1983

Structural and electronic influences on phosphite basicity and its application to heterogeneous and homogeneous catalysis

David Evan Schiff

Iowa State University

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STRUCTURAL AND ELECTRONIC INFLUENCES ON PHOSPHITE BASICITY
AND ITS APPLICATION TO HETEROGENEOUS AND HOMOGENEOUS
CATALYSIS

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Structural and electronic influences on phosphite

basicity and its application to heterogeneous and

homogeneous catalysis

by

David Evan Schiff

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of the

Requirements for the Degree of

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Major: Inorganic Chemistry

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For the Graduate College

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Ames, Iowa

1983

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PREFACE

The steric and electronic properties of phosphorus ligands are known to vary widely. This dissertation discusses work done during the study of the properties of different monocyclic and bicyclic phosphite esters and how these properties influence the catalytic activity of the NiL_4 complexes which they form.

X-ray, PES, and NMR studies of some selected aminophosphite compounds were carried out in order to understand how their unique structural and electronic properties could influence the catalytic properties of their NiL_4 complexes.

We were also successful in producing two new types of heterogenized NiL_4 complexes which we hoped would have properties similar to that of a homogeneous NiL_4 catalyst, yet would also have the desirable characteristics of a heterogeneous catalyst.

In addition, this dissertation will describe the development of an analytical procedure for quantifying alcohols contained within a mixture, by means of a phosphorus derivatizing reagent. The actual analysis entailed the quantitative measurement of the phosphorus-containing alcohol derivative using ^{31}P NMR techniques.

A list of compounds discussed in this dissertation is included in Table 1.

Table 1. Compounds described in this thesis

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Table 1. (Continued)

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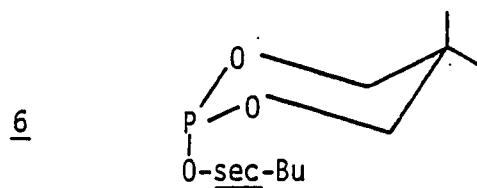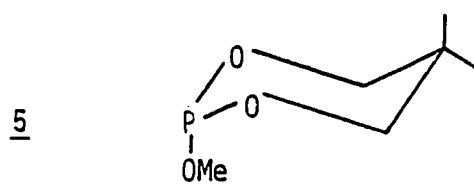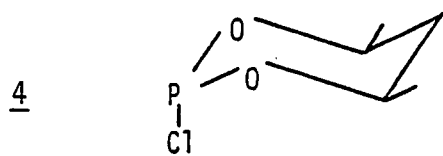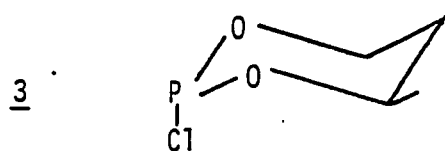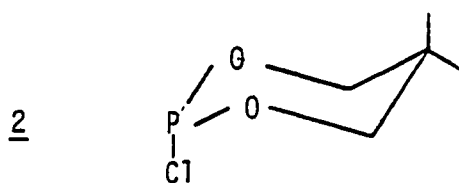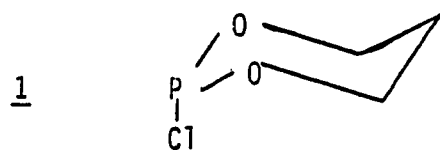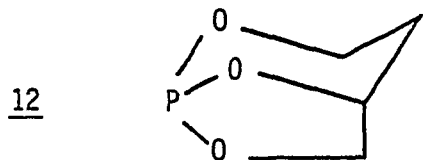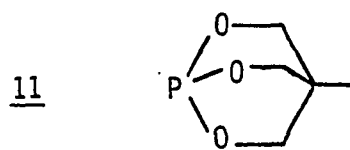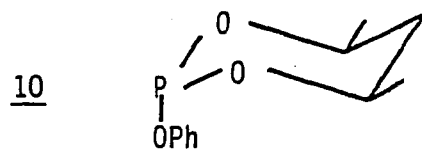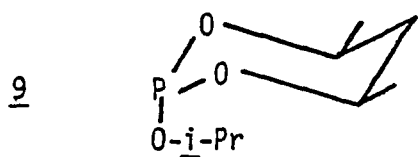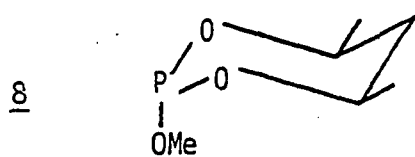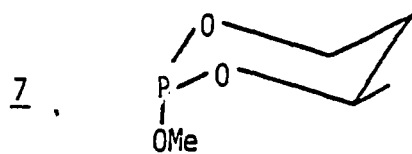
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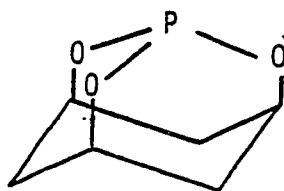
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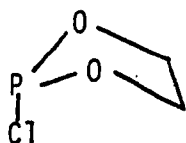
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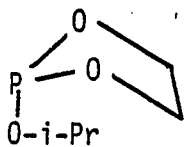
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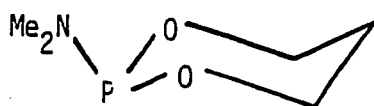
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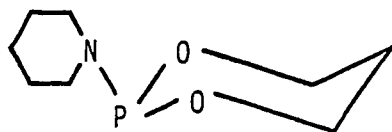
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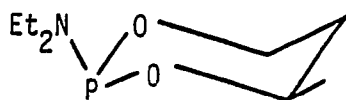
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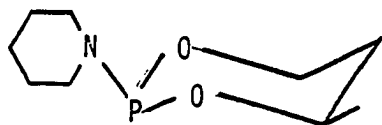
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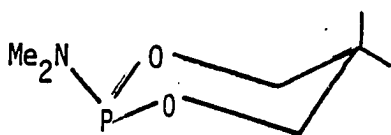
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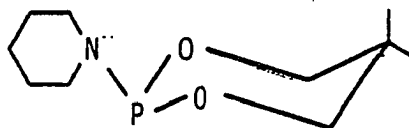
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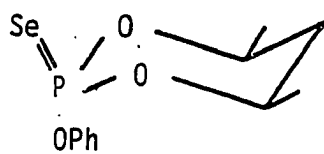
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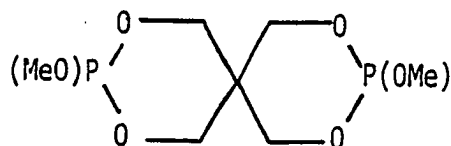
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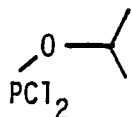
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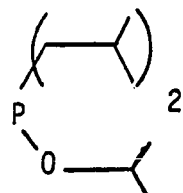
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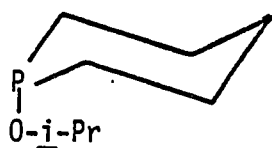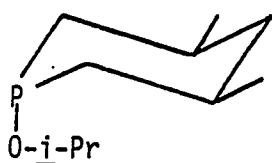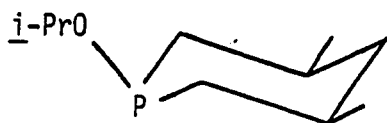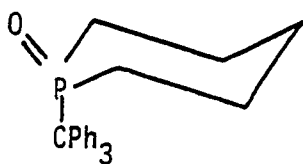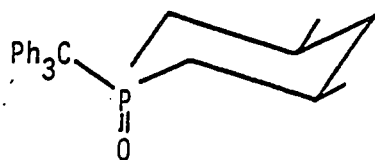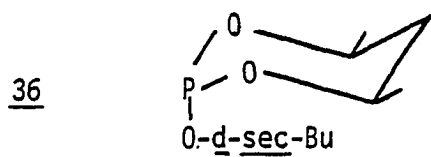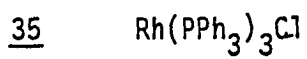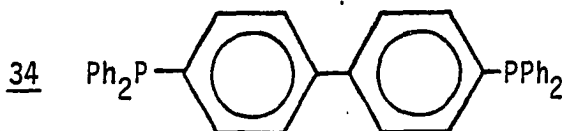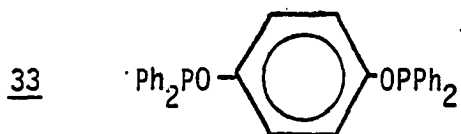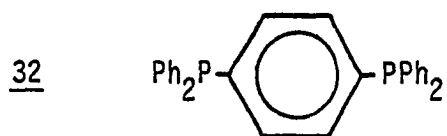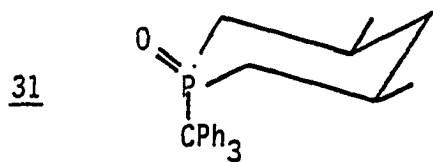
O-i-Pr

27

O-i-Pr

28

i-PrO

29

CPh₃

30

Ph₃C

Table 1. (Continued)

31

32   Ph_2P—⬡—PPh_2

33   Ph_2PO—⬡—$OPPh_2$

34   Ph_2P—⬡—⬡—PPh_2

35    $Rh(PPh_3)_3Cl$

36

Table 1. (Continued)

37   (structure: cyclic phosphite with P–OMe)

38   (structure: MeO-substituted cyclic phosphite)

39   (structure: cyclic phosphite)

40     $(MeO)_2PCl$

41     $(MeO)_2PNMe_2$

42   (structure: cyclic phosphite with P–NMe$_2$)

Table 1. (Continued)

43

44 (MeO)$_2$P(Se)NMe$_2$

45

46

47

48

Table 1. (Continued)

49   (ClCH₂CH₂)₂N

CH₂CH₂Cl

50   OMe

51   Se   OMe

52   Se   OMe

53   MeO   Se

54   O-i-Pr

Table 1. (continued)

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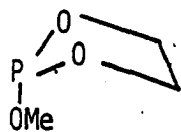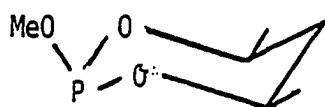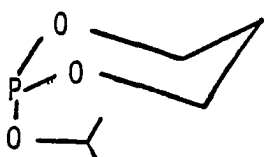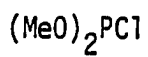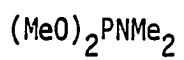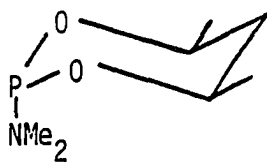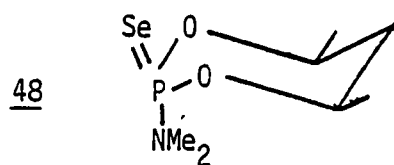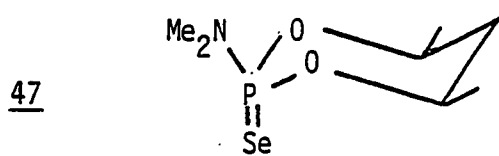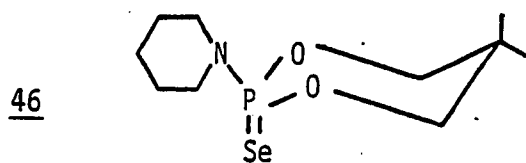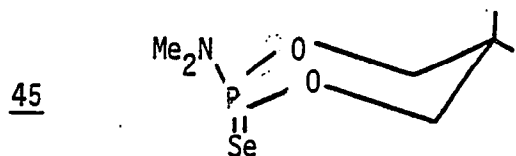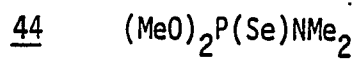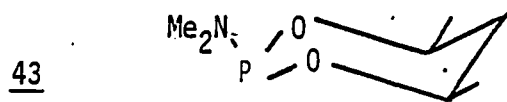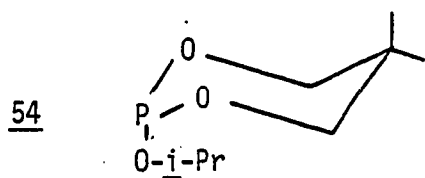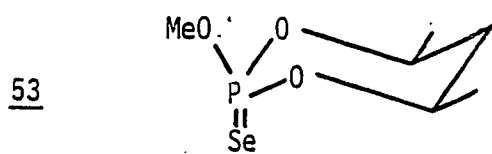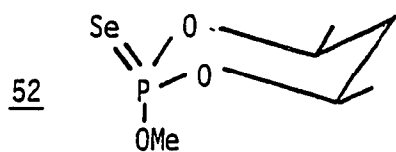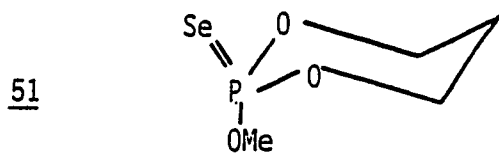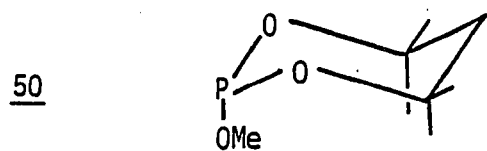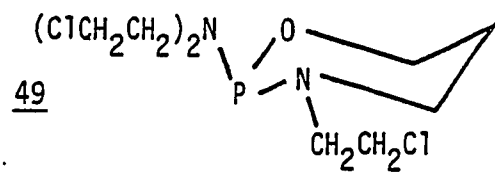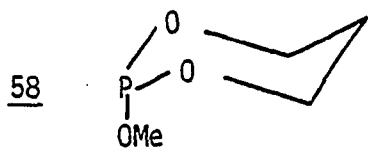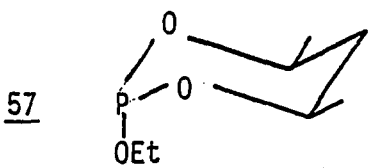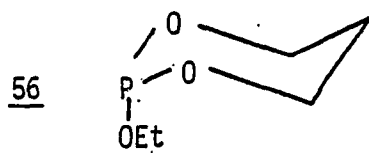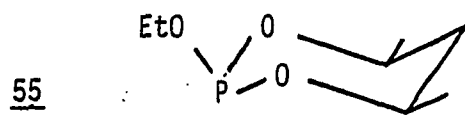
PART 1:

THE CATALYTIC PROPERTIES OF HOMOGENEOUS AND HETEROGENEOUS

NiL_4 (L = PHOSPHITE) COMPLEXES

INTRODUCTION

One of the most novel features of transition metals is their ability to adopt many different oxidation states. This is perhaps one of the most important factors in their capacity to act as catalysts in a variety of organic reactions (1,2). The ability of a transition metal to adopt lower oxidation states is facilitated by the coordination of electron soft ligands such as PR_3, $P(OR)_3$, SR_2, CO, C_6H_6, etc.

In most cases, transition metals bind ligands in a manner which provides 18 electrons in their valence shell. These complexes are then said to be coordinatively saturated. In order for these complexes to act as catalytically active species, they must first dissociate one of their ligands to form electron deficient complexes. In most cases, these are 16 electron intermediates which are then able to bind small molecules such as olefins, hydrogen, nitrogen, alkyl halides, etc. Upon coordination, these small molecules undergo changes in their electronic structure which facilitate their further reaction while coordinated to the metal atom. This feature is best illustrated by the pioneering work of Dewar, and Chatt and Duncanson (3,4) on the bonding of olefins to metal atoms. In their model, the electron density contained in the double bond is donated to the metal atom via a σ bond while at the same time electron density is returned to the olefin through its anti-bonding orbitals. This redistribution of electron density is suggested by the observation of an increase in the C-C distance of the coordinated olefin compared to that found in the uncoordinated olefin (4,5). X-ray crystal-

lographic studies of olefin complexes such as $Ni(CH_2=CH_2)(P(O-\underline{o}-C_6H_4CH_3)_3)_2$ and $Ni(CH_2=CH_2)(PPh_3)_2$ (5) have shown that the olefin loses its planarity upon coordination. This is indicative of extensive rehybridization of the olefinic carbon atoms from sp^2 to sp^3. It is the weakening of the olefin's double bond, which activates it toward reactions with other atoms and smaller molecules, such as H and CO, which are also bound to the metal atom.

The ability of a transition metal to act as a catalyst depends very strongly upon the steric and electronic interactions between the ligands contained in the coordination sphere of the metal atom. The electronic interaction between a ligand such as CO and a metal atom can also be described by the Dewar-Chatt-Duncanson model (Fig. 1) (4). In this model, a pair of electrons is donated to the metal atom from the CO
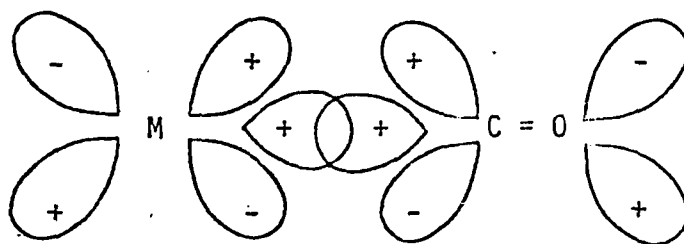
Fig. 1. Bonding in transition metal carbonyl complexes

ligand via a σ bond. At the same time, electron density is returned to the CO ligand via a π bond formed by the antibonding orbitals of the CO and the d orbitals on the metal, which causes a weakening of the C-O bond. Support for this theory has been well-documented by the decrease

in the $\nu(C=O)$ stretching frequency of CO upon coordination to metals such as Fe, Co, etc. (6).

Back donation of electron density has also been postulated to occur in other ligands which contain atoms having low-lying unoccupied d orbitals, such as phosphorus, sulfur, arsenic and selenium. In the case of phosphorus, it has been known for many years that the donor-acceptor properties of the ligands are highly dependent upon the groups bonded to phosphorus (7).

Tolman (8) has been able to quantify the contributions of these substituents from the donor-acceptor properties of phosphorus. The contribution of the substituent to the A_1 CO stretching frequency of various $Ni(CO)_3L$ complexes, where $L = PX_1X_2X_3$, has been quantified by the substituent additivity coefficient (χ_1) of X. The effect of this contribution on the A_1 stretching frequency is given by equation 1.

$$\nu_{(CO)A_1} = 2056 + \sum_{i=1}^{3}\chi_i \, cm^{-1} \qquad (1)$$

The values of χ_1 range from 0.0 for a $\underline{t}$-butyl group to 19.6 for a trifluoromethyl group. Clearly, the more electron withdrawing a group, the higher its χ_i value. It has also been observed that ligands which are good π-acceptors also cause the A_1 CO stretching frequency of these complexes to be higher. Of course, it is impossible to quantify the relative donor-acceptor properties of a phosphorus ligand solely on the basis of a single CO stretching frequency. In fact, it has been argued

that the phosphorus-metal σ bond is the major factor in determining the $\nu(CO)$ frequency for the CO ligands contained within the complex (9,10).

Over the past several years many methods have been developed to quantify the donor properties (or basicity) of phosphorus. Protonation of phosphorus ligands with strong acids such as F_3CCO_2H, followed by subsequent ^{31}P NMR analysis have shown that J_{P-H} is related to the basicity of the phosphorus ligand (10). It has been argued (11,12) that the less basic the phosphorus ligand is, the higher the positive charge at the phosphorus nucleus. This increase in positive charge then causes an increase in the value of J_{P-H} upon protonation.

Other workers have been successful in correlating phosphorus ligand basicity to the 31_P-77_{Se} values of their corresponding selenides (13), the ν_{B-H} values of their borane adducts (14) and the $J_{183_W-31_P}$ values found in $W(CO)_5L$ complexes (15,16). Recent work by Yarbrough and Hall (17) has shown that photoelectron spectroscopy can furnish information which distinguishes π-acceptor and σ-donor properties of a phosphorus ligand. The photoelectron spectra of $LM(CO)_5$ where M = Cr, Mo and W and L = PEt_3, PMe_3, $P(NMe_2)_3$, $P(OEt)_3$, $P(OMe)_3$ or PF_3 were reported. The authors compared the spectra of these complexes to that of the free ligands. Information on the σ donor ability of the ligands was obtained by comparing the difference in the ionization potentials of M-P bond to that of the lone pair in the free ligand. It was assumed that the greater the donor ability of ligand, the smaller the difference in ionization potential of the M-P bond to that of the lone pair in the free ligand. This allowed them to rank the donor ability of these ligands

while complexed to the metal atom in the following order:

$$PEt_3 \sim PMe_3 > P(OEt)_3 \sim P(OMe)_3 > P(NMe_2)_3 > PF_3$$
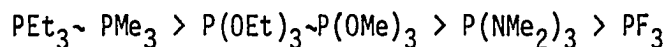
It should be noted that the relative order of $P(OMe)_3$ and $P(NMe_2)_3$ is opposite to what Cowley and co-workers (18) have found for the uncoordinated ligand. The π-acceptor abilities of these ligands were determined by the amount that the t_{2g} orbitals of the metal atom were split into e and b_2 groups by the ligands. The amount of splitting of these orbitals by the ligands fell into the following order:

$$PEt_3 \sim PMe_3 > P(NMe_2)_3 > P(OEt)_3 \sim P(OMe)_3 > PF_3$$
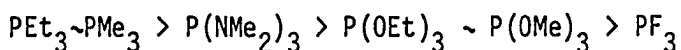
This order is opposite to the order of increasing π-acidity based on electronegativity considerations. The switch in the order of $P(NMe_2)_3$ and the phosphites in going from σ basicity to π-acidity is attributed to the interaction between occupied and unoccupied orbitals on both phosphorus and its substituents.

The steric properties of a phosphorus ligand have also been shown to be important in describing the overall properties of the ligand. Tolman and co-workers (19,20) has shown that the steric properties of the phosphorus ligand play a dominate role in influencing the position of the following equilibrium (Eq. 2).

$$NiL_4 + 4 L' \longrightarrow NiL_{(4-n)} L'_n + (4-n) L' + nL \qquad (2)$$
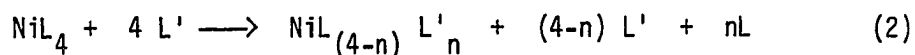
He has shown that the smaller the size of the ligand, the more stable the resulting complex is toward ligand replacement. In order to quantify

steric properties of a ligand, Tolman defines the ligand cone angle as the apex angle of a cylindrical cone, centered at 2.28Å from the center of the phosphorus atom (Fig. 2). (This distance exemplifies the average distance found between a metal atom and a phosphorus ligand.) The cone is constructed so that it just touches the van der Waals radii of the outermost atoms. The value of the ligand cone angle, which can be determined by using space-filling models, ranges from 101° for the rather nonsterically demanding $P(OCH_2)_3CCH_3$ to 212° for the bulky $P(mesityl)_3$ ligand (Table 2).

Having the ability to determine the electronic and steric properties of a ligand, one should be able to relate these properties to the reactivity of a metal complex containing these ligands, toward small molecules such as olefins, hydrogen, or CO, etc. With this knowledge one should be able to custom design a metal complex for use as a catalyst.

A good example of how a ligand can influence a transition metal complex's catalytic behavior is perhaps best demonstrated by Wilkinson's catalyst. Wilkinson catalyst, $Rh(PPh_3)_3Cl$, (21,22) is one of the best known homogeneous hydrogenation catalysts. The proposed mechanism of its role in the hydrogenation of an olefin is :

Ligand dissociation

$$Rh(PPh_3)_3Cl \longrightarrow Rh(PPh_3)_2Cl + PPh_3 \qquad (3)$$

Oxidative addition

$$Rh^I(PPh_3)_2Cl + H_2 \longrightarrow Rh^{III}(H)_2(PPh_3)_2Cl \qquad (4)$$
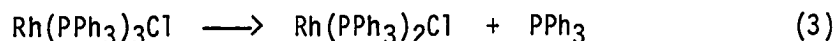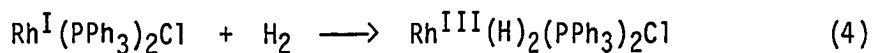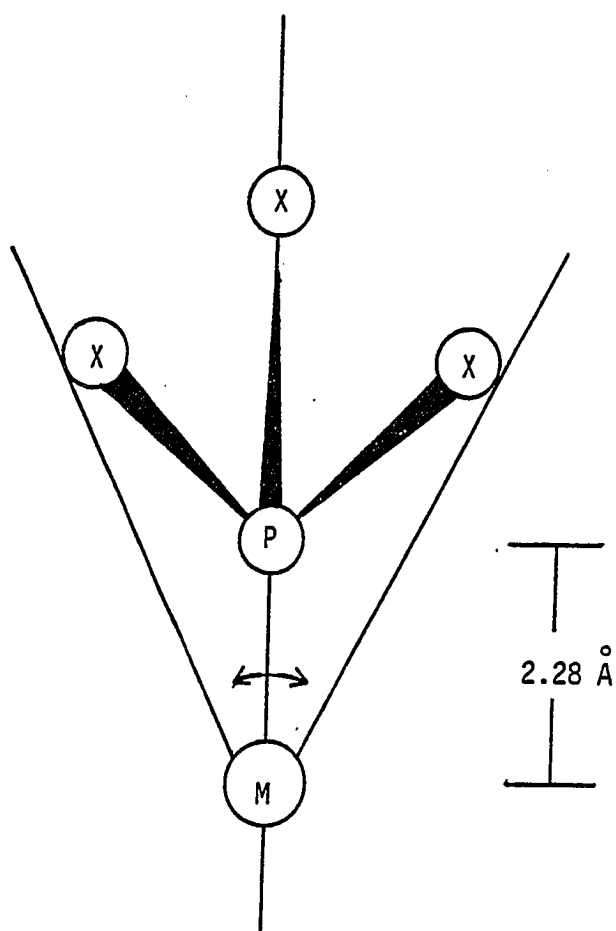
Figure 2. Ligand cone angle as defined by Tolman (19)

Table 2. Various ligand cone angles for some selected phosphorus
ligands (19,20)

Ligand	Cone Angle (°)
$P(OCH_2)_3CCH_3$	101
PF_3	104
$P(OMe)_3$	107
$P(OEt)_3$	109
PCl_3	124
$P(O\text{-}i\text{-}Pr)_3$	130
$P(O\text{-}o\text{-}tol)_3$	141
$P(NMe_2)_3$	157
$P(mesityl)_3$	212

Olefin addition and insertion

$$Rh(H)_2(PPh_3)_2Cl \ + \ CH_2=CH_2 \ \longrightarrow \ Rh(H)_2(PPh_3)_2Cl(CH_2=H_2) \qquad (5)$$

$$Rh(H)_2(PPh_3)_2Cl(CH_2=CH_2) \ \longrightarrow \ RhH(PPh_3)_2Cl(CH_2CH_3) \qquad (6)$$

Reductive elimination

$$Rh(H)(PPh_3)_2Cl(CH_2CH_3) \ \longrightarrow \ Rh(PPh_3)_2Cl \ + \ CH_3CH_3 \qquad (7)$$
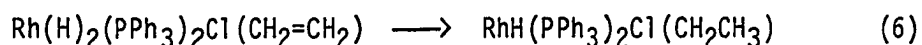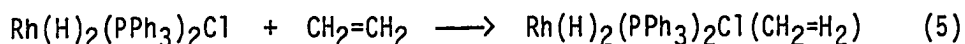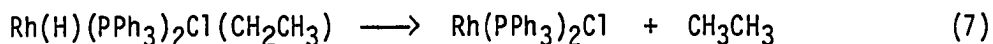
In each of these steps, the properties of the phosphine ligand has a great effect upon this reaction since the analogous phosphite complex $Rh(P(OPh)_3)_3Cl$ has been shown to be completely inactive as a hydrogenation catalyst (21). At first, this difference was attributed to the greater π-acidity of the phosphite over the phosphine, which was believed to lower the amount of electron density on the metal, thus changing the metal's electronic properties. However, this difference in activity has more recently been attributed to the failure of a $P(OPh)_3$ ligand to dissociate and provide an open site for coordination of hydrogen or an olefin (22). This failure to dissociate is a consequence of the reduced steric bulk of $P(OPh)_3$ compared to that of PPh_3. This is borne out by the differences in the ligand cone angle of 128° to 145° for $P(OPh)_3$ and PPh_3, respectively (Table 2) (19).

Over the last two decades, our group has focused interest on the chemistry of various monocyclic, and bicyclic ligands exemplified by structures of the types below (12,23,24). A great deal of work has also been done to understand both the steric and electronic properties of these ligands (24,25,26,27). Based on our present knowledge of these
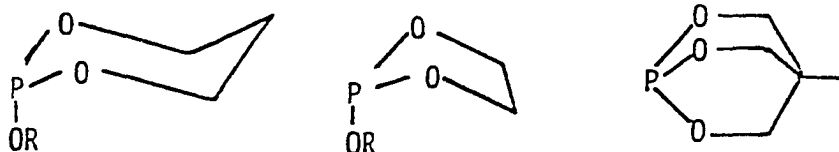
R = alkyl or aryl

ligands it seemed reasonable to attempt to correlate these properties to the catalytic activities of some selected transition metal complexes which they form.

The homogeneous catalytic isomerization of an olefin provides an excellent system to probe the effects of the properties of the ligand on the rate of catalysis by a given complex. This is due in part to the overall relative simplicity of the mechanism involved.

The catalytic isomerization of olefins has been shown to proceed by two different mechanisms (1). The first involves a σ-bonded alkyl intermediate which is formed by olefin insertion into a metal hydride bond. This is then followed by β-hydrogen elimination to give the isomerized product (Eq. 8).

$$RCH_2CH=CH_2 + M-H \longleftrightarrow \underset{M}{R-CH_2CHCH_3} \longleftrightarrow RCH=CHCH_3 + MH \qquad (8)$$
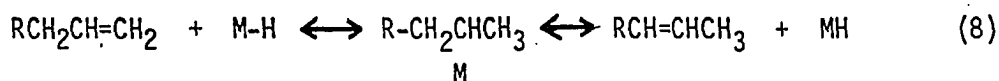
This mechanism requires the formation of a metal hydrogen bond followed by a 1,2-hydrogen shift. In most cases, the hydride is supplied by either a protic acid or molecular hydrogen. Examples of catalytic systems which proceed via such a mechanism are $HCo(CO)_4$ (28), $((C_2H_4)_2RhCl)_2/HCl$ (29), $HNi(P(OEt)_3)_4^+$ (30) and $PtCl_2(PPh_3)_2$ $SnCl_4/H_2$ (31).

The second mechanism requires the formation of a π or σ allyl-metal intermediates. The π-allyl metal hydride mechanism proceeds via reaction (9).

$$RCH_2CH=CH_2 \rightleftharpoons RCH \overset{H-M}{\underset{C-H}{\big|\,CH_2}} \rightleftharpoons RCH=CHCH_3 \qquad (9)$$
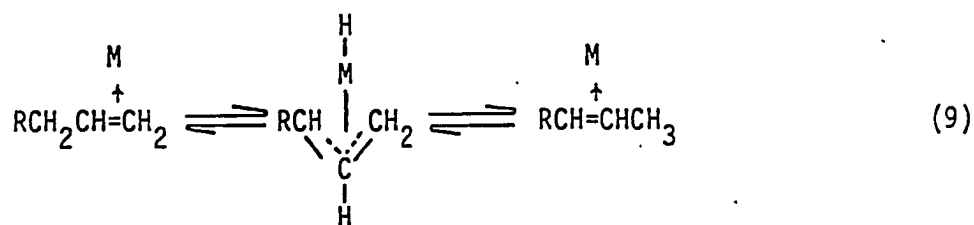
This mechanism was shown to be operative in the isomerization of allyl alcohol to propionaldehyde by $Fe(CO)_5$ (32). Further, deuterium labeling experiments by Hendrix and co-workers (33) confirmed the existence of a 1,3-hydrogen shift, required by the π-allylic mechanism.

Green and Hughes (34,35) proposed a modification of this mechanism which involves the formation of a σ-bonded allyl intermediate (Eq. 10).

$$(10)$$
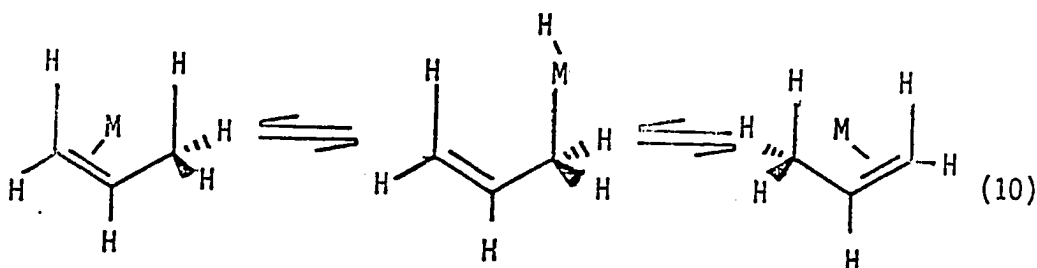
This mechanism requires the metal atom to insert into C-H bond followed by elimination of the metal to reform a new C-H bond with concurrent isomerization of the double bond. This mechanism has been substantiated by the thermal rearrangement of η^2 and η^4-3-methylene-4-vinyldihydro-

furan-2(3H)-one complexes of iron(0) (Scheme 1) (34). Optically active A

in Scheme 1 rearranges regiospecifically, but with extensive racemization

in the formation of C and D. Green and Hughes (35) contend that this

racemization can only occur by means of a terminal σ bonded allylic

intermediate B.

In 1970 C. A. Tolman reported that under strongly acid conditions

Ni(P(OEt)$_3$)$_4$ could be protonated (36). It was found that protonation of

the complex labilized a triethyl phosphite ligand. It was shown by

spectrophotometric methods that the rate constant increased from 4.9 X

10^{-6} sec^{-1} to 1.5 X 10^{-2} sec^{-1} for the dissociation (Eq. 11) of

Ni(P(OEt)$_3$)$_4$ upon addition of acid. Further work has shown that the

$$HNi(P(OEt_3)_4^+ \longrightarrow HNi(P(OEt)_3)_3^+ + P(OEt)_3 \qquad (11)$$
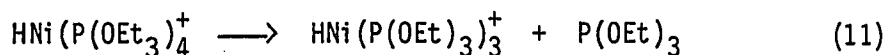
protonated nickel complex can efficiently isomerize 1-butene via the

mechanism proposed in Scheme 2 (36,37). Both spectrophotometric and ^{31}P

NMR (30) analysis indicate that the protonation of Ni(P(OEt)$_3$)$_4$ is

extremely facile. However, the rate-determining step was found to be the

dissociation of a P(OEt)$_3$ ligand to form the coordinatively unsaturated

species, HNi(P(OEt)$_3$)$_3^+$. Dissociation of a P(OEt)$_3$ ligand is probably

facilitated by weakening of the nickel-phosphorus bond. This is due in

part to the decrease in π back donation to the phosphite ligand from the

metal, caused by the coordination of the proton to the nickel. This was

borne out by the work of Gultneh (38) which showed that complexes such as

Ni(11)$_4$ were protonated to a small extent in solution. It is thought
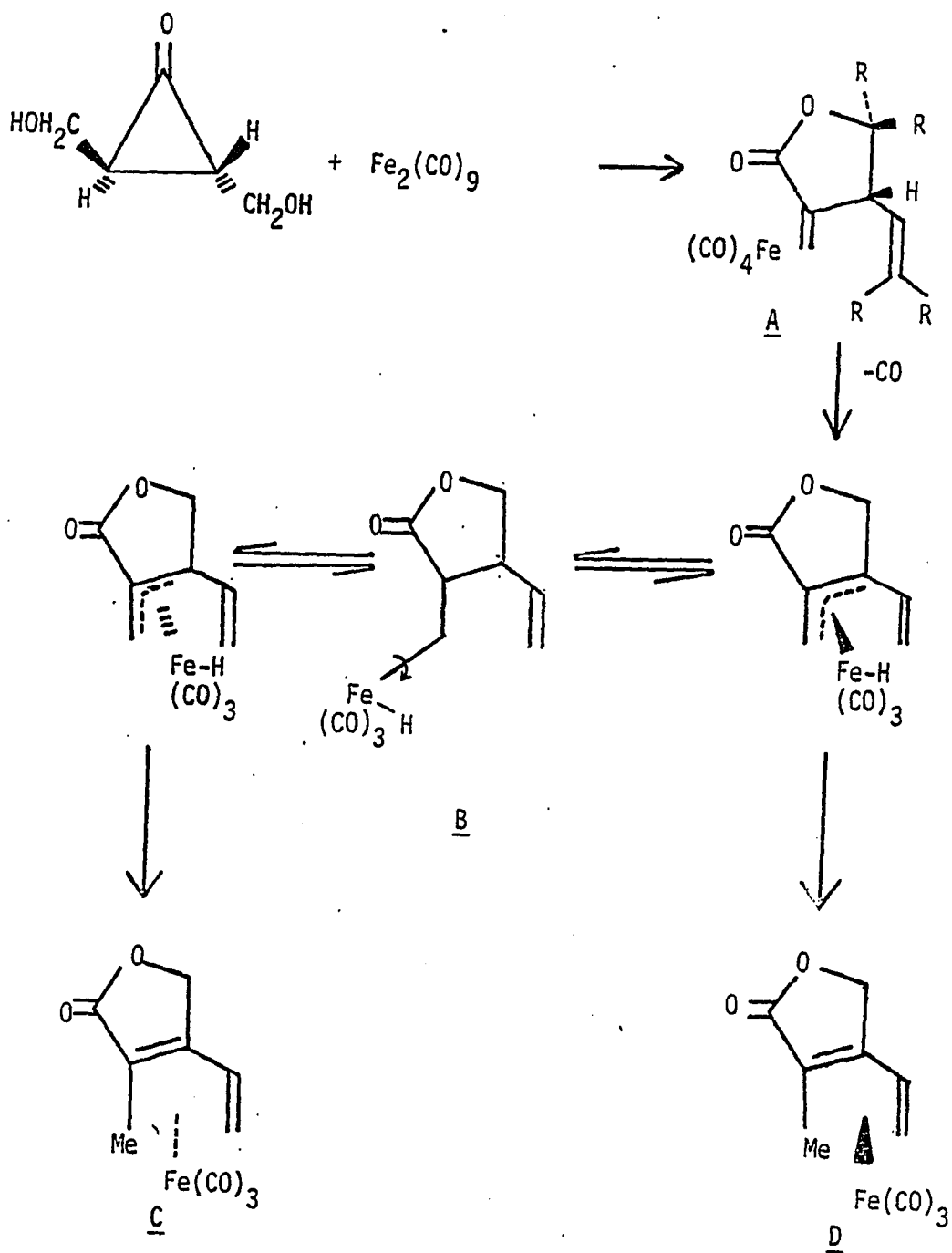
Scheme 1. The mechanism of isomerization of η^2 and η^4-3-methylene -4-vinyl dihydrofuran-2(3H)-one complexes of Fe(0). Note, R groups on compounds succeeding A left off for clarity

$$Ni(P(OEt)_3)_4$$

$$\downarrow \longleftarrow H^+$$

$$HNi(P(OEt)_3)_4{}^+$$

$$\downarrow \longrightarrow P(OEt)_3$$

$$CH_3CH=CHCH_3 \longleftarrow HNi(P(OEt)_3)_3{}^+ \longrightarrow CH_2=CHC_2H_5$$

$$CH_3CH\overset{H}{\underset{CH}{\diagdown}}Ni(P(OEt)_3)_3{}^+ \qquad ((EtO)_3P)_3Ni\overset{+}{\underset{CH}{-H}}$$
$$\underset{CH_3}{|} \qquad \qquad \overset{CH_2}{\underset{CHC_2H_5}{\diagup}}$$

$$\underset{\underset{CH_3}{} \overset{}{} CH_3\diagup^{CH}\diagdown C_2H_5}{(P(OEt)_3)_3}$$
$$Ni^+$$
$$|$$
$$CH$$
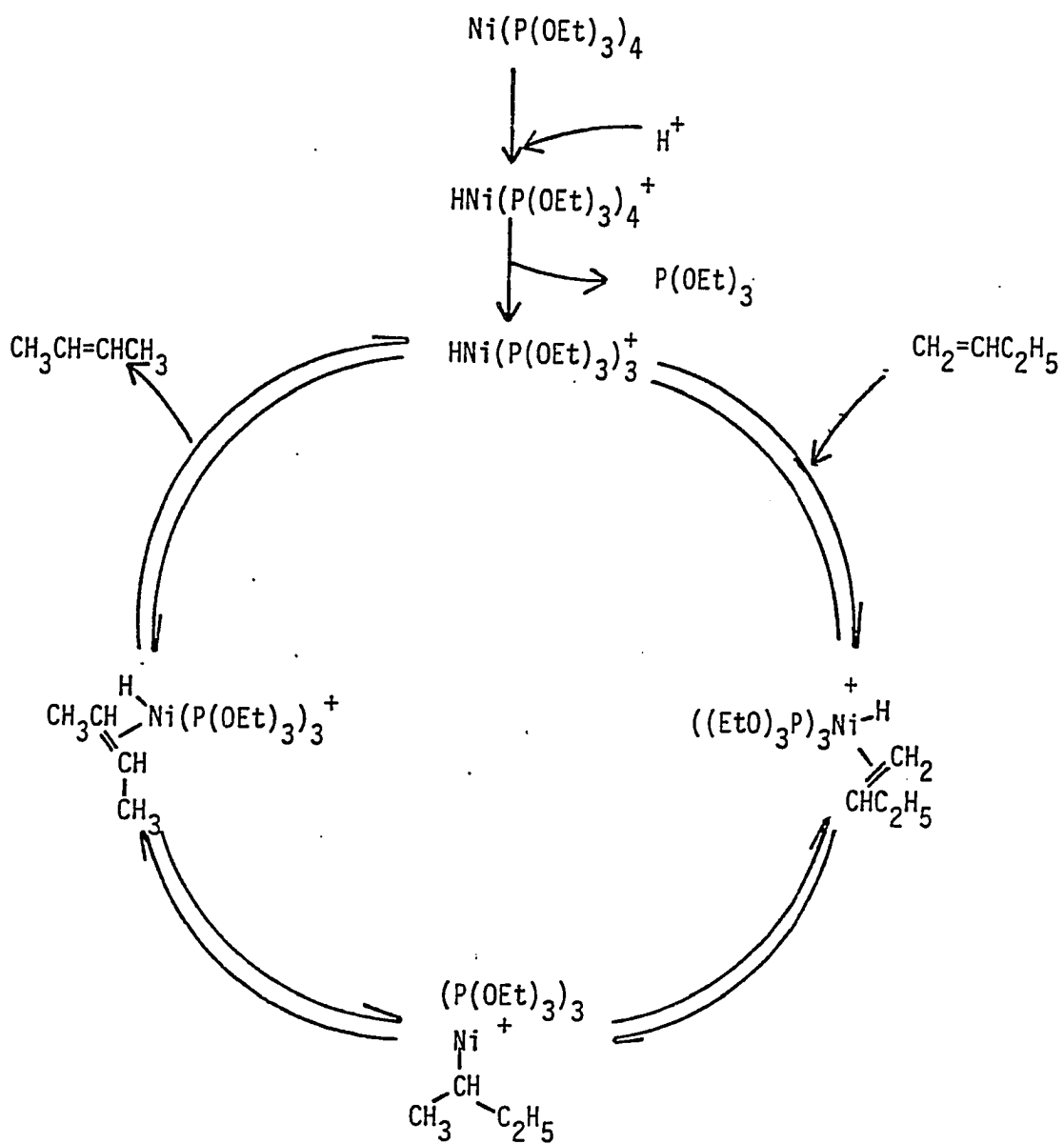
Scheme 2. The mechanism for the isomerization of 1-butene using acidified Ni(P(OEt)$_3$)$_4$ (19)

that the high π-acceptor capacity of 11 sufficiently lowers the basicity of nickel, thus causing it not to be protonated.

The role of the acid in this catalysis mechanism is that of an initiator. Tolman has shown (36) that in D_2SO_4/CH_3OD solutions, $DNiL_4^+$ forms rapidly. However, the deuterium is found in only 1 out of 120 isomerized butene molecules. This indicates that the nickel atom exchanges the deuterium atom for a proton in the isomerizing olefin. Subsequent coordination of a nondeuterated 1-butene which results in the formation of nondeuterated 2-butene. The protonated nickel atom can only redeuterate after it has recaptured a free phosphite ligand to form $HNiL_4^+$ which is then able to exchange with the solvent.

As much as the acid is the key to starting up the catalytic mechanism, it is also the key to ending it. Deactivation of the complex toward catalysis is known to occur via two pathways.

1. Oxidation of the zero-valent nickel atom to Ni(II). Calculation of the E_0 potential for (Eq. 12) yields 0.25 volts.

$$Ni(0) + 2H^+ \longrightarrow Ni(II) + H_2 . \qquad (12)$$
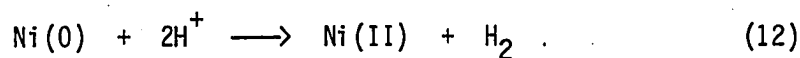
2. Acid-catalyzed solvolysis of dissociated ligands. Examples of acid catalyzed solvolysis of alkyl phosphites have been known for many years (Eq. 13) (39).

$$P(OR)_3 + H^+X^- \longrightarrow H(O)P(OR)_2 + RX \qquad (13)$$
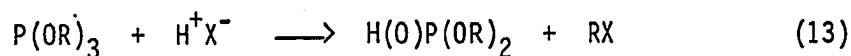
This reaction should be important in the catalysis mechanism since the dissociation of a $P(OEt)_3$ ligand takes place in a highly acidic medium. One might expect that this reaction would favor an increase in the catalysis rate because it shifts the dissociation equilibrium toward $HNiL_3^+$ species. However, in actuality it is presumed that further dissociation takes place leading to the formation of $HNiL_2^+$ and $HNiL^+$ species which are more readily oxidized to $Ni(II)$ in the highly acidic media.

Armed with this basic information, Gultneh and Verkade began a study of the catalytic properties of various NiL_4 complexes where L is'a monocyclic or bicyclic phosphite ligand. One of the most important findings of this study was that small changes in the structure of the phosphite leads to a large increase in the rate of catalytic isomerization of 3-butenenitrile (Table 3). As can be seen in Table 3, the amount of catalysis is maximized for ligands which have methyl groups in the 4,6 equatorial positions. The increased rate of catalysis by the ligand in the NiL_4 complex was found to follow the trend:
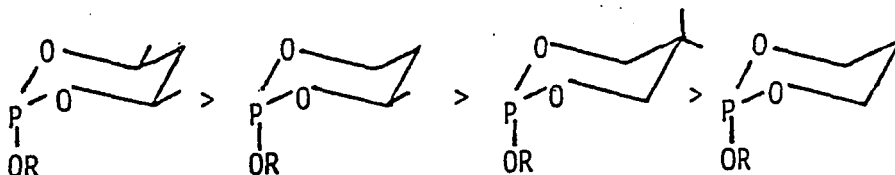
Table 3. Rates of catalytic isomerization of 3-butenenitrile by NiL_4/acid (1/10) systems in benzene at 25°c as a function of the size of the exocyclic phosphorus substituent [a](38)

L	NiL_4/F_3CCOOH			NiL_4/Cl_3CCOOH		
	cyclces over initial 30 min (±3)	$t_{1/2}$ (min) (±0.2 min)	cis/trans (2-butene-nitrile) (±0.2)	cycles over initial 30 min (±3)	$t_{1/2}$ (±0.2 min)	cis/trans (2-butene-nitrile) (±0.2)

OR
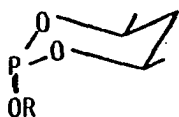
R = Me	(5.0 min)[bc]	<1.0	1.5	107	8.0	1.7
R = n-Pr	(4.0 min)	<1.0	1.6	110	7.5	1.6
R = i-Pr	(3.0 min)[b]	<1.0	1.5	115	7.0	1.6
R = t-Bu	(5.0 min)[c]	<1.0	1.5	104	8.0	1.5
R = sec-Bu	(5.0 min)[d]	<1.0	1.7	104	8.0	1.7
R = l-bornyl	20	>8 hrs	1.6	10	12 hrs	1.5
R = l-menthyl	20	>8 hrs	1.4	10	12 hrs	1.6
R = α-(methoxy- carbonyl)benzyl	0	--	--	--	--	--

R = Me	92	12.0	1.4	62	30.0	1.7
R = i-Pr	108	8.0	1.6	68	29.0	1.5
R = t-Bu	96	9.0	1.5	64	29.0	1.5
R = l-bornyl	0	--	--	0	--	--
R = l-menthyl	0	--	--	0	--	--
R = α-(methoxy-carbonyl)benzene	0	--	--	0	--	--
$P(OMe)_3$	74	15.0	1.3	52	40.0	1.7
$P(OEt)_3$	52	38	1.4	28	115	1.6
$P(O-i-Pr)_3$	35	7 hrs	1.3	25	8 hrs	1.4
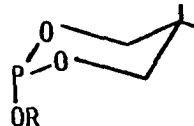
[a] [acid]:[NiL$_4$]:[olefin] = 10:1:124

[b] On increasing the substrate to complex ratio to 992, a rate of 640 cycles in 30 min was obtained.

[c] Under the conditions in footnote b, a rate of 740 cycles in 30 min was obtained.

[d] Under the conditions in footnote b, a rate of 680 cycles in 30 min was obtained.

Table 3 (Continued)

L	NiL$_4$/F$_3$CCOOH			NiL$_4$/Cl$_3$CCOOH		
	cycles over initial 30 min (±3)	$t_{1/2}$ (min) (±0.2 min)	cis/trans (2-butene-nitrile) (±0.2)	cycles over initial 30 min (±3)	$t_{1/2}$ (min) (±0.2 min)	cis/trans (2-butene-nitrile) (±0.2)

R = Me	60	35.0	1.4	30	110	1.6
R = Et	0	--	--	0	--	--
R = i-Pr	0	--	--	0	--	--
R = t-Bu	0	--	--	0	--	--
R = l-bornyl	0	--	--	0	--	--
R = l-menthyl	0	--	--	0	--	--
R = α-(methoxy-carbonyl)benzene	0	--	--	0	--	--

R = Me	92	12.0	1.4	62	30.0	1.7
R = i-Pr	108	8.0	1.6	68	29.0	1.5
R = t-Bu	96	9.0	1.5	64	29.0	1.5
R = l-bornyl	0	--	--	0	--	--
R = l-menthyl	0	--	--	0	--	--
R = α-(methoxy-carbonyl)benzene	0	--	--	0	--	--
P(OMe)$_3$	74	15.0	1.3	52	40.0	1.7
P(OEt)$_3$	52	38	1.4	28	115	1.6
P(O-i-Pr)$_3$	35	7 hrs	1.3	25	8 hrs	1.4

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For complexes containing 4-methyl or 4,6-dimethyl groups, the catalysis rate was found to be maximized when an isopropoxy group was in the exocyclic position. Complexes with ligands which contained either 5,5-dimethyl groups or no substitution at all were found to be active only when a methoxy group was in the exocyclic position. These differences were explained on the basis of increased steric interactions which favored dissociation in complexes with ligands containing 4,6-dimethyl groups.

Studies also revealed that the amount and type of acid used had a great effect on the overall catalysis rate. Maximum rates of isomerization were observed when a ratio of 10 H^+ to 1 Ni was used. At higher ratios there was a marked decrease in the rates of catalysis, probably due to an increase in the amount of solvolysis of the dissociated ligand. The effect of solvolysis of the ligand is that more dissociated nickel species, such as NiL_2 and NiL are produced in solution. These complexes are more easily oxidized than the NiL_4 complexes by the acid to catalytically inactive Ni(II) species. It was also found that for a given complex the amount of catalysis increased with the type of acid used, according to the trend:

$$F_3CCOOH > Cl_3CCOOH > H_3CCOOH$$
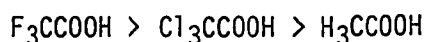
This is reasonable since protonation of the complex is expected to increase with increasing acid strength. Protonation of these NiL_4 complexes can be observed by ^{31}P NMR. All of these complexes show single peaks in the ^{31}P NMR spectrum in the narrow region of 155 to 150 ppm

relative to H_3PO_4. Upon addition of acid to the solution containing the NiL_4 complex, a characteristic yellow color develops, indicative of protonation. Subsequent low temperature ^{31}P NMR analysis shows the formation of a doublet in the range from 134 to 128 ppm with a J_{P-H} of 29-39 Hz. This range of coupling constants has been observed in other compounds that have hydrogen coupling to phosphorus through a metal atom (40).

In all cases, the effect of adding excess ligand retards the rate and extent of catalysis. This is most pronounced for the least catalytically active system, $Ni(\underline{11})_4/F_3CCOOH$. This agrees with the belief that the most catalytically active systems are those which have the most extensive ligand dissociation. Excess ligand would decrease the amount of dissociation to a greater extent in a less easily dissociated system.

Throughout the initial study it was shown that ligand basicity was very important in determining whether a particular complex acted as an efficient catalyst. Complexes of ligands such as $\underline{11}$ and $\underline{15}$ were shown to protonate to only a small extent (~5%) with F_3CCO_2H (in benzene or methylene chloride). This small extent of protonation was shown by the failure of solutions containing these compounds to turn yellow in color upon addition of acid and the appearance of a doublet of relatively small intensity for the protonated species compared to the large singlet which is observed for the unprotonated NiL_4 complex. This lack of protonation is due in large part to the reduced phosphorus basicity of the ligand and the subsequent decrease in the overall nucleophilicity of the complex. The decrease in basicity of these ligands has been evidenced by their

higher J_{P-H} values when protonated, the higher $J_{31_{P}-77_{Se}}$ values for their corresponding selenides, and the higher ν_{CO} values found in their $Ni(CO)_3L$ complexes (38), compared to the corresponding values for the more basic ligands, 8 and 9, which are known to form NiL_4 complexes that fully protonate in solution (38).

The decreased basicity of 11 has been explained via the concept of increased molecular constraint (12). As can be seen in Fig. 3, the oxygen p orbitals in the bicyclic phosphorus ester are orthogonal to the phosphorus lone-pair, resulting in minimal interaction between the lone-pairs. This in turn causes a decrease in the energy of the phosphorus lone-pairs thus making the lone pair less polarizable by electron acceptors such as H^+ and BH_3. At the same time, geometrical constraint of the P-O-C linkage causes the oxygen lone pairs to rehybridize from sp^2 to sp^3 resulting in a reduction of phosphorus-oxygen $d_\pi-p_\pi$ overlap (41). This reduction in overlap results in a decrease in the amount of electron density that is returned to phosphorus, thus causing an increase in the amount of positive charge on phosphorus. It is the combination of the orthogonality of the lone-pairs and the effects of molecular constraint which results in the decrease in basicity of 11 (12,42).

A significant result of these studies (38) was that Lewis acids such as $AlCl_3$, $ZnCl_2$ and $TiCl_3$ were found to act as efficient cocatalysts in place of protic acids, such as F_3CCO_2H. $AlCl_3$ was found to act as efficiently as H^+ in terms of the amount of isomerization catalysis observed over the course of thirty minutes.
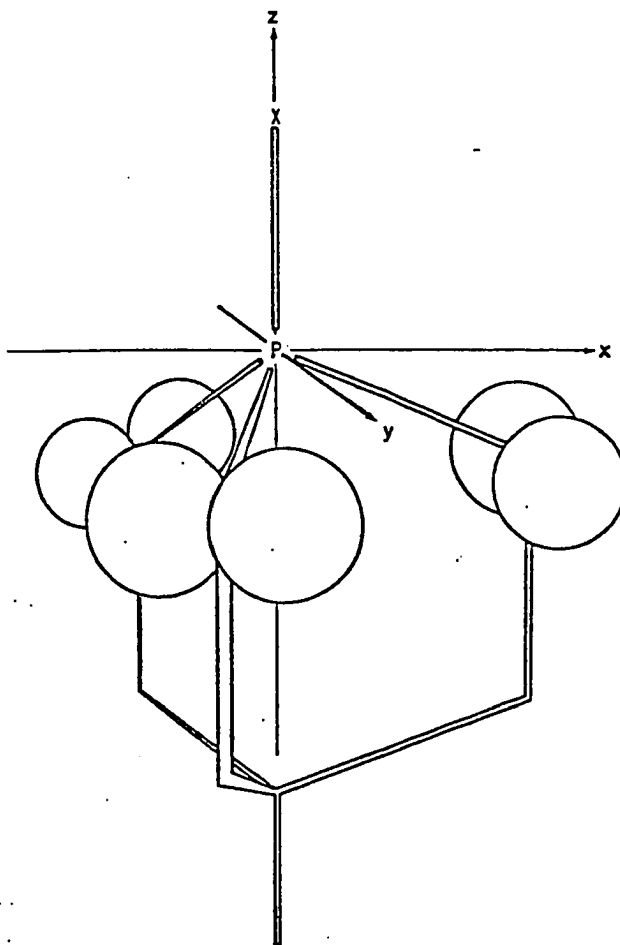
Figure 3. Geometric arrangement of the P, O, and C
atoms and the ester oxygen p orbitals in a
bicyclic phosphorus ester (X = lone pair or
oxygen) if sp^2 hybridization is assumed (12)

Gultneh reports that for AlCl$_3$, the catalytically active species is formed from a NiL$_4$:AlCl$_3$ adduct. Evidence for this adduct is based upon the appearance of a band in the visible spectrum of a NiL$_4$/AlCl$_3$ mixture in CH$_2$Cl$_2$ (λ_{max} 335 nm) which is similar to that observed for the HNiL$_4^+$ species. Gultneh postulates (38) that ligand dissociation to form a catalytically active species occurs upon formation of a positively charged nickel-aluminum intermediate (Eq. 14). The only evidence given

$$NiL_4 + AlCl_3 \rightarrow L_4Ni:AlCl_3 \rightarrow L_4NiAlCl_2^+Cl^- \rightarrow L_3NiAlCl_2^+Cl^- + L \qquad (14)$$
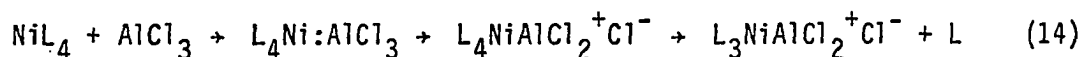
for the existence of such an intermediate is the extremely low molar conductance of 15.4 ohm^{-1} cm^2 mole^{-2}, which was observed for complex Ni($\underline{8}$)$_4$ and AlCl$_3$ in CH$_3$CN. However, this result still does not rule out the possible formation of a NiL$_4$:AlCl$_3$ adduct which is somehow involved in the catalytic machanism, since examples of nickel complexes that form adducts with Lewis acids are known. Examples of these types of complexes are the following (43,44):

(Ph$_3$P)$_2$Ni:Al(CH$_3$)$_3$ (CH$_2$)$_N$ $\begin{array}{c} P^{R_2} \\ \diagdown \\ \diagup \\ P_{R_2} \end{array}$ Ni:Al(CH$_3$)$_3$
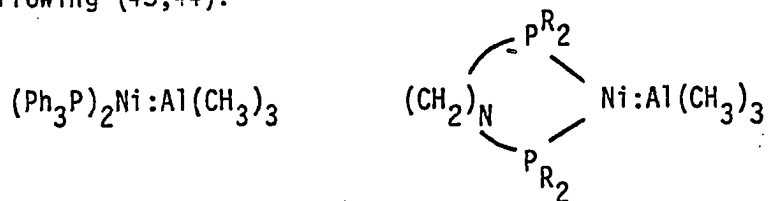
However, an alternate explanation of the role of a Lewis acid in isomerization catalysis will be described in this thesis.

Hydrocyanation of olefins

The catalytic hydrocyanation of olefins has been an area of interest to industrial chemists for many years. This interest has grown primarily because of the economic value in producing compounds such as acrylonitrile and adiponitrile from the hydrocyanation of ethylene and 1,3-butadiene, respectively. As a result, much of the data on this reaction are found in the patent literature (45,46). A recent review by Brown (47) lists many examples of transition metal complexes that are capable of catalyzing the addition of HCN to olefins. For example, $Ru(PPh_3)_3Cl_2$ (48) and $Co_2(CO)_8$ (49) are both known to catalyze the hydrocyanation of $CH_3CH=CHCH_2CN$ to $NC(CH_2)_4CN$ and $CH_3CH(CN)(CH_2)_2CN$. $Co_2(CO)_6L_2$ (48) (where L = PPh_3 or $P(OPh)_3$), is known to catalyze the hydrocyanation of norbornene (Eq. 15).

$$\text{(15)}$$
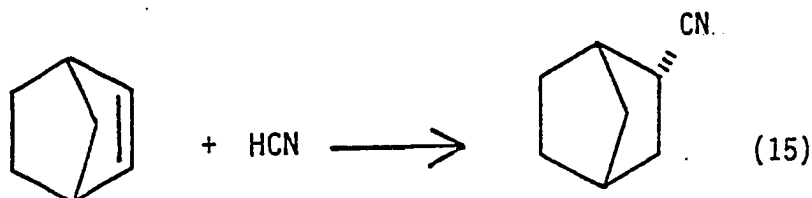
There are even more examples of hydrocyanation catalysts which contain phosphite ligands. In particular, complexes such as $CoH(P(OPh)_3)_4$ (50), $Ni(P(OR)_3)_4$ (51), $Pd(P(OR)_3)_4$ (52) and $Mo(P(OPh)_3)_3(CO)_3/TiCl_3$ (53) have been shown to be effective hydrocyanation catalysts.

The mechanism of hydrocyanation has yet to be totally elucidated but the results of experiments seem to imply the following mechanism (47):

$$M + HCN \rightarrow H-M-CN \qquad (16)$$

$$H-M-CN + olefin \rightarrow H-M(\pi-olefin)(CN) \qquad (17)$$

$$H-M(\pi-olefin)(CN) \rightarrow \sigma-alkyl-M-CN \qquad (18)$$

$$\sigma-alkyl-M-CN \rightarrow alkyl-CN + M \qquad (19)$$
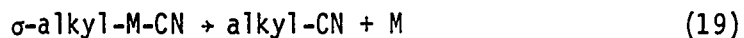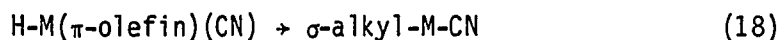
The last step in the mechanism has been a source of dispute. Kwiatek and co-workers (54,55) have proposed, based upon work with the formation of alkyl nitriles from alkylpentacyanocobaltate(III), that equation 19 should be rewritten:

$$\sigma-alkyl-M-CN + HCN \rightarrow alkyl-CN + H-M-CN \qquad (20)$$
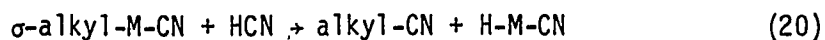
This step is believed to occur via protonation of the coordinated cyanide ligand to form a coordinated hydrogen isocyanide. The isocyanide group then inserts into the metal alkyl bond and then decomposes to form an alkyl nitrile and a protonated metal species (Scheme 3).

$$\sigma-alkyl-M-CN + HCN \rightarrow \sigma-alkyl-M(HNC)CN$$

$$\Downarrow NH$$

$$alkyl-CN + H-M-CN \leftarrow \sigma-alkyl-C-M-CN$$
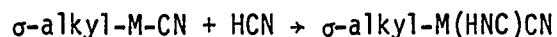
Scheme 3. Decomposition of σ-bound metal alkyl cyanide species to form alkyl nitriles (47,53)

The reason for the use of phosphite ligands rather than phosphines in these catalysts may be due in part to the increased π-acidity of the phosphite which causes the phosphite to impair the extent to which CN⁻ complexes to the metal atom. Other studies have shown that these metal

complexes are eventually inactivated as catalysts due to formation of

metal cyanide compounds such as $Ni(CN)_2$ (47) and $Co(CN)_6^{-3}$ (49). The

decomposition is also inhibited by adding excess ligand which again

impedes the formation of these compounds. It has also been reported

(56,57) that Lewis acids such as $ZnCl_2$ act as efficient cocatalysts in

hydrocyanation. Though the mechanism of its activity is not known, it is

believed that the $ZnCl_2$ in the presence of HCN promotes formation of the

catalytically active species $[HNiL_n]^+[ZnCl_2CN]^-$.

Gultneh (38) has carried out a study of the use of the previously

mentioned NiL_4 complexes as hydrocyanation catalysts. The trend observed

for increased amounts of hydrocyanation of olefins such as allylbenzene,

norbornene, norbornadiene, cyclopentene and cyclooctene with various

monocyclic ligands was :
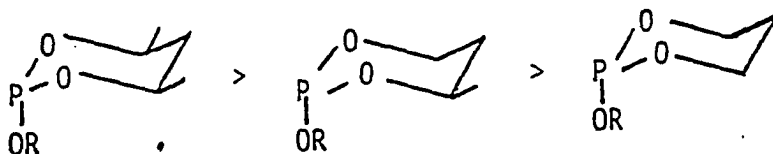
In the case of the 4-methyl and 4,6-dimethyl-1,3,2-dioxa-

phosphorinanes it was observed that by increasing the size of the

exocyclic group from methyl to isopropyl, there was an increase in

catalytic activities of the NiL_4 complexes. The extent of catalysis was

found to decrease when larger groups such as menthyl or bornyl were

placed in the exocyclic positions on the phosphorinane ring. However,

the rates of catalysis still proceeded moderately. This was not the case

in isomerization of 3-butenenitrile wherein such large groups completely

deactivated the complex. Attempts to form catalytically active complexes for the hydrocyanation of olefins with bicyclic and 5-membered ring cyclic phosphite ligands proved to be unsuccessful. This is probably due in part to the reduced overall basicity of these ligands which in turn reduced the basicity of the NiL_4 complexes. Since HCN is itself such a weak acid, the degree to which the nickel atom is protonated is further reduced. The combination of these effects probably led to the inactivity of these complexes.

Previous work has shown that the more active catalyst systems for the hydrocyanation of olefins are those which contain Lewis acids (48). Gultneh (38) found $ZnCl_2$ to be the most active cocatalyst. Attempts to use $AlCl_3$ as a cocatalyst in the hydrocyanation of norbornene showed that the $AlCl_3/NiL_4$ catalyst mixture produced half the number of catalytic cycles as did the $ZnCl_2/NiL_4$ mixture. In attempts to hydrocyanate allylbenzene, the $AlCl_3/NiL_4$ mixture proved be to completely inactive, while the $ZnCl_2/NiL_4$ showed some activity. The failure to hydrocyanate any of the allylbenzene by $NiL_4/AlCl_3$ was in part due to the complete and facile isomerization of the allyl benzene to the more stable conjugated product, 1-phenylpropene. This isomerization occurred before any appreciable amount of hydrocyanation could take place.

As stated previously, the degree of isomerization of 3-butenenitrile was reduced upon adding excess ligand to the catalyst mixture. During the hydrocyanation of olefins, it was found that in many cases the rate of catalysis increased when excess ligand was added. However, it was also observed that the optimum amount of excess ligand added depended

entirely on the ligand used. The optimum ratio of L/NiL_4 varied from 3 for $Ni(P(OEt)_3)_4$ to 18 for $Ni(\underline{8})_4$. The reason for adding excess ligand is to prevent complexation of more than one molecule of HCN to the nickel atom as suggested by the mechanism (Eqs. 21-26) of Gultneh (38) for the deactivation of the NiL_4 catalyst.

$$HCN + Zn^{+2} \longrightarrow ZnCN^+ + H^+ \tag{21}$$

$$NiL_4 + H^+ \longrightarrow HNiL_4^+ \tag{22}$$

$$HNiL_4^+ \longrightarrow HNiL_3^+ + L \tag{23}$$

$$HNiL_3^+ \longrightarrow HNiL_2^+ + L \tag{24}$$

$$HNiL_2^+ + HCN \longrightarrow HNiL_2CN + H^+ \tag{25}$$

$$HNiL_2CN + HCN \longrightarrow NiL_2(CN)_2 + H_2 \tag{26}$$
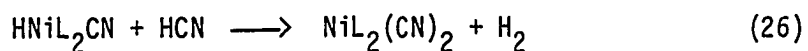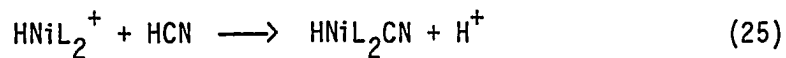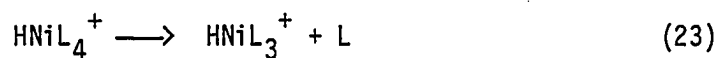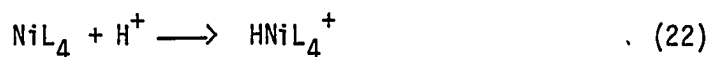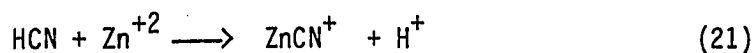
Formation of complexes such as $NiL_2(CN)_2$ would force the catalysis to stop due to the irreversible oxidation of the NiL_4 complexes to these Ni(II) species.

Unanswered questions in Gultneh's work

Though quite extensive, Yilma Gultneh's work left some unanswered questions:

1. Tolman had been very explicit in proving that steric factors were extremely important in determining the extent of dissociation in NiL_4 complexes. However, it would seem reasonable that electronic effects should have some role in the catalytic properties of a given NiL_4 complex. The question was raised if it would be possible to isolate this electronic effect by selectively comparing the catalytic activity of some NiL_4 complexes containing ligands that were heretofore untried. Until now only complexes which contained ligands that had alkoxy exocyclic groups had been tried. We were interested in how the replacement of an alkoxy group by an amine group in the exocyclic position of the ligand would change the activity of the resulting complex. This was of special interest since the electronic properties of these types of ligands have been found to be markedly different from those with alkoxy exocyclic groups (58).

2. In explaining the catalytic properties of the NiL_4 ($ZnCl_2$ or $AlCl_3$) system for the isomerization of olefins, Gultneh (38) proposed that the catalytically active intermediate was a dissociated $[NiL_4ZnCl^+]Cl^-$ complex or an $NiL_4:AlCl_3$ adduct. However, the evidence for the existence of these intermediates was tenuous at best. It was necessary to prove concretely the existence of these intermediates or else develop an alternative mechanism which could better explain the results that had been obtained.

3. Mosbo (58) had shown that 1,3,2-dioxaphosphorinanes existed as two different conformational isomers, A and B.
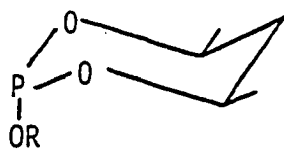
A
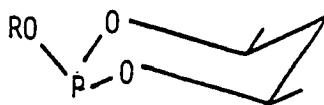
B

It was shown that when the exocyclic group was an alkoxy group, conformation A was the more thermodynamically stable isomer. Isomer B was considered to be the thermodynamically more unstable isomer since the lone-pair on phosphorus was repelled by two lone-pair p orbitals on each of the two cyclic oxygens. A consequence of this isomerism is that the basicity of these isomers are different. Previous work has shown that isomer B is more basic than isomer A (59). This increase in basicity has been ascribed to lone pair interactions which raises the energy of the phosphorus lone pair thus making it more polarizable. Gultneh (38) contends that large exocyclic groups on these 1,3,2-dioxaphosphorinanes are forced to adopt an equatorial position, with respect to the ring, due to steric interactions with the other ligands contained in the complex. This would then change the basicity of the ligand which could then influence the catalytic activity of the complex. In order to prove or disprove this contention, we deemed it worthwhile to attempt an x-ray structural analysis of a NiL_4 complex which contained a ligand with a large exocyclic group. This was done in order to determine if the ligand was forced to adopt the more basic conformation due to steric interactions.

An x-ray structural analysis of one of these complexes would also be helpful in determining if there are indeed steric interactions between

the 4,6 methyl groups on adjacent ligands, which would promote ligand dissociation.

4. Gultneh has shown that there is a 20 fold increase in the catalytic activity of $Ni(\underline{9})_4$ versus its acyclic analogue, $Ni(P(O-\underline{i}-Pr)_3)_4$. In order to investigate the effect of geometrical constraint on the P-O-C angles in the cyclic 4,6-dimethyl phosphorinanes and how that effect influences the catalytic properties of a NiL_4 complex, it was thought useful to prepare the phosphinite analogues $\underline{27}$ and $\underline{28}$. As can be seen in Table 4, there is a marked decrease in the difference in catalytic activity of the NiL_4 complexes of the phosphinite ligands versus the phosphite ligands. It was suggested (38) that there is only a small difference in the steric requirements of $\underline{9}$ and $P(O-\underline{i}-Pr)_3$. Therefore, it was thought that the differences in the catalytic activities of the complexes could be attributed to small differences in the electronic properties of the ligands in going from $P(O-\underline{i}-Pr)_3$ to $\underline{9}$.

In describing the properties of $\underline{27}$, Gultneh (38) gives no information about the distribution of conformational isomers. It is known (60) that analogous phosphorinanes do show a conformational equilibrium between conformers (Eq. 27).

(27)
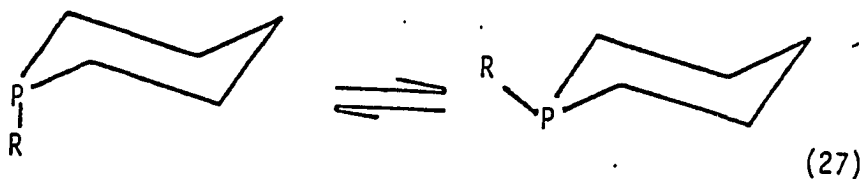
Table 4. Rates of isomerization of 3-butenenitrile by NiL_4/F_3CCOOH systems in benzene at $25°^a$ (38)

L	Cycles over 30 min (± 2)	cis/trans (2-butenenitriles) (± 0.1)
25	32	1.0
28	36	1.1
$P(O-\underline{i}-Pr)_3$	35	1.3
9	740	1.6

$^a Ni/H^+/$3-butenenitrile = 1/10/124

The equilibrium position is determined in part by the steric bulk of the exocyclic R group. Quin and Featherman (60) have shown that when R = CH_3, the equatorial conformation is preferred by only a small margin ($k_{e/a}=2.03$). Therefore, in the case of 27 and 28 it should be reasonable to assume that a similar isomeric distribution between equatorial and axial isopropoxy groups should exist. Since the literature provided no information on the conformational distribution of these cyclic phosphinites, it was thought to be important to determine this first and then attempt to separate 27 from 28. Once this separation was completed, it would be possible to prepare NiL_4 complexes of both isomers and investigate any differences in their catalytic activities. In fact, by using a mixture of isomers it would be possible to prepare up to five different complexes of the type $Ni(27)_{4-n}(28)_n$ where n = 0,1,2,3,4. Since separation of these complexes would be difficult, there would be no

way of knowing if either ligand caused the complex to be more active than the other.

5. The use of optically active ligands in transition metal catalysts used for asymmetric synthesis has become very important (61,62). It was found that $Ni((-)-\underline{7})_4$ acted as catalyst for the asymmetric isomerization of prochiral olefins (Eq. 28).

$$CH_3CH_2(CH_3)C=CH_2CH_2CN \xrightarrow[\substack{F_3CCO_2H/C_6H_6 \\ 25\,^0C}]{Ni((-)-\underline{7})_4} CH_3CH_2(CH_3)\overset{*}{C}HCH=CHCN \quad (28)$$
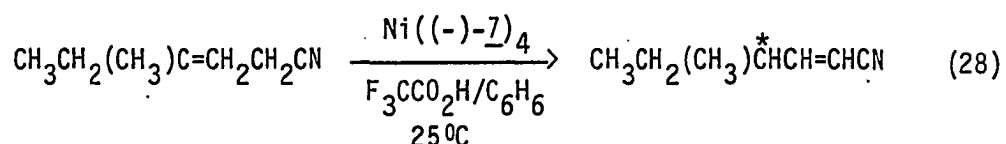
By the use of chiral shift reagents, it was determined that a 52% enantiomeric excess for (Eq. 28) had been obtained. It was thought that by using an optically active ligand which contained a methyl group at the equatorial 4,6 positions, a higher degree of conversion and enantiomeric excess might be obtained. The use of $Ni(\underline{36})_4$ as an asymmetric isomerization catalyst in equation 28 will be detailed herein.

6. The use of NiL_4 complexes (where L = 2-alkoxy-1,3,2-dioxaphosphorinane) as efficient hydrocyanation catalysts are now well documented (38). However, the use of these complexes in hydrocyanating 1,3-butadiene to form adiponitrile had yet to be explored. Due to its industrial applications, it was of interest to see if our best hydrocyanation catalysts, $Ni(\underline{8})_4$ and $Ni(\underline{9})_4$ could assist in the production of adiponitrile from 1,3-butadiene.

Heterogenized homogeneous catalysts

The use of catalysts in chemical reactions has become one of the most important areas of chemical research (63). When discussing this

area, one must differentiate between two main classes; namely,

heterogeneous and homogeneous catalysis. Heterogeneous catalysis implies

that the catalytic reaction takes place at the interface of two or more

phases. For example, in the catalytic hydrogenation of an olefin by a

metal, studies have shown that the actual reaction takes place at the

interface of the gas and solid phases (63). Homogeneous catalysis

usually implies that the reaction occurs in the same phase, as is the

case when the catalyst and reactants are dissolved in a solvent. As can

be seen in Table 5, the advantages and disadvantages of both types of

catalysis are numerous. In recent years, many reviews have been

published which detail previous attempts to prepare heterogenized

homogeneous catalysts in which a transition metal complex, which is known

Table 5. Relative advantages and disadvantages of different types of.
catalysts

Type of catalysis	Advantages	Disadvantages
Heterogeneous	1. ease of separation 2. high mechanical strength 3. high activity 4. use in packed and fluidized bed reactors	1. lack of knowledge of actual active sites 2. limited access to catalyst's active site 3. High temperatures and pressures needed
Homogeneous	1. well documented mechanistic information available 2. mild operating conditions 3. electronic and steric properties of ligands can be changed to improve catalysis	1. difficult to separate catalyst from reaction mixture 2. catalysts tend to be more sensitive to O_2, H_2O and temperature

to act as a homogeneous catalyst, is bound to a solid support

(64,65,66). These hybrid catalysts have been shown to possess properties

which incorporate the best features of each class of catalyst, while at

the same time reducing some of the disadvantages of both. In particular,

it has been found that these hybrid catalysts allow for easy separation

of the catalyst from a reaction mixture, in some cases resulting in a

reduction in the loss of valuable precious metal catalyst. At the same

time, these catalysts are often more durable than their homogeneous

analogues, allowing for in some cases several recycles of the supported

catalysts (66).

Two basic types of solid supports have been used to anchor

homogeneous catalysts. The first type includes organic polymer supports,

usually consisting of a polystyrene divinyl benzene resin which is

functionalized with phosphine, cyclopentadiene, bipyridyl, or benzene

ligands. Equation 29 illustrates a common technique used to prepare

these types of functionalized supports.

$$-(CH_2CH)_{\overline{n}} \quad + \quad Cl_2 \longrightarrow -(CH_2CH)_{\overline{n}} \quad + \quad LiPPh_2 \longrightarrow -(CH_2CH)_{\overline{n}} \quad (29)$$
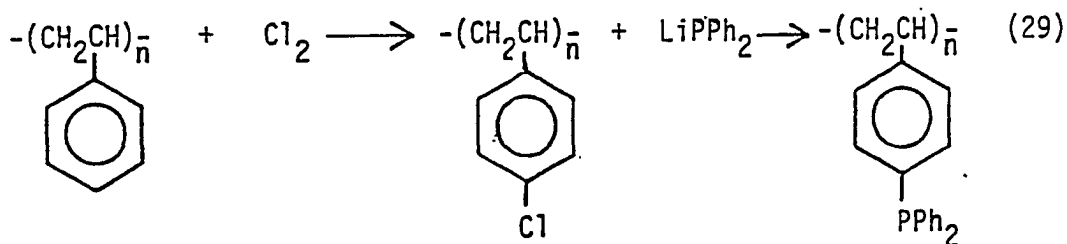
The metal complex is then anchored on the support by exchanging one

of its ligands with a -PPh$_2$ group. Grubbs and co-workers have used this

technique to heterogenize Rh(PPh$_3$)$_3$Cl (67). This type of support has

also been used to anchor $H_4Rh_4(CO)_{12}$(68), $Ni(CO)_2(PPh_3)_2$ (69) and $W(CO)_6$ (70), to cite just a few of many examples.

Polystyrene-divinylbenzene co-polymers have also been used to directly bind metal carbonyls such as $Cr(CO)_6$ (Eq. 30).

$$[-(CH_2CH_2)-(CH_2CH)-]_n + Cr(CO)_6 \longrightarrow [-(CH_2CH_2)-(CH_2CH)-]_n + 3CO \quad (30)$$
$$\underset{\bigcirc}{} \qquad \underset{\underset{Cr(CO)_3}{\bigcirc}}{}$$
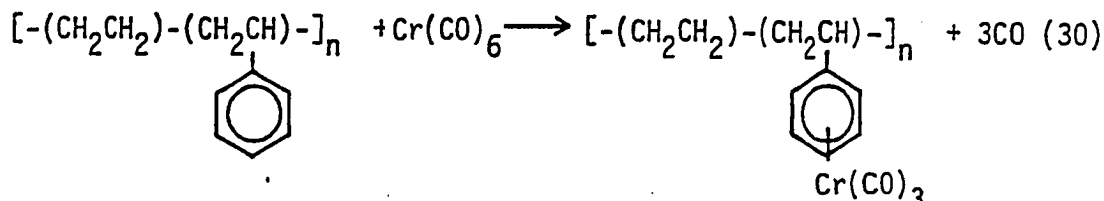
Complexation has been accomplished by subjecting a mixture of polystyrene resin, metal carbonyl, and solvent, to conditions such as heat (71), high pressure (72), and ultra violet radiation (73).

Pittman (73) and Masuda and Stille (74) have been successful in forming heterogeneous catalysts by polymerizing soluble metal complexes which contain ligands having functionalities such as olefins. Stille has also been successful in producing polymers which contain optically active ligating groups that can bond to certain metal complexes. These polymers have been used successfully as catalysts for asymmetric synthesis (75).

One of the advantages of these catalysts is their ability to stabilize complexes which are not stable in solution. Gubtosa and Brintzinger (76) have shown that a $Fe(CO)_2H$ unit can be stabilized on cyclopentadienyl functionalized polystyrene (Eq. 31). The resulting

$$P -CH_2-C_5H_4 + Fe_2(CO)_9 \longrightarrow P -CH_2-\eta_5-C_5H_4-Fe(CO)_2H \quad (31)$$
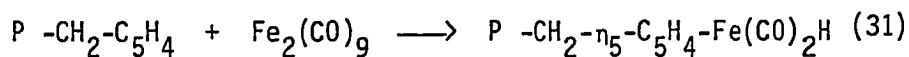
$$P = \text{polymer backbone}$$

anchored complex has been found to be indefinitely stable, whereas in solution, $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ quickly dimerizes with subsequent loss of hydrogen to form $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (76). They have also shown that a $Co(CO)_2$ unit can be supported similarly, by reaction of the cyclopentadienyl-derivatized resin and $Co_2(CO)_8$. Subsequent irradiation of the polymer causes a loss of CO to form a bis-arene complexed cobalt resin (Eq. 32):

$$P\text{-}CH_2\text{-}(\eta^5\text{-}C_5H_4) - Co(CO)_2 \longrightarrow$$

P = polymer

$$CH_2\text{-}(\eta^5\text{-}C_5H_4)\text{-}Co$$

n = 1 or 2

(32)
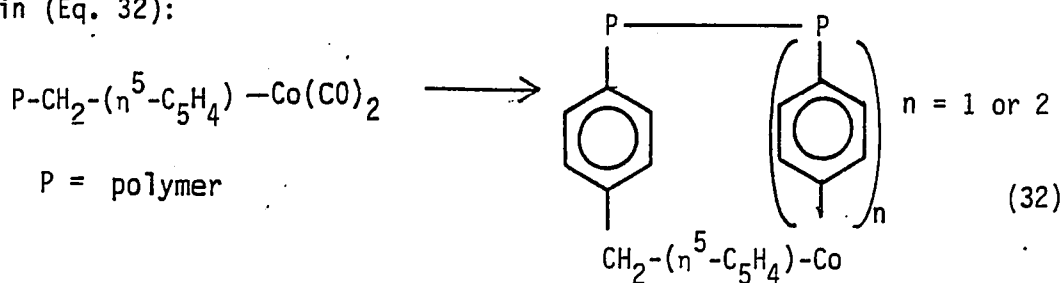
Whereas, complexes of the type $\eta^5\text{-}(C_5H_5)_2Co_2(CO)_2$, $\eta^5\text{-}(C_5H_5)_2Co_2(CO)_3$, and $\eta^5\text{-}(C_5H_5)Co_3(CO)_3$ were observed to form upon irradiation of solutions containing the homogeneous analogue $\eta^5\text{-}(C_5H_5)Co(CO)_2$ (77). Thus, these types of polymers can be used to stabilize metal moieties that would be otherwise unstable in solution. This provides the possibility of producing new types of catalysts that could not be obtained by any other means.

One of the main disadvantages in the use of these catalysts is that the rates of catalysis are often lower than those observed for the analogous homogeneous catalysts. Pittman and co-workers (78) have shown that $Cr(CO)_6$ can be supported on polystyrene and that methyl sorbate can be hydrogenated with such a catalyst (Eq. 33). At 160°, the selectivity

$$\text{CH}_3\text{CH=CH-CH=CH-CO}_2\text{Me} \xrightarrow[\text{500 psi}]{\text{H}_2 \;\; 140\text{-}150^\circ} \quad \text{CO}_2\text{Me} \;+\; \text{CO}_2\text{Me} \;+\; \text{CO}_2\text{Me} \qquad (33)$$
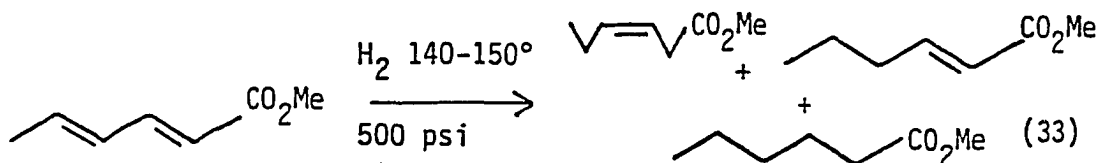
for (Z)-methyl-3-hexenoate is 96-98% for 100% conversion in 24 hrs, while at 140° the selectivity is 99%. . Cais and co-workers (79), however, have reported 95% conversion for the hydrogenation of methyl sorbate using $Cr(CO)_6$ under the same conditions in only 7 hrs. Pittman and co-workers (80) have also reported a retardation in the rate of hydroformylation of 1-pentene using $Rh(PPh_3)_3H(CO)$ bound to polystyrene. It was found that at 40° and 250 psig, the polymer-bound $Rh(PPh_3)_3H(CO)$ was 0.22 times as active as the homogeneous catalyst. While at 60° and 800 psig the ratio of activity increased to 1.08. It has also been found (80) that the rate at which anchored $Ni(PPh_3)_2(CO)_2$ cyclooligomerizes butene at 112°C is equal to the rate at which the analogous homogeneous catalyst operates at 90°.

These reductions in catalysis rates have been ascribed to diffusional limitations created by the resin for migration of the substrate into the active site. The rate of diffusion is dependent upon the pore size within the resin which in turn is dependent upon the amount by which the resin swells upon being placed in a solvent. However, the rate of diffusion of the substrate into the resin is also dependent upon

polarity gradients which develop between the bulk solvent and active sites within the resin. Therefore, by carefully choosing the degree of crosslinking in the resin (the more crosslinking the smaller the pore size), and the type of solvent system used, one is able to control the selectivity of the catalyst toward a particular reaction or substrate (66).

In order to circumvent the problems of swelling of organic polymers as supports for transition metal catalysts, many workers have tried anchoring these complexes to inorganic supports such as silica, alumina, zeolites or derivatized silica and alumina due to their increased rigidity (66). Metal carbonyls such as $Cr(CO)_6$ (81) and $Ru_3(CO)_{12}$ (82) have been supported on Al_2O_3 and SiO_2, respectively, and shown to function as hydrogenation catalysts. In these types of catalysts, the adherence of the complex to the support is maintained by strong carbonyl-surface interactions (81,82).

Attachments of metal complexes can also be accomplished by placing ligands on the metal which contain functional groups which further react and bind to OH groups on the surface on the support. Recently, Wrighton and Liu (83) have shown that $Ru_3(CO)_{12}$ can be supported on silica in two ways (Scheme 4).

Wrighton has shown that these supported compounds can act as isomerization or hydrosilylation catalysts under the proper conditions. Capka and Hetflejs (84) have also succeeded in attaching groups as $-PPh_2$, $-SiCH_2CH_2PPh_2$ and $-Si(CH_3)_2(CH_2)_3CN$ to inorganic materials such as γ-alumina, zeolites, and glass in order to prepare similar types of catalysts.

$$Ru_3(CO)_{12} \quad + \quad 3 \ (EtO)_3SiCH_2CH_2PPh_2$$

$$\downarrow$$

$$[(EtO)_3SiCH_2CH_2PPh_2]_3Ru_3(CO)_9$$

$h\nu$ ↙ $-CO$ ↘ $[Si-OH]_n$

$$[(EtO)_3SiCH_2CH_2PPh_2]Ru(CO)_4$$

$$\left[\begin{array}{c} -Si\diagdown_O \\ -Si-O \\ -Si\diagup^O \end{array} \right. -SiCH_2CH_2PPh_2]_3Ru_3(CO)_9 \ + \ 9 \ EtOH$$

$$\downarrow \ [Si-OH]_n$$

$$\left[\begin{array}{c} -Si\diagdown_O \\ -Si-O \\ -Si\diagup^O \end{array} \right. -SiCH_2CH_2PPh_2]Ru(CO)_4 \ + \ 3 \ EtOH$$

$[Si-OH]_n$ = silica gel

$$\left[\begin{array}{c} -Si \\ -Si \\ -Si \end{array} \right.$$ = silica gel backbone
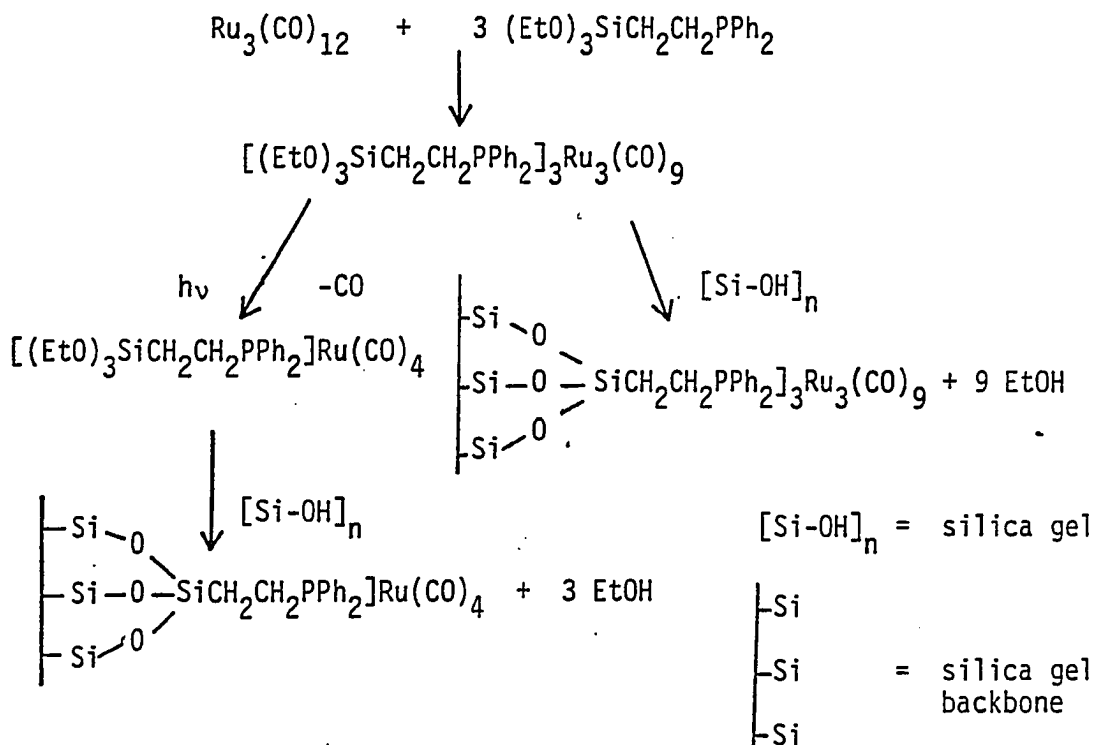
Scheme 4. Attachment of metal carbonyl compounds to derivatized silica gel (83)

Based upon our knowledge of the NiL_4/H^+ catalyst system we began a study to find ways to heterogenize these homogeneous catalysts. We were successful in designing a new type of polymeric complex, which also functions as an isomerization catalyst. The polymer produced was of the type:

$$\begin{array}{ccc} L & L & L \\ -(P-P)-M-(P-P)-M-(P-P)-M-(P-P)- \\ L & L & L \end{array}$$
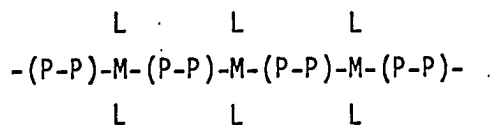
where M is a metal atom which is connected to other atoms by P-P, a diphosphorus nonchelating ligand. This ligand was designed to mimic as closely as possible the electronic and steric properties of the ligands contained within the homogeneous catalyst. The synthesis and properties of these types of catalysts will be described in this thesis.

We have also been able to heterogenize these NiL_4 catalysts by supporting them on cation exchange resins. In our case, macroreticular resins were used to ensure diffusion of the NiL_4 complex into the bead. The preparation, activities, and formulations of these catalysts will be discussed.

EXPERIMENTAL PROCEDURES

All solvents were reagent grade or better. The following solvents were further purified by distillation from drying agents: diethyl ether (K metal); tetrahydrofuran, toluene and benzene (Na), methanol and pyridine (CaH_2); acetonitrile (P_4O_{10}); acetone (molecular sieves).

These chemicals were obtained from the following suppliers and were used as received: pentaerythritol, 2,2-dimethyl propanediol, 1,3-butanediol, 1,1,1-trishydroxymethylethane, triphenyl phosphine, 1,3,5-trihydroxy benzene, 1,2,4-butanetriol, diethylaluminum chloride (1 M solution in hexane), and triethylaluminum were obtained from Aldrich Chemical Co. Nickel carbonyl, nickel tetraflouroboratehexahydrate, and the macroreticular resins were obtained from Alfa-Ventron, Inc. 1,4-Dibromo-benzene and 4,4-dibromobiphenyl were obtained from Eastman Kodak. 3-Methyl-1-pentene-3-ol was obtained from Fluka A.G. Rhodium trichloride trihydrate was obtained from Engelhard Minerals.

Proton NMR spectra were obtained on either a Varian EM-360 or a Perkin-Elmer/Hitachi RB-20 NMR spectrometer. Me_4Si was used as an internal standard in all cases. ^{31}P NMR spectra were obtained on samples contained in 10 mm tubes on either a Bruker HX-90 spectrometer operating at 36.4 MHz or a Bruker WM-300 spectrometer operating at 121.5 MHz. In both cases, the spectrometers operated in the FT mode with an internal ^2H lock provided by ^2H atoms contained in the solvent. The external standard was 85% H_3PO_4 sealed in a 1 mm capillary tube held coaxially in the sample tube by a Teflon vortex plug. All downfield shifts of H_3PO_4

were considered positive. ^{13}C NMR spectra were obtained on a JEOL FX 90Q spectrometer operating at 22.5 MHz in the FT mode. An internal ^2H lock was provided by the ^2H atoms contained in the solvent. The carbon atoms of the solvent ($CDCl_3$) acted as a reference. ^{27}Al NMR spectra were obtained on a Bruker WM-300 spectrometer operating in the FT mode at a frequency of 78.21 MHz. A sealed 1 mm diameter capillary tube containing a 1 M solution of $AlCl_3$ dissolved in D_2O acted as both an external reference and an external ^2H lock. ^{11}B NMR spectra were also obtained on a Bruker WM-300 NMR spectrometer operating at 96.3 MHz in the FT mode. An internal ^2H lock was maintained by the ^2H atoms contained in the solvent. All spectra were referenced to $Et_2O:BF_3$.

Mass spectra were obtained on a Finnegan 4000 or an AE1 MS902 mass spectrometer. UV-visible spectra were obtained on a Perkin-Elmer 320 UV-visible spectrometer. Quartz cells (1 cm x 1 cm x 10 cm) were used to obtain spectra of compounds contained in organic solvents. Fisher brand polystyrene (10 mm x 10 mm x 45 mm) cuvets were used to obtain spectra of compounds contained in aqueous solutions. Infrared spectra were obtained using a Perkin-Elmer 281 double beam infrared spectrometer. In all cases, the spectra were obtained on liquid solutions contained in matched NaCl solution in cells.

Analysis of catalytic isomerization was performed on a Varian series 1700 gas chromatograph equipped with a thermal conductivity detector. Separations were carried out on a 8' x 0.25" copper column packed with 10% diisodecylphthalate on chromosorb P. The column and support were prepared by a previously described method (85,86). Analyses of mixtures

obtained in the catalytic hydrocyanation of 1,3-butadiene were carried out using a Varian model 3700 gas chromatograph equipped with a flame ionization detector, automatic peak integrator, and a glass capillary column containing SE-30 as a stationary phase.

All preparations of NiL_4 complexes were carried out under a nitrogen atmosphere. All manipulations involving these complexes were done using the appropriate Schlenk vessels or nitrogen-filled glove bags.

Experiments on the catalytic isomerization of 3-butenenitrile were carried out using the following procedure. The NiL_4 complex (0.10 mmole) was placed in a 25 ml nitrogen-flushed roundbottom flask, equipped with a stirring bar and rubber septum. The flask was then placed in a water bath maintained at 25°C ± 0.2°C. Benzene (5.0 ml) was added via a syringe through the septum into the flask. The flask and its contents were equilibrated for 30 min. in the cooling bath and timing began after addition of 0.88 g (12 mmole) of 3-butenenitrile and 1 ml of a 1.0 M solution of F_3CCO_2H in benzene. Periodically, 0.5 ml samples were removed from the solution for GC analysis. Calculations of yields of isomerized products were carried out by cutting out and weighing the peaks in the chromatogram. The yields were calculated based upon response factors which were determined independently for 3-butenenitrile, cis-2-butenenitrile, and trans-2-butenenitrile. The presence of cis and trans 2-butenenitrile in the mixture was initially confirmed by preparative gas chromatography and subsequent proton NMR analysis.

Catalytic hydrocyanations of olefins were carried out by the following procedure. HCN was prepared before each run by adding

approximately 10 mls of 18 M sulfuric acid to approximately 20 g of NaCN contained in a nitrogen-flushed 100 ml flask. The gaseous hydrogen cyanide produced was transferred via a cannula into a N_2 filled centrifuge tube which was stoppered with a rubber septum. The tube was chilled to -78°C in order to facilitate the collection of the HCN.

Attempts to hydrocyanate norbornene were then carried out using the method of Gultneh (38). Attempts to hydrocyanate 1,3-butadiene were carried out by the procedure of Drinkard and Lindsey (51). The NiL_4 complex (0.07 mmole) was placed in a nitrogen-flushed 3-necked 25 ml flask which had been fitted with a rubber septum. Xylene (4.0 mls) was then added to the flask via a syringe. In some experiments, the flask would also be charged with $ZnCl_2$ and excess ligand. The flask was then heated to 120° ± 0.5°C and allowed to equilibrate for 15 minutes. The 1,3-butadiene was bubbled slowly (10 ml/1 min.) into the centrifuge tube containing the liquid HCN held at 0°. The HCN/1,3-butadiene gas mixture was transferred from the tube into the flask via a cannula which was held below the level of the NiL_4/xylene solution. Upon addition of the equivalent of 1 liquid ml of HCN over the course of 2 hrs., the experiment was ended and samples were removed for capillary gas chromatographic analysis. The yields of adiponitrile and other products from the reaction were obtained by integration of the peaks contained in the chromatogram. The existence of adiponitrile in the mixture was confirmed by comparison of the chromatogram to a chromatogram of pure adiponitrile recorded under the same conditions.

The purity of a particular ligand or phosphorochloridite was determined by its boiling point and ^{31}P NMR spectrum. The purity of a NiL_4 compound was determined by its ^{31}P NMR spectrum exclusively. It was observed (38) that the different classes of compounds showed single peaks within a narrow range of chemical shifts (Table 5). In all cases, these compounds appeared as sharp singlets in the ^{31}P NMR spectrum. A particular compound was judged to be pure if it exhibited no other peaks in the ^{31}P NMR spectrum or if the area of the peak comprised 95% or greater of the total area of all peaks contained in the spectrum.

Preparations

KSeCN   This compound was prepared via the procedure of Waitkins and Shutt (87).

$Ni(CH_2=CHCN)_2$ This compound was first prepared by Schrauzer (88). However, the compound was prepared here by the following simplified procedure. $Ni(CO)_4$ (6.60 g, 38.6 mmole) and 60.0 ml of acrylonitrile was added to a nitrogen-flushed 250 ml 2-necked flask equipped with a condenser and nitrogen inlet. The mixture was refluxed under nitrogen for 2 hrs and then cooled to room temperature. The orange precipitate which formed was allowed to settle and the supernatant was removed via a cannula. The product was washed three times with 25 ml portions of dry, degassed ether and the resulting solid was dried under a stream of nitrogen gas. The material was used immediately without further purification.

Table 6. Ranges of chemical shift (rel. to H_3PO_4) for compounds discussed in this thesis.

Class of compound	^{31}P NMR chemical shift range (ppm)

R = Me or H in various combinations
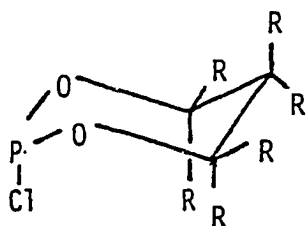
160-180
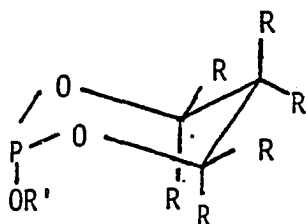
R = Me or H in various combinations

R' = Me, Et, $\underline{i}$-Pr, $\underline{sec}$-Bu, $\underline{t}$-Bu, or Ph

120-135

NiL_4

140-170

L = Phosphite

2-Chloro-1,3,2-dioxaphosphorinane (<u>1</u>)   This compound was prepared

via the method of Verkade and co-workers (89) with the following

adjustment. Triethyl amine was not employed; instead, the HCl produced

by the reaction of the diol and PCl_3 was removed by passing a slow stream

of nitrogen through the flask during the course of the reaction. The

compound was obtained in 62% yield after distillation (b$_4$ = 47-50°, lit.

b$_5$ = 36-38° (89); ^{31}P NMR (C$_6$D$_6$) 150.8, lit. 153.5 (89)).

2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (<u>2</u>)   This compound

was prepared in 59% yield from the reaction of 2,2-dimethyl-1,3,-

propanediol and PCl_3 via the same procedure used to prepare <u>1</u> (b$_{12}$ = 70°,

lit. b$_{12}$ = 70° (89); ^{31}P NMR (C$_6$D$_6$) 146.1, lit. 146.0 (89)).

2-β-Chloro-4-α-methyl-1,3,2-dioxaphosphorinane (<u>3</u>)   This compound

was prepared in 59% yield by the reaction of 1,3-butanediol and PCl_3 by

the procedure used for <u>1</u>. (b$_3$ = 59°, lit. b$_{0.5}$ = 30° (89); ^{31}P NMR (C$_6$D$_6$)

150.8).

2-β-Chloro-4,6-α,α-dimethyl-1,3,2-dioxaphosphorinane (<u>4</u>)   This

compound was prepared in 55% yield by the reaction of <u>meso</u>-2,4-

pentanediol and PCl_3 using the procedure of <u>1</u>. (b$_{13}$ = 72°, lit. B$_{12}$ = 71-

73°; ^{31}P NMR (C$_6$D$_6$) 148.0).

2-Methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane (<u>5</u>)   This

compound was prepared via the method of Gultneh (38).

2-sec-Butyl-5,5-dimethyl-1,3,2-dioxaphosphorinane (<u>6</u>)   This

compound was prepared via the method of Gultneh (38).

2-β-Methoxy-4-α-methyl-1,3,2-dioxaphosphorinane (7)   This

compound was prepared via the method of Gultneh (38).

2-β-Methoxy-4,6-α,α-dimethyl-1,3,2-dioxaphosphorinane (8)   This

compound was prepared via the method of Gultneh (38).

2-β-Phenoxy-4,6-α,α-dimethyl-1,3,2-dioxaphosphorinane (10)   To a

solution of 10.0 g (0.0595 mol) of 4 in 50 ml of dry ether at 0°C was

added a solution of 5.61 g (.0597 mole) of phenol and 6.00 g (0.0594

mole) triethyl amine in 25 ml of ether. The addition was carried out

dropwise over a period of 0.5 hour. The mixture was stirred for an

additional hour and then filtered. The ether was removed on a rotary

evaporator. The product was distilled in 76% yield. (b$_5$ = 115-120°; ^{31}P

NMR (C$_6$D$_6$) 119.2; ^{1}H NMR (CDCl$_3$) 7.15m 5H C$_6$H$_5$, 4.65m 2H CH, 1.6m 2H CH$_2$,

1.2d (J$_{H-H}$ = 6 Hz) 6H CH$_3$).

4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (11)   This

compound was prepared via the method of Verkade and co-workers (90).

2,7,8-Trioxa-1-phosphabicyclo[3.2.1]octane (12)   This compound

was prepared via a literature method (91).

2,8,9-Trioxa-1-phosphaadamantane (13)   This compound was prepared

via the method of Hutteman (92).

2-Chloro-1,3,2-dioxaphospholane (14)   This compound was prepared

via a literature method (93).

2-Isoproproxy-1,3,2-dioxaphospholane (15)   This compound was

prepared via a literature method (93).

2-R-1,3,2-dioxaphosphorinane (R = diethylamino (16), R = piperdino

(17)) These compounds were prepared by reacting 0.10 moles of $\underline{1}$ and

0.20 moles of the corresponding amine in 100 ml of ether via a method

similar to one described by Denney and Chang (94). Compounds $\underline{16}$ and $\underline{17}$

were obtained in 65 and 81% yield, respectively, upon distillation ($\underline{16}$:

b_{15} = 78-84°; ^{31}P NMR (C_6D_6) 146.6; ($\underline{17}$): b_{10} = 90-95, ^{31}P NMR (C_6D_6)

141.3).

2-α-R-4-α- methyl-1,3,2-phosphorinane (R = Diethylamino (18), R =

piperdino (19)) These compounds were prepared via the method of

Denney and Chang (94).

2-R-5,5-dimethyl-1,3,2-dioxaphosphorinane (R = dimethylamino (20)

R = piperdino (21)) These compounds were prepared by reacting 0.1

mole of $\underline{2}$ and 0.2 mole of the corresponding amine in 150 ml of ether at

0°C. The amine hydrochloride was filtered and washed with ether. The

ether was removed on a rotary evaporator and the resulting solid was

sublimed. Compound $\underline{20}$ was sublimed at 27°/0.05 Torr resulting in a yield

of 88%. Compound $\underline{21}$ was sublimed at 60°/0.25 Torr resulting in a yield

of 71% (($\underline{20}$): m = 28-29°, ^{31}P NMR (C_6D_6) 144.0; ($\underline{21}$): m = 65°-67°, ^{31}P

NMR (C_6D_6) 142.3).

Ni(P(OMe)$_3$)$_4$ This compound was prepared by a literature

procedure (95).

Ni(P(OEt)$_4$)$_4$ This compound was prepared via the method of Vinal

and Reynolds (96).

Ni(P(OPh)$_3$)$_4$ This compound was prepared by a literature

procedure (97).

NiL$_4$(L = $\underline{5}$, $\underline{6}$, $\underline{7}$, $\underline{8}$, $\underline{9}$, $\underline{10}$, $\underline{12}$, $\underline{15}$)   These compounds were

prepared via the procedure of Gultneh (38).

Ni($\underline{13}$)$_4$ To a suspension of 0.25 g (0.0015 mole) of Ni(CH$_2$=CHCN)$_2$

in 10 ml of toluene was added 0.98 g (0.0061 mole) of $\underline{13}$ dissolved in 5

ml of toluene. A white solid precipitated after 30 min of stirring. The

solid was recrystallized from ethanol in 48% yield (m = decomp > 265°,

^{31}P NMR (C$_6$D$_6$) 153.0, lit. 153.0 (98)).

Ni($\underline{18}$)$_4$ To a suspension of 0.49 g (0.0029 mole) of Ni(CH$_2$=CHCN)$_2$

was added 2.1 g (0.012 mole) of $\underline{18}$ dissolved in 5 ml of toluene. The

mixture was stirred for 1 hr. and the toluene was removed under vacuum to

yield a yellowish-white solid. The solid was chromatographed on an

alumina column to yield a white powdery solid in 42% yield (^{31}P NMR

(C$_6$D$_6$) 163.6).

2-β-Phenoxy-4,6-α,α-dimethyl-2-α-seleno-1,3,2-dioxaphosphorinane

($\underline{22}$)   Neat $\underline{10}$ (2.00 g (0.00881 mole)) was added to a solution of 1.26

g (0.00881 mole) of KSeCN dissolved in 25.0 ml of dry acetonitrile and

the mixture was stirred for 2 hrs. The solution was filtered and the

acetonitrile was removed on a rotary evaporator. A white solid was

obtained in 94% yield (^{31}P NMR (CD$_3$CN) 57.4d $J_{31_{P}-77_{Se}}$ = 1024 Hz).

3,9-Dimethyl-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane

(23)   This compound was prepared by White (99). However, attempts

to repeat this preparation were unsuccessful. Therefore, the following

procedure was used. In a 50 ml flask equipped with a distillation

apparatus was placed 6.8 g (0.051 mole) of $C(CH_2OH)_4$ and 11.8 g (0.0952

mole) of $P(OMe)_3$. The flask was heated to 100°C and methanol slowly

began to distill off. Heating was maintained for approximately five

hours. At this point, not quite all the $C(CH_2OH)_4$ had dissolved in the

$P(OMe)_3$. The mixture was placed under vacuum in order to remove any

residual trimethyl phosphite and methanol. Sublimation of the crude

material at 95°/2 mm yielded the product in 30% yield (m = 122-125°, lit.

124-7° (99); ^{31}P NMR (C_6D_6) 126.1).

[Ni(23)(L')$_2$]$_n$ L' = $P(OMe)_3$, 5, 7   In 20 ml of dry acetonitrile

contained in a nitrogen-flushed 50 ml flask was dissolved 0.0010 moles of

the NiL'_4 complex and 0.25 g (0.0010 mole) of 23 dissolved in 5 ml of

acetonitrile was added to the flask via syringe. After 2 minutes of

stirring, a thick gelatinous precipitate formed in the flask. The

mixture was stirred for an additional 30 min., then filtered and

repeatedly washed with fresh acetonitrile to remove any unreacted NiL'_4,

23, or L'. The white solid obtained was dried for several hours under

vacuum. Attempts to dissolve this solid in various organic solvents

proved to be unsuccessful.

Reaction of [Ni(23)(P(OMe)$_3$)$_2$]$_n$ and O_3 A sample of

[Ni(23)(P(OMe)$_3$)$_2$]$_n$ (0.090 g, 0.00016 mole) was placed in a 100 ml flask

fitted with a medium fritted filter stick. Fifty ml of CH_2Cl_2 was added to the flask, which was then cooled to -78°C. Ozone produced from an ozone generator designed and built in the Chemistry Department at Iowa State University was bubbled through the flask for 2 hr resulting in the solution turning dark blue. The flask was warmed to room temperature and the blue color faded. The CH_2Cl_2 was removed by distillation at atmospheric pressure. ^{31}P NMR analysis of the remaining oil showed only two peaks at 2.2 and -0.63 ppm in the ratio of 0.9 to 1. ^{31}P NMR spectra of authentic samples of $(MeO)_3P=O$ and $(MeO)_2(O)P(OCH_2)_2C(CH_2O)_2P(O)OMe$ exhibited single peaks at 2.2 and -6.3 ppm, respectively.

Nickel analysis of $[Ni(\underline{23})(P(OMe)_3)_2]_n$ and $[Ni(\underline{23})(7)_2]_n$

A sample of the polymer weighing 0.1800 g was placed in a 25 ml Erlenmeyer flask. A mixture consisting of 2 ml 70% HNO_3 and 2 ml 72% $HClO_4$ was added to the flask. The mixture was then slowly heated in a silicon oil bath to 200°C. The solution was allowed to boil vigorously for 30 seconds and the flask was then removed from the oil bath and allowed to cool to approximately 130°C. To ensure that all of the polymer had been properly digested, the flask was again heated to 200°C for an additional 2.5 minutes. The resulting green solution was cooled to room temperature and a gravimetric nickel analysis was carried out as previously described by Skoog and West (100). Results of these analyses can be found in the results and discussion section of this chapter.

meso-2,4-Dimethyl-1,5-dibromopentane   This compound was prepared

via the method of Noller and Pannell (101) (Scheme 5), which was amended

$$CH_3CH(CO_2Et)_2 \quad + \quad Na^+OEt^- \quad \longrightarrow \quad CH_3C(CO_2Et)_2^-$$

meso + d,l

$(EtO_2C)_2$ CO$_2$Me

HCl
H$_2$O

HO$_2$C CO$_2$H

(CH$_3$CO)$_2$O

meso only

LAH

OH
OH

PBr$_3$

Br
Br
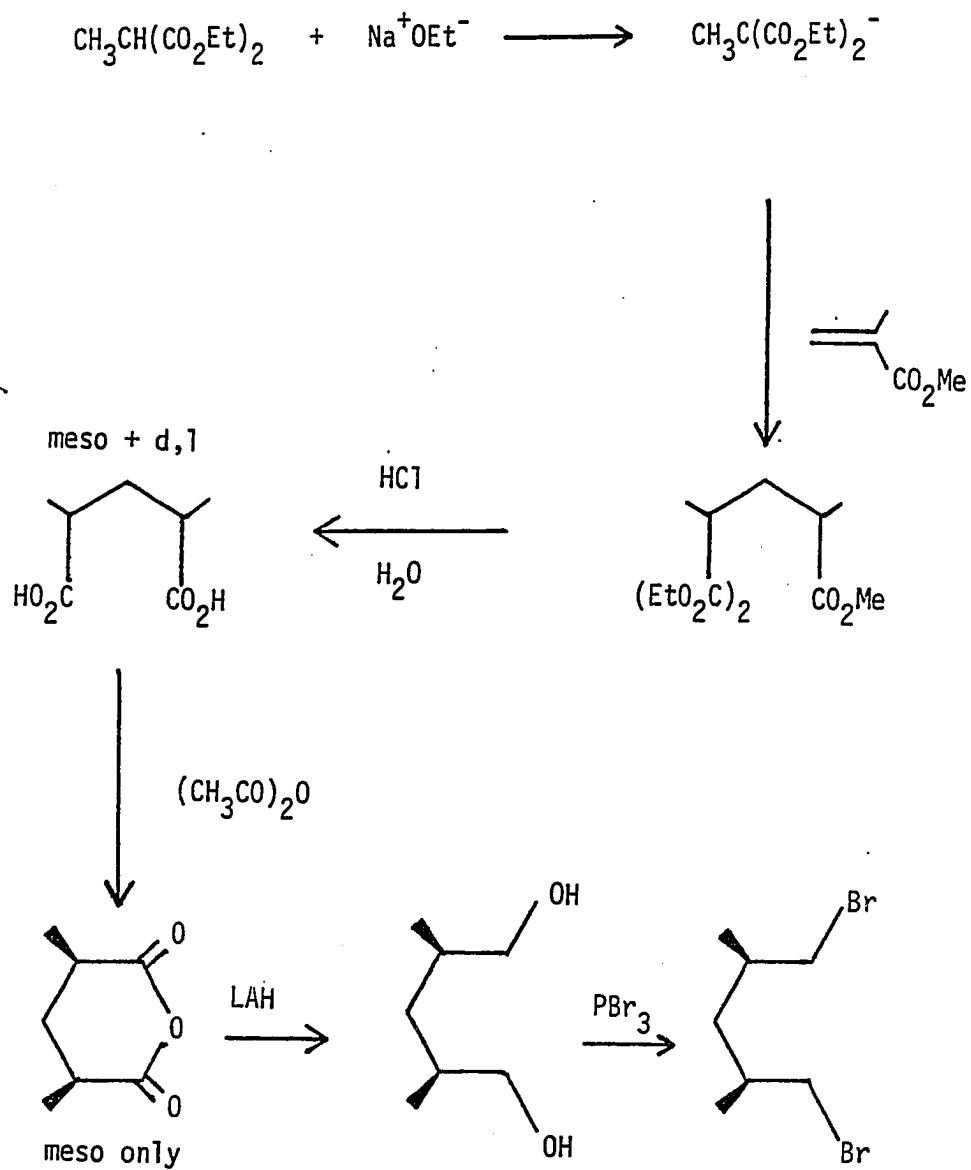
Scheme 5. The synthesis of meso-2,4-dimethyl-1,5-dibromo
pentane

as follows. The reaction conditions for the preparation of meso-
α,α-dimethyl gluturic acid were not changed. However, the work up
procedure used was the following. The resulting aqueous solution
containing the glutaric acid was vacuum distilled to remove the water.
The residual water was then removed by azeotropic distillation with
benzene (30 ml benzene/10 g solid). When all the water had been removed,
approximately 50% of the benzene was removed and a volume of heptane
equal to half the volume of the remaining benzene was added. The
resulting mixture was heated to redissolve any solid which had
precipitated from solution. The product was obtained by cooling the
solution at 5°C for 24-48 hr. The compound was obtained in 69.5% yield
as opposed to the literature yield of 74% (101) (m = 98°-104° lit. 101-
109° (101), ^{1}H NMR (CDCl$_3$) 11.5s 2H COOH, 2.6-2.2m 2H CH, 1.9-1.6m 2H CH,
1.2d (J_{H-H} = 10 Hz) 6H CH$_3$). For the meso-2,4-dimethyl-1,5-pentanediol
the reaction conditions were not changed. However, the product was
obtained in 83% yield (lit. 88.5%) (101) using the workup procedure of
Fieser and Fieser (102) (B$_2$ = 95-99°, lit. 97-99°; ^{1}H NMR (CDCl$_3$) 4.45d
J_{H-H} = 11 Hz 4H CH$_2$O, 3.3s 2H OH, 1.9-1.5m 4H CH$_2$ and CH, 1.95d J_{H-H} = 12
Hz 6H CH$_3$).

Dichloroisopropylphosphinite (24)   This compound was prepared by
the method of Gultneh (38).

Bis-(2-methyl-n-propyl)isopropylphosphinite (25)   In a 3-neck
1000 ml flask equipped with a dropping funnel and mechanical stirrer was
added 125 ml dry Et$_2$O and 3.2 g (0.13 mole) of Mg turnings. To the

solution was added 0.5 ml $BrCH_2CH_2Br$ and the mixture was stirred for 15

minutes. 2-Methyl-1-bromopropane (11.9 g, 0.0875 mole) in 50 ml of ether

was added over a period of one hour. After the completion of the

addition, the resulting solution was stirred for an additional 30 min.

The reaction mixture was then cooled to -78°C. A solution of 24 (7.0 g,

0.043 mole) and pyridine (14.0 g, 0.167 mole) in 25 ml of dry ether was

added drop-wise over 30 minutes. After stirring for an additional 30

minutes, the mixture was warmed to room temperature and stirred for 1.5

hours. After filtering in a nitrogen-filled glove bag, the ether was

removed from the filtrate via distillation at 30 Torr. The product was

obtained in 63% yield (^{31}P NMR (C_6D_6) 122.0; ^1H NMR ($CDCl_3$) 4.2-3.4m 1H

CH, 2.1-0.7m 24H CH_3, CH, and CH_3).

2-Isopropyl-2-phosphorinane (26)   This compound was prepared in

the same manner as 25, using 20.0 g (0.0871 mole) of 1,5-dibromopentane,

10.0 g (0.411 moles) Mg turnings, 14.1 g (0.090 moles) 24, and 27.5 g

(0.348 moles) of pyridine. A clear oil weighing 1.9 g was obtained. The

^{31}P NMR spectrum of the oil showed only two peaks at 108.7 and 126.0 ppm

in the ratio of 20 to 1. Attempts to distill the product at reduced

pressure (1 Torr) resulted in its decomposition. This was evidenced by

the disappearance of the peaks at 108.7 and 126.0 ppm and the appearance

of new peaks from +70 to 40 ppm.

2-β-Isopropoxy-4,6-α,α-dimethyl-2-phosphorinane (27), 2-α-iso-

propyl-4,6-α,α-dimethyl-2-phosphorinane (28)   Attempts were made to

prepare this compound from meso-2,4-dimethyl-1,5-dibromopentane and 24

via the method of Gultneh (38) and the method used to prepare 26. All attempts to prepare a pure sample of this compound were unsuccessful as evidenced by the existence of many peaks in the ^{31}P NMR spectrum of the brown oil obtained. Three sets of peaks in the regions of 220-205 ppm, 111 to 106 ppm and 60 to 40 ppm showed that many different compounds formed in the reaction. Attempts to distill this material according to the conditions (56-58°/2 Torr) of Gultneh were unsuccessful. In fact, heating this mixture during the distillation resulted in the disappearance of the peaks located at 220 to 205 and 111 to 106 ppm with the subsequent appearance of new peaks in the region of 70 to 40 ppm.

2-Triphenylmethyl-2-oxophosphorinane (29)   ·The oil (1.7 g)

obtained in the synthesis of 26, 3.0 g (0.011 mol) of triphenylmethyl chloride and 30 ml of dry degassed acetonitrile were refluxed for 5 hr. The acetonitrile was removed on a rotary evaporator and the resulting oily yellow solid was chromatographed on silica gel using a 3 to 1 mixture of hexane and acetone. The yellowish oil which was obtained (0.46 g) showed only one spot on TLC (using hexane and acetone as solvents) (^{31}P NMR ($CD_3C(O)CD_3$) 52.0; ^{1}H ($CDCl_3$) 7.65-7.20m 15H C_6H_5, 2.15-1.40m 10H CH_2; ν(P=O) ($CHCl_3$) 1147 cm^{-1}; $P^+ \frac{m}{e}$ = 360.1 meas., 360.1 calc).

2-α-Triphenylmethyl-2-β-oxo-4,6-α,α-2-phosphorinane (30),

2-β-Triphenylmethyl-2-α-oxo-4,6-α,α-2-phosphorinane (31)   In 30 ml of

dry acetonitrile which contained 3.0 g (0.011 mole) of triphenylmethyl chloride was dissolved 1.2 g of the brown oil containing 27 and 28. The

mixture was refluxed under N_2 for 2 hours. A yellow solid was obtained

upon removal under vacuum of the acetonitrile. The ^{31}P NMR spectrum of

this material showed several peaks from +80 to +34 ppm, including 2 peaks

at 56.0 ppm and 53.6 ppm in an approximately 4 to 1 ratio.

Chromatography of this solid on a column of silica gel using a 9 to 1

mixture of hexane and acetone yielded only a brownish oil. Large

colorless crystals were observed in the oil after one week. The crystals

which were extracted from the oil with cold acetone showed a single peak

in the ^{31}P NMR at 53.2 ppm. The remaining oil showed a single resonance

at 55.7 ppm ((30) ^{31}P NMR $(CD_3C(O)CD_3)$ 53.2 ppm; $P^+ \frac{m}{e}$ = 388.1 meas.,

388.7 calc; (31) ^{31}P NMR $(CD_3C(O)CD_3)$ 55.7 ppm; $P^+ \frac{m}{e}$ 388.1, meas. 388.7

calc).

X-ray experimental details for 30   A clear colorless crystal 0.2

x 0.3 x 0.3 mm was sealed in a 0.3 mm Lindemann capillary tube and

mounted on a Syntex P_2 diffractometer equipped with a monochromator and

Cu X-ray tube. Analysis of the crystal showed it to be orthorhombic with

a = 16.554(7)Å, b = 17.628(3)Å, and c = 14.910(3)Å ; V = 4351(8)Å^3, ρ =

1.18 $\frac{g}{cm^3}$ (calcd), N = 8. Data were collected using an ω scan technique

out to a 2θ limit of 100.0°. A variable scan rate was used to collect

data at a minimum rate of 4°/min and a maximum rate of 29°/min. A total

of 3717 reflections were measured. Repeated measurement of a single

strong reflection after every 75 reflections showed no evidence of

crystal decay. Analysis of the data showed the systematic absences h00,

h = 2n; 0kl, l = 2n; 0k0, k = 2n; h0l, h = 2n; 00l, l = 2n; hk0, k = 2n

indicative of the orthorhombic space group P_{cab}. Data averaging yield 1473 reflections $(F_0 > 3\sigma)$. The positions of all nonhydrogen atoms were found using MULTAN (103). The refinement proceeded without difficulty to yield a final R of 0.083. Hydrogen atom positions were then calculated and their positions were refined with no apparent improvement in the final agreement factor. A final difference map showed no unexplained electron density.

X-ray experimental details for Ni(6)$_4$ Ni(6)$_4$ (0.3 g) was dissolved in a minimum ($\sim$1 ml) of boiling heptane contained in a 15 dram vial. The vial was placed in a small Dewar. The top of the Dewar was packed with a paper towel and then placed in a freezer which was maintained at -15°C. After cooling for 24 hours, the vial was removed from the dewar and large (3 x 3 x 3 mm average) crystals were observed on the bottom. The heptane supernatant was decanted off and the crystals were then allowed to air dry. The compound appeared to have no air sensitivity.

Analysis of the crystals under a microscope showed that many of them were twinned. However, a small (0.3 x 0.3 x 0.3 mm) nontwinned fragment was cut off of a larger crystal and then mounted in a 0.3 mm Lindemann capillary. A data set was collected at room temperature using a four-circle X-ray diffractometer designed and built in the Ames Laboratory. Data were obtained using graphite monochromated molybdenum radiation. The quality of the data set obtained at room temperature appeared poor owing to the fact that many of the reflections proved to be unobserved.

However, the data set was reduced and averaged. All nonhydrogen atom positions were found successfully using this data set. Refinement of the structure proceeded until it was noticed that the isotropic temperature factors for the exocyclic secbutyl carbons were found to be equal to about 29.0. This indicated that there was excess thermal motion in the molecule.

The refinement was suspended and a new data set was collected at -95°C ± 2°C. The crystal was found to be monoclinic with a = 13.873(1) Å, b = 17.195(1) Å, c = 20.351(3) Å, β = 101.97(1)°, z = 4, v = 4748.8(7) Å^3 and ρ = 1.23 9/cm^3 (calcd). The only systematic absence, h0l, l = 2 n, indicated the space group $P_{2/c}$ which was later confirmed by solution of the structure. Data collection yielded 3879 reflections measured over 3 octants with a 2θ limit of 50°. There was no observed decomposition of the crystal based upon repeated observation of three standard reflections. Averaging of equivalent data yielded 1987 independent reflections ($F_0 > 3\sigma$). Block matrix least squares isotropic refinement of the nonhydrogen positions yielded a conventional R of 0.135 and a weighted R of 0.149. A full matrix anisotropic refinment of the nonhydrogen atoms led to a final conventional R of 0.086 and a weighted R of 0.108. An electron difference map of the unit cell failed to show any unexplained electron density.

1,4-Bis(diphenylphosphino)benzene (32)   This compound was

prepared by the procedure of Baldwin and Chang (104).

1,4-Bis(diphenylphosphinito)benzene (33)   Hydroquinone (4.0 g,

0.036 mole) and 11.0 g (0.109 mole) triethyl amine were dissolved in 100

ml of dry ether. The solution was cooled to 0°C and 16.0 g (0.072 mole)

diphenylchlorophosphine in 100 ml of dry ether was added dropwise over 30

min. The solution was stirred with the aid of a mechanical stirrer for a

period of 1 hr. The mixture was filtered and the ether was removed on a

rotary evaporator. The yellow oil obtained was dissolved in boiling n-

propanol and long slender crystals formed upon cooling. The product was

obtained in 11.1% yield (m = 130-131°; ^{31}P NMR (C_6D_6) 112.4; ^1H NMR

($CDCl_3$) 7.4m 2OH C_6H_5, 6.95m 4H C_6H_4).

4,4'-(Diphenylphosphino)biphenyl (34)   A solution of 8.6 g (0.028

mole) of 4,4'-dibromobiphenyl in 35 ml of dry THF was placed in a 3-neck

250 ml flask equipped with a nitrogen inlet, dropping funnel and

mechanical stirrer. The solution was chilled to -78°C and 30 ml (0.066

mole) of 2.2 M solution of n-butyl lithium in hexane was added dropwise

over one hour. Upon completion of the addition, 12.3 g (0.056 mole) of

diphenylchlorophosphine was added to the reaction mixture over 10 min.

The solution was stirred for an additional thirty minutes and then

filtered. The solid which was obtained was washed with water and then

refluxed overnight in methanol to remove any remaining unreacted 4,4'-

dibromobiphenyl. The remaining solid was filtered and dried under vacuum

for several hours. The product was obtained in 15.3% yield (m = 189-

190°, lit. = 192-194° (105); ^{31}P NMR (C_6D_6) -6.0; ^1H ($CDCl_3$) 7.50m C_6H_5,

C_6H_4).

Rh(P(C$_6$H$_5$)$_3$)$_3$Cl (35)   This compound was prepared using the

procedure of Osborn and Wilkinson (106).

Reaction of 32 and 35   In order to obtain polymers similar to

those obtained with NiL$_4$ complexes, 0.23 g (0.00025 mole) of 35 and 0.12

g (0.00026 mole) of 32 were mixed in 20 ml of methylene chloride. The

mixture was stirred overnight with no evidence of any polymer

formation. Further refluxing of this material for 24 hrs. also failed to

produce any polymeric material.

Reaction of 34 and 35   In 20 ml of methylene chloride was mixed

35 (0.16 g, 0.00017 mole) and 34 (0.088 g, 0.00017 mole). After 32 hrs.

of stirring at room temperature and 16 hrs. of refluxing, no polymeric

material was observed to have formed.

Reaction of 33 and 35   In 20 ml of chloroform was mixed 35 (0.31

g, 0.00033 mol) and 33 (0.17 g, 0.00033 mole). The mixture was refluxed

for 30 min. After stirring overnight, a dark red precipitate was

observed to have formed. The solid (0.1 g) was filtered and dried in

vacuum. Attempts to dissolve this material in any organic solvents were

unsuccessful. Attempts were made to use this material as a catalyst for

the hydrogenation of 1-hexene according to the procedure of Gultneh (38);

however, the compound proved to be catalytically inactive.

1-chloro-3-methyl-2-pentene   Attempts to prepare this material by

the procedure of Gultneh (38) failed. The following amended procedure

was used. To a mixture of 32.5 g (0.276 mole) of 3-methyl-pentene-3-ol

and 28.8 g (0.343 mole) of pyridine in 125 ml of ether was added

dropwise, 43.6 g (0.366 mole) of freshly distilled thionyl chloride, over

the course of 30 min. at room temperature. The mixture was stirred for

an additional 2 hours and then filtered. The ether was removed and the

residual yellow liquid was vacuum distilled to give the product in 36.7%

yield (b_{160} = 85°; ^{1}H (CDCl$_3$) 6.2-4.8m 1H CH, 3.9d J_{H-H} = 12 1H CH$_2$Cl,

2.3-1.8m 2H CH$_2$, 1.65s 3H CH$_3$, 0.85t J_{H-H} = 10 Hz 3H CH$_3$).

3-methyl-3-hexenenitrile   A solution of 6.0 g (0.051 mole) of 1-

chloro-3-methyl-2-pentene, 4.0 g (0.083 mole) of NaCN, and 0.3 g (0.003

mole) of KI in 125 ml of acetone was refluxed for 16 hrs. The mixture

was cooled to room temperature and filtered. The acetone was removed and

the remaining liquid was vacuum distilled to give the product in 27.0%

yield (B_{12} = 35-38°; ν(C≡N) = 2255 cm^{-1}; ^{1}H NMR (CDCl$_3$) 5.5-5.0m 1H CH,

3.1d J_{H-H} = 12 Hz 2H CH$_2$CN, 2.3-1.9m 2H CH$_2$, 1.7s 3H CH$_3$, 1.1dt 6H CH$_3$).

Supported NiL$_4$ complexes on macroreticular resins   The resin

(0.53 g, 0.0016 mole of H$^+$), 3.5 g (0.0048 mole) of Ni(P(OEt)$_3$)$_4$ and 10

ml of dry, degassed toluene were placed in a nitrogen-flushed 50 ml round

bottom flask equipped with a stirring bar. The mixture was stirred for

12 hr. under nitrogen at room temperature. The toluene was then removed

and the resin was washed with four 15 ml aliquots of fresh toluene. The

beads were then immediately used as catalysts. Resins containing

different NiL$_4$ complexes were prepared in an analogous manner using the

same ratios of reagents.

Analysis of NiL$_4$-supported macroreticular resins   The resins were
digested with HNO$_3$/HClO$_4$ mixtures using the same procedure used in the
nickel analysis of the [Ni(23)$_2$L']$_n$ complexes. The resulting acid
solutions were analyzed quantitatively for nickel using the previously
described procedure of Snell (107).

Results and discussion

The catalytic properties of a NiL$_4$ complex are due in large measure
to the ability of the complex to dissociate. Dissociation of a ligand
provides an open site which is available for coordination of small
molecules such as olefins. Ordinarily, only NiL$_4$ complexes which contain
bulky ligands, as defined by their ligand cone angles, are extensively
dissociated in solution. Examples of these types of ligands are P(O-i-
Pr)$_3$ and P(O-o-tolyl)$_3$. In fact, nickel(0) complexes of these ligands
have been shown to dissociate extensively in solution to NiL$_3$ complexes
(108). However, for complexes with smaller ligands, dissociation does
not occur until the complex is protonated in solution. As stated
previously in the introduction, dissociation of a ligand upon protonation
is probably facilitated by reduced π-back donation of electron density
from the nickel atom to the phosphorus atom. The reduction in π-back
donation is caused by the electrophilicity of the proton upon
coordination. The decrease in back donation reduces the strength of the
Ni-P bond which promotes dissociation. Though Tolman contends that
dissociation in complexes containing ligands with small ligand cone
angles is aided by protonation of the complex, he maintains that the

steric properties of the ligand determine the extent to which these complexes dissociate.

Gultneh has used steric arguments to explain why adding methyl groups to the equatorial 4,6 positions of the phosphorinane ring causes the NiL_4 complexes of these ligands to be more efficient catalysts. Gultneh has also observed that large groups in the exocyclic positions on phosphorus also brought about an increase in the catalytic activity of the complex. This effect is maximized by having an isopropyl group in this position. Groups larger than isopropyl tend to cause a decrease in the catalytic activity of the complex. Gultneh erroneously contends that the main cause for the decrease in activity of NiL_4 complexes containing ligands which have these larger groups is the increased basicity of the phosphorus atom. This increase in phosphorus basicity was thought to be due to either increased amounts of electron donation to phosphorus by the alkyl groups, or, by the steric interactions within the complex which cause the larger exocyclic groups to adopt the more basic equatorial position. However, on the basis of J_{P-H} data given in his thesis, the change in relative phosphorus basicity of the ligands would appear to be slight (Table 7). Moreover, an X-ray structural analysis of $Ni(\underline{6})_4$ (given later in this thesis) indicates that large exocyclic groups are not forced to adopt an equatorial position at least in the solid state. The reduction in activity is probably due to the larger steric bulk of these groups which impedes the ability of an olefin to coordinate to the nickel atom.

Table 7: ^{31}P NMR chemical shift and J_{P-H} values of some selected monocyclic phosphite ligands upon protonation with FSO_3H at -50°C (38).
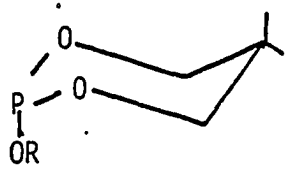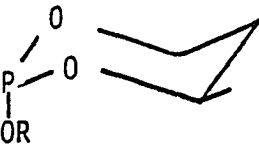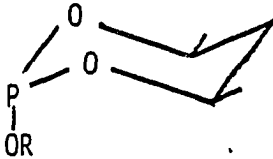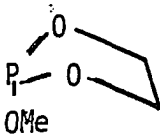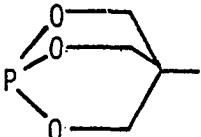
L	δ $^{31}P(HL^+)$ ppm	J_{P-H} ($\pm$ 4 Hz)

R = Me	18.0	861
i-Pr	16.5	852
l-methyl	16.9	853
l-bornyl	16.2	856

R = Me	17.5	871
i-Pr	16.8	855
l-menthyl	16.9	865
l-bornyl	17.2	854
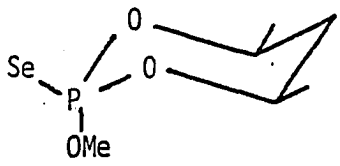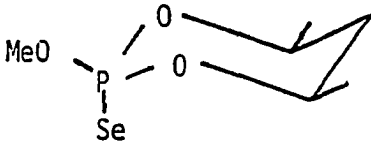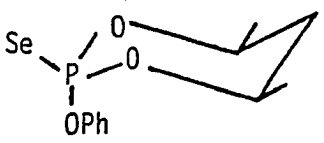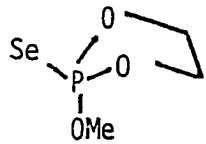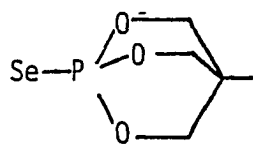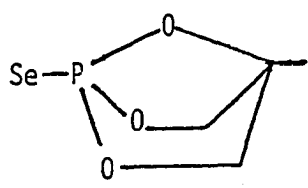
Table 7. (continued)

L	$\delta\ ^{31}P(HL^+)$ ppm	J_{P-H} (±4 Hz)

R = Me	16.5	861
= i-Pr	16.8	853
= l-menthyl	16.9	853
= bornyl	16.6	854

	43.7	913[a]

	21.4	899[b]

[a]Reference (109).

[b]Reference (110),

Tolman (19) has suggested that the steric properties of a ligand are the major factors in determining the extent to which it dissociates from the complex. However, in order to see if the electronic properties of the ligand had any role in shaping the catalytic properties of a complex, several new ligands and their NiL_4 complexes were prepared and tested as isomerization catalysts. $Ni(\underline{10})_4$ was shown to be completely inactive as a catalyst. Gas chromatographic analysis showed that the complex failed to isomerize 3-butenenitrile to cis and trans-2-butenenitrile. This seemed unreasonable in view of the high activity of $Ni(\underline{9})_4$. Models of $Ni(\underline{10})_4$ seem to show that the phenoxy groups have almost the same steric properties as an isopropyl group. This is also illustrated by the similarity in the ligand cone angles of $P(O-\underline{i}-Pr)_3$ and $P(OPh)_3$ of 130° and 128°, respectively. In order to determine the relative basicity of this ligand, its corresponding selenide was prepared and its $J_{31_{P}-77_{Se}}$ value was measured (19). This value was found to be 1024 Hz. As can be seen in Table 8 this coupling constant is much higher relative to the coupling constant of the selenide of $\underline{8}$ (compound $\underline{8}$ was shown by J_{P-H} data to be electronically similar to $\underline{9}$). In fact, ligand $\underline{10}$ would seem to have electronic properties much closer to the constrained phosphites, $P(OCH_2)_3C(Me)$, $OCH_2CH_2OP(OMe)$ and $P(OCH_2)_2CO(Me)$. The reduced basicity of $\underline{10}$, which seems similar to that of the 5 member ring phosphite $\underline{37}$, probably is due to resonance delocalization of electron density from the oxygen to the phenyl ring as shown in fig. 4. The build up of positive charge on oxygen brings about a build up of positive charge on

Table 8. $^{31}P-^{77}Se$ spin-spin couplings and ^{31}P NMR chemical shifts (rel. to H_3PO_4) of some selected selenophosphoryl compounds(13)

Compound	δ ^{31}P (± 0.1 ppm)	$J_{^{31}P-^{77}Se}$ ($\pm$ 1 Hz)
SeP(OMe)$_3$	78.0	954
	66.8	996
	68.8	949
	57.4	1024
	88.0	1011
	60.1	1053
	61.4	1099
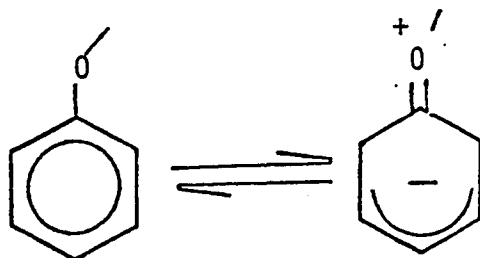
Fig. 4. Resonance structures for a phenoxy group.

phosphorus thus reducing its basicity and decreasing the extent to which the NiL_4 complex is protonated. This is evidenced by the failure of a solution of $Ni(\underline{10})_4$ to turn yellow upon addition of acid. Such a failure of the solution to turn yellow has been shown in the past (38) to stem from the lack of protonation of the NiL_4 complex.

This reduced basicity argument has been used to explain why NiL_4 complexes containing 5-member ring phosphite ligands such as $\underline{37}$ also fail to act as catalysts for olefin isomerization (38). Structural studies of these types of ligands have shown their P-O-C angles to be constrained, thus causing a decrease in their phosphorus basicity as discussed previously (111). This reduction in basicity and hence the basicity of the nickel is observed by the low degree (5% by ^{31}P NMR) to which $Ni(\underline{37})_4$ protonates in acidic solution. This decrease in the extent of protonation is also demonstrated by the failure of solutions of $Ni(\underline{37})_4$ to turn yellow in color upon addition of acid. The effect of decreased phosphorus basicity by molecular constraint on 5-member ring phosphites

is so great that it can not be overcome by large electron donating groups

in the phosphorus exocyclic position. This was exemplified by the

preparation of Ni$(\underline{15})_4$, which contains an isopropyl group in the

exocyclic position, and its observed inactivity as an isomerization

catalyst. ^{31}P NMR analysis showed that the complex failed to protonate

in solution.

In order to investigate the effect of increased phosphorus ligand

basicity on the catalytic activity of complexes, several ligands were

prepared which contained amine functions in the exocyclic position. The

increase in phosphorus basicity by replacing the alkoxy group with an

amino group is best illustrated by the decrease in $J_{31_{P}-71_{Se}}$ of

Se=P(OMe)$_3$ compared to Se=P(NMe$_2$)$_3$ from 954 to 784 Hz (19). In order to

test this effect, the series of aminophosphite ligands, $\underline{16}$, $\underline{17}$, $\underline{18}$, $\underline{19}$,

$\underline{21}$ and $\underline{22}$ were prepared along with their corresponding series of NiL$_4$

complexes. In every case, all of these complexes were shown to be

totally inactive as isomerization catalysts. Attempts were made to

measure the J_{P-H} values of the protonated forms of these ligands using

^{31}P NMR in order to estimate their relative basicity. However, in all

cases, upon adding FSO$_2$H to the NMR tube containing the ligand according

to the procedure of Weiss and co-workers (111), a darkening of the

solution was observed. Subsequent ^{31}P NMR analysis indicated that the

ligand had undergone extensive decomposition upon mixing with the acid.

In an attempt to determine how this decomposition of the ligand

might have been responsible for the inactivity of the complexes, a low-

temperature ^{31}P NMR analysis of the protonation of one of these complexes

was carried out. Fig. 5 is an example of what is observed in the ^{31}P NMR

when a nickel complex of a phosphite, 6, is protonated in a 5 to 1 H^+ to

Ni ratio. As can be seen upon addition of acid, the singlet at 154.6 ppm

corresponding to the NiL_4 complex shrinks with subsequent formation of a

doublet at 136.8 ppm (J_{P-H} = 33 Hz), indicative of protonation. In the

case of Ni(20)$_4$ (δ ^{31}P = 163.8 ppm), addition of even one equivalent of

acid brings about apparent decomposition of the NiL_4 complex as evidenced

by formation of new peaks in the ^{31}P NMR spectrum at 172, 169, 165, 145,

140, 133 and 116 ppm (Fig. 6). Upon addition of another equivalent of

acid (Fig. 7), even more decomposition is observed. At a ratio of 10

acid to 1 Ni (the ratio which was shown to give an optimum rate of

catalysis for phosphite complexes (38)), the ^{31}P NMR spectrum seems to

suggest that all of the NiL_4 complex has decomposed (Fig. 8). However,

there appears to be a small doublet centered at 127.5 ppm which shows a

coupling constant of 32 Hz, suggestive of a protonated NiL_4 complex.

Integration of this doublet shows that it comprises only about 4% of the

total area of all the peaks in the spectra, however.

On the basis of these experiments, the inactivity of these complexes

as catalyst can be explained by their decomposition in acid solution. It

is possible that instead of the nickel being protonated, as occurs with

phosphite complexes, the nitrogen of the ligand is preferentially

protonated. The protonation of the nitrogen facilitates weakening of the

P-N bond thus leading to decomposition of the ligand and subsequently the

NiL_4 complex.
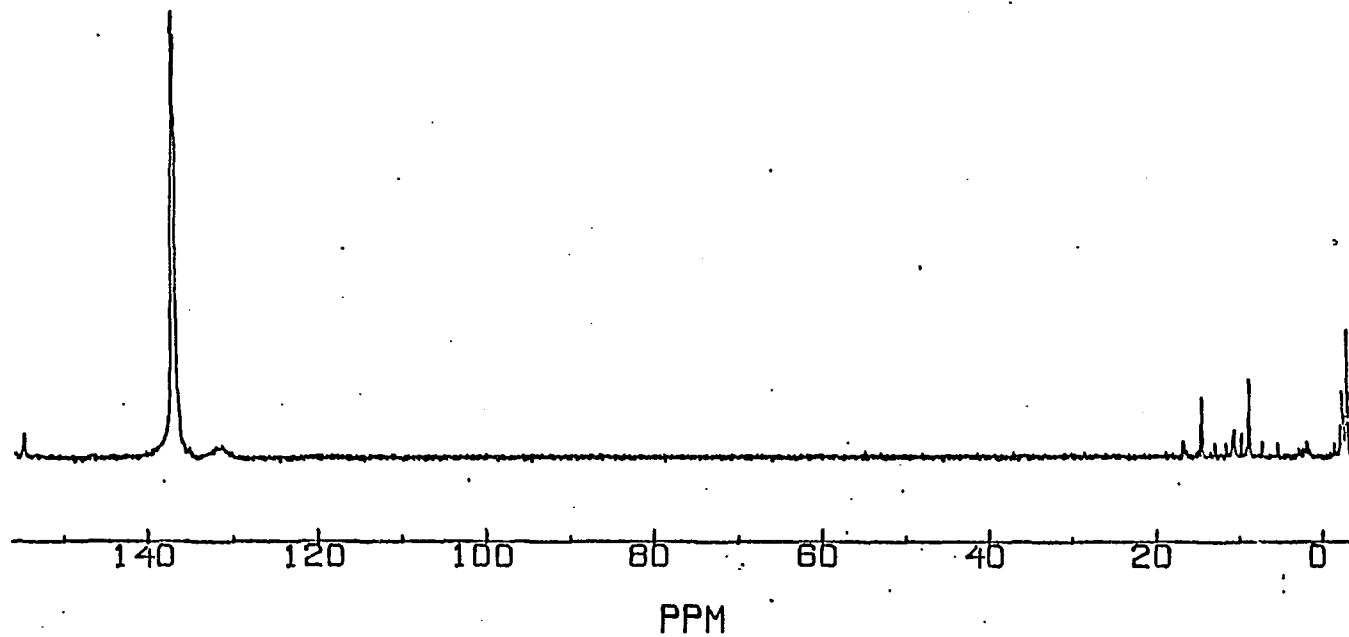
Figure 5. ^{31}P NMR spectrum of a C_6D_6 solution of $Ni(\underline{6})_4$ acidified with 5 equivalents of F_3CCOOH at room temperature
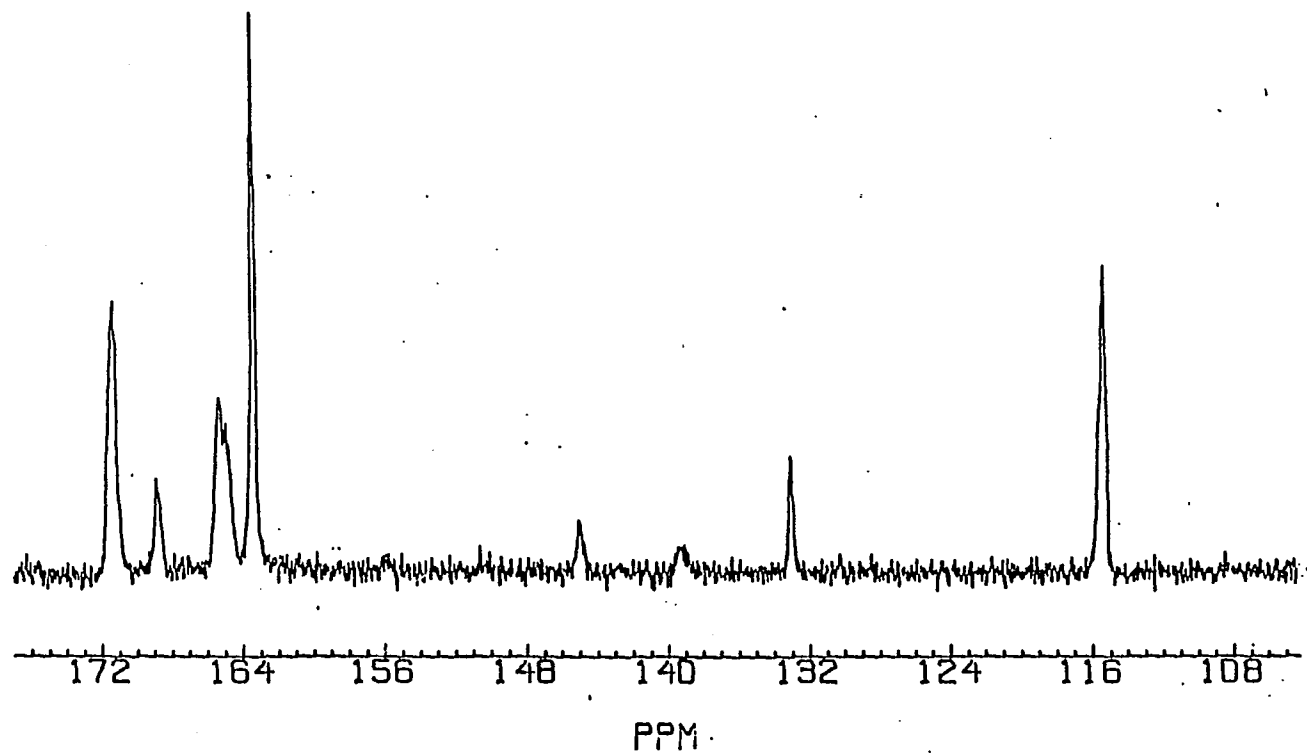
Figure 6. ^{31}P NMR spectrum of a C_6D_6 solution of Ni(20)$_4$ acidified
with 1 equivalent of F$_3$CCOOH at 200 K
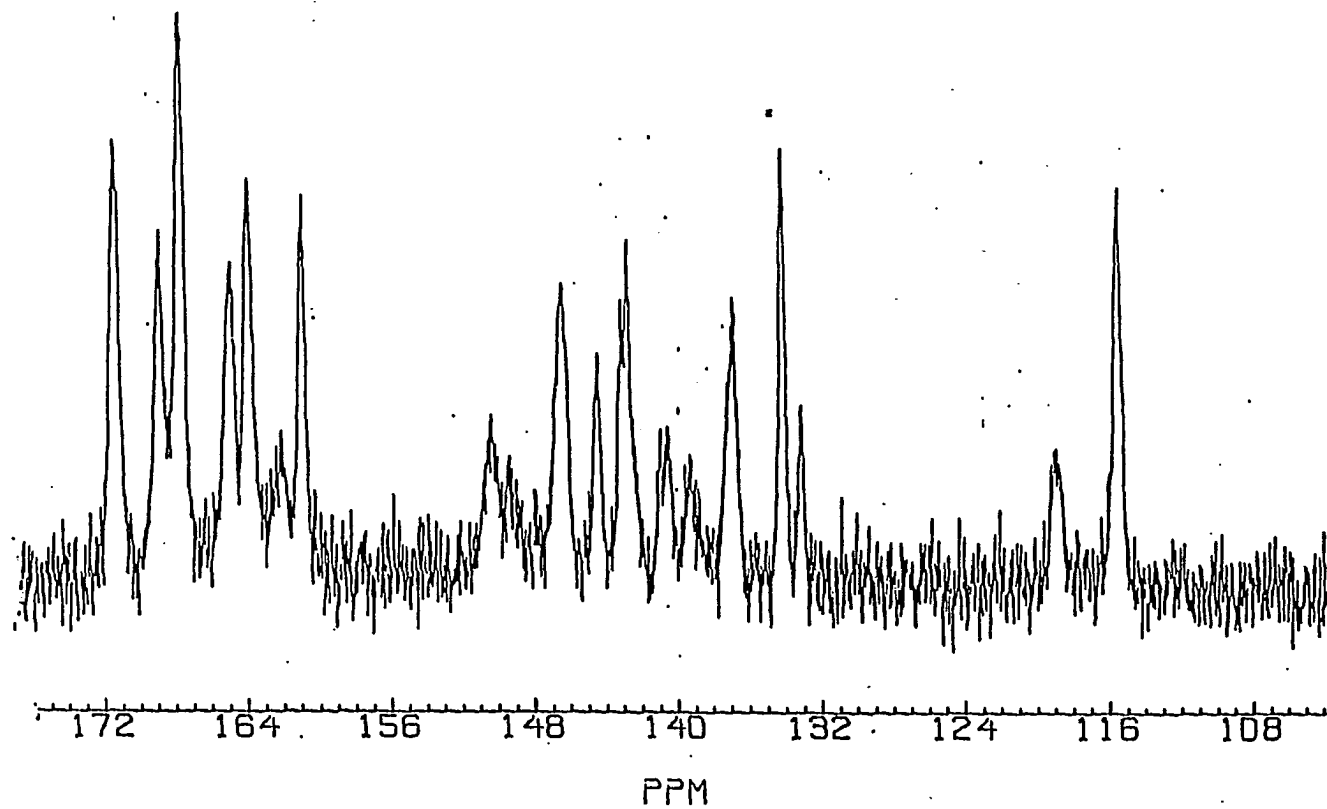
Figure 7. ^{31}P NMR spectrum of a C_6D_6 solution of $Ni(\underline{20})_4$ acidified with 2 equivalents of F_3CCOOH at 200 K
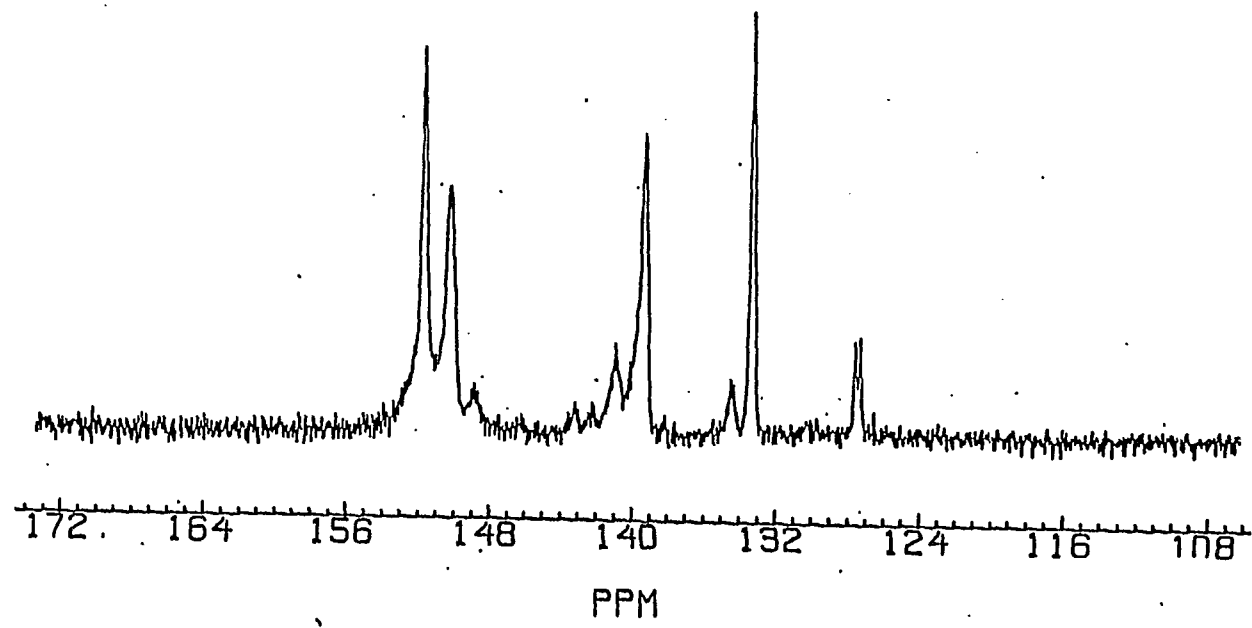
Figure 8. ^{31}P NMR spectrum of a C_6D_6 solution of Ni$(\underline{20})_4$ acidified with 10 equivalents of F_3CCOOH at 200 K

On the basis of these results, it would appear that the electronic properties of the ligand are very important in determining the extent to which an NiL_4 complex is protonated in solution. However, it also seems that as long as the nickel atom is able to undergo protonation, the steric properties of the ligand influence the catalytic activity of the complex in two ways: firstly, by promoting dissociation of a ligand, and secondly, as will be seen in the work with asymmetric catalysis, by influencing the extent of olefin coordination to the metal atom.

Use of Lewis acid cocatalysts in the isomerization of 3-butenenitrile

Gultneh observed that Lewis acids such as $AlCl_3$, $TiCl_3$, and $ZnCl_2$ acted as efficient cocatalysts in the isomerization of olefins. It was observed that in most cases the rates of catalysis using these compounds were similar to that observed with protic acids (Table 9).

It was found that benzene solutions containing catalytically active mixtures of NiL_4 complexes and Lewis acids were yellow in color, as was observed in protic acid solutions. In fact, the visible spectra of these solutions exhibited absorption maxima in the region of 355 nm as was also observed with H^+/NiL_4 systems (38). Moreover, addition of $P(OMe)_3$ to solutions containing a NiL_4 complex, (L = 2-alkoxy-1,3,2-dioxaphosphorinane) and a Lewis acid such as $AlCl_3$ brought about redistribution of the ligands to form complexes of the type $NiL_x(P(OMe)_3)_{4-x}$ (38). This was confirmed by ^{31}P NMR analysis (38).

Based upon the similarities between the Lewis and protic acid systems, Gultneh contended that the role of Lewis acid in the catalysis

Table 9. Comparison of activity of Lewis acids to H^+ as cocatalyst in the isomerization of 3-butenenitrile [a,b,c,]

Ligand	Lewis acid		
	cycles in 30 min (±2)		
	$AlCl_3$	$ZnCl_2$	H^+
5	54	15	25
7	88	20	60
8	124 (4.0 min)	30	124 (4.0 min)

[a][Lewis acid]/[NiL_4]/3-butenenitrile = 1/1/124.

[b]Time (± 0.2 min) taken to complete 124 cycles.

[c]Ref. (38).

was similar to H^+. His proposal of a $NiL_4:AlCl_3$ adduct was based upon the visible absorbance which was previously mentioned. However, at the time, the exact bonding interaction between the nickel and aluminum was not understood. Based upon the presence of a molar conductivity of 15.4 ohm^{-1} cm^2 $mole^{-2}$ in CH_3CN for a 1 to 1 mixture of Ni($\underline{9}$)$_4$ and $AlCl_3$, the following mechanism was proposed for the interaction of a NiL_4 complex

$$NiL_4 + AlCl_3 \rightarrow L_4NiAlCl_3 \rightarrow L_4NiAlCl_2^+ Cl^- \rightarrow L_3NiAlCl_2^+ Cl^- + L$$

Scheme 6. Proposed mechanism of Gultneh for the interaction of a NiL_4 complex and $AlCl_3$

with $AlCl_3$. It was also reported that addition of excess ligand to these catalyst mixtures decreased the rate of catalysis.

The conductivity reported was extremely low for what would have been expected for a 1 to 1 electrolyte in CH_3CN (120-160 ohm^{-1} cm^{22} $mole^{-2}$) (112). A recheck of the conductivity of $Ni(\underline{9})_4/AlCl_3$ under nitrogen using freshly sublimed $AlCl_3$ and CH_3CN freshly dried from P_4O_{10}, showed that the system had no detectable conductivity. It is possible that the previously described value was caused from the partial hydrolysis of $AlCl_3$ by water contained within the system (Eq. 34).

$$AlCl_3 + H_2O \rightarrow Al(OH)Cl_2 + H^+ + Cl^- \qquad (34)$$
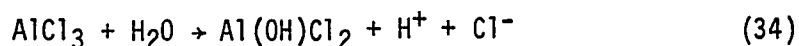
Since attempts by Gultneh (38) to isolate these adducts had failed, we sought to find a new way of proving or disproving their existence. A UV-visible spectroscopic study was carried out in order to achieve this goal and the following observations were made:

1. Addition of $Ni(\underline{9})_4$ in benzene showed no absorption in the visible spectrum. Likewise, $\underline{9}$ showed no visible adsorption.

2. Addition of $Ni(\underline{9})_4$ to CH_2Cl_2 caused the solution to turn slightly yellow in color. A slight absorption ($\varepsilon = 2.7 \times 10^1$) at 340 nm was seen in the visible spectrum.

3. A 1 to 1 molar mixture of $Ni(\underline{9})_4$ and $AlCl_3$ in CH_2Cl_2 shows absorptions at 420 nm ($\varepsilon = 9.6 \times 10^{-1}$) and 340 nm ($\varepsilon = 2.3 \times 10^1$).

4. Addition of excess ligand to the mixture described in 3 causes an increase in the size of the peak at 420 (ε = 1.1 x 10^1) and a decrease in the size of the peak at 340 (ε = 9.0).

5. The visible spectrum of $AlCl_3$ and free ligand $\underline{9}$ in CH_2Cl_2 showed an absorption at 420 nm (ε = 6.0).

The data would seem to suggest that the peak at 340 nm is from a NiL_3 species while the peak at 420 nm is from an adduct which forms between the $AlCl_3$ and the free ligand.

Tolman and Gosser (108) have previously shown that NiL_3 species such as $Ni(P(O-\underline{o}-tolyl)_3)_3$ exhibits an absorption maximum at 420 nms, while a solution of $Ni(P(O-\underline{i}-Pr)_3)_4$ exhibits an absorption maximum at 430 nm upon heating, indicative of the formation of $Ni(P(O-\underline{i}-Pr)_3)_3$. The reasons for the lower wavelength absorption at 340 nm of $Ni(\underline{9})_4$ (in CH_2Cl_2) as compared to the 410 nm absorption of $Ni(P(O-\underline{i}-Pr)_3)_3$ are not known as yet. It is perhaps caused by a difference in the value of 10 Dq, resulting from the difference in the ligand basicity and steric arrangement in the resulting $Ni(\underline{9})_3$ complex. The above results suggest that the role of $AlCl_3$ in this system is that of a dissociation promoter (Eq. 35).

$$NiL_4 + AlCl_3 \longrightarrow NiL_3 + L:AlCl_3 \tag{35}$$
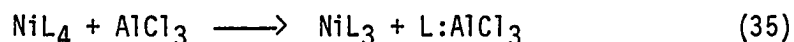
The $AlCl_3$ in this case assists in shifting the equilibrium toward the coordinatively unsaturated NiL_3 species which can then isomerize 3-butenenitrile through a π-allylic mechanism. In order to further substantiate these ideas, an ^{27}Al NMR study was carried out in order to

determine what changes, if any, take place around the aluminum atom when the $AlCl_3$ is added to the NiL_4 complex.

Aluminum has been found to be a very good NMR nucleus (113). Reasons for this are: the aluminum-27 isotope is 100% abundant and the relative receptivity of the nucleus to the NMR experiment is 20% that of hydrogen (phosphorus having a receptivity of only 6.6% relative to that of hydrogen). Although the aluminum-27 nucleus possesses a quadrupole moment with a spin of 5/2, it is still possible to obtain spectra which contain very narrow lines. However, this is observed only when there is a high degree of symmetry around the aluminum atom. Thus, the highly symmetric $Al(H_2O)_6^{+3}$ ion has been shown to have a line width of only 3 Hz (114).

Aluminum-27 NMR chemical shifts (relative to $Al(H_2O)_6^{+3}$) have been shown to be dependent upon the type of coordination around the aluminum atom (113). Complexes which possess octahedral symmetry are usually found to exhibit chemical shifts in the region of +20 ppm to -50 ppm. While tetrahedrally coordinated compounds are found to have chemical shifts from -28 to +221 ppm. Therefore, upon obtaining both line width and chemical shift data, it is found that aluminum-27 NMR provides an extremely useful tool in determining the chemical environment around an aluminum atom.

The existence of stable adducts between phosphorus bases and aluminum containing Lewis acids has been known for some time. Vriezen and Jellinek (115) have shown that AlX_3, (X = Cl or Br) can form stable adducts with trialkylphosphines. They found that the following

equilibrium (Eq. 36) is maintained in solutions containing these compounds.

$$R_3P + AlX_3 \rightleftharpoons R_3PAlX_3 \overset{R_3P}{\rightleftharpoons} (R_3P)_2AlX_3 \qquad (36)$$

$$R = Me \text{ or } Et \qquad X = Cl \text{ or } Br$$
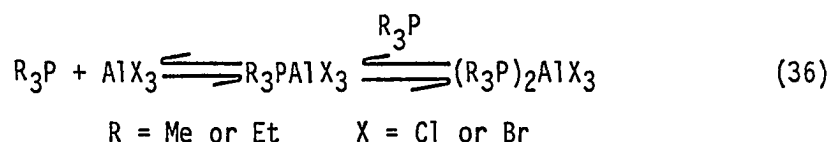
It was observed that the relative concentrations of the mono and diphosphorus adducts could be controlled by adjustment of the ratio of PR_3 to AlX_3 in solution. Titration of the $AlCl_3$ with PEt_3 in toluene showed that the ^{27}Al resonance varied from +109.9 ppm (rel. to $Al(H_2O)_6^{+3}$) for a 1 to 1 adduct, to a limiting value of 55.9 ppm for $(R_3P)_2AlCl_3$. The rather large difference in chemical shift (54 ppm) was attributed to the change from sp^3 hybridization in Et_3PAlCl_3 to dsp^2 hybridization in $(Et_3P)_2AlCl_3$ (115).

As can be seen in Table 10, the ^{27}Al chemical shifts for the aluminum species produced from a 1 to 1 mixture of $AlCl_3$ and free ligand ($P(OEt)_3$ or 9), is about 103.7 ppm. The peak falls in the same region as is observed for a 1 to 1 $AlCl_3/PEt_3$ adduct. It should also be noticed that the same chemical shift is observed for a 1 to 1 mixture of $AlCl_3$ and the corresponding NiL_4 complex. It would be highly coincidental if the chemical shift of an adduct formed between the $AlCl_3$ and the nickel atom, as proposed by Gultneh, came at the same place as the shift of an $AlCl_3$/phosphite adduct. Therefore, on the basis of this evidence we are fairly confident that the role of a Lewis acid, in particular $AlCl_3$, is to promote ligand dissociation, as shown in equation 33. As further

Table 10. ^{27}Al NMR data for various $AlCl_3$, ligand, and NiL_4 complex mixtures[a,b]

components in mixture	ratio of components	$\delta\ ^{27}$Al (ppm)	Line width (Hz)
$AlCl_3$	---	91.0	300
$AlCl_3/P(OEt)_3$	1/1	103.5	50
$AlCl_3/Ni(P(OEt)_3)_4$	1/1	103.9	50
$AlCl_3/(\underline{9})$	1/1	103.6	132[c]
$AlCl_3/Ni(\underline{9})_4$	1/1	103.9	10[c]

[a]Rel. to $Al(D_2O)_6^{+3}$.

[b]In toluene solution.

[c]The reason for the large difference in the line width between the spectra of the NiL_4 complex and the ligand is not known as yet.

evidence for this mechanism, the same type of study was done with the $AlCl_3/Ni(\underline{11})_4$ system. A 1 to 1 mixture of $AlCl_3$ and $\underline{11}$ exhibits a ^{27}Al NMR shift of 104.0 ppm. However, a 1 to 1 mixture of $AlCl_3$ and $Ni(\underline{11})_4$ shows only a peak at +91.0 ppm indicative of $AlCl_3$ dissolved in solution. It would appear that in this case an adduct fails to form between $(\underline{11})$ and $AlCl_3$. This can be explained by the lack of dissociation of a ligand from the $Ni(\underline{11})_4$ complex due to the high strength of the Ni-P bond.

Attempts to observe the chemical shift of an adduct formed between $AlCl_3$ and $\underline{12}$ were also unsuccessful. It appears that $\underline{12}$ is not sufficiently basic enough to form an adduct with aluminum. In fact, the J_{P-H} value of $H(\underline{12})^+$ (929 Hz) indicates that it is even less basic than $\underline{11}$ ($H(\underline{11})^+$, J_{P-H} = 899 Hz (109)).

For the $AlCl_3$/phosphite adduct, there exists the possibility of two different modes of coordination of the phosphite to $AlCl_3$. Coordination can take place through either the lone pair on phosphorus or through one of the lone pairs on oxygen. Cohen and Smith (116) have shown that coordination occurs exclusively through the lone pair on phosphorus, however. This was illustrated by a ^1H NMR study of the adduct formed between $P(OMe)_3$ and $AlMe_3$. The ^1H NMR resonance for the methoxy protons appeared as a single doublet. This suggests that either all the methoxy groups were equivalent due to phosphorus coordination to aluminum or the aluminum was rapidly exchanging coordination with all the oxygens of the phosphite. However, IR studies showed very little change in the P-O-C stretching frequencies upon coordination of the aluminum. Therefore, Cohen and Smith suggested that coordination takes place exclusively through the phosphorus atom.

This mode of coordination was also found to be consistent with ^{13}C NMR data taken on a 1 to 1 mixture of $P(OEt)_3$ and $AlCl_3$. The ^{13}C NMR spectrum of $P(OEt)_3$ in C_6D_6 shows two doublets at 57.67 (J_{C-P} = 13.5 Hz) and 16.85 (J_{C-P} = 6 Hz) ppm. Upon addition of one equivalent of $AlCl_3$, there appears to be no change in any of chemical shifts, nor in the values of J_{C-P}.

It was observed that a major limitation in working with $AlCl_3$ was its low solubility in aromatic solvents, namely, 0.7% by weight in toluene (117). In order to investigate the effect of higher concentrations of Lewis acid on the rate of catalysis, $AlEt_3$ was tried as a cocatalyst due to its much higher solubility in solvents such as

benzene. Catalytic isomerization of 3-butenenitrile involving $Ni(P(OEt)_3)_4/AlEt_3$, in a 1 to 1 ratio, showed the system to be completely inactive. Higher Al to Ni ratios were also shown to be inactive as catalyst systems. In ratios higher than 3 to 1, it appeared that the $AlEt_3$ led to decomposition of the $Ni(P(OEt)_3)_4$ complex as evidenced by ^{31}P NMR spectroscopy.

Attempts to use $Ni(\underline{9})_4/AlEt_3$ in a 1 to 1 ratio as cocatalysts were also unsuccessful as shown by the lack of any isomerized product produced in 24 hrs. However, using a 10 to 1 ratio of $AlEt_3$ to $Ni(\underline{9})_4$, 116 cycles were observed in 24 hrs for the isomerization of 3-butenenitrile (cis/trans = 1.2). This decrease in activity as compared to $AlCl_3$ is probably due to reduced electrophilicity of aluminum by the electron donating ethyl groups. This effect is thought to interfere with the extent to which adducts form between the $AlEt_3$ and the dissociated ligand.

In order to achieve a compromise between increased solubility and electrophilicity, $AlEtCl_2$ was tried as a cocatalyst. ^{27}Al NMR data for the $Ni(\underline{9})_4/AlEtCl_2$ system is shown in Table 11. The large downfield shift of 130.7 ppm for $AlEtCl_2$ as compared to 91.0 ppm for $AlCl_3$ and 87.1 for neat $Al(\underline{i}-Bu)Cl_2$ (118) is presently unexplained. This large downfield shift may be attributed to concentration or solvent effects. However, addition of 1 equivalent of free ligand $(\underline{9})$ to $AlEtCl_2$ causes the resonance to shift upfield to 103.8 ppm. A 1 to 1 molar ratio of

Table 11. ^{27}Al NMR data for various $AlCl_2Et$, ligand, and NiL_4 complex mixtures[a]

Mixture	Ratio of components	δ ^{27}Al (ppm)
$AlCl_2Et$	---	130.7 ppm
$AlCl_2Et/\underline{9}$	1/1	103.8 ppm
$AlCl_2Et/$ $Ni(\underline{9})_4$	1/1	104.0 ppm

[a]Relative of $Al(D_2O)_6^{+3}$.

$Ni(\underline{9})_4$ and $AlEtCl_2$ also shows a single resonance in about the same position (104.0 ppm). Attempts to use $AlEtCl_2$ as a cocatalyst were successful only when the $Ni(\underline{9})_4$ and $AlEtCl_2$ were present in a 1 to 1 molar ratio. This ratio of $AlEtCl_2$ proved to be a much better cocatalyst than $AlEt_3$ as illustrated by the 115 cycles achieved in 1.75 hrs. for the isomerization of 3-butenenitrile. Attempts were made to carry out the isomerization at higher ratios of Al to Ni such as 5 to 1 and 10 to 1. However, these attempts proved to be unsuccessful and ^{31}P NMR studies revealed the decomposition of the NiL_4 complex at these higher concentrations of $AlEtCl_2$. The reason for this decomposition may be due in part to rearrangement of the ligands. Cohen and co-workers (119) have found that the $(MeO)_3PAlEtCl_2$ adduct rearranges to form the phosphonate complex, $(MeO)_2MePOAlEtCl_2$. Adducts formed from either $(\underline{i}-PrO)_3P$ or $(\underline{t}-BuO)_3P$ with $AlEtCl_2$ were not obtained, as they spontaneously decomposed to give olefins, ethane, and alkyl chlorides.

Phosphites are also known to form adducts with boron compounds, such as BH_3 and BF_3. Gultneh (38) found that BF_3 fails to act as a cocatalyst in the isomerization of 3-butenenitrile. An attempt was made to use BH_3 as a cocatalyst. It was observed that these systems were catalytically inactive. The NiL_4 complex appeared to completely decompose upon addition of BH_3 (as BH_3:THF complex). ^{11}B NMR was employed to investigate the mode of decomposition of this system. A 1 to 1 mixture of 9 and BH_3 in C_6D_6 showed a doublet in the ^{11}B NMR spectrum at -42.7 ppm, (J_{B-P} = 102 Hz). This chemical shift and coupling constant is consistent with what is observed for other BH_3 adducts of various phosphites (120). However, addition of 1 equivalent of THF:BH_3 to an equivalent of Ni(9)$_4$ in C_6D_6 failed to show any peaks in the region of -42 ppm. The only peaks observed were at +17.5 and -0.06 ppm. The peak at -0.06 was later shown to be from unreacted THF/BH_3 complex (120). The peak at +17.5 ppm was found to be consistent with the resonance observed for other alkyl borates (120). In particular, B(O-i-Pr)$_3$ exhibits a resonance at +17.5 ppm (120).

It would appear that instead of promoting dissociation of NiL_4 complexes, as was the case with $AlCl_3$, BH_3 coordinates to one of the oxygens in the phosphite and facilitates the breaking of the P-O bond and subsequent formation of a B-OR linkage. Decomposition of the ligand probably occurs while it is coordinated to the nickel atom, since it is known that stable adducts form when the ligand is uncoordinated. It is conceivable that this decomposition occurs with the breaking of either or both the exocyclic and cyclic P-O-C linkages. ^{11}B NMR analysis

of a 1 to 1 mixture of Ni$(11)_4$ and THF:BH_3 showed the presence of a single peak in the borate region of the spectrum at +18.3 ppm. Due to the bicyclic structure of 11 this would seem to indicate that BH_3 can cleave a cyclic P-O-C linkage. It is thus reasonable to believe that BH_3 can also open up the P-O-C linkage in the phosphorinane ring. The resulting B-O-R linkage produced is structurally similar to a B-O-i-Pr group, thus giving an identical chemical shift.

Crystal and molecular structure of Ni$(6)_4$

As was previously stated, work with 2-alkoxy-1,3,2-dioxaphosphorinanes showed that these ligands can adopt conformations wherein the alkoxy group is equatorial or axial with respect to the ring. When methyl groups are placed in the equatorial 4,6 positions of the ring it is possible to isolate products isomeric at phosphorus (58). The rings are locked into their conformations since 1,3-diaxial interactions between methyl groups would occur if the ring changed its conformation. However, when these methyl groups are not present the ring can easily exchange conformation via a ring flip. Support for this statement comes from the small ΔH value of 1.34 kcal/mole for equilibrium in Equation 37 (58).

$$ (37) $$
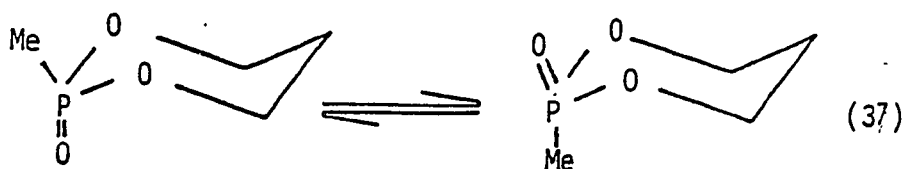
As previously stated, this isomerization at phosphorus leads to differences in the phosphorus basicity of the ligands. In discussing the differences in the catalytic activity of various NiL_4 complexes, Gultneh (38) suggested that the lack of activity of complexes with ligands which do not contain 4,6 methyl groups arises from changes in conformation of the ligand upon coordination. This would account for changes in the electronic properties of the ligand and hence the complex. In complexes containing 2-alkoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane ligands, it is conceivable that 1,3-syndiaxial steric interactions could force the exocyclic groups to adopt an equatorial conformation via a flipping of the ring. In the 4-methyl or 4,6-dimethyl systems, such a ring flip would be energetically unfavorable, but it still would be possible for the ring to adopt a twist boat conformation which could lead to differences in the steric properties of the ligand.

In order to see if the ligand could change conformation upon coordination to a zero valent nickel atom, an X-ray structural analysis was carried out. First, an X-ray crystallographic analysis of $Ni(\underline{54})_4$ was attempted. However, attempts to solve the structure proved unsuccessful due to the apparent high symmetry of the ligand and the complex it formed. In order to eliminate the problem of high symmetry, $Ni(\underline{6})_4$ was prepared. In this complex, the isopropyl group was replaced with a less symmetric sec-butyl group. Upon making this change, subsequent solution of the structure was carried out successfully. Final positions, bond distances and angles, and anisotropic thermal parameters for $Ni(\underline{6})_4$ can be found in Tables 12, 13, 14, and 15, respectively.

Table 12. The final positional parameters for atoms contained in Ni $(\underline{6})_4$
with their estimated standard deviations (in parentheses) [a]

atom	x	y	z
Ni	0.0	0.2735(1)	0.2500
PA	0.4381(2)	0.8418(2)	0.3164(2)
O1A	0.3269(5)	0.8715(5)	0.2894(4)
O2A	0.4283(5)	0.7973(5)	0.3852(4)
O3A	0.4863(6)	0.9254(5)	0.3441(4)
C1A	0.2727(12)	0.9056(9)	0.3365(8)
C2A	0.3729(11)	0.8322(10)	0.4294(7)
C3A	0.2656(11)	0.8486(11)	0.3947(8)
C4A	0.2132(10)	0.7736(10)	0.3686(8)
C5A	0.2150(12)	0.8931(13)	0.4459(8)
C6A	0.5929(10)	0.9318(8)	0.3624(9)
C7A	0.6279(12)	0.9222(12)	0.4393(8)
C8A	0.6160(13)	1.0100(12)	0.3330(13)
C9A	0.7255(30)	1.0181(14)	0.3523(17)
PB	0.6178(2)	0.7077(2)	0.3040(2)
O1B	0.7022(5)	0.6815(5)	0.2644(4)
O2B	0.6821(5)	0.7535(5)	0.3683(4)
O3B	0.6012(7)	0.6229(5)	0.3358(6)
C1B	0.7953(11)	0.6532(10)	0.3033(9)
C2B	0.7760(10)	0.7181(10)	0.4028(8)
C3B	0.8468(9)	0.7109(10)	0.3557(8)
C4B	0.9419(10)	0.6690(11)	0.3967(9)
C5B	0.8716(9)	0.7864(8)	0.3247(8)
C6B	0.5163(11)	0.6096(11)	0.3653(10)
C7B	0.4779(13)	0.5242(11)	0.3422(11)
C8B	0.5558(16)	0.6186(15)	0.4401(12)
C9B	0.4766(20)	0.6086(18)	0.4758(15)

[a]Positional parameters are listed in fractional unit cell coordinates.

Table 13. Bond distances (Å) and their estimated standard deviations (in parentheses) for Ni $(\underline{6})_4$ [a]

Ni-PA	2.103(3)	Ni-PB	2.101(3)
PA-O1A	1.609(7)	PB-O1B	1.618(9)
PA-O2A	1.627(9)	PB-O2B	1.626(8)
PA-O3A	1.636(8)	PB-O3B	1.629(9)
O1A-C1A	1.457(20)	O1B-C1B	1.451(16)
O2A-C2A	1.430(19)	O2B-C2B	1.477(16)
O3A-C6A	1.453(16)	O3B-C6B	1.447(22)
C1A-C3A	1.555(23)	C1B-C3B	1.520(22)
C3A-C2A	1.536(20)	C3B-C2B	1.514(23)
C3A-C4A	1.520(24)	C3B-C4B	1.580(20)
C3A-C5A	1.571(26)	C3B-C5B	1.514(23)
C6A-C7A	1.548(23)	C6B-C7B	1.599(26)
C6A-C8A	1.533(27)	C6B-C8B	1.515(30)
C8A-C9A	1.495(43)	C8B-C9B	1.448(40)

[a]For symmetry nonrelated ligands.

Table 14. Bond angles (°) and their estimated standard deviations (in parentheses) for Ni(6)₄ᵃ

PA-Ni-PB	109.97(13)		
Ni-PA-O1B	116.68(34)	Ni-PB-O1B	116.97(33)
Ni-PA-O2A	114.11(35)	Ni-PB-O2B	113.41(33)
Ni-PA-O3A	121.35(39)	Ni-PB-O3B	122.08(35)
O1A-PA-O2A	101.38(46)	O1B-PB-O2B	101.69(42)
O2A-PA-O3A	102.55(47)	O2B-PB-O3B	102.37(48)
O1A-PA-O3A	97.63(44)	O1B-PB-O3B	97.15(49)
PA-O1A-C1A	119.48(75)	PB-O1B-C1B	118.38(93)
PA-O2A-C2A	119.70(87)	PB-O2B-C2B	117.74(84)
PA-O3A-C6A	118.46(77)	PB-O3B-C6B	119.94(96)
O1A-C1A-C3A	111.76(1.27)	O1B-C1B-C3B	113.63(1.26)
C1A-C3A-C2A	104.88(1.30)	C1B-C3B-C2B	103.04(1.22)
C1A-C3A-C4A	111.71(1.25)	C1B-C3B-C4B	107.05(1.33)
C1A-C3A-C5A	107.79(1.46)	C1B-C3B-C5B	112.43(1.31)
C3A-C2A-O2A	112.55(1.15)	C3B-C2B-O2B	110.84(1.19)
O3A-C6A-C7A	109.90(1.36)	O3B-C6B-C7B	105.82(1.50)
O3A-C6A-C8A	104.52(1.11)	O3B-C6B-C8B	104.16(1.37)
C6A-C8A-C9A	105.24(1.67)	C6B-C8B-C9B	109.74(1.85)
C7A-C6A-C8A	116.15(1.49)	C7B-C6B-C8B	114.70(1.77)
C2A-C3A-C4A	110.64(1.41)	C2B-C3B-C4B	106.44(1.28)
C2A-C3A-C5A	107.93(1.20)	C2B-C3B-C5B	115.27(1.37)

ᵃFor symmetry nonrelated ligands.

Table 15. Thermal parameters and their estimated standard deviations (in parentheses) for Ni$(\underline{6})_4$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	3.8(1)	4.8(1)	5.5(1)	0.0(0)	0.2(1)	0.0(0)
P1	4.3(2)	5.3(2)	5.5(2)	0.5(1)	0.1(1)	-0.1(1)
P2	4.6(2)	4.8(2)	6.4(2)	0.3(1)	0.2(1)	0.3(1)
O1A	4.4(3)	6.7(4)	5.9(4)	0.9(3)	0.4(3)	0.2(4)
O2A	5.9(4)	7.7(5)	5.2(4)	1.3(4)	0.9(4)	0.7(4)
O3A	5.9(4)	5.5(4)	8.3(5)	-0.4(3)	0.5(4)	-1.6(4)
O1B	4.7(4)	5.9(4)	8.2(5)	1.1(3)	1.5(4)	-0.9(4)
O2B	4.6(4)	6.5(4)	6.3(4)	0.8(3)	-0.7(3)	0.2(4)
O3B	6.0(4)	5.4(4)	11.8(7)	0.6(4)	0.8(5)	2.3(4)
C1A	6.7(6)	8.4(9)	7.4(9)	2.6(8)	0.1(7)	-1.0(8)
C2A	6.6(9)	11.0(12)	6.7(8)	0.5(8)	1.9(7)	1.4(9)
C3A	7.1(8)	12.1(12)	6.3(8)	4.2(9)	1.5(6)	1.0(9)
C4A	6.1(7)	10.7(11)	9.7(10)	-1.9(8)	0.4(6)	0.9(9)
C5A	10.2(10)	17.8(16)	7.5(8)	5.9(10)	3.8(8)	-1.1(10)
C6A	6.0(8)	4.4(7)	11.6(11)	-0.7(6)	0.7(7)	-1.1(7)
C7A	8.9(9)	17.2(15)	6.6(9)	-1.1(10)	-1.4(8)	-0.9(10)
C8A	4.3(8)	8.6(11)	18.9(20)	0.5(7)	-0.3(10)	-0.3(12)
C9A	17.5(21)	11.1(15)	24.3(25)	-0.2(15)	4.3(19)	2.1(16)
C1B	6.2(9)	7.8(9)	12.4(15)	2.9(8)	1.4(8)	-0.2(10)

[a]The form of the anisotropic thermal parameter is $\exp[-(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + (B_{12}a^*b^* hk + B_{13} a^*c^*hl + B_{23}b^*c^*kl)/2]$.

Table 15. (continued)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C2B	5.8(7)	9.9(10)	5.9(8)	1.5(7)	-1.4(7)	1.4(7)
C3B	4.3(6)	9.6(10)	7.7(8)	2.2(7)	-0.2(6)	-1.4(8)
C4B	6.2(7)	13.8(13)	11.1(11)	4.4(8)	-1.0(7)	2.6(10)
C5B	5.9(7)	6.6(7)	10.0(9)	-1.0(6)	0.2(6)	0.9(7)
C6B	6.3(7)	11.3(12)	9.3(11)	0.8(8)	1.8(8)	3.3(9)
C7B	9.3(10)	9.3(10)	17.6(17)	-3.8(9)	4.4(11)	1.3(11)
C8B	11.9(13)	14.5(15)	11.7(15)	-0.1(14)	5.7(12)	1.4(14)
C9B	16.3(18)	19.7(23)	20.1(23)	5.4(18)	7.4(17)	5.1(20)

Structure factors for the complex can be found in Appendix 1. An ORTEP diagram of the fragment containing the nickel atom and two of its four symmetry nonrelated ligands is shown in Fig. 9. For clarity, the symmetry-related ligands are not shown.

Solution of the structure revealed that a slightly distorted tetrahedral coordination was maintained around the nickel atom ($<$ P-Ni-P = 110.0°). This coordination has been found in other zero-valent nickel complexes such as $Ni(PPh_3)_2(CO)_2$ (121), $Ni(CH_2=CHCN)_2(P(OPh)_3)_2$ (5) and $Ni(CO)_3(P(\underline{t}-Bu)_3)$ (122). This geometry is consistent with sp^3 hybridization on nickel due to its filled d^{10} configuration.

The ligand used in the preparation of $Ni(\underline{6})_4$ is believed to contain the $\underline{sec}$-butyl group primarily in the axial conformation (38) in its uncoordinated state. It thus appears that this remains the case upon coordination.
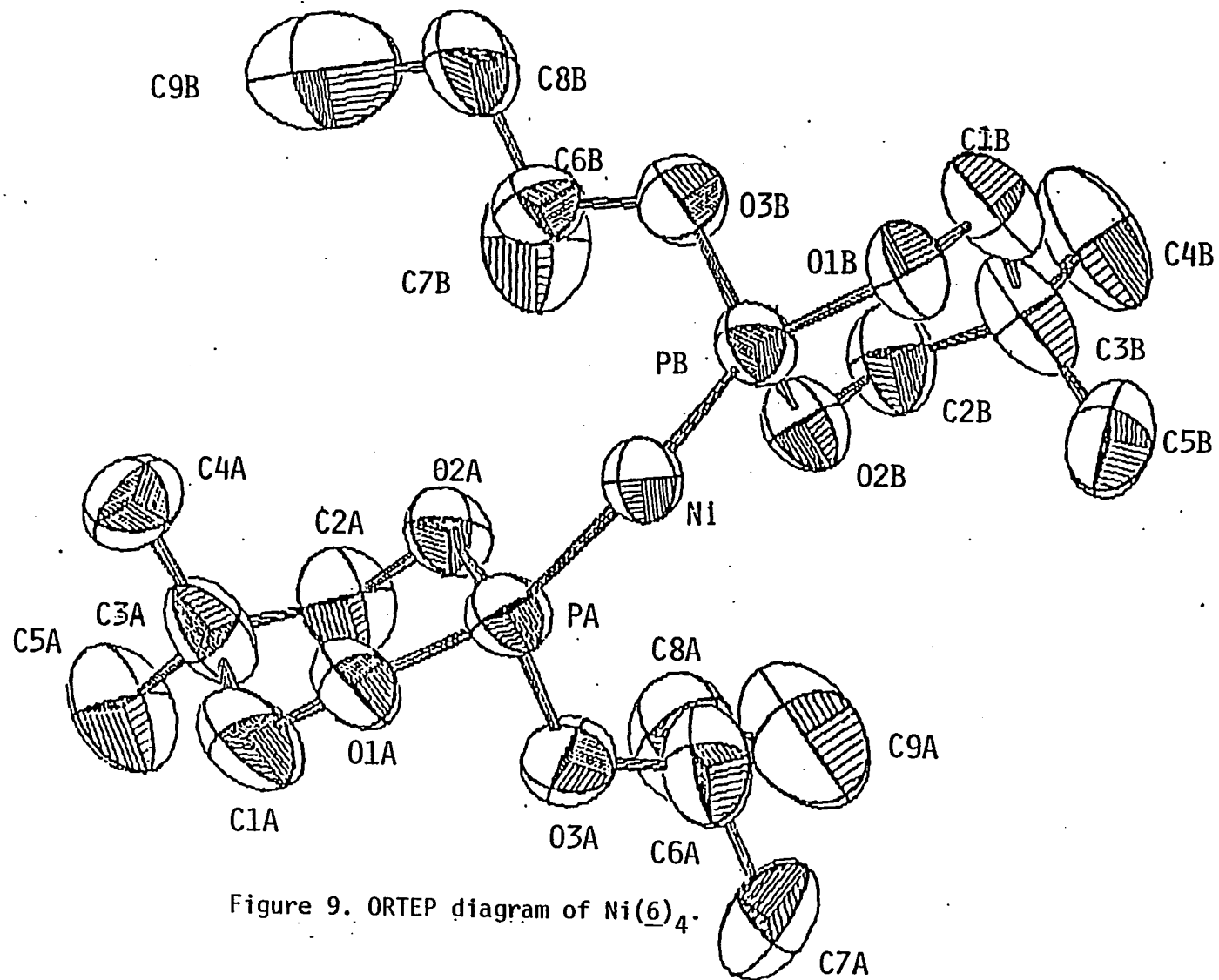
Figure 9. ORTEP diagram of Ni(6)₄.

One of the most interesting features of the structure is the extremely short nickel phosphorus bond distance of 2.109(3)Å. In fact, this distance is as short as the 2.116(10)Å which has been observed in Ni(PF$_3$)$_4$ (123,124). This shorter distance is surprising considering the high degree of π-back donation from nickel to phosphorus which is believed to strengthen the Ni-P bond. The possible effect of increased π-back bonding may also be illustrated by shortening of the Ni-P bond in Ni(P(OMe)$_3$)$_4$ Br$^+$ versus Ni(PMe$_3$)$_4$Br$^+$; however, steric effect may be dominant. The averages for the axial and equatorial Ni-P distances in Ni(P(OMe)$_3$)$_4$Br^4 are 2.18 Å and 2.22 Å, respectively (125), while in Ni(PMe$_3$)$_4$Br$^+$ the distances are 2.25 Å and 2.25 Å, respectively (126). However, the reason for the short Ni-P distance in Ni(6)$_4$ is not known at this time. Further analysis revealed that all the phosphorinane bond distances and angles in Ni(6)$_4$ are consistent with those found in the similar phosphorinane complex, cis-Mo(CO)$_4$ (38)$_2$ (127). These bond distances and angles were also similar to those found in uncomplexed phosphorinane compounds (128). As previously stated, the ligands adopt a chair conformation with an axially oriented sec-butoxy group. Each of the symmetry nonrelated ligands failed to show any twist in their chair conformation as the torsional angles described by atoms O1B, O2A, C2A, C1A and O1B, O2B, C1B, C2B were equal to 0.0° and 1.39°, respectively. Molecular models of the complex indicate that there could be favorable hydrogen bonding interactions between an exocyclic oxygen and the hydrogen on the CH group of its symmetry related (C$_2$) sec-butoxy group.

The calculated H-O distance of 3.3 Å is at the outer limit of this type of bonding interaction (129).

One of the goals of this structural analysis was to understand the possible interactions between ligands which could account for the increased activity of a complex containing ligands with equatorial 4,6-dimethyl groups. Unfortunately, we were unable to crystallize a complex which contained these types of ligands. However, using data from the structural analysis of $Ni(\underline{6})_4$, we were able to calculate the imaginary positions of equatorial 4,6 methyl groups using a C4 to methyl distance of 1.54 Å and C(methyl)-C4-H(ax) angle of 109.5°. From these calculations, the distance between methyl groups on adjacent ligands is 6.0 Å, which is larger than the sum of the van der Waals radii (4 Å) of two methyl groups. Inspection of a model of the structure revealed that significant steric interactions exist only between methyls in the 4 and 6 positions of the ring and the exocylic groups of other ligands. Calculations of the distance between the imaginary C4 and C6 methyl groups of the ring to the C8 methylene and C7 methyl groups contained on other ligands varied from 3.6 to 4.6 Å. These distances seem to suggest that there is the possibility of steric interactions among these groups. The structure also seems to suggest that as the exocyclic group grows larger from methyl to isopropyl, an interaction begins to develop between these groups and the methyl groups located in the equatorial 4,6 positions of the adjacent phosphorinane rings. However, when the exocyclic groups become exceedingly large, (e.g., t-butyl or bornyl), the exocyclic groups swing away from each other in order to reduce steric

interactions. This results in an increase in the distance between the exocyclic groups and 4,6 equatorial methyl groups on adjacent ligands, thus decreasing the steric interactions between the ligands.

These types of steric interactions may serve to increase the extent of ligand dissociation in these $HNiL_4^+$ complexes, thus resulting in the higher rates of catalysis for the isomerization of 3-butenenitrile. The reason why $Ni(\underline{9})_4$ gives the highest rate of catalysis may be due to optimization of this steric effect when an isopropyl group is in the exocyclic position.

A decrease in the rate of catalysis was observed upon placing groups larger than isopropyl in the exocyclic position of the ring. A possible explanation of this result is that these groups sterically interfere with coordination of the olefin to the metal atom. However, this argument loses some of its attractiveness when one considers that if the phosphorinane ring fails to contain any methyl groups in the equatorial 4,6 positions, catalysis is observed only when a methoxy group is bound in the exocyclic position. Since no catalysis is observed with compound $Ni(\underline{39})_4$, while catalysis is observed with $Ni(\underline{9})_4$, it would seem unreasonable that the exocyclic group interferes with olefin coordination to the nickel. Therefore, it is more likely that the presence of 4,6 equatorial methyl/exocyclic group interactions account for the large changes in the observed rates of catalysis.

Effect of substitution of oxygens in the phosphorinane ring by carbon

As was mentioned earlier, a striking result of Gultneh's work was the tremendous increase in catalytic activity of $Ni(\underline{9})_4$ compared to its acyclic analogue, $Ni(P(O-\underline{i}-Pr)_3)_4$. Gultneh contended that the source of this difference in activity was due to subtle changes in the electronic properties of the ligand. Verkade (12) has shown that some cyclic phosphites have a smaller P-O-C angle than what is observed in their acyclic analogues. This decrease in the P-O-C angle has been shown to bring about a decrease in the basicity of the phosphite. This decrease in basicity can be shown by measurement of the J_{P-H} value upon protonation of the ligand.

As previously described, the more basic the phosphite, the smaller the value of J_{P-H}. The J_{P-H} value for $HP(O-\underline{i}-Pr)_3^+$ was found to be 795 Hz (109), while Gultneh (38) found the J_{P-H} for $H(\underline{9})^+$ to be 853 Hz. Clearly, the acyclic ligand is the one which is more basic. This increased basicity should impart more basicity to the nickel atom, thus facilitating protonation. This increase in the extent of protonation should cause an increase in ligand dissociation, and hence increase the catalytic activity of the complex. However, this turns out to be directly opposite to what is observed experimentally.

Solutions which contain $Ni(P(O-\underline{i}-Pr)_3)_4$ are yellow in color. Addition of acid to these solutions brings about an increase in the intensity of the yellow color. However, solutions of $Ni(\underline{9})_4$ appear colorless. The development of the yellow color occurs only when acid is added. It has been shown fairly conclusively (108) that this yellow

color indicates the presence of NiL_3 species in solution. Based upon either of the previously described isomerization mechanisms, $HNiL_3^+$ or NiL_3 are known to be the catalytically active intermediates. The question then posed is the following: If $Ni(P(O-\underline{i}-Pr)_3)_4$ is more dissociated in solution than $Ni(\underline{9})_4$, then why is it a poorer catalyst than $Ni(\underline{9})_4$? In order to explain this difference in activity, Gultneh contends that $Ni(P(O-\underline{i}-Pr)_3)_4$ decomposes more quickly in the strongly acid media than $Ni(\underline{9})_4$. However, results of the present work have shown that there is very little difference in the rate of decomposition of both complexes in acid solution. This decomposition is evidenced by the solution turning from yellow to green, indicative of the formation of $Ni(II)$ species. Gultneh also contends that electronic factors cause a difference in the extent to which both compounds dissociate in solution. He also states, based upon previous work, that the steric difference between $P(O-\underline{i}-Pr)_3$ and $\underline{9}$ is minor. These conclusions do not appear credible since: a) Tolman (19) has shown that steric factors are more important than electronic factors in the extent to which a NiL_4 complex will dissociate; b) Based upon the increase in the extent of dissociation which is observed from $Ni(P(O-\underline{i}-Pr)_3)_4$ over $Ni(\underline{9})_4$ it would appear that $P(O-\underline{i}-Pr)_3$ has greater steric bulk than $\underline{9}$. This increased extent of dissociation is evidenced by solutions of $Ni(P(O-\underline{i}-Pr)_3)_4$ being yellow in color as opposed to solutions of $Ni(\underline{9})_4$ which are colorless. Tolman and Gosser have previously stated (108) that the yellow color stems from the presence of dissociated $Ni(P(O-\underline{i}-Pr)_3)_3$ species. Unfortunately, measurement of the cone angle of the free ligand may not

provide any useful information about the steric demands of the ligand upon coordination to a metal, since there is no way of determining the exact orientation of the substituents on phosphorus in either a NiL_4 or NiL_3 complex. However, it can be argued that the number of degrees of freedom of the OR group on phosphorus are less in $\underline{9}$ than in $P(O-\underline{i}-Pr)_3$ due to the cyclization of the ring. In fact, the isopropyl groups in $P(O-\underline{i}-Pr)_3$ should be free to adopt any geometry which minimizes their interactions. It is believed that the isopropyl group in the resulting $Ni(P(O-\underline{i}-Pr)_3)_3$ complex could partially block coordination of the olefin to the nickel atom, thus reducing the activity of the system. This argument can be extended to the $HNi(P(O-\underline{i}-Pr)_3)_3^+$ species which forms in protic media.

Tolman and Gosser have suggested (108) that the geometry of a NiL_3 species is trigonal planar. His assertion is supported by a recent x-ray structural analysis of the isoelectronic compound $Pt(PPh_3)_3$ which was observed to be trigonal planar (130). Molecular models of $Ni(P(O-\underline{i}-Pr)_3)_3$ would suggest that due to the higher degrees of freedom for the isopropyl arms of the ligand it is reasonable to expect that some of these isopropyl groups will spend part of their time situated above and below the nickel atom. This geometry is also stabilized by weak hydrogen bonding interactions which could develop between the CH of one isopropyl group and oxygens contained on adjacent ligands. One would expect that this geometry would hinder olefin coordination to the metal and thus slow the rate of catalysis.

However, with Ni$(\underline{9})_4$ it would appear that steric interactions between the ligands are not large enough to cause ligand dissociation to take place in the unprotonated complex. Dissociation is thus only made facile upon protonation of the nickel. Once protonation does occur, the Ni-P bond is weakened sufficiently so that the steric interactions which occur in the complex can promote dissociation. Since there is less freedom of movement for the OR groups in the cyclic ligands, it should be more difficult for these groups to situate themselves directly above and below the nickel atom; thus, the olefin can easily coordinate to the metal atom and undergo isomerization.

In order to see if constraint of the P-O-C angles in $\underline{9}$ as compared to P(O-$\underline{i}$-Pr)$_3$ could account for the large difference in activity of the complexes, Gultneh prepared the corresponding phosphinite ligands $\underline{25}$ and $\underline{28}$. In these ligands, molecular constraint of oxygen can not be present since the oxygens are replaced by CH$_2$ groups. It was reported that Ni$(\underline{28})_4$ is a more effective catalyst than its acyclic analogue, Ni$(\underline{25})_4$. However, the 12% difference in the number of catalytic cycles/30 min. that each produced was small compared to the 2000% difference that was observed with the analogous phosphites during same time period. It was suggested (38) that the large difference in rates between the phosphite and the phosphinite complexes was due to the presence of the oxygens contained in the phosphite ligands.

In the discussion of the phosphinite complexes, no mention was made of the presence of the conformational isomers $\underline{27}$ and $\underline{28}$. It was known that the conformation of the exocyclic group on phosphorus influences the

phosphorus basicity (19). Since it had been shown that both conformers 8 and 38 could be prepared and isolated, it seemed reasonable that conformers 27 and 28 could be prepared and isolated. It was thought that perhaps one of the conformers would produce a more active complex than the other due to basicity and/or steric differences. Perhaps the activity which was observed with the phosphinites was due to the weighted averages of the amount of each isomer coordinated to the nickel atom.

Attempts to prepare a sample of the free ligand according to the procedure of Gultneh (38) met with repeated failure (Eqs. 38, 39).

$$+ \ 2 \ Mg \ \xrightarrow{\ Et_2O\ } \qquad (38)$$

$$+ \ Cl_2PO\text{-}\underline{i}\text{-}Pr \longrightarrow \underline{i}\text{-}PrO$$

$$+ \ 2 \ MgBrCl \qquad (39)$$
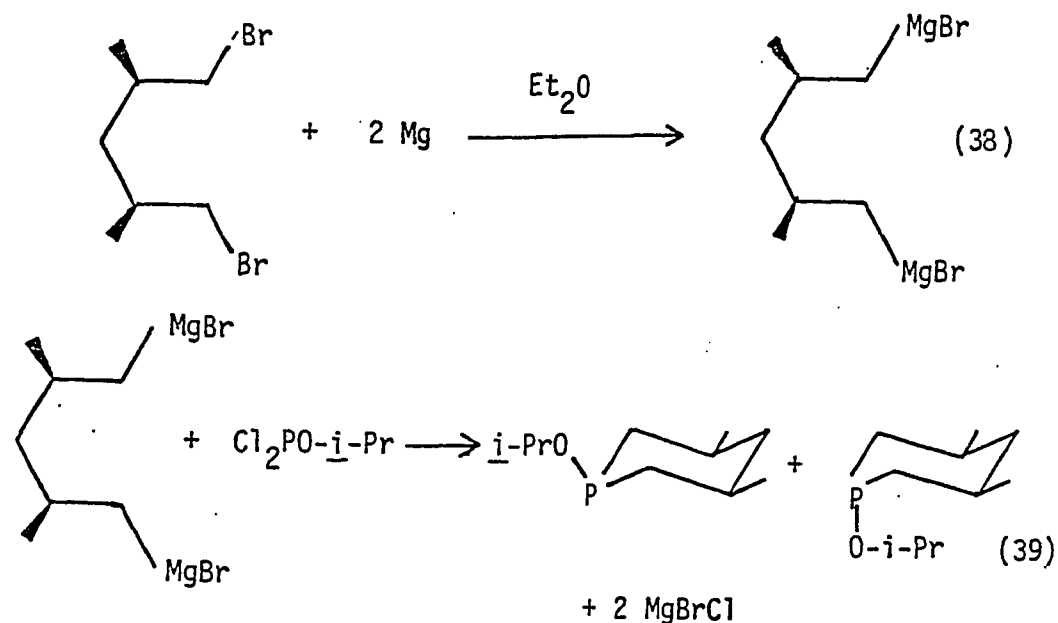
This problem was further complicated by the fact that the meso-2,4-dimethyl-1,5-dibromopentane was obtained in only 7.2% overall yield as described in scheme (5). In order to determine the optimum conditions

for producing _27_ and _28_, attempts were made to prepare the unsubstituted ring compound _26_ via Equations 40 and 41 using the commercially available 1,5-dibromopentane.

$$\text{(40)}$$

$$\text{(41)}$$
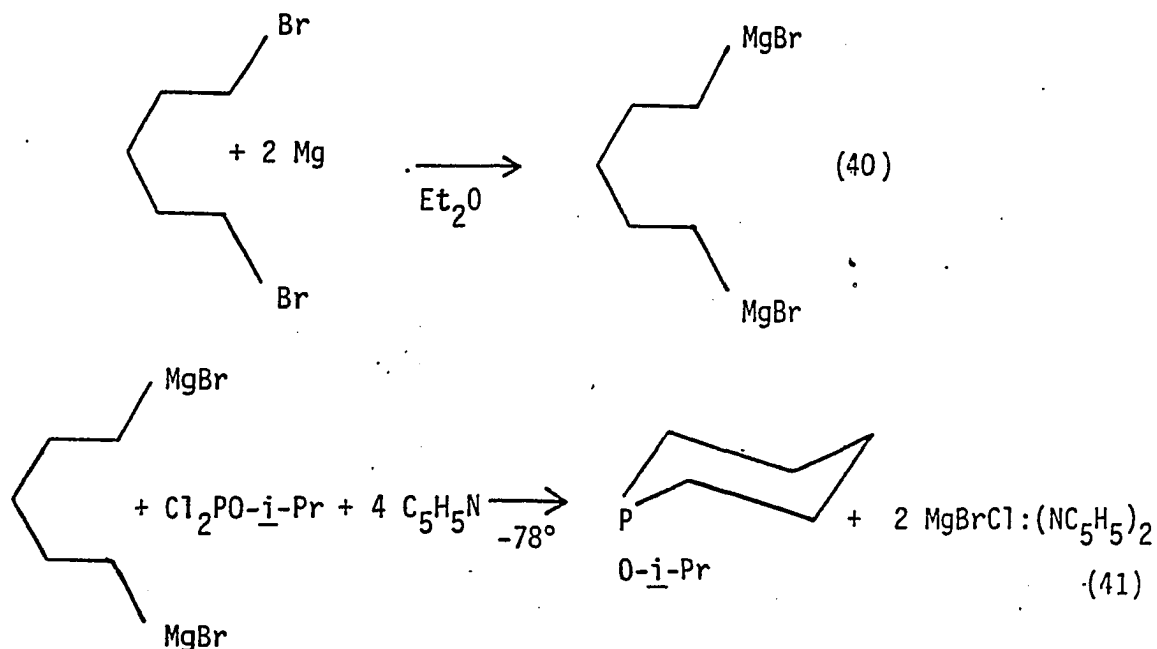
It was found that by adding pyridine to the reaction of the Grignard reagent and $Cl_2P(OiPr)$ (Eq. 41), the yield of cyclic phosphinite (_26_) could be enhanced. Kabachnik and Tsvetkov (131) were the first to show that the yield of a phosphinite $(R_2P(OR))$ in these types of Grignard reactions could be greatly improved by the presence of pyridine. It appeared that the pyridine assisted in the displacement of the phosphinite from their complexes with the magnesium halide, which was produced in the above reaction.

As previously stated in the experimental section, the oil which was obtained from reaction (40) was shown to contain two phosphorus species

in a ratio of 20 to 1 by ^{31}P NMR spectroscopy. Integration of the ^{1}H NMR

spectrum of the oil which was obtained was found to be consistent with

the proposed structure of 26. Attempts to purify the material by

distillation were unsuccessful due to decomposition that took place

during heating. Kosolopoff and Maier have shown (132) that similar

phosphinites are unstable towards rearrangement to tertiary phosphine

oxides upon heating (Eq. 42).

$$R_2P-OR' \longrightarrow R_2P(O)R' \tag{42}$$

To further confirm the identity of the product of reaction (41), the oil

which was obtained was derivatized by an Arbusov reaction (Eq. 43) using

triphenylmethyl chloride. The ^{1}H NMR, ^{31}P NMR and mass spectral
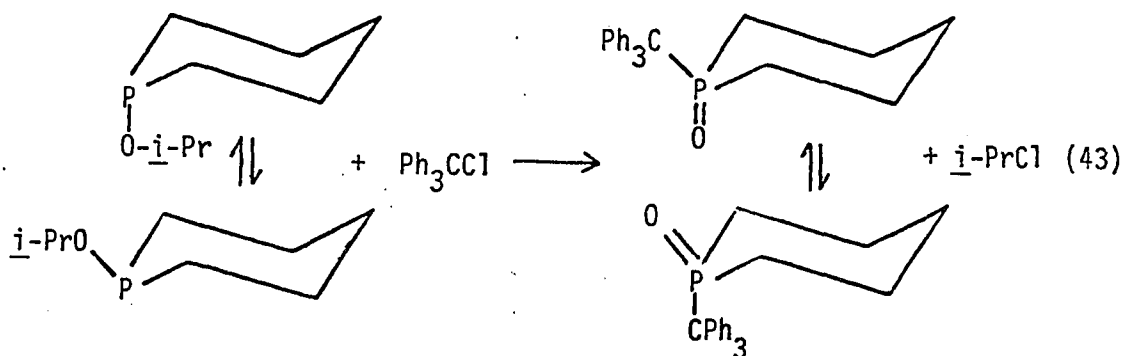
data which were obtained on the product 29 was consistent with its

proposed structure.

Upon developing the proper reaction conditions for the synthesis of

these types of cyclic phosphinites, reactions 38 and 39 were reattempted.

In order to determine the conformational distribution of 27 and 28

contained in the product, the mixture was immediately reacted with

triphenylmethyl chloride in order to obtain more stable derivatives.
White (99) has shown that the Arbusov rearrangement of 8 and 38 with
triphenylmethyl chloride proceeds with retention of configuration.
Therefore, the relative amounts of compounds 29 and 30 should indicate
the amounts of 27 and 28 in the original reaction mixture.
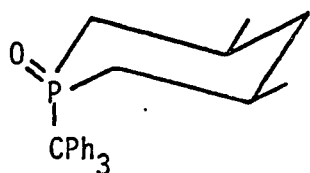
29
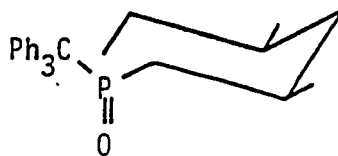
30

^{31}P NMR analysis of the crude solid obtained from the reaction of 27
and 28 with triphenylmethyl chloride showed the presence of many peaks.
However, two peaks at 56.0 ppm and 53.6 ppm were observed in a 3 to 1
ratio. Chromatographic separation of the mixture yielded an oil which
exhibited only these peaks in the same ratio. Upon standing, crystals
formed in the oil which exhibited a ^{31}P NMR chemical shift of 53.6 ppm.
The remaining oil showed the other chemical shift at 55.7 ppm. Mass
spectral analysis of both the oil and the crystals showed that they
contained compounds which were similar in structure due to the similarity
of their fragmentation patterns (Figs. 10 and 11) and the fact that they
both yielded parent ions with m^+/e values of 388.1. An X-ray
crystallographic analysis was carried out in order to determine whether
conformer 29 or 30 was contained in the crystals. The analysis revealed
the identity of the crystals to be 30. The final atomic positions, bond
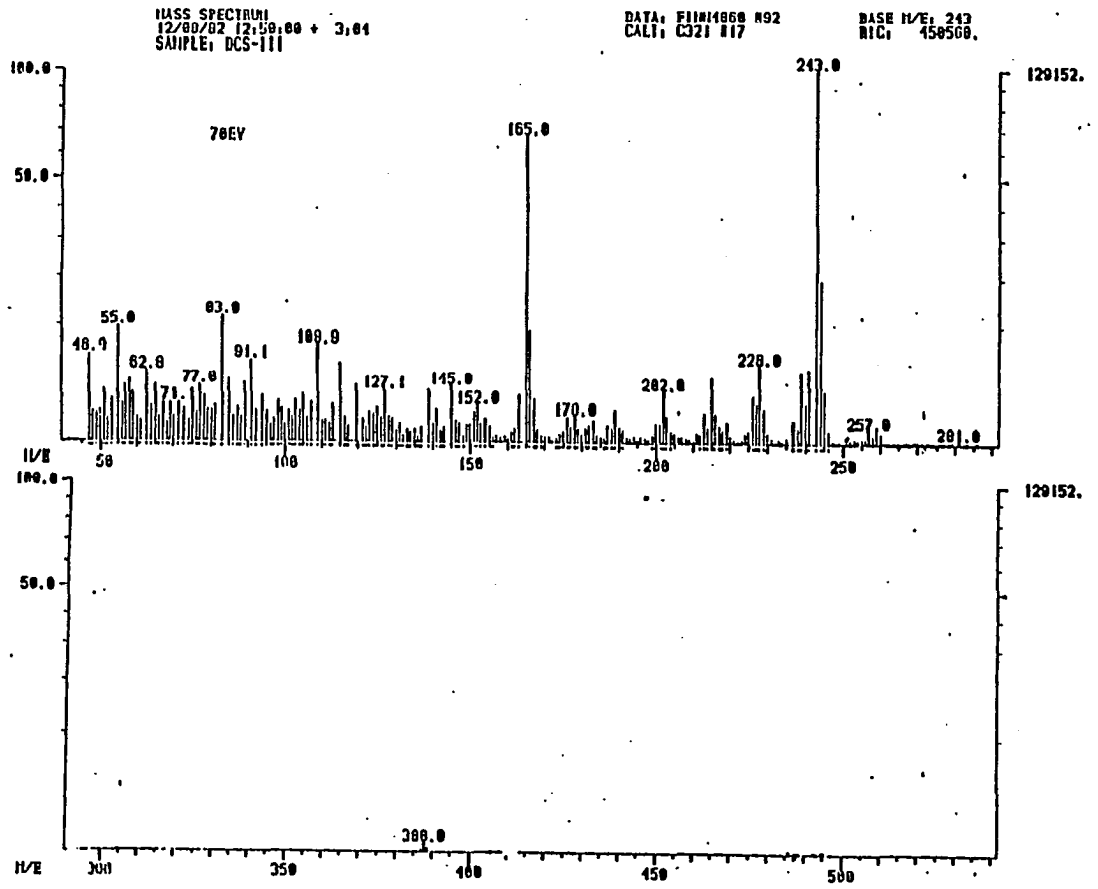
Figure 10. Mass spectrum of <u>29</u>
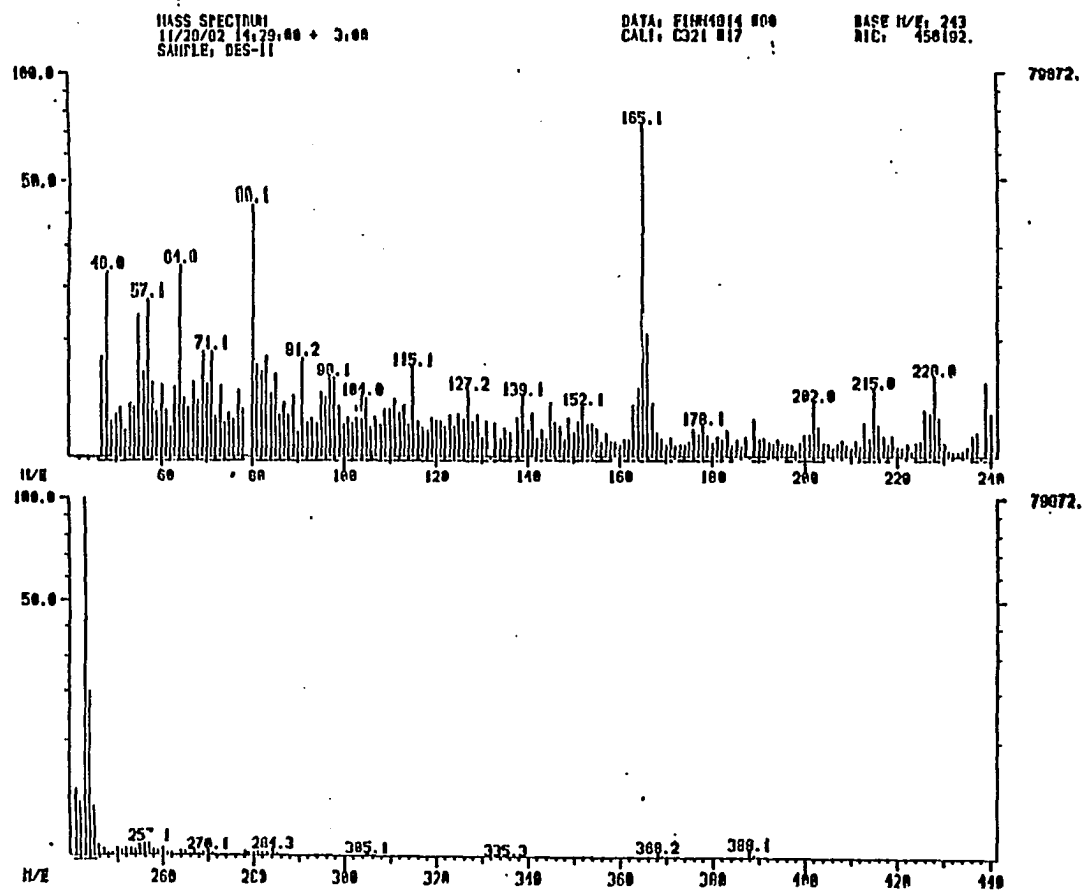
Figure 11. Mass spectrum of 30

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lengths and angles, and anisotropic thermal parameters appear in Tables
16, 17, 18 and 19, respectively. Structure factors for the compound are
found in Appendix 2. An ORTEP diagram of the structure can be found in
Fig. 12. A view of the unit cell is shown in Fig. 13.

Table 16. Final positional parameters and their estimated standard
deviations (in parentheses) for meso-
$(C_6H_5)_3C(O)P[CH_2C(CH_3)H]_2CH_2$ (30)[a]

atom	x	y	z
P	0.0637(1)	0.0752(1)	0.2462(1)
O	0.1319(3)	0.0268(3)	0.2306(3)
C	0.0971(4)	0.1413(4)	0.3559(4)
C1A	0.0246(4)	0.1665(4)	0.4119(5)
C2A	0.0142(5)	0.1472(4)	0.5012(5)
C3A	-0.0545(5)	0.1675(5)	0.5493(5)
C4A	-0.1154(5)	0.2068(5)	0.5089(6)
C5A	-0.1089(5)	0.2274(4)	0.4198(6)
C6A	-0.0384(5)	0.2082(5)	0.3718(5)
C1B	0.1407(4)	0.2080(4)	0.3103(4)
C2B	0.2040(4)	0.1922(4)	0.2535(5)
C3B	0.2472(5)	0.2499(5)	0.2114(5)
C4B	0.2282(5)	0.3257(5)	0.2291(6)
C5B	0.1663(6)	0.3417(4)	0.2877(5)

[a]Position parameters are listed in fractional unit cell coordinates.

Table 16. (continued)

atom	x	y	z
C6B	0.1231(4)	0.2834(4)	0.3287(5)
C1C	0.1570(4)	0.1015(4)	0.4171(5)
C2C	0.1552(5)	0.0226(5)	0.4335(6)
C3C	0.2069(5)	-0.0105(5)	0.4963(6)
C4C	0.2623(5)	0.0300(5)	0.5435(5)
C5C	0.2655(5)	0.1086(5)	0.5264(5)
C6C	0.2138(5)	0.1424(5)	0.4640(5)
C1	0.0201(5)	0.1292(4)	0.1725(5)
C2	-0.0143(6)	0.0742(6)	0.1017(5)
C3	-0.0530(7)	0.1235(6)	0.0243(6)
C4	-0.0786(5)	0.0244(5)	0.1433(5)
C5	-0.1227(6)	-0.0802(6)	0.2496(7)
C6	-0.0524(6)	-0.0283(5)	0.2192(5)
C7	-0.0227(4)	0.0189(4)	0.3009(5)

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Table 17. Bond distances (Å) and their estimated standard deviations (in parentheses) for meso-$(C_6H_5)_3C(0)P[CH_2C(CH_3)H]_2CH_2$ (30)

P-0	1.501(5)	C1C-C2C	1.413(11)
P-C	1.879(7)	C2C-C3C	1.397(12)
P-C1	1.816(8)	C3C-C4C	1.359(12)
P-C7	1.824(8)	C4C-C5C	1.411(12)
C1-C2	1.542(12)	C5C-C6C	1.398(11)
C2-C3	1.580(13)	C6C-C1C	1.374(11)
C2-C4	1.513(13		
C4-C6	1.528(12)		
C6-C5	1.548(14)		
C6-C7	1.556(11)		
C-C1A	1.528(10)		
C-C1B	1.539(10)		
C-C1C	1.519(10)		
C1A-C2A	1.385(11)		
C2A-C3A	1.392(11)		
C3A-C4A	1.364(12)		
C4A-C5A	1.381(12)		
C5A-C6A	1.41(11)		
C6A-C1A	1.409(11)		
C1B-C2B	1.376(10)		
C2B-C3B	1.393(11)		
C3B-C4B	1.398(11)		
C4B-C5B	1.375(12)		
C5B-C6B	1.393(11)		
C6B-C1B	1.387(10)		
C1C-C2C	1.413(11)		
C2C-C3C	1.397(12)		
C3C-C4C	1.359(12)		
C4C-C5C	1.411(12)		
C5C-C6C	1.398(11)		
C6C-C1C	1.374(11)		

Table 18. Bond angles (°) and their estimated standard deviations (in parentheses) for meso-$(C_6H_5)_3C(O)P[CH_2C(CH_3)H]_2CH_2$ (30)

O-P-C	111.96(31)	C2B-C1B-C6B	118.44(67)
O-P-C1	110.19(33)	C1B-C2B-C3B	121.26(69)
O-P-C7	112.38(34)	C2B-C3B-C4B	119.92(73)
C-P-C1	109.88(34)	C3B-C4B-C5B	118.84(76)
C-P-C7	110.46(33)	C4B-C5B-C6B	120.69(75)
C1-P-C7	101.50(36)	C1B-C6B-C5B	120.78(73)
P-C-C1A	110.25(48)	C-C1C-C2C	122.93(66)
P-C-C1B	106.88(43)	C-C1C-C6C	120.68(66)
P-C-C1C	110.06(49)	C2C-C1C-C6C	116.29(69)
C1A-C-C1B	112.77(59)	C1C-C2C-C3C	120.95(75)
C1A-C-C1C	108.63(54)	C2C-C3C-C4C	122.81(79)
C1B-C-C1C	108.21(57)	C3C-C4C-C5C	116.59(74)
C-C1A-C2A	123.38(65)	C4C-C5C-C6C	121.01(73)
C-C1A-C6A	120.16(64)	C1C-C6C-C5C	122.34(74)
C2A-C1A-C6A	116.36(67)	P-C1-C2	109.44(56)
C1A-C2A-C3A	122.23(71)	C1-C2-C3	107.69(74)
C2A-C3A-C4A	120.52(74)	C1-C2-C4	110.11(66)
C3A-C4A-C5A	119.99(78)	C3-C2-C4	109.47(79)
C4A-C5A-C6A	119.35(75)	C2-C4-C6	117.17(76)
C1A-C6A-C5A	121.52(70)	C4-C6-C5	111.27(79)
C-C1B-C2B	118.24(62)	C4-C6-C7	110.07(73)
C-C1B-C6B	123.15(64)	C5-C6-C7	108.99(69)
		P-C7-C6	107.71(53)

Table 19. Thermal parameters and their estimated standard deviations[a] (in parentheses) for meso-$(C_6H_5)_3C(O)P[CH_2C(CH_3)H]_2CH_2$ (30)

atom	B_{11}	B_{12}	B_{33}	B_{12}	B_{13}	B_{33}
P	6.0(1)	6.1(1)	4.8(1)	-0.5(1)	-0.1(1)	0.0(1)
O	6.6(3)	7.3(3)	6.8(3)	0.6(3)	1.0(2)	-1.0(3)
C	5.5(5)	6.1(4)	3.9(4)	0.5(4)	-0.4(3)	-0.4(4)
C1A	6.0(5)	5.6(5)	5.9(4)	-0.3(5)	-0.1(4)	-0.2(4)
C2A	6.2(6)	7.0(6)	5.4(4)	0.0(5)	1.0(4)	1.0(4)
C3A	9.2(6)	8.3(6)	5.7(6)	-0.7(6)	1.3(5)	0.4(5)
C4A	8.1(7)	8.1(6)	7.3(6)	0.1(6)	2.1(5)	0.10(5)
C5A	7.0(6)	8.1(6)	7.0(6)	0.9(5)	-0.1(5)	-0.6(5)
C6A	7.6(8)	7.9(6)	5.2(5)	0.4(5)	0.8(5)	-0.5(5)
C1B	5.8(5)	5.3(5)	4.9(4)	-0.0(4)	-0.6(4)	-0.4(4)
C2B	6.1(5)	6.1(5)	6.2(5)	-0.7(4)	0.1(5)	0.4(4)
C3B	6.8(6)	8.1(6)	6.5(5)	-0.8(6)	-0.1(4)	-0.2(5)
C4B	7.8(6)	8.0(7)	7.3(6)	-2.2(6)	-0.6(5)	1.2(6)
C5B	9.5(7)	5.9(6)	7.9(6)	0.5(6)	-0.5(5)	0.1(5)
C6B	7.6(6)	5.9(5)	6.2(5)	-0.27(5)	0.1(4)	-0.1(4)
C1C	5.2(5)	6.6(5)	5.0(4)	-0.7(4)	-0.3(4)	-0.4(4)
C2C	7.5(6)	6.7(6)	7.8(6)	-0.5(5)	-2.6(5)	0.2(5)
C3C	9.5(6)	7.0(5)	8.4(6)	-0.3(5)	-3.1(6)	0.6(5)

[a]The form of the anisotropic thermal parameter is $\exp[-(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^{*2} + B_{33}c^{*2}l^2)/r + (B_{12}a^*b^* hk + B_{13}a^*c^*hl + B_{23}b^*c^* kl)/2]$.

Table 19. (continued)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{33}
C4C	7.0(6)	7.9(6)	6.4(5)	0.7(6)	-1.11(5)	1.1(5)
C5C	6.6(6)	9.2(7)	6.0(5)	-1.0(5)	-1.3(5)	0.1(5)
C6C	6.9(5)	7.1(5)	5.9(5)	0.2(5)	-0.7(4)	1.4(5)
C1	8.1(5)	6.3(5)	4.2(4)	0.5(4)	-0.5(4)	0.8(4)
C2	11.7(7)	9.5(6)	6.1(5)	-3.8(6)	-1.9(5)	0.6(5)
C3	15.2(8)	9.9(7)	6.9(6)	-1.7(6)	-4.9(6)	2.9(5)
C4	8.0(6)	9.9(7)	5.8(5)	-1.2(5)	-1.3(5)	-0.9(5)
C5	11.8(8)	12.2(8)	10.3(7)	-7.3(7)	0.5(7)	-0.1(7)
C6	11.5(7)	9.7(6)	5.5(5)	-3.7(6)	-2.7(5)	0.9(5)
C7	5.6(4)	7.5(5)	5.9(4)	-1.9(4)	1.3(4)	0.8(4)

As can be seen in Fig. 12, the triphenylmethyl group adopts the equatorial position with respect to the phosphorinane ring. The ring adopts the chair conformations which appears to be free of any twist as the torsional angles described by atoms P, C1, C2, C4 and P, C7, C6, and C4 are equal to 59.7° and -60.8, respectively. The acute angle formed by the planes C1-P-C7 and C7-C6-C2-C1 is 53.6°, which is fairly close to the 60° angle found in the perfect chair conformation of cyclohexane. The rear of the phosphorinane ring comprised of the C2, C4, and C6 atoms does appear to be somewhat flattened since the acute angle between the least square planes encompassing the C2, C4, C6 and C1, C2, C6, C7 atoms is
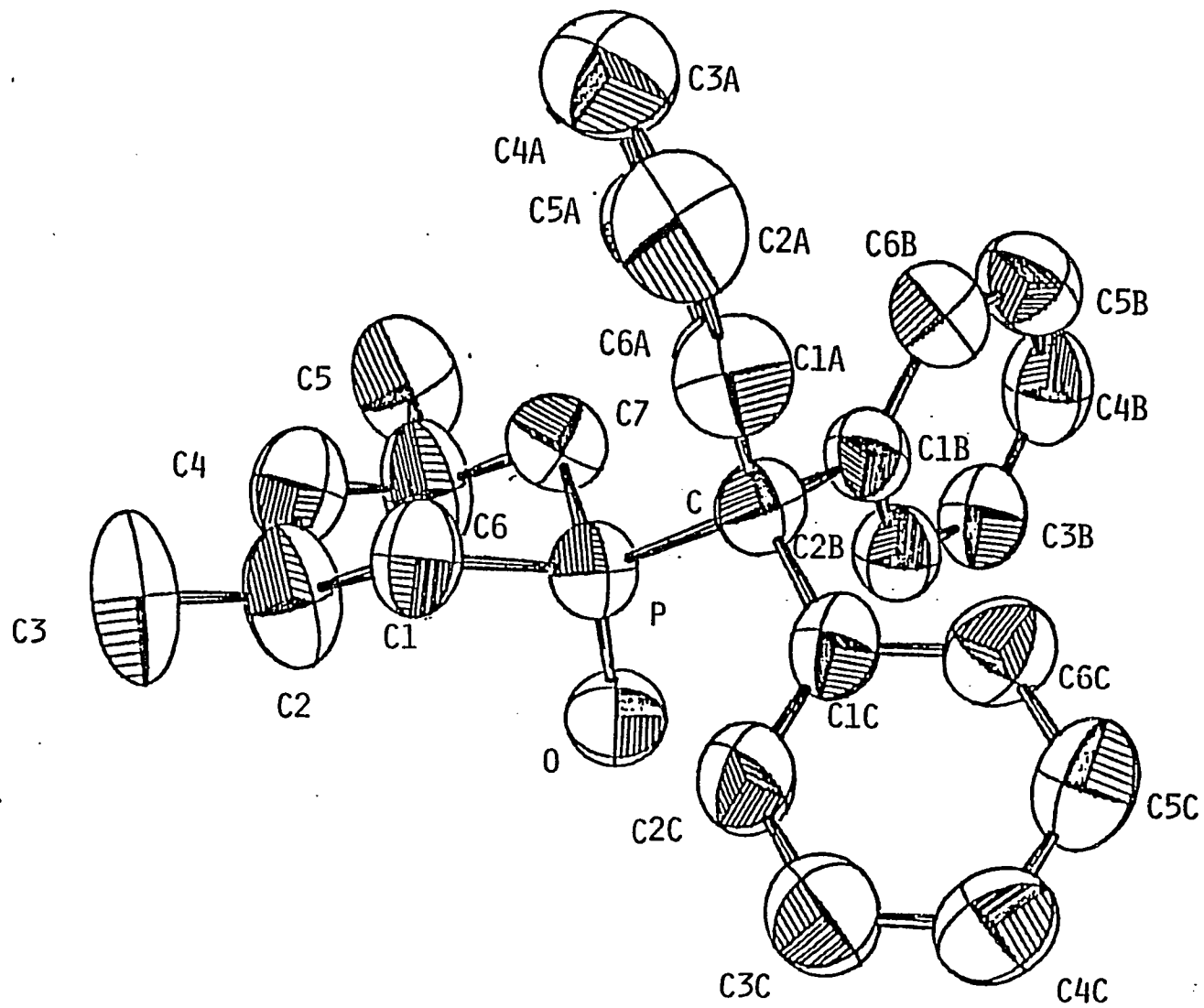
Figure 12. ORTEP diagram of 30.
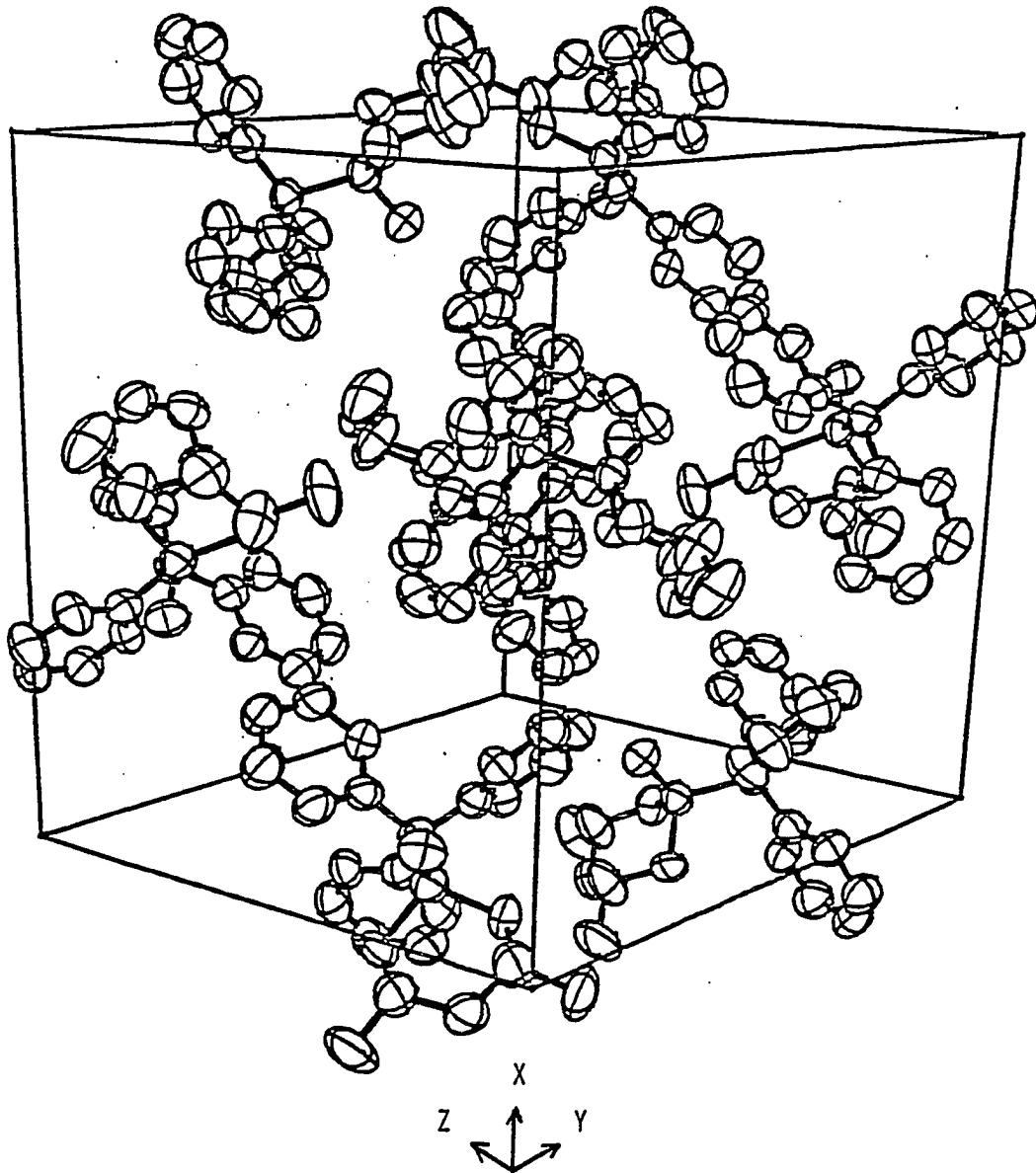
Figure 13. Unit cell diagram of 30.

equal to 39.2°. This deviation from 60° can only be ascribed to packing forces within the crystal, since there appears to be no steric interactions with any other parts of the molecule which could account for this flattening. All other bond distances and angles are consistent with those found in other 2-alkoxy-2-oxo-1,3,2-dioxaphosphorinanes (99).

Reactions of cyclic phosphites and triphenylmethyl chloride are known to yield Arbusov products in which the original conformation about phosphorus is retained (133). Since the reaction of the phosphinite and triphenylmethyl chloride presumably takes place by the same mechanism as with a phosphite, the percentage of each configuration in the resulting tertiary phosphine oxide mixture should be the same as in the starting phosphinite mixture. Based upon information supplied by the X-ray crystallographic analysis, we are able to assign the peak at 53.6 ppm of the phosphine oxide mixture to configuration 30 while the peak at 56.0 ppm is assigned to 29. Since the ratio of the peak areas in the ^{31}P NMR spectrum is 3 to 1, this should correspond to a ratio of 3 to 1 in the original phosphinite mixture.

As stated previously, in 2-alkoxy-1,3,2-dioxaphosphinanes the conformation with the axial alkoxy group and an equatorial lone pair is preferred. This conformation is preferred in order to minimize electronic interactions between the lone pairs on phosphorus and the lone pairs on oxygen. However, phosphorinanes which do not contain oxygen in the ring prefer to adopt the conformation which has the alkoxy group in an equatorial position and a lone pair in the axial position. This

conformation reduces the steric interaction between the exocyclic group
and the rest of the ring (19).

The 3 to 1 ratio of configurations was also verified by a ^{31}P NMR
analysis of the product mixture obtained in reactions (37 and 38).
Previous work had shown that compound 26 exhibited a sharp singlet at
108.8 ppm. Close scrutiny of the NMR spectrum of the mixture showed
three peaks at 111.1, 109.4, and 107.4 ppm in a ratio of 1 to 3 to 1.
The peaks at 109.4 and 107.4 ppm were assigned to compounds 27 and 28,
respectively. While the peak at 111.1 was ascribed to possibly
oligomeric products formed in the reaction. The peaks were assigned as
shown since work with the derivatized material indicated a 3 to 1 mixture
of starting phosphinites. Also, it appeared that these peaks were
observed to have ^{31}P NMR chemical shifts which were on either side of the
corresponding unsubstituent phosphinite. As can be seen in Table 20, the
decreasing ^{31}P NMR chemical shifts fall in the order: 55, 56, and 57.
Though the magnitudes of the differences in chemical shifts between
compounds may be different in phosphites and phosphinites, the trends in
chemical shifts may be expected to be the same due to the similarity of
the compounds.

Attempts to prepare and separate 27 and 28 had proved
unsuccessful. ^{31}P NMR peak integration has shown that the compounds were
prepared in less than 10% yield. Due to the low yield of the compounds
and the fact that there was no known way of converting back the
derivatized products to their starting phosphinites, it seemed that

Table 20. ^{31}P NMR Chemical shifts for selected phosphorinane compounds

Compound	Chemical shift (ppm)	Compound	Chemical Shift (ppm)
55	132.9	27	109.4
56	130.0	26	108
57	127.1	28	107.4

[a]Reference (38).

[b]Reference (133).

separation of the isomers would not be feasible. However, it was known (38) that NiL$_4$ complexes of 28 and 27 could be made by reaction of the ligand obtained in reaction (38) with Ni(CH$_2$=CHCN)$_2$. The amount of Ni(CH$_2$=CHCN)$_2$ to be used was determined by the ^{31}P NMR spectrum of the oil which indicated the relative amount of 27 and 28 contained in a specific amount of the mixture. Unfortunately, repeated attempts to synthesize Ni(27,28)$_4$ were met with failure. In every case, unrecognizable products were obtained. ^{31}P NMR analysis of this material indicated the lack of any of the NiL$_4$ complex as Gultneh (38) had described. However, attempts to prepare Ni(25)$_4$ were successful. The final product obtained by chromatography under N$_2$ was a greyish white solid which exhibited only one ^{31}P NMR chemical shift at +144.9 ppm, 22.9 ppm downfield of the free ligand. In all the previously discussed

complexes, a downfield shift of approximately 20 ppm was observed for the ligand upon coordination.

Attempts to use this compound in the catalytic isomerization of 3-butenenitrile were unsuccessful. It was observed that upon addition of the acid to a benzene solution of the complex the solution took on a yellow-orange color. However, after about fifteen minutes the color had changed to green, indicative of nickel oxidation. This observation agrees with work of Carriatta and co-workers (134) who showed that only zero-valent platinum phosphine complexes could be protonated by acid. Attempts to protonate the analogous tetrakis phosphine palladium and nickel complexes yielded only nickel and pallium salts of the corresponding acid.

This instability of NiL_4 complexes of phosphines and phosphinites toward acids can be explained by the electronic properties of the ligands. Since these ligands are known to be more basic than phosphites, they should impart more electron density to the nickel atom thus making it easier for its oxidation by acids. On the other hand, the phosphite is able to decrease the electron density on the nickel atom due to its increased π-acceptor and poorer σ donation properties. It is this reduced electron density on nickel which prevents immediate oxidation by the acid. However, this reduction in electron density is still not enough to entirely prevent oxidation of the Ni(0) species. It only serves to slow down oxidation as evidenced by oxidation of a $Ni(P(OR)_3)_4$ complex in acid approximately 6 hrs. (under anaerobic conditions). Fortunately, during this period, the $HNiL_3^+$ species, which is generated

from the NiL$_4$ complex in protic acids, and the NiL$_3$ species generated with nonprotic acids can act as catalysts for olefin isomerization. However, it should also be realized that removal of electron density from the nickel by strong π-acceptor ligands can become so great, as in the case of 11 and 12, that the corresponding NiL$_4$ fails to protonate; or in the case of nonprotic acid media, fails to dissociate sufficiently. Thus, it would appear that the unique electronic properties of phosphite ligands facilitate their use in NiL$_4$/acid catalyst systems.

Asymmetric isomerization of (CH$_3$CH$_2$)(CH$_3$)C=CHCH$_2$CN

Gultneh (38) found that Ni((-)-7)$_4$ catalyzed the asymmetric isomerization of Et(Me)C=CHCH$_2$CN to Et(Me)CHCH=CHCN. He observed that approximately 70% of the starting prochiral olefin could be isomerized, and a 52% enantiomeric excess could be achieved in a period of 2 hrs.

Results obtained in the isomerization of 3-butenenitrile had shown that the most active catalysts were those which contained methyl groups in the equatorial 4 and 6 positions on the ring. It was thought that by synthesizing a chiral ligand with methyl groups in these positions and incorporating it in a NiL$_4$ complex, isomerization of the above compound could be carried out more quickly with possibly a higher degree of enantiomeric excess. Compound 36 was prepared by the reaction of 4 and d-sec butanol in the presence of triethyl amine. The NiL$_4$ complex was prepared using the aforementioned method. Subsequent ^{31}P NMR analysis showed that the complex was completely protonated by a 10 to 1 acid to nickel ratio. This was evidenced by the disappearance of a singlet at

151.3 ppm for the NiL_4 species and the appearance of a doublet at 131.8

ppm $(J_{H-M-P} = 30 Hz)$ upon addition of acid.

The complex was tried as a catalyst for the isomerization of $Et(Me)C$

$= CHCH_2CN$. However, repeated attempts showed that the complex was

completely inactive as a catalyst. However, other experiments showed

that the compound could efficiently isomerize 3-butenenitrile to cis and

trans 2-butenenitrile (90 cycles/30 min). On the basis of these results,

it was felt that $Ni(\underline{36})_4$ failed to isomerize the prochiral olefin due to

the latter's larger size compared to 3-butenenitrile. It would appear

that $Ni(\underline{7})_4$ was able to isomerize the prochiral olefin since the ligand

was smaller than $\underline{36}$ and thus the prochiral olefin could more easily

coordinate to the metal center and undergo isomerization.

These results would seem to suggest, as was previously suggested by

Parshall (1), that when designing a metal complex to be used as a.

catalyst, one must not only take into account the steric requirements of

the ligands about the metal, but also the steric requirements of the

substrate.

Hydrocyanation of 1,3-butadiene to adiponitrile

The catalytic hydrocyanation of olefins has been of interest to

industrial chemists for many years. The hydrocyanation of butadiene to

adiponitrile $(NC(CH_2)_4CN)$ is of considerable interest, because of the use

of adiponitrile as a chemical intermediate in the production of synthetic

polymers, such as nylon. Chemists at Dupont have patented the use of

cuprous halides and nickel(0) complexes containing phosphite ligands, in

particular $P(OPh)_3$ (51) as catalysts for the production of adiponitrile from butadiene. The reaction of butadiene and HCN in the presence of these catalysts is thought to proceed via the following series of Equations 44-47.

$$CH_2=CHCH=CH_2 + HCN \xrightarrow{M} CH_3CH=CHCH_2CN \qquad (44)$$

$$+$$

$$CH_2=CH-CH(CH_3)CN$$

$$CH_2=CH-CH(CH_3)CN \xrightarrow{M} CH_3CH=CHCH_2CN \qquad (45)$$

$$CH_3CH=CHCH_2CN \xrightarrow{M} CH_2=CHCH_2CH_2CN \qquad (46)$$

$$CH_2=CHCH_2CH_2CN + HCN \xrightarrow{M} NC(CH_2)_4CN \qquad (47)$$

$$M = Ni(P(OR)_3)_4$$
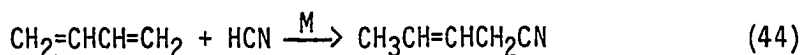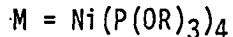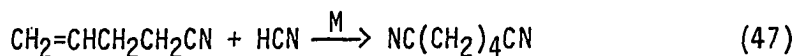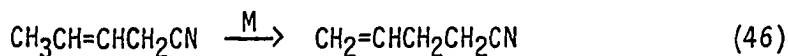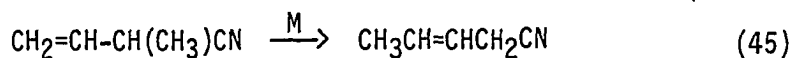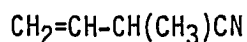
It is claimed that complexes such as $Ni(O-\underline{o}-tolyl)_3$ can affect the conversion of 1,3-butadiene to adiponitrile in high yield and with high selectivity (1).

It should also be noted that Monsanto Corporation has patented a process for the production of adiponitrile by electrodimerizing acrylonitrile (135). Acrylonitrile can be easily prepared by addition of HCN to acetylene via the use of catalysts such as $Co_2(CO)_8$ and $Ni(P(OEt)_3)_4$ (47). The advantage of this process is that the adiponitrile can be produced without production of unwanted isomers as is the case with 1,3-butadiene.

Gultneh (38) found that the NiL_4 complexes he used for olefin isomerization were also effective hydrocyanation catalysts. It was observed that the most efficient isomerization catalysts were also the most efficient for hydrocyanation. However, two major differences were observed. Though hydrocyanation of olefins such as norbornene was maximized with NiL_4 complexes containing ligands with methyl groups in the equatorial 4,6 positions of the phosphorinane ring, changing the size of the exocyclic group had only a small effect in controlling the activity of the complex. It was observed that placement of an isopropyl group in the exocyclic position did seem to maximize the amount of catalysis observed in 4,6-dimethyl phosphorinane system. However, increasing the exocyclic group size to a t-butyl group only reduced the number of turnovers per hour by 15%, whereas in isomerization the rate decreased by 60%. Secondly, addition of excess ligand to the hydrocyanation system brought about an increase in the amount of hydrocyanated product formed. This is opposite to what was observed in the isomerization of 3-butenenitrile, where addition of excess ligand brought about a decrease in the extent of catalysis. The probable explanation of this observation is that excess ligand limits the extent to which hydrogen cyanide complexes to the nickel atom, hence slowing down the rate of oxidation of the catalyst to catalytically inactive $Ni(CN)_2$ species.

Since Gultneh had found that these complexes were active catalysts for the hydrocyanation of olefins such as norbornene, allylbenzene, and 1,5-octadiene, it seemed worthwhile to attempt to hydrocyanate 1,3-

butadiene using the catalysts he found to be the most active, namely, $Ni(\underline{8})_4$ and $Ni(\underline{9})_4$. The reactions were carried out under the same conditions as used by Drinkard and Lindsey for the production of adiponitrile (46). The mixtures were analyzed for adiponitrile using capillary gas chromatography. As can be seen in Table 21, the yields of adiponitrile were quite low. The values which were obtained are even considerably lower than what was obtained in the hydrocyanation of the previously mentioned olefins. Analysis of the results suggest that $Ni(\underline{8})_4$ in the presence of $ZnCl_2$ and excess ligand produced the most active catalyst mixture. It also appeared that having a methyl group instead of an isopropyl group in the exocyclic position produced a more active catalyst. This result is opposite to what was observed by Gultneh for the olefins which he used. The precise reasons for the increased activity of the methyl complex is not yet known. However, it is possible that subtle differences in the steric properties of the ligands cause $Ni(\underline{8})_4$ to be a more efficient catalyst for the hydrocyanation of 1,3-butadiene. As seen in Table 21, the highest number of turnovers for the $Ni(\underline{8})_4$ is observed when excess ligand is present. As previously stated, this is probably due to excess ligand preventing complexation of excess HCN to the Ni atom. We are currently unable to give a justification for the lower amount of turnovers observed for the 1/1/8 $Ni(\underline{9})_4/ZnCl_2/\underline{9}$ system as compared to the 1/1 $Ni(\underline{9})_4/ZnCl_2$ system. Previous work (38) would have led to the expectation of a larger number of catalytic cycles for the former system.

Table 21. The preparation of adiponitrile from butadiene and HCN using various catalyst systems at 120°C in xylene

Catalyst mixture	mole of adiponitrile produced mole of Ni/2 hr (±1)
Ni($\underline{8}$)$_4$	4.0
Ni($\underline{8}$)$_4$/ZnCl$_2$/$\underline{8}$: 1/1/17	13.6
Ni($\underline{9}$)$_4$	0.0
Ni($\underline{9}$)$_4$/ZnCl$_2$: 1/1	6.7
Ni($\underline{9}$)$_4$/ZnCl$_2$/$\underline{9}$: 1/1/8	3.0
Ni($\underline{9}$)$_4$/ZnCl$_2$/$\underline{9}$: 1/1/15	5.4

It would appear that these catalysts, though good for the hydrocyanation of some olefins, are poor at converting 1,3-butadiene to adiponitrile. Attempts were made to carry out the reaction at 25°C in order to increase the residence time of the butadiene (bp = -4.4°C) and HCN (bp = 26°C) in the flask. However, experiments with $Ni(\underline{9})_4$, $ZnCl_2$ and $\underline{9}$ in a ratio of 1/1/15 at 25° failed to produce any adiponitrile. It is possible that the reaction fails to proceed at this temperature and the residence time of the reagents may not even be a factor in the lack of activity.

GC-MS analysis of the reaction mixture showed that besides adiponitrile being produced in these reactions, pentenenitrile and compounds of higher molecular weight than adiponitrile were also produced. The yields of these compounds were found to be approximately equal to that of adiponitrile. The identities of these higher molecular weight compounds are not known at this time. However, they are probably oligomers of either 1,3-butadiene or pentenenitrile since Tolman has shown previously that $Ni(P(OR)_3)_4$ complexes are efficient catalysts for the codimerization of olefins (136). No further work was done with this system due to the apparent lack of activity or selectivity for the production of adiponitrile.

Heterogenized NiL_4 catalysts

As stated in the introduction of this chapter, the advantages in the use of heterogeneous catalysts are numerous. Based upon our knowledge of the NiL_4 catalyst system, we sought to find ways to heterogenize these

catalysts. We were well aware of previous attempts to heterogenize

homogeneous catalysts (66). Generally, these techniques involved

substitution of a ligand in a homogeneous complex with a ligand bound to

a polymer support. However, we decided to attempt a markedly different

approach, that of directly incorporating the active metal center in a

polymer framework. By doing this, it was hoped that it would be possible

to prepare a catalyst which would function heterogeneously while at the

same time providing easy access of the substrate to the catalytically

active metal site.

First, attempts were made to prepare metal complex polymers of the

following type (Fig. 14):

$$-(P---P)-\underset{|}{M}-(P---P)-\underset{|}{M}-(P---P)-\underset{|}{M}-(P---P)-\underset{|}{M}-(P---P)-$$

$$-(P---P)-\underset{|}{M}-(P---P)-\underset{|}{M}-(P---P)-\underset{|}{M}-(P---P)-\underset{|}{M}-(P---P)-$$

(P---P) = nonchelating diphosphorus ligand
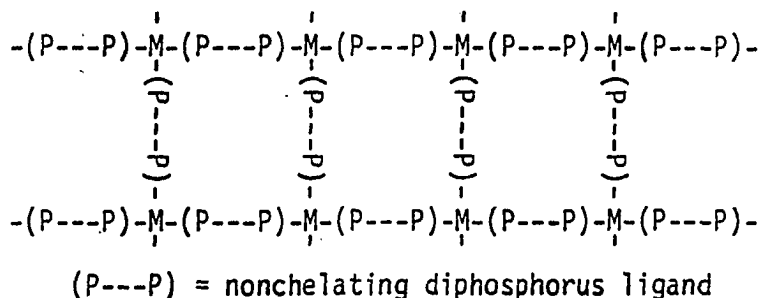
Figure 14. Proposed structure of metal complex polymer

In selecting a ligand which would link metal centers it was deemed

necessary that the ligand: 1) not chelate the metal atom, and 2) mimic as

closely as possible the structural and electronic properties of the

ligand it replaced in the homogeneous NiL_4 complex. Compound 23 was

selected to be used as the linking ligand. A recent x-ray structural

analysis had shown (41) that the phosphorus lone pairs were unable to

chelate a metal atom due to the structural features of the molecule; at

the same time its six member ring structure was similar to that shown to

be effective in our homogeneous reaction studies. Attempts to prepare a polymer of the type $[Ni(\underline{23})_2]_n$ were carried out via the following reactions.

$$Ni(H_2O)_6(BF_4)_2 + 6\ CH_3C(OMe)_2CH_3 \longrightarrow Ni(BF_4)_2 + 12\ MeOH \qquad (48)$$
$$+ 6\ CH_3C(O)CH_3$$

$$Ni(BF_4)_2 + 2.5\ (\underline{23}) \xrightarrow[\text{acetone}]{} [Ni(\underline{23})_{2.5}](BF_4)_2 \qquad (49)$$

$$2[Ni(\underline{23})_{2.5}]_n(BF_4)_2 + 2NaHCO_3 \xrightarrow[H_2O]{} 2[Ni(\underline{23})_2]_n + 2NaBF_4 + O{=}(\underline{23}){=}O$$
$$+ 2HBF_4 + 2CO_2 \qquad (50)$$
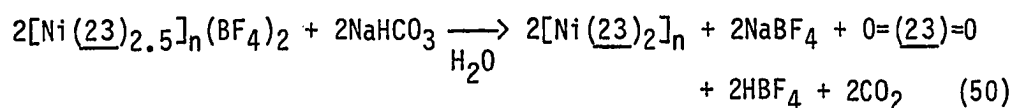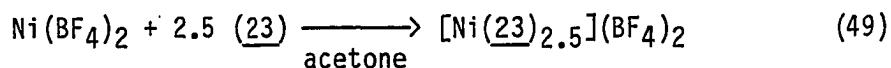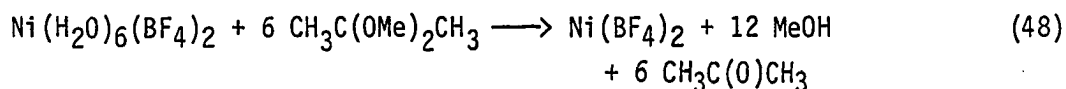
Previously, work with nickel(II) phosphite complexes had shown them to be pentacoordinate (137). Since each molecule of $\underline{23}$ contains two phosphorus atoms it was deemed necessary that a 2.5 to 1 ratio of $\underline{23}$ to nickel ratio should be used. The product from reaction (47) was a bright yellow orange solid which was observed to be insoluble in all solvents including water. The powder was ground very finely and then added to an aqueous bicarbonate solution. Gas evolution was observed as had been observed in similar reactions of $Ni(P(OR)_3)_5^{+2}$ and $KHCO_3$ (138). Upon stirring for 2 hr under N_2 the orange solid had turned white, indicative of a Ni(0) species.

Attempts to reduce $[Ni(\underline{23})_{2.5}]_n(BF_4)_2$ with $LiAlH_4$ and $NaBH_4$ at room temperature proved to be unsuccessful as evidenced by the brownish-green

intractable solids produced in the reactions. However, reduction with NaBH$_4$ at -78°C did prove to be successful in producing a white solid.

The white solids which were obtained in these reactions were tried as catalysts in the isomerization of 3-butenenitrile. The solid was suspended in a benzene solution which contained the 3-butenenitrile. Upon addition of acid to the suspension, the solid turned yellow in color, indicative of protonation of the nickel. Subsequent analysis of the solution showed that the polymer was incapable of isomerizing the olefin.

The inactivity of this catalyst was probably due to its inability to undergo ligand dissociation. As previously stated, the important step in the isomerization mechanism is the dissociation of a ligand from the HNiL$_4^+$ complex to form a coordinatively unsaturated HNiL$_3^+$ species. In this type of polymer, ligand dissociation is limited since most of the ligands are part of the polymer framework. In order to overcome this problem, a new type of polymer was designed (139). It was thought that by exchanging ligands between a NiL$_4$ complex and 23, a new type of polymer could be formed (Eq. 49).

$$NiL_4 \; + \; \text{(ligand structure)} \rightarrow \left\{ NiL_2(\text{(ligand structure)}) \right\}_n + \; 2L \quad (51)$$
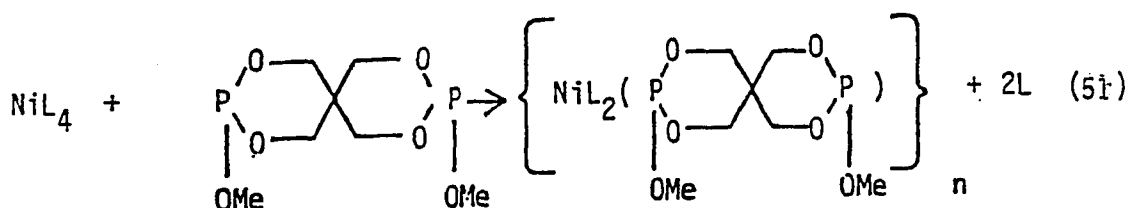
The advantages of this type of catalyst over the previous polymer was that it contained monodentate phosphite ligands(L) which could now undergo dissociation upon protonation of the metal. The strand-like nature of this polymer might also allow for an increase in the availability of the metal atom to coordination of an olefin. Total utilization of all the nickel atoms in the other polymer would not be possible since most of the nickel atoms were buried deep within the polymer framework.

Reaction (51) was found to proceed when L = $\underline{5}$, $\underline{7}$, and P(OMe)$_3$. Surprisingly, the reaction failed when L = $\underline{8}$. One of the main problems in characterizing these materials was the complete insolubility in all organic solvents, which is indicative of their polymeric nature. This ruled out their analysis using most standard spectroscopic techniques. In order to determine the ratio of $\underline{23}$ to L in these types of polymers, a sample of [Ni($\underline{23}$)(P(OMe)$_3$)$_2$]$_n$ was subjected to ozonolysis for 2 hours. ^{31}P NMR showed that the only products obtained in this reaction were (MeO)(O)P(OCH$_2$)$_2$C(CH$_2$O)$_2$P(O)(OMe) and (MeO)$_3$PO in a ratio of 1.1 to 1 (based on phosphorus), which is slightly greater than the 1 to 1 ratio which would have been expected. A gravimetric nickel analysis was done to determine the percent of nickel in the polymer. [Ni($\underline{23}$)(P(OMe)$_3$)$_2$]$_n$ was found to contain 9.4% nickel whereas 10.4% would be expected for a compound of that formulation. [Ni($\underline{23}$)($\underline{7}$)$_2$]$_n$ analyzed slightly better with a value of 9.1% Ni as compared to an expected value of 9.5%. The polymers were all tried as catalysts in the isomerization of 3-butenenitrile, and all were shown to function as catalysts. However,

there was a sharp decline in the activity of these compounds as opposed to their homogeneous analogues (Table 22).

In order to prove that these catalysts operated heterogeneously, the following experiment was carried out. A freshly prepared sample of [Ni(23)(P(OMe)$_3$)$_2$]$_n$ was divided in half. One half was used to make sure that the sample could isomerize 3-butenenitrile to cis/trans 2-butene-nitrile. Once the activity of the sample had been established, the other half was used in an identical catalysis experiment. As soon as the complex started to isomerize the olefin (as shown by gas chromatography), the reaction mixture was filtered under a nitrogen atmosphere. The

Table 22. The number of turnovers per unit time produced by various [Ni(23)$_2$(L)$_2$]$_n$ polymers versus their homogeneous NiL$_4$ complexes for the isomerization of 3-butenenitrile[a]

L	[Ni(23)(L)$_2$]$_n$ Turnovers/time ($\pm$ 10)	NiL$_4$[b] Turnovers/time ($\pm$ 10)
P(OMe)$_3$	120/18 hrs	74/30 min
5	0	60/30 min
7	72/24 hrs	92/30 min

[a]3-Butene nitrile/acid/Ni = 124/10/1.

[b]Ref. (38).

yellow solid could be easily filtered out by glass wool placed at the end

of pipette to yield a clear, colorless solution. Subsequent analysis of

the solution revealed that the catalysis had stopped upon filtration of

the catalysts. The reduced activity of these complexes as compared to

their homogeneous counterparts is probably due in part to the following

two factors:

1. The different steric environment around the nickel atom in these

polymers as compared to the homogeneous NiL_4 complexes could have

inhibited olefin coordination and isomerization.

2. These polymers contain only two ligands that are completely free

to dissociate ((23) is used to maintain the polymer framework) whereas

there are four ligands which are free to dissociate in the corresponding

NiL_4 complex. Therefore, the polymer's ability to dissociate a ligand

and provide an open site for the coordination of olefin is reduced.

Attempts were also made to polymerize Wilkinson's catalyst. Again,

linking ligands were selected on their ability not to chelate the metal

atom, and their similarity to the monodentate ligands they were to

replace. Initial attempts to polymerize $Rh(PPh_3)_3Cl$ via reaction (51)

proved unsuccessful, as no polymeric materials were obtained. Attempts

were then made to use 34 as a linking ligand. This ligand was used in an

attempt to provide more distance between the $(RhClPPh_3)$ units in the

event that their size and proximity inhibited formation of a polymer.

The reaction of a 1 to 1 mixture of 33 and $Rh(PPh_3)_3Cl$ was carried out.

The reaction yielded a small amount of solid which was close in

appearance to $Rh(PPh_3)_3Cl$ but yet did not exhibit any of the solubility

characteristics of the complex. An attempt was made to hydrogenate 1-hexene using this material via the procedure of Osborn and co-workers (21). However, analysis of the catalysis mixture by gas chromatography showed that none of the hexene had been hydrogenated.

Since it was known that PPh_3 was able to dissociate from $Rh(PPh_3)_3Cl$ (22), whereas dissociation of $P(OMe)_3$ from $Ni(P(OMe)_3)_4$ was limited (19), it was felt that perhaps the linking ligand dissociated too quickly from the rhodium atom, thus inhibiting polymer formation. Therefore, (33) was prepared in the hope that it would bind more tightly to the rhodium atom and help ensure polymerization. However, attempts to prepare a polymer from this ligand and $Rh(PPh_3)_3Cl$ were also unsuccessful.

As stated in the introduction, many workers had been successful in finding ways of supporting transition metal complexes on functionalized resins in order to heterogenize homogeneous catalysts. Most of these preparations involved some sort of ligand exchange reaction between the complex and the support. Generally, this technique employed the use of complexes which were observed to undergo facile ligand exchange (i.e. $Rh(PPh_3)_3Cl$). However, in order to anchor appreciable amounts of a complex on the support it was necessary to stir a mixture of the complex and the resin in a solvent for up to three weeks (64). It was known that the NiL_4 (L=$P(OR)_3$) complex did not undergo appreciable rates of ligand exchange unless acid was added (38). The use of an acid catalyst to speed up the rate of ligand exchange between a NiL_4 complex and a functionalized support was ruled out, since it was felt that the acid would oxidize most of the complex before it would have a chance to be

anchored to the support. It did seem reasonable to suppose, however, that a NiL_4 complex could be supported on a cation exchange resin via reaction (Eq. 52). In this case the resin would actually act as the acid

$$\underset{SO_3^-H^+}{\overset{P}{\bigcirc}} \quad + \quad NiL_4 \quad \longrightarrow \quad \underset{SO_3^-HNiL_4^+}{\overset{P}{\bigcirc}} \quad (52)$$
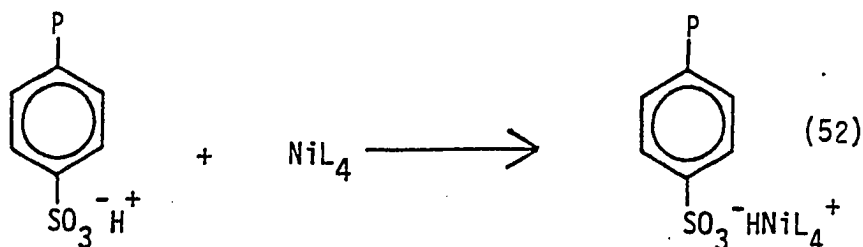
which would protonate the complex. At the same time the complex would be anchored on the resin and therefore would act as a heterogeneous catalyst.

In order to maximize diffusion of the NiL_4 complex into the resin, it was decided that macroreticular resins, which are known to have large porosities would be used. Amberlyst IR-15 and XN-1010 were two such resins which have porosities of 32% and 47%, respectively (140). However, the XN-1010 resins had a larger surface area of 540 sq.m/gm. as compared to the 45 sq.m/gm of IR-15 (140). It was thought that the high porosity and surface areas would help diffusion of the NiL_4 complex and substrate into the resin.

The catalyst was prepared by stirring the beads in a toluene solution containing a two fold excess of NiL_4 complex based upon the amount of H^+ in the resin, for approximately 12 hrs. Analysis of the resin indicated that additional hours of stirring failed to significantly

increase the amount of nickel in the bead.

At first, the IR-15 resin was used to investigate the activity of these types of catalysts. The catalyst was prepared as described, and after stirring, the excess NiL_4 complex was removed. This was accomplished by washing the resin under nitrogen with 4 to 5 portions of toluene with each portion being equal in volume to the original amount of toluene used. Proof of heterogeneity of the catalyst was provided by the same experiment that had been used with the polymer catalyst. When a sample was proved active, the catalyst was removed and the catalytic isomerization was observed to have stopped.

In order to determine the amount of nickel present in the resin, the resins were digested in a $HNO_3/HClO_4$ solution. Due to the low concentration of nickel contained in the resin (at most 3.3 mmole/gram resin), the exact amount of nickel present was determined spectrophotometrically. The nickel was complexed using 4-(2-pyridylazo) resorcinol and its concentration was established by measurement of the visible adsorption at 494 nm (107). Each time a new portion of catalyst was prepared, it was analyzed for its nickel content. Table 23 shows the numbers of H^+ cations per nickel atom found. As can be seen for the acyclic phosphites, the larger the ligands, the smaller the amount of complex which was observed to be contained in the resin. The three cyclic compounds were observed in ratios that fell in a small range, with $Ni(\underline{8})_4$ appearing to have the highest concentration of nickel in the resin.

Table 23. Amount of H^+/nickel found in NiL_4/XN-1010 resin catalysts[a]

Ligand L	Moles H^+/Moles Ni (± 0.5)
$P(OMe)_3$	5.5
$P(OEt)_3$	6.6
$P(OiPr)_3$	8.7
(7)	6.0
(8)	4.6
(58)	7.1

[a]3.3 Meq. H^+/gm of resin.

These resins were used as catalysts in the isomerization of 3-butenenitrile under the same conditions as was used in the homogeneous catalyses with the exception that no acid was added. As can be seen in Table 24, in all cases the heterogeneous catalysts were much less efficient than their homogeneous analogues. The reasons for this reduction in rate could lie in any of the following reasons.

Gultneh had found that the highest rates of catalysis were obtained at a 10 to 1 acid to nickel ratio. This allowed for the complete protonation of the NiL_4 as shown in Equation 53. Within the resin, this

$$NiL_4 + H^+ \longrightarrow HNiL_4^+ \qquad (53)$$

Table 24. Number of turnovers/unit time of supported NiL_4 complexes
versus their homogeneous analogue for the isomerization of 3-
butenenitrile

L	Turnovers per unit time for isomerization of 3-butenenitrile (± 5)	
	Supported catalysts	Homogeneous catalyst
$P(OMe)_3$	0	74/30 min
$P(OEt)_3$	130/24 hrs	52/30 min
$P(OiPr)_3$	0	35/30 min
(7)	128/12 hr	92/30 min
(8)	132/12 hr	640/30 min
(58)	0	124 cycles/23 min

high ratio could not be achieved since addition of excess acid would have

led to the formation of $HNiL_4^+$ species in solution which could then

diffuse out of the resin resulting in homogeneous catalysts.

Secondly, the environment around the NiL_4 complex may not have been

conducive to olefin coordination. Since sulfonic acid groups are

attached to styrene groups, it is possible that the phenyl rings of the

styrene group impede coordination of the olefin to the metal upon ligand

dissociation.

Thirdly, the diffusion of a polar olefin such as 3-butenenitrile

into the bead may have been limited due to the lack of polar gradients

which develop between the resin (which is largely aromatic due to its

styrene makeup) and the aromatic solvent (toluene) used (66).

Hence, due to the reduced activity of these catalysts as compared to

their homogeneous counterparts, no further work was deemed warranted.

PART II:

STEREOELECTRONIC EFFECTS OF CYCLIZATION IN

AMINOPHOSPHINE SYSTEMS: A STRUCTURAL,

PES, AND NMR STUDY OF $Me_2NP(OCH_2)_2CMe_2$

AND $CH_2(CH_2CH_2)_2NP(OCH_2)_2CMe_2$

INTRODUCTION

The chemistry of phosphorinanes has been an area of great interest over the past several years (141,142). Much work has been done to elucidate their structures in both the solid and solution phases. The results of previous work have shown that in all cases phosphorinanes adopt a chair conformation. However, this conformation has been found to be slightly modified from that found in cyclohexane (142). In most compounds, the phosphorinane ring has been observed to be slightly flattened at the phosphorus end. This flattening has been attributed to steric interactions which develop between the exocyclic groups on phosphorus and the rest of the phosphorinane ring. Studies have also shown that the exocyclic groups on phosphorus can adopt either the axial or equatorial positions with respect to the ring. Quin and co-workers have prepared many 2-alkyl-(aryl) phosphorinanes (143) and have studied their conformational equilibria (Eq. 27) using NMR techniques (60).

$$(27)$$
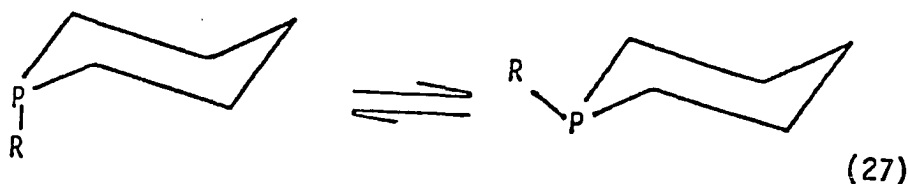
They have found that at lower temperatures (130-150 K) the conformer with an equatorial exocyclic group is slightly favored ($K_{e/a}$ = 2.03 (CH_3), 2.10 (C_2H_5), 2.33 (C_6H_5)). The axial conformation is thought to be destabilized by interactions between the exocyclic group and the axial

4,6 protons. It was also observed that the entropy change was significant for Equation 52 (ΔS= -3.4 eu (CH_3), -3.2 eu (C_2H_5), -2.5 eu (C_6H_5)), while the ΔH was low (-0.68 kcal/mol for R = CH_3) (60). As a consequence, upon heating solutions of these compounds to 300 K the equilibrium was found to shift toward the axial conformer ($K_{e/a}$ = 0.56 (CH_3), 0.65 (C_2H_5), 0.72 (C_2H_5)) (60).

Over the past ten years our group has focused particular attention upon the 2-alkoxy-1,3,2-dioxaphosphinanes system (24). Unlike the previously mentioned phosphine analogues, we have found that these compounds overwhelmingly adopt the conformation with an axial R group (24). This would seem to suggest that steric factors are less important than electronic factors in determining the conformation of the ring. Hudson and Verkade (144) have shown that when the lone pair on phosphorus is in the axial position with respect to the ring, there arises an interaction between it and a lone-pair contained in a p orbital on a ring oxygen. As a result, the conformation with an axial OR group and an equatorial lone-pair is preferred. Mosbo (58) found that when the -OR group was replaced with an NR_2 group, the conformation with an axial lone-pair and an equatorial NR_2 group was preferred. The factor which stabilizes this conformation is the steric interaction which develops between a nitrogen methyl group and the axial 4,6 hydrogens of the ring which are present within conformation a and not in b (Fig. 15). The dimethylamino group is forced to adopt the orientation as shown with respect to the ring due to the repulsion of the lone-pair on phosphorus and the N-P π MO (145).
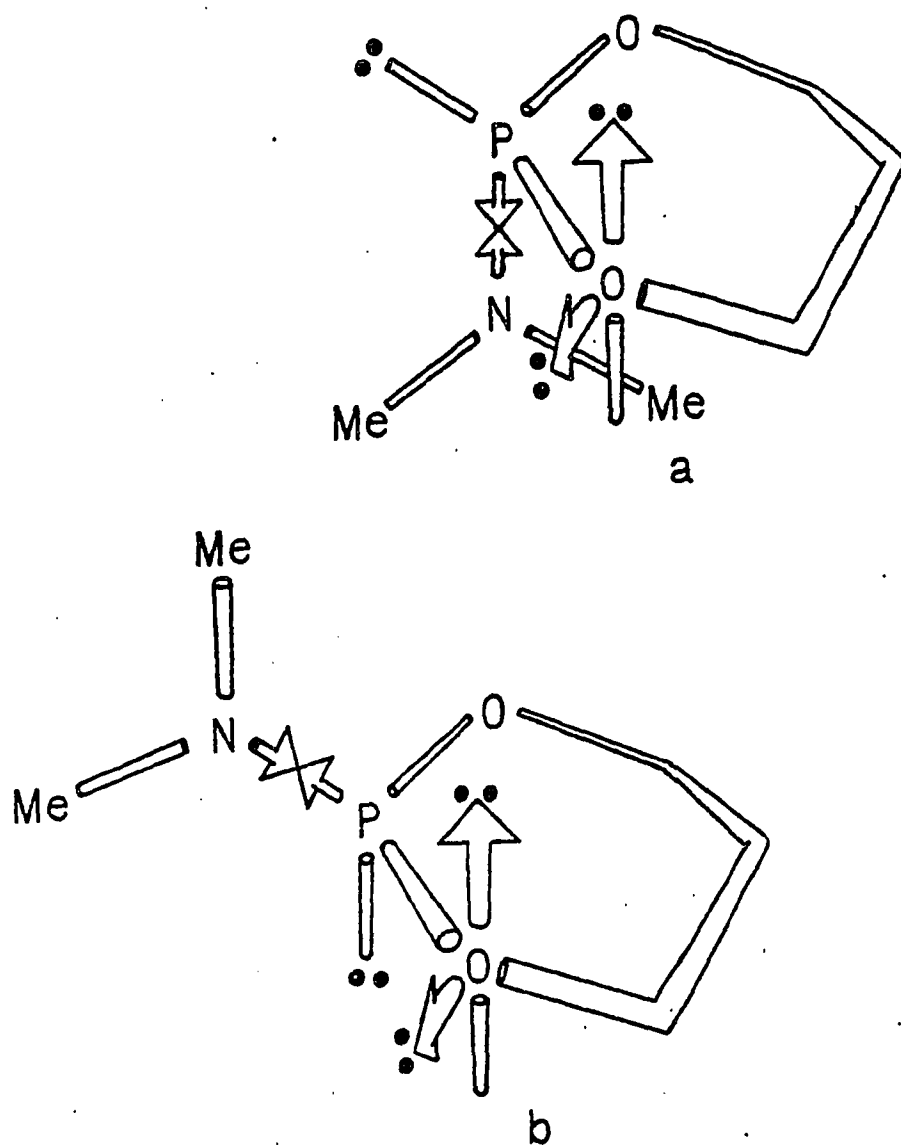
Figure 15. Orientation of electron lone pairs
in each of the two possible conformations
of 2-dimethylamino-1,3,2-dioxaphosphorinane

In the past, there has been much interest in the structural and electronic properties of aminophosphorus compounds, in particular $P(NMe_2)_3$ (27). However, much of the solid state structural information which is known about 2-amino-1,3,2-dioxaphosphorinanes is inferred from analogous compounds in which the phosphorus is pentavalent. In fact, proof of the preference of the Me_2N group to be equatorial originally came from dipole moment studies of the corresponding 2-amino-1-oxo-1,3,2-dioxaphosphorinanes (58). Since 20 and 21 were trivalent and solids at ambient temperatures, an opportunity was provided to compare their structural and conformational preferences to their pentavalent analogues via the use of X-ray diffraction. We also sought to investigate the electronic properties of these cyclic compounds and compare them to their acyclic analogues using photoelectron spectroscopy and the J_{P-Se} coupling data of their corresponding selenides. It was hoped that their electronic properties could be rationalized using information obtained in the X-ray structural analysis.

In this chapter, we will report that compounds 20 and 21 prefer the same conformation in the solid, solution and gaseous states, that the nitrogens are nearly planar in the solid state, and that 20 and 21 are less basic than their acyclic analogue $(Me_2N)P(OMe)_2$ in the gas and solution states.

Experimental procedures

All solvents and other materials were of reagent grade or better. Diethyl ether was dried by refluxing over NaK alloy. Acetonitrile was

dried over P_4O_{10}, benzene was dried by refluxing over Na metal.

Trimethyl phosphite and dimethylamine were obtained from Eastman Kodak

Company. Piperdine was obtained from Fisher Chemical Company, while 2,2-

dimethyl-1,3-propanediol was obtained from the Alrich Chemical Company.

All the above reagents were used as received with no further

purification.

All ^1H NMR spectra were obtained on deuterated chloroform solutions

contained in 5 mm tubes. Chemical shifts were obtained relative to the

internal standard tetramethylsilane. All ^1H NMR spectra were obtained

using a Varian EM-360 NMR spectrometer. All ^{31}P NMR spectra were

obtained on either C_6D_6 or $CD_3C(O)CD_3$ solutions contained in 10 mm

tubes. The spectra were obtained on a Bruker WM-300 NMR spectrometer

operating in the FT mode at 121.5 MHz. The external standard was a

sealed capillary tube containing 85% H_3PO_4. The capillary was held

coaxially in the tube by means of a Teflon vortex plug. The spectrometer

operated using a ^2H lock provided by the deuterium atoms contained in the

solvent.

All ^{13}C NMR spectra were obtained using a Jeol FX-90Q spectrometer

operating at 22.5 MHz in the FT mode, while locked on the deutrium atoms

contained in the solvent $CO_3C(O)CD_3/CF_2Cl_2$. The spectra were obtained

using the carbon atoms of the solvent as a reference. All mass spectral

data were obtained using a Finnegan 4000 mass spectrometer. All melting

point data were collected on a Thomas-Hoover Unimelt apparatus. Melting

points were obtained uncorrected. PES data were recorded as described

earlier (27).

Preparations

2-β-Chloro-4,6-α,α-dimethyl-1,3,2-dioxaphosphorinane (4)   The

preparation of this compound can be found in chapter one of this thesis.

Dimethylphosphochlorodite (40)   This compound was prepared via

the procedure of Ramirez and co-workers (146).

Dimethyldimethylphosphoramidite (41)   Attempts to prepare this

compound via the reaction of 1 equivalent of tris(dimethyl

amino)phosphine and two equivalents of methanol in the presence of a

catalytic amount of dimethylamine hydrochloride via the method of

Bentrude and co-workers (147) were unsuccessful. The compound was

successfully prepared via the reaction of 40 and dimethylamine in a

manner similar to a procedure described previously (128). The compound

was obtained in 73% yield via distillation (b_{42} = 42-45°, lit. b_{45} = 50-

51° (147); ^{1}H NMR (CDCl$_3$) 3.4d J_{P-H} = 12 Hz 6H OCH$_3$, 2.6d $J_{P=H}$ = 9 Hz 6H

-N(CH$_3$)$_2$, lit. (147) 3.3d J_{P-H} = 12 Hz 6H OCH$_3$, 2.6d J_{P-H} = 9 Hz 6H

N(CH$_3$)$_2$).

2-Dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane (20)   This

compound's preparation is described in Chapter One of this thesis.

2-Piperdino-5,5-dimethyl-1,3,2-dioxaphosphorinane (21)   This

compound's preparation is described in Chapter One of this thesis.

2-β-Dimethyl amino-4,6-α,α-dimethyl-1,3,2-dioxaphosphorinane (42),

2-α-dimethylamino-4,6-α,α-dimethyl-1,3,2-dioxaphosphorinane (43)

Mixtures of these compounds were first prepared via two procedures described by Mosbo (58). The first procedure entailed the reaction of $\underline{4}$ and dimethylamine, while the second used the reaction of meso-2,4-pentanediol and tris (dimethylamino) phosphine. In both procedures, Mosbo reports a conformational ratio of 9 to 1 for $\underline{43}$ and $\underline{42}$, respectively. However, upon repeating this work it was found that the first procedure produced a 2 to 1 mixture of $\underline{43}$ and $\underline{42}$, while the second procedure yielded a 4 to 1 mixture of $\underline{43}$ and $\underline{42}$. Heating a neat mixture of $\underline{43}$ and $\underline{42}$ for 3 hr. under N_2 at 130°C failed to affect any change in the conformational distribution obtained in either reaction. A 4 to 1 mixture of $\underline{43}$ to $\underline{42}$ could be obtained from a 2 to 1 starting mixture by heating 0.5 g of the neat 2 to 1 mixture with 5 mg of para-toluenesulfonic acid at 90°C for 3 hr. Determination of the isomeric distribution was made by integration of each set of dimethylamino resonances in the ^1H NMR spectrum. The compounds were obtained as a mixture of isomers in 81% yield by distillation. No attempts were made to separate the isomers ($b_3 = 46°$, lit. $b_2 = 44-46°$ (58); (($\underline{43}$) ^{31}P NMR (C_6D_6) 141.4, lit. 141.0 (58), ^1H NMR ($CDCl_3$) 4.3-3.7m 2H CH, 2.5d J_{P-H} = 9 Hz, 6H $N(CH_3)_2$, 1.1d J_{H-H} = 6 Hz, 6H CH_3, 1.0m 2H CH_2; ($\underline{42}$) ^{31}P NMR (C_6D_6) 137.6, lit. 137 (58); ^1H NMR ($CDCl_3$) 4.3-3.7m 2H CH, 2.3d J_{P-H} = 8 Hz 6H $N(CH_3)_2$, 1.1d J_{H-H} = 6 Hz 6H CH_3, 1.0m 2H CH_2).

KSeCN   This compound was prepared via the procedure of Waitkins and Shutt (87).

Dimethyldimethylselenophosphoramidate (44)   This compound was

prepared by reacting 0.55 g (0.0039 mole) KSeCN and 0.53 of 41 in 25 ml

of acetonitrile. The mixture was stirred for 3 hr. at room temperature

and filtered. The compound was obtained in 94% yield upon removal of the

acetonitrile using a rotary evaporator. No further purification was

necessary as evidenced by ^{31}P NMR (^{31}P NMR ($CD_3C(O)CD_3$) 87.1d J_{P-Se} = 903

Hz).

2-Dimethylamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane (45)

This compound was prepared by the reaction of 0.81 g (0.0056 mole) of

KSeCN and 0.83 g (0.0055 mole) of 20 in 20 ml of acetonitrile. The

solution was stirred for 4 hrs, then filtered, and the acetonitrile was

removed under vacuum to yield a white solid. The product was obtained in

86% yield via sublimation at 85°/1.5 Torr (^{31}P NMR ($CD_3C(O)CD_3$) 79.2d

J_{P-Se} = 914 Hz).

2-Piperdino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane (46)

This compound was kindly provided by Dr. Steven Socol.

2-α-Dimethylamino-2-β-seleno-4,6-α,α-dimethyl-1,3,2-dioxaphorinane

(47), 2-β-Dimethyl amino-2-α-seleno-4,6-α,α-dimethyl-1,3,2-dimethyl-

1,3,2-dioxaphosphorinane (48)   This compound was prepared via the

reactions of a 4 to 1 mixture of 43 and 42 and KSeCN via the procedure

described for 44. The resulting liquid which was obtained in 81% yield

was used without further purification ((47)^{31}P NMR ($CD_3C(O)CH_3$) 75.1d

J_{P-Se} = 895 Hz; (48) ^{31}P NMR ($CD_3(C(O)CD_3$) 77.6d J_{P-Se} = 924 Hz).

Experimental details for X-ray data collection for compounds 20 and 21

Crystals of both 20 and 21 suitable for x-ray diffraction were grown by separately sealing approximately 0.5 g of the purified compound in an evacuated (~0.1 Torr) 10 cm long 1/4" ID glass tube. The bottom of the tube was placed in a sand bath and slowly heated. Compounds 20 and 21 sublimed at 27° and 60°, respectively. Due to the low melting point of compound 20 (28°C), it was necessary to select and mount crystals in a cold room which was maintained at 14°C. A colorless crystal of 20 in the shape of a paralelepiped (0.3 x 0.4 x 0.2 m) was mounted in a 0.5 mm I.D. Lindemann capillary. The capillary was sealed to prevent hydrolysis by atmospheric moisture. The crystal was found to be triclinic with a = 6.542(1)Å, b = 11.731(3)Å, c = 6.440(2)Å, α = 101.53(4), β = 83.52(3) and γ = 90.96(3)Å. A density of 1.22 g/cm^3 was computed on a volume of 481.1(2)Å^3. A Howells, Phillip, and Rodgers' plot (148) indicated a centrosymmetric lattice which led unambiguously to the space group $P\bar{1}$ which was later confirmed by subsequent solution and refinement of the structure. The data were collected at -130 ± 3° on a Syntex diffractometer with graphite monochromated MoK$_\alpha$ radiation (λ = 0.70954 Å) employing a previously described procedure (149). Low-temperature data were collected in order to minimize thermal motions. Four octants were collected within the sphere of 2θ < 50° yielding 2645 measured intensities. There was no significant crystal decomposition as judged by repeated measurements of three standard reflections. Averaging of equivalent data yielded 1270 observed reflections (F$_0$ > 3σ (F$_0$)).

Lattice constants were obtained by a least squares refinement of the $\pm 2\theta$ ($|2\theta| > 20°$) measurements of 24 standard reflections.

The structure was solved by standard heavy atom procedures following location of the phosphorus atom from interpretation of the Patterson maps. Refinement of the structure was carried out using block matrix least-squares methods. Fourier-difference maps and least squares refinements led to location of the positions of all nonhydrogen atoms. Isotropic refinements of these positons gave a conventional R factor of 0.19 and a weighted R factor of 0.265. Anisotropic refinement of these positions gave a conventional R factor of 0.114 and a weighted R factor of 0.172. Ring hydrogen positions were calculated and a final full matrix least-squares refinement of all atoms led to a final conventional R of 0.074 and weighted R of 0.121.

The structure of compound 21 was determined using the same methods as used on compound 20. Initial attempts at solving the structure of compounds at -130°C were unsuccessful due to computational problems which arose from apparent pseudosymmetry in both the nitrogen and phosphorus rings. Re-collection of the data at 21°C $\pm$ 3° seemed to allow for more thermal movement in both rings which eliminated the pseudosymmetry.

The pyramidal shaped crystal (0.4 x 0.2 x 0.2 mm) was found to be orthorombic with a = 8.464(1)Å, b = 9.868(2)Å, c = 27.832(2)Å, Z = 8, volume = 2323.9(6)Å^3 and ρ = 1.24 g/cm^{-1} (calculated). Systematic absences 0k0 k = 2n; h0l for h + l = 2n; 0kl, k = 2n; hk0 for h=2, and 00l for l = 2n indicated the space group P_{bna} which was later confirmed by solution of the structure.

Data were collected on a four circle diffractometer designed and built in the Ames Laboratory, equipped with a scintillation counter and interfaced to a PDP-15 computer. The data were collected with graphite monochromated MoK_α radiation with 1465 reflections in 2 octants being observed within a sphere of $2\theta < 50°C$.

There was no observed decomposition of the crystal based upon repeated observation of three standard reflections. Averaging of equivalent data yielded 560 independent reflections $(F_0 > 3\sigma (F_0))$. Block matrix least square isotropic refinement of the nonhydrogen positions yielded a conventional R of 0.103 and a weighted R of 0.141. Hydrogen positions were calculated and a final full matrix anisotropic refinement of the nonhydrogen positions led to a final conventional R of 0.084 and a weighted R of 0.117.

Results and discussion
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Tables 25 and 26 list the bond angles and bond distances for compounds 20 and 21, respectively. Tables 27 and 28 list their respective fractional coordinates, while Tables 29 and 30 give their respective anisotropic thermal parameters. The structure factors for 20 and 21 can be found in Appendices 3 and 4 of this thesis.

ORTEP drawings of 20 and 21 may be found in Figs. 16 and 17. Unit cell drawings of these compounds are shown in Figs. 18 and 19. As can be seen, each of the compounds adopts the chair conformation with the amino group in the equatorial position with respect to the ring. Previous structural investigations of other 2-amino-2-oxo-1,3,2-dioxaphosphorinane

Table 25. Bond distances (Å), angles (°), and their standard deviations for $Me_2NP(OCH_2)_2CMe_2$ (20)

Bond distance		Bond angle	
P-01	1.640(4)	N-P-01	99.23(22)
P-02	1.652(4)	N-P-02	101.50(22)
P-N	1.642(5)	01-P-02	97.73(20)
01-C3	1.452(7)	C1-N-C2	115.12(49)
02-C4	1.453(7)	C1-N-P	125.30(45)
N-C1	1.447(7)	C2-N-P	119.58(37)
N-C2	1.469(9)	P-01-C3	114.75(24)
C3-C5	1.525(7)	P-02-C4	112.32(29)
C4-C5	1.532(8)	01-C3-C5	111.80(38)
C5-C6	1.549(9)	02-C4-C5	109.92(34)
C5-C7	1.547(7)	C3-C5-C4	108.80(30)
		C3-C5-C6	108.08(40)
		C3-C5-C7	111.83(36)
		C4-C5-C6	108.11(37)
		C4-C5-C7	109.99(35)
		C6-C5-C7	110.63(35)

Table 26. Bond distances (Å), angles (°) and their standard deviations
for $CH_2(CH_2CH_2)_2NP(OCH_2)_2CMe_2$ (21)

Bond distance		Bond angles	
P-01	1.675(16)	01-P-02	97.39(79)
P-02	1.623(18)	N-P-01	100.61(93)
P-N	1.637(12)	N-P-02	100.18(90)
01-C3	1.461(32)	C1-N-P	120.88(95)
02-C4	1.426(33)	C2-N-P	124.33(106)
N-C1	1.505(22)	C1-N-C2	114.25(118)
N-C2	1.502(21)	P-01-C3	115.87(140)
C3-C5	1.515(44)	P-02-C4	114.77(137)
C4-C5	1.556(43)	01-C3-C5	112.18(188)
C5-C6	1.53(21)	02-C4-C5	112.76(186)
C5-C7	1.556(20)	C3-C5-C6	110.61(222)
C1-C3N	1.582(28)	C3-C5-C7	109.65(228)
C2-C4N	1.521(30)	C4-C5-C6	110.00(238)
C3N-C5N	1.501(26)	C4-C5-C7	111.82(74)
C4N-C5N	1.632(27)	C6-C5-C7	107.53(119)
		N-C7-C3N	108.04(161)
		C1-C3N-C5N	112.22(151)
		C3N-C5N-C4N	106.27(143)
		C5N-C4N-C2	110.13(153)
		C4N-C2-N	109.55(173)

Table 27. Final positional parameters and their standard deviations for $Me_2NP(OCH_2)_2CMe_2$ (20)[a]

	x	y	z
P	0.0848(2)	0.2816(1)	-0.0080(2)
01	0.1347(5)	0.2862(3)	0.7382(6)
02	0.8443(5)	0.2385(3)	0.9884(6)
N	0.2044(7)	0.1593(4)	0.9917(8)
C1	0.2081(10)	0.0559(5)	0.8250(11)
C2	0.3179(9)	0.1496(6)	0.1718(11)
C3	0.0011(8)	0.3625(4)	0.6617(8)
C4	0.7134(8)	0.3200(5)	0.9214(9)
C5	0.7770(7)	0.3247(4)	0.6869(8)
C6	0.6428(9)	0.4184(5)	0.6277(10)
C7	0.7458(9)	0.2044(5)	0.5442(9)
H1A	-0.0889	0.4281	0.7654
H1B	-0.0681	0.3363	0.5204
H2A	0.7278	0.4031	1.0200
H2B	0.5597	0.2929	0.9398

[a]Fractional coordinates of unit cell.

Table 28. Final positional parameters and their standard deviations for $CH_2(CH_2CH_2)_2NP(OCH_2)_2CMe_2$ (21)[a]

	x	y	y
P	0.7472(10)	0.1762(3)	0.0892(1)
O1	0.5972(15)	0.2863(15)	0.0932(4)
O2	0.8897(10)	0.2834(15)	0.0997(3)
N	0.7355(27)	0.1019(13)	0.1417(4)
C1	0.7189(31)	0.9509(17)	0.1458(5)
C2	0.7156(28)	0.1738(18)	0.1884(6)
C3	0.6058(29)	0.4026(27)	0.0615(7)
C4	0.8967(27)	0.3957(27)	0.0670(8)
C5	0.7503(40)	0.4895(14)	0.0710(5)
C6	0.7641(39)	0.6043(16)	0.0338(5)
C7	0.7385(29)	0.5567(15)	0.1214(5)
C3N	0.8435(21)	0.8985(21)	0.1838(6)
C4N	0.8394(24)	0.1263(20)	0.2240(6)
C5N	0.8203(20)	0.9624(18)	0.2322(6)
H3A	0.4962	0.4596	0.0656
H3B	0.5996	0.3654	0.0244
H4A	0.9970	0.4601	0.0761
H4B	0.9108	0.3650	0.0371
H1A	0.6171	1.000	0.1581
H1B	0.7611	1.000	0.1148
H2A	0.7281	0.2795	0.1839
H2B	0.5995	0.1561	0.2028
H3NA	0.9593	0.9221	0.1710
H3NB	0.8330	0.7946	0.1875
H4NA	0.8006	0.0688	0.2557
H4NB	0.9410	0.0744	0.2155
H5NA	0.7123	1.019	0.2397
H5NB	0.9126	1.200	0.2489

[a]Fractional coordinates of unit cell.

Table 29. Final thermal parameters and their standard deviations (in parentheses)[a] for $Me_2NP(OCH_2)_2CMe_2$ (20)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	2.4(1)	2.5(1)	2.9(1)	0.3(4)	-0.8(4)	0.3(1)
O1	2.4(1)	3.1(2)	3.6(2)	0.3(1)	-0.1(1)	1.0(1)
O2	2.4(2)	4.3(2)	3.4(2)	0.2(2)	-0.4(1)	1.9(1)
N	3.1(2)	3.3(2)	4.0(2)	0.5(2)	-1.2(2)	0.7(2)
C1	4.3(3)	2.6(2)	5.0(3)	0.5(2)	-0.7(2)	-0.1(2)
C2	3.6(3)	5.3(3)	5.0(3)	0.7(2)	-1.8(2)	2.3(2)
C3	3.0(2)	2.8(2)	3.3(2)	0.1(2)	-0.6(2)	1.1(2)
C4	2.1(2)	4.4(3)	3.4(3)	0.8(2)	0.0(2)	1.6(2)
C5	2.2(2)	2.9(2)	2.9(2)	-0.1(2)	-0.7(2)	1.1(2)
C6	3.4(3)	4.2(3)	5.3(3)	0.3(2)	1.1(2)	2.3(3)
C7	4.8(3)	3.6(3)	4.0(3)	-1.2(2)	-2.0(2)	0.6(2)

[a]The form of the anisotropic thermal parameter is $\exp[(-B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2)/4 + (B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)/2]$.

Table 30. Final thermal parameters and their standard deviations (in parentheses)[a] for $CH_2(CH_2CH_2)_2NP(OCH_2)_2CMe_2$ (21)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	4.2(2)	2.6(1)	2.5(1)	-0.3(4)	0.5(6)	-0.1(1)
O1	1.6(7)	2.8(8)	3.9(6)	0.4(6)	-0.1(6)	0.4(7)
O2	3.2(8)	3.8(9)	3.0(7)	0.3(7)	-0.2(6)	-0.3(6)
N	5.7(9)	3.1(6)	3.1(5)	0.6(13)	-0.3(10)	-0.3(4)
C3	7.5(16)	1.7(15)	2.0(8)	-1.2(18)	1.0(11)	-0.2(10)
C4	1.7(15)	6.5(15)	3.6(10)	-1.6(18)	-0.3(11)	1.0(12)
C5	2.5(9)	2.4(6)	3.8(6)	-1.4(22)	-1.9(14)	-0.2(5)
C6	3.7(10)	3.4(7)	4.3(7)	2.1(16)	1.6(13)	1.4(6)
C7	3.0(9)	3.0(7)	3.9(7)	-0.2(15)	1.0(13)	-0.1(6)
C1	5.8(16)	3.9(8)	2.2(6)	0.9(11)	-0.1(8)	0.5(6)
C2	9.7(18)	3.2(7)	4.0(7)	2.0(12)	1.6(11)	0.2(8)
C3N	4.5(11)	3.2(8)	5.0(10)	1.0(10)	-1.0(8)	-0.2(8)
C4N	7.7(15)	3.5(9)	2.6(7)	0.1(10)	0.4(8)	0.3(7)
C5N	3.3(11)	3.2(9)	4.9(9)	-0.0(7)	1.3(7)	-1.3(7)

[a]The form of the anisotropic thermal parameter is $\exp[(-B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2)/4 + (B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)/2]$.

investigation indicates for the first time that this preference persists when phosphorus is trivalent. Each of the compounds contains nitrogens which are planar. This is illustrated by the sum of the angles around nitrogen being equal to 360.0° and 359.5° for 20 and 21, respectively.
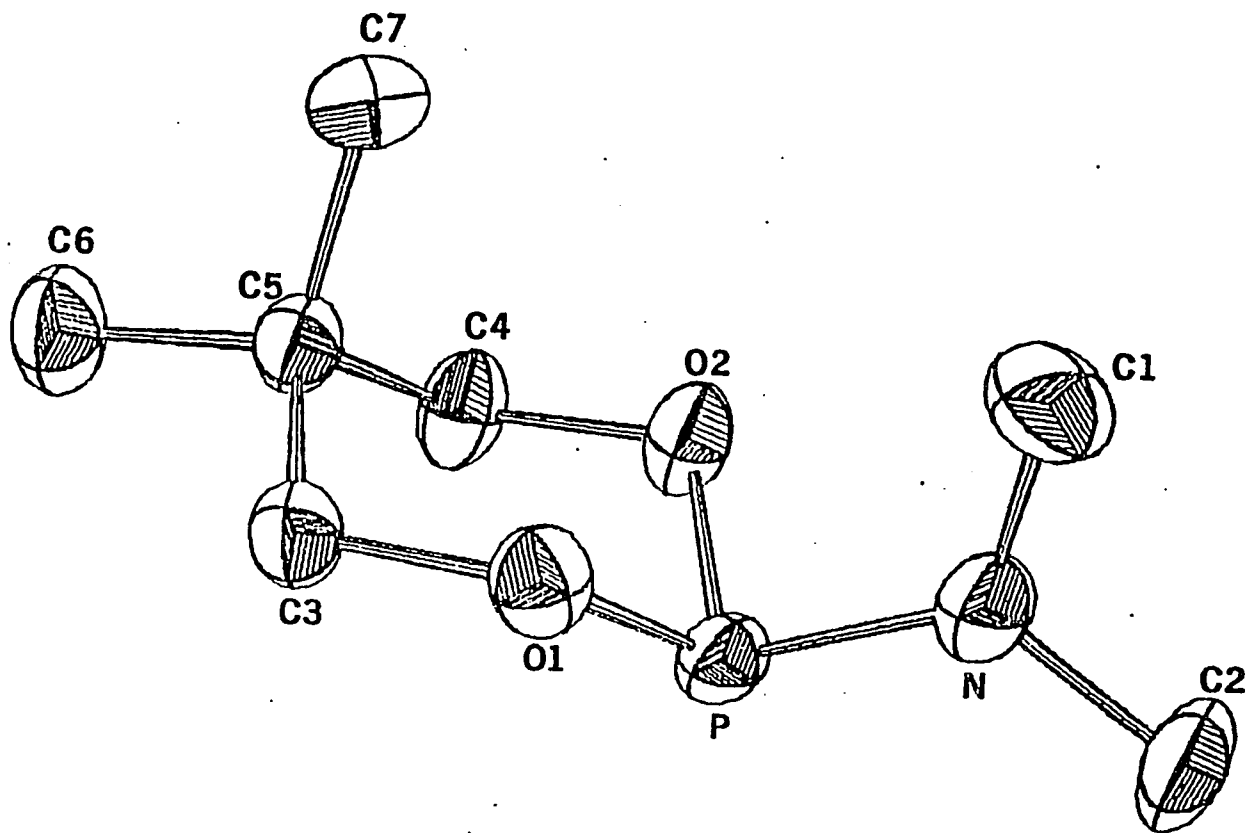
Figure 16. ORTEP diagram of 20
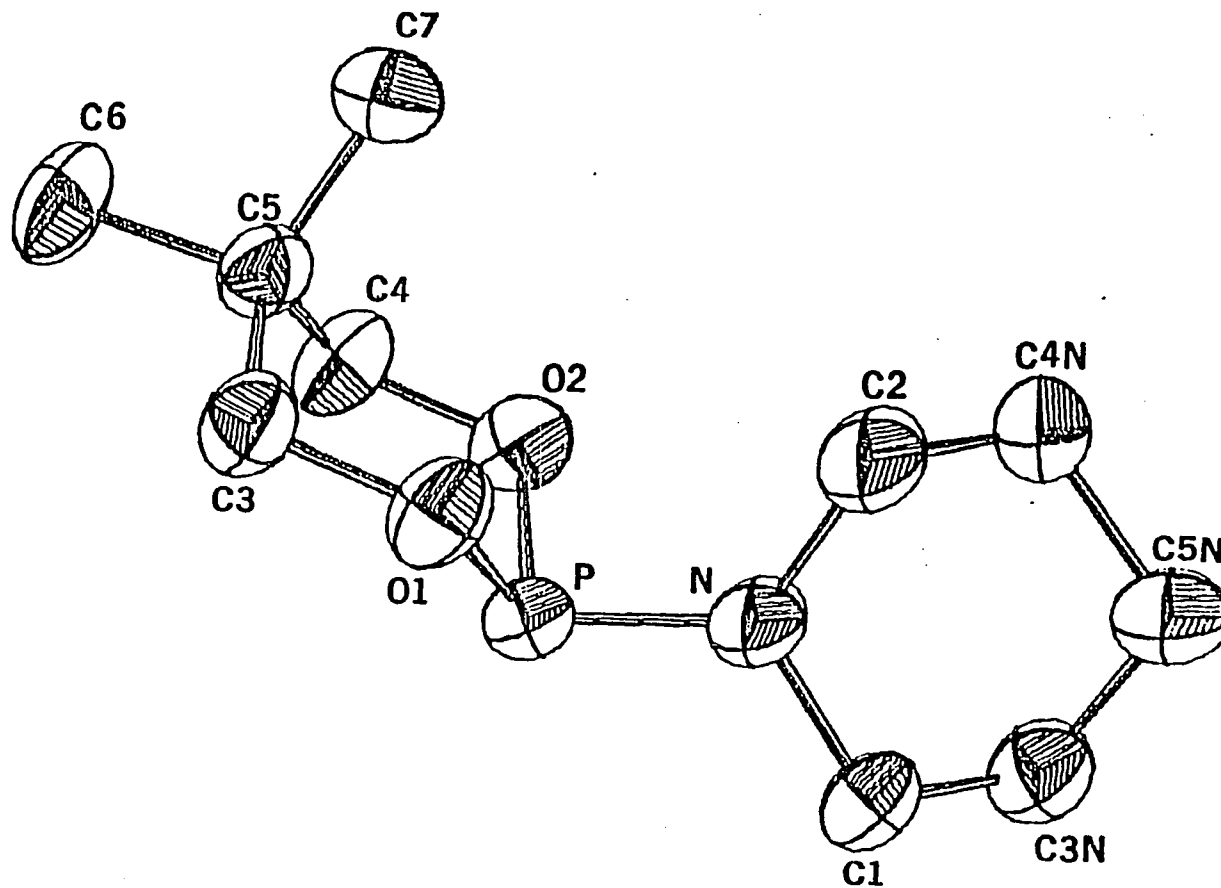
Figure 17. ORTEP diagram of 21
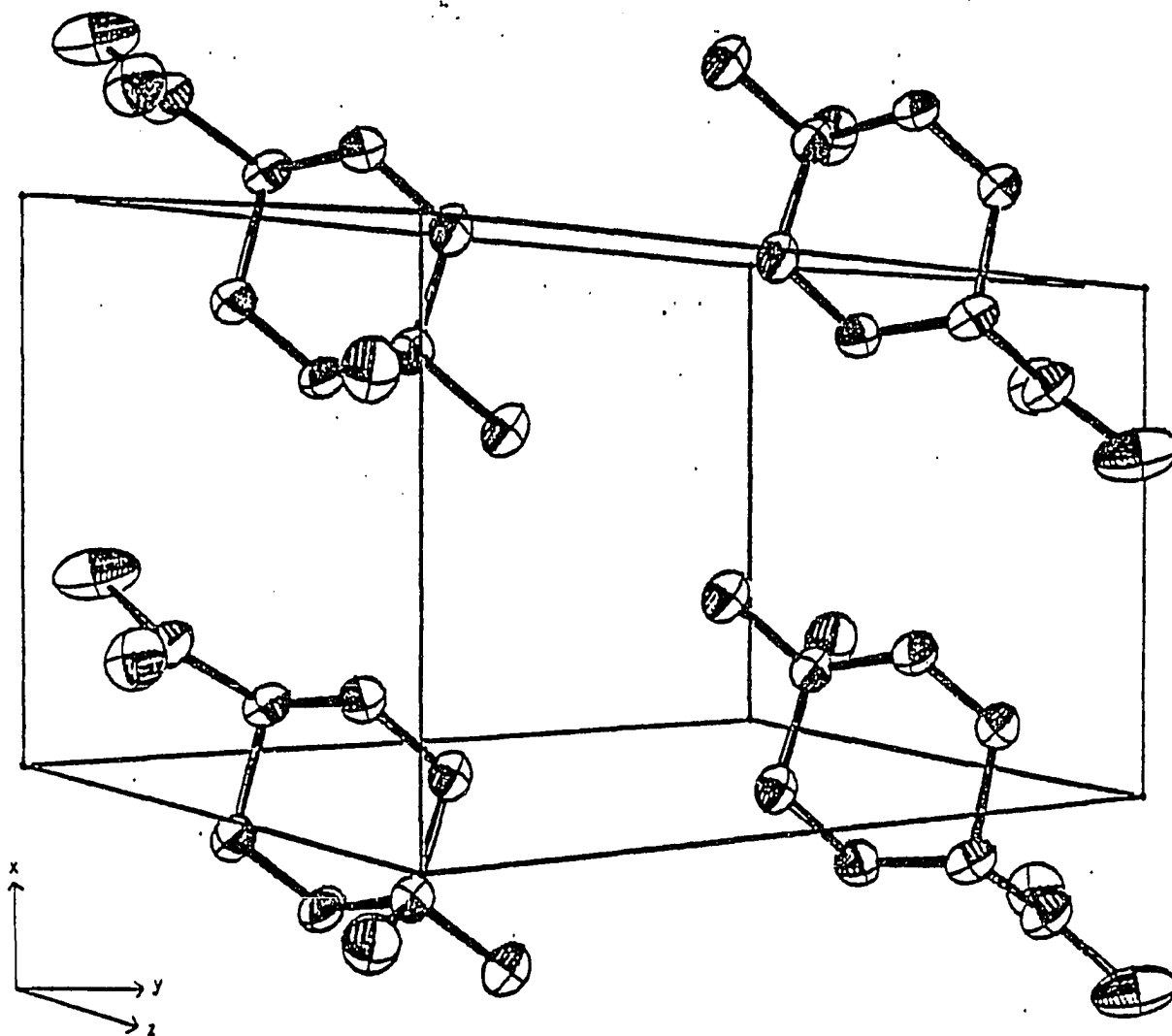
Figure 18. Unit cell diagram of <u>20</u>
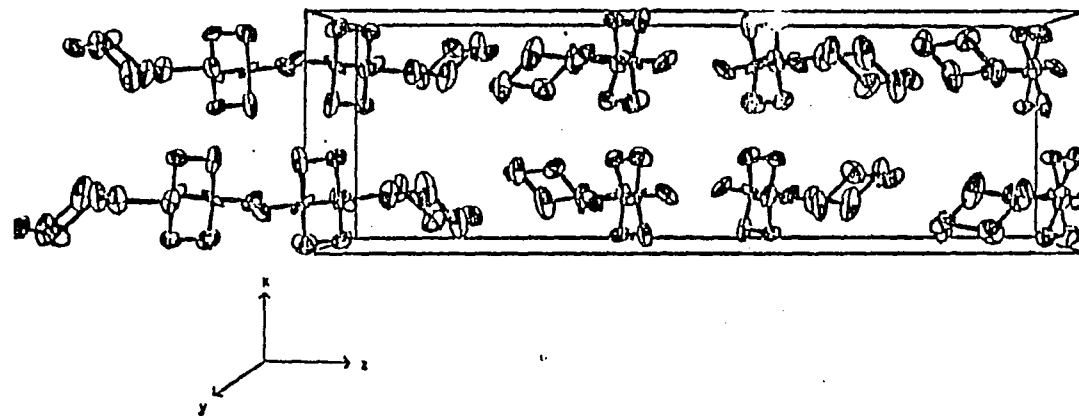
Figure 19. Unit cell diagram for 21

The nitrogen is rehybridized from sp^3 to sp^2 as illustrated by its

planarity and the short N-P bond distance of 1.642(5)Å and 1.637(12) Å in

20 and 21, respectively. These distances clearly indicated the presence

of some multiple bonding between nitrogen and phosphorus. Previous

workers have accepted a nitrogen-phosphorus single bond to be 1.769 Å

long (as is found in $Na[H_3NPO_3]$ (151)), while a nitrogen-phosphorus

double bond is accepted to be 1.52 Å long (as is found in $[NPCl_2]_5$

(152)). The source of this multiple bonding between nitrogen and

phosphorus stems from the presence of electronegative substituents on

phosphorus such as oxygen in 20, 21, and 49 (153) or halogens in R_2NPX_2

(154). These electronegative groups cause a buildup in positive charge

on phosphorus which in turn causes an increased interaction to develop

between the lone-pair on nitrogen and an empty d-orbital on phosphorus,

resulting in multiple bonding between the atoms. Recent X-ray structural

studies of $SeP[N(CH_2CH_2)CH_2]_3$ (155) and $P[N(CH_2CH_2)CH_2]_3$ (156) shows that

each compound contains only 2 planar nitrogens while the other is

tetrahedral. It is probable that in these cases all three nitrogens

render the phosphorus insufficiently electronegative to maintain the

planarity of all three nitrogens. This has also been observed by Socol

and Verkade (157) in the solid state structure of $Ag(P(NMe)_3)_2^+$ BPh_4^-.

It was found that only two of the nitrogens on each phosphorus were

planar while the third was tetrahedral. Since 20 and 21 each contain two

oxygen atoms, phosphorus is rendered sufficiently electronegative to

preserve the planarity of the nitrogen. It appears that the tendency

toward planarity of the nitrogen is strong enough to overcome the

puckering tendency of the piperidine ring in compound 21. This is also

true in $P(N(CH_2CH_2)_2CH_2)_3$ (156) and $SeP[N(CH_2CH_2)_2CH_2]_3$ (155). This has

also been observed in the corresponding morpholino compounds

$SeP[N(CH_2CH_2)_2O]_3$ and $P[N(CH_2CH_2)_2O]_3$ (155). The piperidine ring in 21

is able to accommodate the planar nitrogen by increasing the C_1-N-C_2 bond

angle to 114° and by flattening the C_1-N-C_2 plane with respect to the C1-

C3N-C4N-C2 plane. The acute angle between both planes is 53° as opposed

to the 60° angle found in the cyclohexane chair conformation. The

reasons for the long C4N-C5N distance (1.632 Å) in the piperidine ring

are not known at this time, since the anisotropic thermal parameters for

these atoms are not unusual nor are there any close intermolecular

contacts within the unit cell.

Typical of R_2NPX_2 (154,158,159) and $R_2NP(O)X_2$ (X_2 = OCCCO or OCCCNR)

ring systems (153) is the tendency of the C_2NP plane to be nearly

perpendicular to that of the bisector of the PX_2 angle. This

conformational property is also seen in 20 and 21, wherein the C_2N planes

are rotated from perpendicularity to the PO_2 plane by 2.2° and 1.9°,

respectively. This observation is consistent with the notion that the

nitrogen and phosphorus lone-pairs avoid repulsion and the nitrogen lone-

pair enhances its opportunity to pi bond with phosphorus by adopting the

observed conformation. Rotation of the P-N bonds in these compounds is

apparently facile since the ^{13}C NMR of 20 shows no perceptible change

down to -84° in $(CD_3)_2CO/CF_2Cl_2$.

The P-N bonds in 20 and 21 (1.642(5) and 1.637(1)Å, respectively)

are typical of those observed for several P(III)-N compounds (160), a

result which is consistent with the presence of pi bonding in the P-N bond. Further evidence for enhanced P-N pi bonding in 20 and 21 can be construed to emanate from their P-O-C angles which average 113.5 and 115.3°, respectively. These angles are distinctly smaller than the POC angles in the rings of 23 which average 119.9° (41). This is consistent with the idea that the hybridization around the oxygens in 20 and 21 is closer to sp^3 whereas in 23 it is nearer to sp^2. The exocyclic POC angle in 23 (117.80°) is also larger than the POC angles in 20 and 21 (41). These results are consistent with the idea that the R_2N substituent is more capable of N-P pi bonding than a methoxy group. This postulate is also supported by the slightly longer average P-O bond distances in 20 and 21 (1.646(4) and 1.649(4), respectively) compared with 23 (1.617(5)Å). A consequence of the larger POC angle in 23 is that the esteratic portion of each chair is more flattened than in 20 and 21. Thus, the acute angle between the planes made by the 01-P-02 and 01-02-C3-C4 portions of the ring in 1 and 2 is 74.1° and 76.5°, respectively. This compares with the corresponding angle of 36.9° in 23. The sum of the angles around phosphorus in P(III) compounds generally falls in the range 295-300° (155). The corresponding sums in 1 and 2 are not unusual in this respect (298.5° and 298.8°, respectively).

In order to determine the electronic properties of 20 and 21, a UV photoelectron study of these compounds was carried out in collaboration with Cowley and co-workers. The He(I) UV-PE spectra of these compounds can be found in figures 20 and 21. Table 30 shows the possible band assignments for 20 and 21 and several related compounds including 16.

IONIZATION ENERGY (eV)
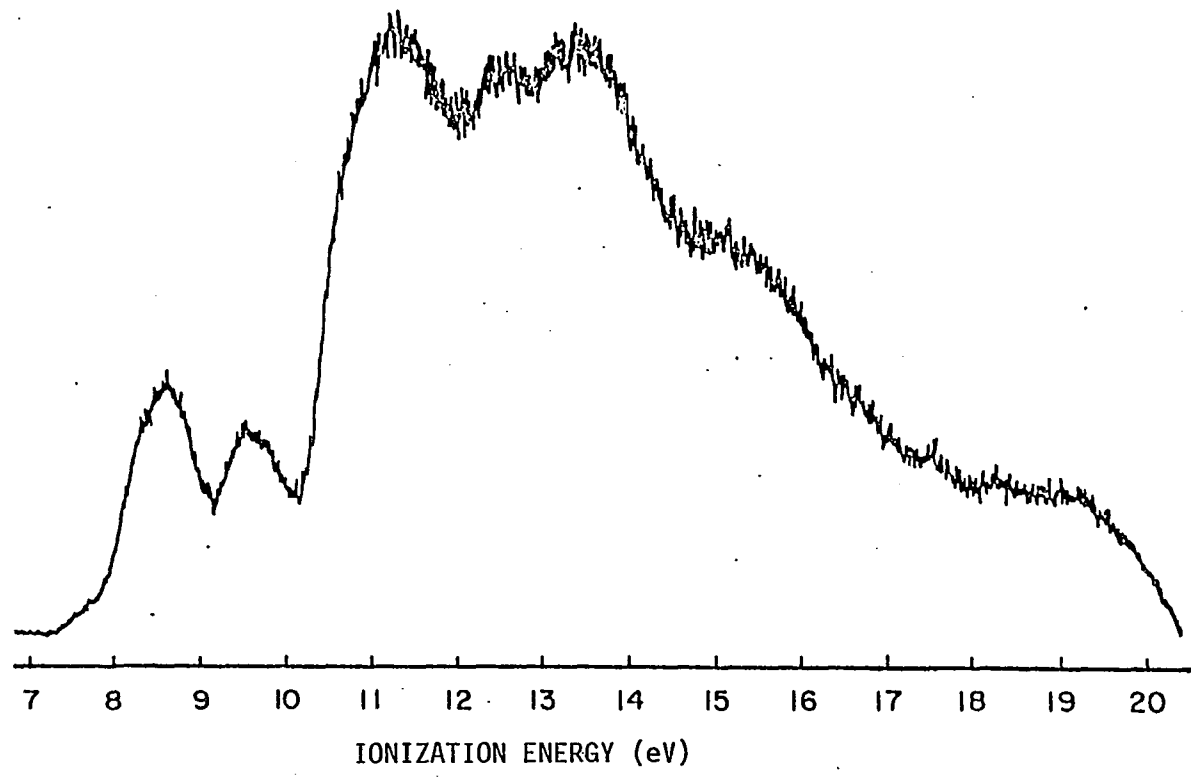
Figure 20. UV photoelectron spectrum of 20

178

IONIZATION ENERGY (eV)
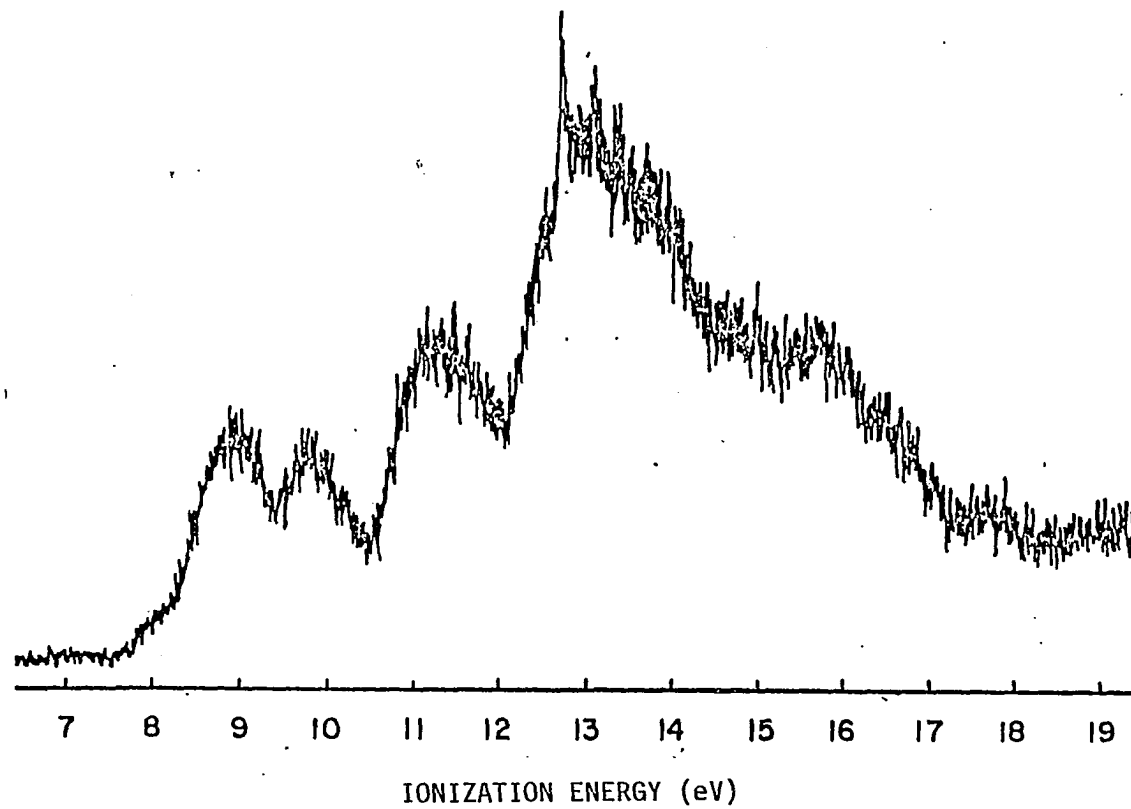
Figure 21. UV photoelectron spectrum of 21

Table 31. Ionization energies[a]

	IE_N		IE_P	IE_O
$P(OMe)_3$[b]			9.22	10.54, 11.11, 11.3
$Me_2NP(OMe)_2$[c]		8.63	8.93	10.56(a',a"), 11.01(nσ)
20[d]	a)	8.95	8.95	9.80(a',a"), 11.30(nσ)
	b)	8.95	9.80	11.30(a',a"), 12.53(nσ)
21[d]	a)	8.56	8.56	9.60(a',a"), 11.30(nσ)
	b)	8.56	9.60	11.30(a',a"), 12.53(nσ)
16[e]		8.70	8.70	10.0, 11.26
$(Me_2N)_2POMe$[c]	7.80(a"), 9.15(a')		8.59	10.63
$P(NMe_2)_3$[f]	7.89(a"), 8.77(a')		7.58	
	9.90(a')			

[a] In eV. "Lone pair" energies unless stated otherwise.

[b] Ref. 161.

[c] Ref. 162.

[d] This work.

[e] Ref. 163.

[f] Ref. 27.

The values of IE_N for 20 and 21 bracket closely the value for $Me_2NP(OMe)_2$. All three of these values are larger than the average of the IE_N for $(Me_2N)_2POMe$ (8.48 ev), as might be expected from the presence of a second electron donating Me_2N group and one less electron

withdrawing alkoxy group on phosphorus. Although the averages of the first two values of IE_N for $P(NMe_2)_3$ are lower than the IE_N energies for 20, 21 or $Me_2NP(OMe)_2$, the third value for $P(NMe_2)_3$ is unexpectedly higher. The difference in IE_N values of the nitrogens in $P(NMe_2)_3$ has been attributed to an interaction between one of the nitrogen lone-pairs and the lone-pair on phosphorus (27). This interaction is evidenced by the differences in the experimentally observed IE_P value for $P(NMe_2)_3$ versus what one would normally expect. The stepwise decrease in IE_P from $P(OMe)_3$ to $Me_2NP(OMe)_2$ to $(Me_2N)_2POMe$ is approximately 0.3 ev. If one assumes that the decrease in IE_P from the last compound to $P(NMe_2)_3$ should be the same, then the IE_P for $P(NMe_2)_3$ should be 8.3 ev. However, the experimentally found value is 7.6 ev. If the difference in these two values (0.7 ev) is applied to the 9.90 ev value of IE_N, this then results in an average IE_N for $P(NMe_2)_3$ of 8.6 ev. This is still 0.3 ev higher than the average of the other two IE_N values. This 0.3 ev difference can be rationalized by the fact that X-ray structural analysis of compounds such as $SeP(NMe_2)_3$ have shown (155,156) one of the nitrogens to be . tetrahedral as opposed to planar, thus leading to an increase in the ionization energy of its lone-pair. This interaction between the nitrogen and phosphorus lone-pairs is illustrated by the MO diagram illustrated in fig. 22.

As can be seen in Table 31, there are two possible assignments for the ionization energies of the lone-pairs on phosphorus and oxygen in compounds 20 and 21. Originally, assignment b) was favored on the basis of the greater .sp^3 character of the oxygens in 20 and 21 as opposed to 23

ENERGY
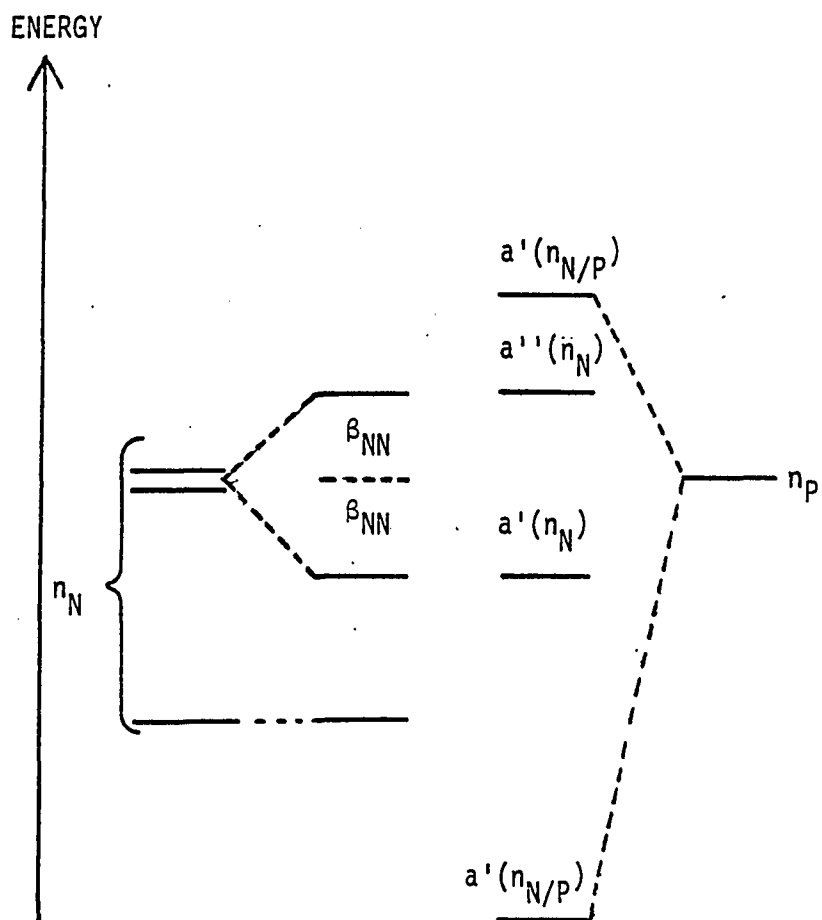
Figure 22. MO diagram for nitrogen and phosphorus
lone pairs in P(NMe$_2$)$_3$

and $P(OMe)_3$. The greater sp^3 hydrization was evidenced by the smaller P-O-C angles of 113.5° and 115.3° in compounds 20 and 21 as compared to 120° angle found in 23 and $P(OMe)_3$. It was felt that this increase in sp^3 hydrization should lead to a decrease in π-bonding from O to P in 20 and 21 which would lead to a higher positive charge on phosphorus and a higher IE_P. The higher IE_0 values for assignment b) in compounds 20 and 21 as compared to $P(OMe)_3$ could be attributed to an increase in s orbital involvement between oxygen and phosphorus upon rehybridization. However, it was also observed that assignment b) failed to agree with the $J_{31_{P}-77_{Se}}$ data obtained on the selenides of 20, 21 and other similar compounds.

One bond $^{31}P-^{77}Se$ coupling constants have been observed over a wide range of frequencies (500 Hz) (13). The use of these coupling constants have been shown to be an effective method of measuring the inductive effects on phosphorus stemming from variations in substituent electronegativities and from molecular constraint (13). Table 32 shows the $\delta^{31}P$ and $J_{31_{P}-77_{Se}}$ values for the corresponding selenides of 20 and 21 along with the values of some related compounds. Previous work has shown that as the positive charge on phosphorus increases, either by molecular constraint or increased substituent electronegativity, the value of $J_{31_{P}-77_{Se}}$ increases. Therefore, as can be seen, the value of $J_{31_{P}-77_{Se}}$ increases upon replacement of Me_2N groups by MeO groups. Although the values of $J_{31_{P}-77_{Se}}$ for 45 and 46 are larger than that for $Me_2N(Se)P(OMe)_2$, as would be expected on the grounds of increased molecular constraint, it is very surprising that the couplings are

Table 32. ^{31}P NMR chemical shifts (ppm) and $J_{31_{P}-77_{Se}}$ coupling constants (Hz)

	$\delta^{31}P$ (±0.5)	$^{1}J_{31_{P}-77_{Se}}$ (±1 Hz)
. SeP(OMe)$_3$[a]	78.0	954
<u>51</u>[a]	68.6	985
. <u>52</u>[a]	66.8	996
<u>53</u>[a]	68.8	949
Me$_2$N(Se)P(OMe)$_2$[b]	87.1	903
<u>45</u>[b]	79.2	914
<u>46</u>[b]	76.9	909
<u>47</u>[b]	75.1	895
<u>48</u>[b]	77.6	924
SeP(NMe$_2$)$_3$[a]	82.5	784

[a]See ref. 13.

[b]This work.

substantially lower than for SeP(OMe)$_3$. This would not be expected due to the lower IE_p values for P(OMe)$_3$ as compared to those given in assignment b for <u>20</u> and <u>21</u>. Secondly, it is odd that a small change in $J_{31_{P}-77_{Se}}$ from Me$_2$NP(Se)(OMe)$_2$ to <u>45</u> (11 Hz) would correspond to a 0.9 ev difference in IE_p values of the parent phosphites, whereas the small change in $J_{31_{P}-77_{Se}}$ values of 5 Hz in going from SeP(OMe)$_3$ to <u>53</u> corresponds to a much smaller difference in IE_p (0.16 eV) of their parent phosphites (26). Thirdly, it is not yet clear why the approximately sp^3

hybridizational character of oxygen in 20 and 21 (used to support

assignment b) in Table 31 is not at least similar in $Me_2NP(OMe)_2$, thus

leading to a higher IE_p value than the 8.93 ev assigned to this acyclic

analogue by others (162). Fourthly, given the structural similarity of

21 and 16, it seems questionable that there should be such a large

increase in IE_p (0.8 ev). Fifthly, the conformation of $Me_2NP(OMe)_2$ as

calculated by semi-empirical MNDO methods should be that of C_s symmetry

Fig. 23 (162). The arrangement of lone-pairs in this conformation should

cause a higher IE_p than for the conformation of 20 and 21 (as illustrated

by the conformations of lone-pairs in similar compounds (Fig. 24)

(163)). This is due to lack of interaction between the lone-pairs on

oxygen and phosphorus in the acyclic compounds, which would normally tend

to raise the energy of the phosphorus lone-pair. However, the

approximate equivalence of the IE_p values under assignment a) with that

of $Me_2NP(OMe)_2$ may be due to greater sp^3 character in the ring oxygens of

20 and 21 which would tend to reduce lone-pair interactions between

phosphorus and oxygen.

The photoelectron assignments given in a) would seem best since they

remove all five objections to assignment b). At the same time the values

in assignment a) for 20 and 21 are in agreement with those found for

$Me_2NP(OMe)_2$ (162) and 16 (163). However, it would appear that the IE_0

for the a',a" interactions of the p AO's on the oxygens in 20 and 21 are

quite low compared to those for $Me_2NP(OMe)_2$. This would not be expected

especially if the oxygens in 20 and 21 possess more sp^3 character.
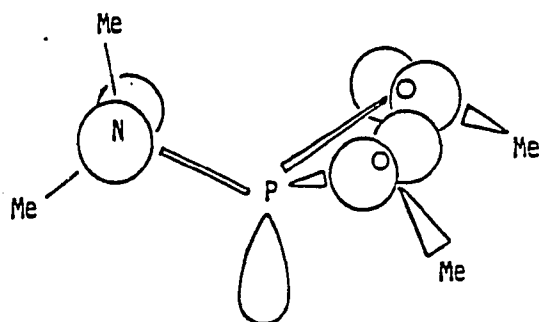
Figure 23. Conformation of $Me_2NP(OMe)_2$ as calculated by semiempirical MNDO methods (162)
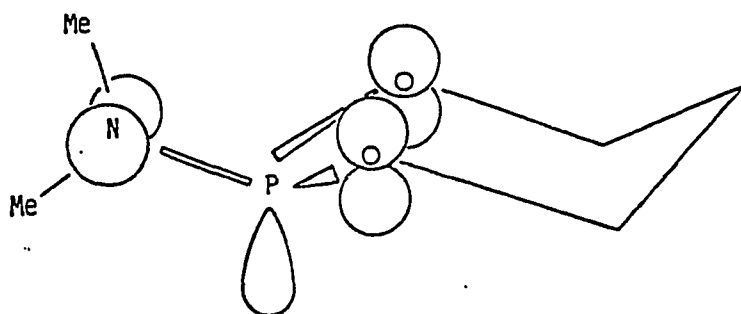
Figure 24. Proposed conformation of 16 (163)

We now know that compounds such as 20 and 21 adopt the equatorial amino group conformation in the solid phase. Previous work by Mosbo and this work confirm that this conformation is preferred in the solution phase. It is logical to question if this conformational preference holds in the gas phase wherein their PE spectra are measured. Upon analysis of the PE data, we believe this to be the case due to the following observations. The PE spectrum of 58 (which is known to be 100% in the axial MeO conformation in solution as judged by the exclusive presence of this conformation upon equilibration of 8 and 38) is similar to the PE spectra of 8 but is quite different from the PE spectrum of 38 (26). Therefore, since the methoxy derivative shows the same conformation in the gas phase as that observed in the solution phase it seems reasonable that the equatorial Me_2N group is favored in the gas phase as it is in the solution phase. This conclusion seems reasonable since it is steric factors and not electronic factors which dominate in the solid and solution phases and there is no reason to assume that electronic factors would become dominant in the gas phase and cause the axial Me_2N conformer to become favored.

PART III:

THE USE OF PHOSPHORUS CONTAINING DERIVATIZING

REAGENTS FOR THE ANALYSIS OF ALCOHOLS

INTRODUCTION

NMR spectroscopy has become an extremely important analytical tool over the past twenty five years. This is particularly true of ^{1}H NMR, as it has become the main method of structural analysis of organic compounds. During the same period, ^{31}P NMR has also proved to be an important technique in the study of phosphorus-containing compounds.

One of the advantages of ^{31}P NMR is that the range of chemical shifts is large (ca. 500 ppm) as compared to 40 ppm for ^{1}H NMR. Since different classes of phosphorus compounds (phosphines, phosphites, phosphates, etc.) have markedly different chemical shifts, a ^{31}P NMR analysis of a mixture of phosphorus compounds can afford information on the types of compounds contained within the mixture.

NMR can also be used as a quantitative method of analysis. As is the case with ^{1}H NMR, under optimum conditions, the peak areas contained in continuous wave ^{31}P NMR spectra are proportional to the relative amounts of each of the phosphorus compounds contained in the sample. However, over the past ten years Fourier Transform (FT) techniques have been applied to ^{31}P NMR and essentially replaced the use of continuous wave techniques. The use of FT techniques has allowed ^{31}P NMR to be used as a rapid method of qualitative analysis for phosphorus compounds in concentrations of 10^{-2} M or higher.

The area under a peak contained in an NMR spectrum depends upon several factors (Eq. 52);

$$\text{Peak area} \quad \alpha \frac{NB_1\mu^2}{KT(1 + \gamma B_1{}^2T_1T_2)^{1/2}} \qquad (52)$$

where N = number of nuclei giving the signal, B_1 = applied magnetic field, μ = magnetic moment, T_1 = spin-lattice relaxation time and T_2 = spin-spin relaxation time (164). As seen in Equation (52), the T_1 value can have a great effect on the peak area observed for a particular compound. Under continuous wave conditions relaxation time has little effect on the observed peak area. However, in order to obtain accurate peak areas under FT conditions, it is important to maintain the pulsing frequency sufficiently slow to allow the observed nuclei enough time to relax before being pulsed again. This point is especially important when compounds contained in the sample have very different T_1 values.

The spin-lattice relaxation times (T_1) for various phosphorus compounds vary over a wide range, from 1 to 25 seconds (165,166). It has been suggested (165) that in order to obtain valid analytical data using FT-NMR techniques one must allow three times the longest T_1 between successive pulses in order to obtain an accuracy of $\pm$ 5%. With compounds such as $P(O-\underline{i}-Pr)_3$, which has a T_1 of 18 sec (165), this represents a delay of approximately 1 minute between each pulse. Under conditions of low concentration, where a large number of scans is required to achieve an reasonable signal to noise ratio, such a procedure would be unacceptable.

The most common method of reducing large T_1 values is to add a small amount of paramagnetic material to the NMR sample. Gurley and Ritchey (167) have reported the use of Fe(III) complexes as relaxation agents in the analysis of inorganic phosphates. Kasler and Tierney (168) have also used $Cr(acac)_3$ in the quantitative analysis of phosphorus contained in various organic compounds. However, most trivalent phosphorus compounds can function as ligands. Due to differences in their ligating properties, it is possible that their relaxation properties may be different upon coordination to an iron or chromium atom. It is also possible that ligand exchange processes between the phosphorus compounds and these metals could lead to excessive line broadening which would render any quantitative NMR analysis of these compounds inaccurate (165).

In order to solve this problem, Stanislawski and Van Wazer (165) have investigated the use of the 4-hydroxy and 4-amino derivatives of 2,2,6,6-tetramethyl piperidinooxy free radical as shiftless relaxagents. It was observed that these free radicals, to which phosphorus can not directly bond, could lower the T_1 values of compounds such as PPh_3 and $(C_2H_5O)_3PO$ from 12.5 and 16.8 seconds to 0.58 and 0.63 seconds, respectively (molar concentration of P = 0.6 and molar concentration of free radical = 0.07).

It occurred to us that quantitative ^{31}P NMR could be applied to the analysis of alcohol mixtures via the use of the following reaction (Eq. 55).

$$R_2P\text{-}Cl + ROH + Et_3N \rightarrow R_2P\text{-}OR + Et_3NH^+Cl^- \tag{55}$$
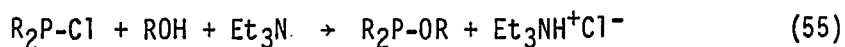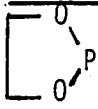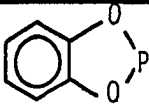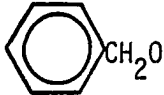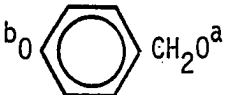
The use of this reaction to derivatize alcohols seemed attractive since equation (55) was known to proceed quantitatively (24). However, it was important that the proper derivatizing reagent be selected so as to be able to discern the types of alcohols in a mixture on the basis of resolution of the chemical shifts of the products esters.

Though gas chromatographic methods of analysis for mixtures of alcohols were already known (169), this method seemed promising for such uses as the analysis of alcohols contained in more heterogeneous mixtures, such as coal. In the past, investigators have used $(CF_3CO)_2O$ (170) and $(CH_3)_3SiCl$ (171) to characterize -OH, -NH, and -SH groups contained in coal. The use of the aforementioned chlorophosphorus compounds as derivatizing reagents seemed promising since reaction (55) was known to proceed in high yield and ^{31}P NMR analysis of the derivatized coal could give information on the types of -OR groups bound to phosphorus. Analysis of the observed chemical shifts, followed by comparison to those of known model compounds (derivatives of both aliphatic and aromatic alcohols) could provide information on the types of alcohols contained within the coal.

Preliminary work by Squires and co-workers (172) indicated that derivatizing reagents containing five membered rings, such as 14, gave the greatest difference in chemical shifts between compounds with different exocyclic groups. As can be seen in Table 33 (172) the 1,3,2-dioxaphospholanyl compounds exhibited the largest chemical shift difference (6 ppm) between aliphatic and aromatic alcohol derivatives.

Table 33. Phosphorus chemical shifts of model compound derivatives[a]

$$R_2PCl + R'OH \rightarrow R_2P\text{-}OR' + HCl$$

R'O	R_2P		
	O-P-O (catechol-type, aliphatic)	O-P-O (benzene-fused)	Ph_2P
phenoxy (O)	128.1	127.0	---
benzyloxy (CH_2O)	134.7	127.1	113.9
$CH_3CH_2CH_2CH_2O$	134.6	127.2	111.0
^bO-phenyl-CH_2O^a	[a]135.1 [b]128.4	[a]127.0 [b]126.7	---

[a]ppm downfield from external 85% H_3PO_4.

In this chapter is discussed further use of 14 as a derivatizing reagent for the analysis of various types of alcohols, the use of 2,2,6,6-tetramethyl piperidinooxy free radical as a shiftless relaxagent, the NMR parameters used in the development of this analysis technique and extension of this procedure to the analysis of alcohols contained in some selected coal-pyridine extracts and coal tars.

EXPERIMENTAL PROCEDURES

All solvents were reagent grade or better. All chemicals were used as received with the exception of phenol which was sublimed before use. The synthesis of the derivatizing reagent, 14, is described in chapter one of this thesis. The 4-amino-2,6-dimethylpiperidinooxy free radical was obtained from Aldrich Chemicals. ^{31}P NMR spectra were obtained on samples contained in 10 mm tubes on a Bruker WM-300 NMR spectrometer operating at 121.5 MHz. The spectrometer operated in the FT mode with an internal ^2H lock provided by ^2H atoms contained in the solvent. The external standard was 85% H_3PO_4 sealed in a 1 mm capillary tube held coaxially in the sample tube by a Teflon vortex plug. All downfield shifts of H_3PO_4 were considered positive. Various pulse sequences used during the collection of NMR data were generated by an Aspect 2000 computer system which was interfaced to the spectrometer.

A typical analysis of a particular alcohol or alcohol mixture was carried out in the following manner: In a 25 ml vial was placed 2.00 mmole of the alcohol or alcohols, 0.512 g (2.00 mmole) of triphenyl phosphine (acting as internal standard), 0.7 ml (0.005 mole) of triethylamine, 5.0 ml of $CHCl_3$, and 0.7 (0.006 mole) of 14. The mixture was shaken for approximately 1 minute. Approximately 1.5 ml of this mixture were added to a 10 mm NMR tube which already contained 1.5 ml of $CDCl_3$ and 0.3 mmole of 2,2,6,6-tetramethylpiperidinooxy free radical.

Analysis of coal tar mixtures was carried out in the same manner, with the exception that 0.15 g of coal tar was used instead of the

alcohols. Preparation of the coal tars is described elsewhere (173).

Analysis of the pyridine coal extract was carried out in the following

manner. The coal extract (0.524 g) was mixed with 20 ml of fresh

pyridine and sonocated for 10 min. The solution was filtered through a

0.05 μm millipore filter. To a 10 mm NMR tube was added 1.5 ml of this

solution, 0.0700 g (0.267 mmole) of PPh_3, 0.3 mmole of the above-

mentioned free radical, and 1.5 ml of $CDCl_3$. The ^{31}P NMR spectrum of

this mixture was then collected. Preparation of the pyridine coal

extract was described previously (174).

A spectrum of the mixture was collected with either continuous or

gated decoupling techniques. Continuous decoupling involves leaving the

proton decoupler on at all times during the entire spectrum

acquisition. Gated decoupling entails having the decoupler on only

during data acquisition. The decoupler is then turned off during the

delay time between pulses. A delay time between pulses of eight seconds

was used. It was felt that eight seconds was sufficient to ensure the

complete relaxation of the phosphorus nuclei in the presence of the

piperidinooxy free radical since Stanislowski and Van Wazer had shown

that similar compounds had T_1 values of 0.5 sec in the presence of a

similar free radical (165).

Upon completion of collection of the spectrum, the peaks

representing the PPh_3 (the internal standard) and the derivatized alcohol

or alcohols ($\overline{OCH_2CH_2O}POR$) were expanded (0.25 ppm/1 inch of paper) and

integrated with the aid of a planimeter in order to yield the relative
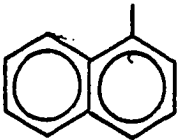
amounts of the alcohols compared to the standard contained in the mixture.

Results and discussion

The use of NMR techniques to identify and quantify materials is widespread. The technique described herein represents the first time that alcohols have been identified and quantified using phosphorus-containing derivatizing reagents. As seen in Table 34, the 1,3,2-dioxaphospholanyl derivatives possess a ca. 6 ppm difference in chemical shift between the aliphatic and aromatic oxygen derivatives. It would appear that due to the closeness of the chemical shifts within a particular class, the method would be inappropriate for distinguishing between, for example, t-butanol and sec-butanol in an unknown mixture. However, it certainly appears possible to identify and quantify the presence of both aliphatic and aromatic alcohols in a mixture.

Table 35 shows the ratio of integrated areas of 1,3,2-dioxaphospholanyl oxygen derivatives to PPh_3 compared to what was known to be present in the mixture. Accumulation of NMR data was obtained under continuous broad band proton decoupling. Table 36 shows the same information; however, accumulation of the spectrum was done with gated proton decoupling. As can be seen, the agreement between the determined and actual ratios is much closer under conditions of gated decoupling. The explanation of this result lies in the fact that under gated decoupling conditions the NOE enhancement of the ^{31}P NMR signal by the

Table 34. Phosphorus chemical shifts of 1,3,2-dioxaphospholanyl derivatives of various alcohols ($\overline{OCH_2CH_2OP}$-OR)[a,b]

R	Chemical shift (ppm) (±0.3 ppm)
n-Bu	135.6
sec-Bu	136.5
t-Bu	135.2
PhCH$_2$	135.7
Ph	129.7
	129.1
PhCH$_2$$\overset{O}{\overset{|}{C}}$	128.5
Ph$\overset{O}{\overset{\|}{C}}$	129.0
trans-PhCH=CHC(O)	128.4

[a]Relative to 85% H$_3$PO$_4$.

[b]Chemical shift of $\overline{OCH_2CH_2OP}$Cl is 169.2 ppm.

Table 35. Comparison of ratios of peak areas of 1,3,2-dioxaphospholanyl derivatives ($\overline{OCH_2CH_2OP}OR$) to PPh_3 under conditions of broad band decoupling
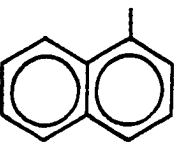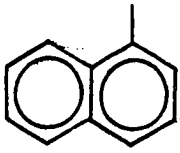
R	actual ratios of moles PPh_3 to moles of ROH in mixture (±0.007)	Ratio of peak areas for moles of PPh_3 to moles of $\overline{OCH_2CH_2OP}(OR)$ found by NMR (±0.07)
n-Bu	1.062	1.03
sec-Bu	0.756	0.68
t-Bu	0.770	0.55
$PhCH_2$	0.974	1.06
Ph	0.943	0.76
(naphthyl)	0.889	0.70
$Ph-\overset{O}{\overset{\|}{C}}-$	0.813	0.72

Table 36. Comparison of ratios of peak areas of 1,3,2-dioxaphospholanyl derivatives ($\overline{OCH_2CH_2OP}$(OR)) to PPh_3 under conditions of gated decoupling

R	Actual ratio of moles PPh_3/moles ROH in mixture (± 0.007)	Ratio of peak area for moles of PPh_3 to moles of $\overline{OCH_2CH_2OP}$(OR) found by NMR (± 0.07)
n-Bu	0.960	1.01
sec-Bu	0.631	0.61
t-Bu	0.676	0.67
PhCH$_2$	0.914	0.92
Ph·	0.876	0.88
(naphthyl structure)	1.422	1.29
$\overset{O}{\overset{\|\|}{Ph-C-}}$	0.700	0.65

broad band decoupling of the protons is eliminated. Under conditions of continuous broad band decoupling, NOE enhancement of phospholanyl derivatives may differ from that of the PPh_3, thus causing the lineshape of their NMR peaks to vary independently. This of course would render inaccurate any comparative integration of the peaks contained in the spectrum.

The procedure was also applied to mixtures of alcohols. Several different mixtures were prepared and analyzed. Table 37 gives a comparison of the actual percentages of a particular alcohol in the mixture to the percentages found in the analyses using broad band decoupling techniques. Table 38 gives the same comparison, using gated decoupling techniques. As was observed in the single alcohol analyses, gated decoupling gave the more accurate results. Again, this result must

Table 37. Results of ^{31}P NMR analysis of alcohol mixtures using 14 as derivatizing reagent, PPh$_3$ as an internal standard, and broad band decoupling

Mixture	R	Actual percentage of ROH in mixture (± 0.2)	Found percentage in mixture (± 0.2)
1	n-Bu	32.3	27.2
	sec-Bu	38.9	39.0
	Ph	28.8	33.8
2	sec-Bu	43.3	47.1
	PhCH=CHC(0)	13.7	12.0
	2-naphthyl	42.9	40.9
3	sec-Bu	36.2	35.8
	Ph	23.0	29.9
	PhC(0)	11.3	17.8
	PhCH$_2$	29.6	16.5

Table 38. Results of ^{31}P NMR analysis of alcohol mixtures using 14 as derivatizing reagent, PPh$_3$ as an internal standard, and gated decoupling techniques

Mixture	R	Actual percentage of ROH in mixture (±0.2)	Found percentage of ROH in mixture (±0.2)
1	n-Bu	28.5	27.2
	sec-Bu	39.0	39.0
	Ph	32.4	33.7
2	sec-Bu	41.4	41.1
	PhC(O)	33.3	33.7
	2-naphthyl	25.2	25.3
3	sec-Bu	37.5	35.7
	Ph	27.6	29.9
	PhC(O)	18.0	17.8
	PhCH$_2$	16.8	16.6

be due to removal of nonuniform NOE enhancement of the 1,3,2-dioxaphospholanyl derivatives contained within the mixture.

Attempts were made to qualify and quantify the types of -OH groups in coal tars and pyridine coal extracts using the above techniques. Due to the similarity of the chemical shifts of similar aliphatic and aromatic alcohol derivatives it does not appear feasible to differentiate sec-butyl alcohols from t-butyl alcohols or phenols from naphthols contained within the coal by-products. However, aliphatic alcohols can be differentiated from aromatic alcohols.

Subsequent analysis of coal tars and pyridine extracts of Kentucky #8 coal revealed that the amount of -OH functional groups in these materials was rather small. Previous analyses of these materials had shown them to contain only 8% oxygen by weight (175). In all cases, small humps were observed in the baseline of the gated decoupled ^{31}P NMR spectra of the derivatized coal products. These humps were centered at 134 and 128 ppm. This would seem to be indicative of the presence of both aliphatic and aromatic alcohols contained in the coal products. Due to their small size, accurate integration of these humps against a PPh$_3$ internal standard was not possible. However, it appeared as though the peak at 134 was approximately twice as large as the peak at 128 ppm. This would seem to imply that there was twice as much aliphatic alcohol as aromatic alcohol contained within the coal products. This result does not seem reasonable considering the highly aromatic nature of coal (175). Analysis of blanks (no extract or tar present) did show the presence of a small peak (< 4%) of area of peak for 14 at 134 ppm. Since the reported chemical shift of $\overline{OCH_2CH_2OPOCH_2CH_2OP}OCH_2CH_2O$ is 133 ppm (176), it is possible that part of the peak at 134 ppm stems from traces of oligomeric impurities contained within the derivatizing reagent. These impurities could give the false impression that there is more aliphatic than aromatic alcohol in the coal extracts and tars. Though this procedure appears to be inappropriate for the analysis of -OH in coal, this procedure is useful for the analysis of alcohols when they are present in higher concentrations.

CONCLUSIONS

As shown in this dissertation the catalytic properties of a NiL_4 complex depend in large measure upon the steric properties of the ligands contained within the complex. An X-ray structural analysis of $Ni(\underline{6})_4$ showed the nickel atom to be tetrahedrally coordinated and there appeared to be no change in the ligand's conformation upon coordination. The results of this structural investigation suggests that the large differences in the catalytic properties of the complexes investigated stem from steric interactions between ligands contained within the complex.

This work suggests that the role of a Lewis acid cocatalyst is that of a ligand dissociation promoter. A Lewis acid, such as $AlCl_3$, was found to promote the formation of a coordinatively unsaturated NiL_3 species from the parent NiL_4 complex. The NiL_3 species is thought to bring about olefin isomerization via a π-allyl olefin isomerization mechanism as opposed to the σ-bonded alkyl isomerization mechanism which is invoked for the NiL_4/H^+ system. Attempts were made at heterogenizing these NiL_4 catalysts. However, in all cases these catalysts were found to be much less active than their homogeneous analogues. This reduction in activity was attributed to the structural characteristics of these hybrid catalysts.

An X-ray structural study of two aminophosphites, $\underline{20}$ and $\underline{21}$, showed each compound to have a planar stereochemistry about the nitrogen. Analysis of the structure also revealed substantial N-P multiple

bonding. Examination of PES data for 20 and 21 reveals that alternate

assignments for the phosphorus lone-pair IEs had to be considered, one

which suggests that these molecules are considerably less basic than

their acyclic analogue, $Me_2NP(OMe)_2$. The other assignment suggests that

the basicity of all three molecules is the same. Solution $31p-77_{Se}$ NMR

coupling data would seem to suggest that the basicity of all three

compounds is the same.

Finally, a procedure was developed to quantify the amounts and types

of alcohols contained within a mixture using a phosphorus-containing

derivatizing reagent. The procedure uses quantitative 31_P NMR techniques

to determine the actual amount of alcohol (or alcohols) contained within

a mixture. Attempts to analyze alcohols contained in coal tars and coal

pyridine extracts were unsuccessful due to the low concentration of OH

groups in coal.

REFERENCES

1. Parshall, G. W., "Homogeneous Catalysis: the Application and Chemistry of Catalysis by Soluble Transition Metal Complexes", John Wiley and Sons, New York, 1980.

2. Shaw, B. L.; Tucker, N. I., "Organo-Transition Metal Compounds and Related Aspects of Homogeneous Catalysis", Pergamon Press: Oxford, 1973.

3. Dewar, M. J. S. Bull. Soc. Chim. Fr. **1957**, _18_, C17.

4. Chatt, J.; Duncanson, L. A. J. Chem. Soc. **1953**, _2_, 959.

5. Guggenberger, L. J. Inorg. Chem. **1973**, _12_, 499.

6. Braterman, P. S. Struct. Bonding **1976**, _26_, 1.

7. Tolman, C. A. Chem. Rev. **1977**, _77_, 313.

8. Tolman, C. A. J. Am. Chem. Soc. **1970**, _92_, 2953.

9. Angelici, R. J.; Malone, J. D. Inorg. Chem. **1967**, _6_, 1731.

10. Bigorgne, M. J. Inorg. Nucl. Chem. **1964**, _26_, 107.

11. McFarlane, W.; White, R. F. M. J. Chem. Soc., Chem. Commun. **1969**, 744. Sheldrick, G. M. Trans. Faraday Soc. **1967**, _63_, 1077.

12. Verkade, J. G. Phosphorus and Sulfur **1976**, _2_, 251.

13. Kroshefsky, R.; Weiss, R.; Verkade, J. G. Inorg. Chem. **1979**, _18_, 469.

14. Watanabe, H.; Nagasawa, K. Inorg. Chem. **1967**, _6_, 1068.

15. Keiter, R. L.; Verkade, J. G. Inorg. Chem. **1969**, _8_, 2115.

16. McFarlane, W.; Rycroft, D. S. J. Chem. Soc., Chem. Commun. **1973**, 336.

17. Yarbrough, L. W.; Hall, M. B. Inorg. Chem. **1978**, _17_, 2269.

18. Cowley, A. H.; Lattman, M.; Stricklen, P. M.; Verkade, J. G. Inorg. Chem. **1982**, _21_, 543.

19. Tolman, C. A. J. Am. Chem. Soc. **1970**, _92_, 2956.

20. Tolman, C. A.; Seidel, W. C.; Gosser, L. W. J. Am. Chem. Soc. **1974, 96**, 53.

21. Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. J. Chem. Soc. **1966**, 1711.

22. Jardine, F. H.; Osborn, J. A.; Wilkinson, G. J. Chem. Soc. **1967**, 1574.

23. Mosbo, J. A.; Verkade, J. G. J. Am. Chem. Soc. **1973, 95**, 204.

24. White, D. C.; Bertand, R. D.; McEwen, G. K.; Verkade, J. G. J. Am. Chem. Soc. **1970, 92**, 7125.

25. Hudson, R. F.; Verkade, J. G. Tetrahedron Lett., **1975**, 3231.

26. Hodges, R. V.; Houle, F. A.; Beauchamp, J. L.; Montag, R. A.; Verkade, J. G. J. Am. Chem. Soc. **1980, 102**, 932.

27. Cowley, A. H.; Lattman, M.; Montag, R. A.; Verkade, J. G. Inorg. Chim. Acta **1977, 25**, L151.

28. Taylor, P.; Orchin, M. J. Am. Chem. Soc. **1971, 93**, 6504.

29. Cramer, R. J. Am. Chem. Soc. **1966, 88**, 2272.

30. Tolman, C. A. J. Am. Chem. Soc. **1972, 94**, 2994.

31. Adams, R. W.; Batley, G. E.; Bailar, J. C. J. Am. Chem. Soc. **1968, 90**, 6051.

32. Emerson, G. F.; Petit, R. J. Am. Chem. Soc. **1962, 84**, 4591.

33. Hendrix, W. T.; Cowherd, F. G.; von Rosenberg, J. L. J. Chem. Soc., Chem. Commun. **1968**, 97.

34. Green, M.; Hughes, R. P.; J. Chem. Soc., Dalton Trans. **1976**, 1907.

35. Green, M.; Hughes, R. P. J. Chem. Soc., Chem. Comm. **1975**, 619.

36. Tolman, C. A. J. Am. Chem. Soc. **1970, 92**, 4217.

37. Rix, C. J.; Verkade, J. G. Coord. Chem. Rev. **1975, 16**, 129.

38. Gultneh, Y., Ph.D. Thesis, Iowa State University, Ames, Iowa, **1981**.

39. Walker, B. J. "Organophorus Chemistry", Penguin Book Ltd.: Middlesex, 1972.

40. Drinkard, W. C.; Eaton, D. R.; Jesson, J. P.; Lindsey Jr., R. V. Inorg. Chem. **1970**, 9, 392.

41. Carpenter II, L. E.; Jacobson, R. A.; Verkade, J. G. Phosphorus and Sulfur **1979**, 6, 475.

42. Milbrath, D. S.; Springer, J. P.; Clardy, J. C.; Verkade, J. G. J. Am. Chem. Soc. **1976**, 98, 5493.

43. Bogdanovic, A. B.; Wilke, G.; Benneman, P. Angew. Chem. Int. Ed. **1967**, 6, 804.

44. Shriver, D. R. J. Am. Chem. Soc. **1963**, 85, 3509.

45. Drinkard, W. C. U. S. Patent 3,496,218; Fr. Patent 1,544,658; Neth. Patent 67 06555; Brit. Patent 1,112,539; Belg. Patent 698,332.

46. Drinkard, W. C.; Lindsey, R. V.; Brit. Patent 1,104,140; Chem. Abstr., 68,77795 (1968); U. S. Patent 3,496,215; Belg. Pat. 698,333; Neth. Patent 67 05556; U. S. Patent 3,496,217.

47. Brown, E. S. Aspect. Homo. Catal. **1974**, 2, 57.

48. Drinkard, W. C.; Ger. Patent 1,807,088; Chem. Abstr., 71, 38383 (1969); Belg. Patent 723,381; Neth. Patent 68 15,746.

49. Arthur, P., England, D. C.; Pratt, B. C.; Whitman, G. M. J. Am. Chem. Soc., 70, 5364 (1954).

50. Drinkard, W. C.; Taylor, B. W.; Belg. Patent 723,383; Neth. Patent 68 15,812.

51. Drinkard, W. C.; Lindsey, R. V.; U. S. Patent 3,496,215.

52. Rick, E. A.; Brown, E. S. J. Chem. Soc. D **1969**, 112.

53. Drinkard, W. C.; Taylor, B. W. Ger. Patent 1,807,089; Chem. Abstr. 71,101350 (1969); Belg. Patent 723,380; Neth. Patent 68 15744 and 68 15746.

54. Kwiatek, J.; Seyler, J. K. J. Organomet. Chem. **1965**, 3, 433.

55. Johnson, M. D.; Tobe, M. L.; Wong, L. Y. J. Chem. Soc. A **1969**, 929.

56. Drinkard, W. C. Ger. Patent OLS 1,806,096; Chem. Abstr. 71,30093, (1969); Neth. Patent 68 15560; Belg. Patent 723,126.

57. King, C. M.; Seidel, W. C.; Tolman, C. A. U. S. Patent 3,925,445.

58. Mosbo, J. A., Ph.D. Thesis, Iowa State University, Ames, Iowa, **1970.**

59. Mosbo, J. A.; Verkade, J. G. J. Am. Chem. Soc. **1973,** 95, 4659.

60. Quin, L. D.; Featherman, S. L. J. Am. Chem. Soc. **1973,** 95, 1699.

61. Merrill, R. D. Chemtech **1981,** 11, 118.

62. Apsimon, J. W.; Seguin, R. P. Tetrahedron **1981,** 35, 2797.

63. Haggin, J. Chem. Eng. News, Nov. 15, **1982,** 11.

64. Bailar, J. C. Catal. Rev. Sci. Eng. **1977,** 10, 17.

65. Grubbs, R. H. Chemtech **1977,** 7, 512.

66. Bailey, D. C.; Langer, S. H. Chem. Rev. **1981,** 81, 109.

67. Grubbs, R. H.; Kroll, L. C.; Sweet, E. M. J. Macromol. Sci. Chem. **1973,** A7, 1047.

68. Otero-Schipper, Z.; Lieto, J.; Gates, B. C. J. Catal. **1980,** 63, 175.

69. Evan, G. O.; Pittman, C. U.; McMillan, R.; Beach, R. T.; Jones, R. J. J. Organomet. Chem. **1974,** 67, 295.

70. Wauvel, S.; Buschmeyer, P. Angew. Chem., Int. Ed. Engl. **1978,** 17, 137.

71. Pittman, C. U.; Marlin, G. V.; Rounsefell, T. D. Macro. Mol. Sci. **1973,** 6, 1.

72. Gray, H. B.; Rembaum, A.; Gupta, A. Ger. Patent 2,633,959; Chem. Abstr. 87, 173430q (1977).

73. Pittman, C. U. Organomet. React. Synth. **1977,** 6, 1.

74. Masuda, T.; Stille, J. K. J. Am. Chem. Soc. **1978,** 100, 268. Takaishi, N.; Imai, H.; Bertelo, C. A.; Stille, J. K. J. Am. Chem. Soc. **1978,** 100, 264.

75. Padmakumari Amma, J.; Stille, J. K. J. Org. Chem. **1982,** 47, 468.

76. Gubtosa, G.; Brintzinger, H. H. J. Am. Chem. Soc. **1977,** 99, 5174.

77. Lee, W. S.; Brintzinger, H. H. J. Organomet. Chem. **1977**, 87, 127.

78. Pittman, C. U.; Kim, B. T.; Douglas, W. M. J. Org. Chem. **1975**, 40, 540.

79. Cais, M.; Frankel, E. N.; Butterfield, R. O. Tetrahedron Lett. **1968**, 1919 (1968).

80. Pittman, C. U.; Smith, L. R.; Hanes, R. M. J. Am. Chem. Soc. **1975**, 97, 1742.

81. Brenner, A.; Hucul, D. A.; Hardwick; S. J. Inorg. Chem. **1979**, 18, 1478.

82. Robertson, J.; Webb, G. Proc. Royal Soc. London, Ser. A. **1974**, 341, 383.

83. Wrighton, M. S.; Liu, D. K. J. Am. Chem. Soc. **1982**, 104, 898.

84. Capka, M.; Hetflejs, J. J. Coll. Czech. Chem. Commun. **1974**, 39, 154.

85. Barltrop, J. A.; Carless, H. A. J. J. Am. Chem. Soc. **1972**, 94, 1951.

86. McGreer, D. E.; Page, D. P.; Kaushal, D. P. Can. J. Chem. **1973**, 51, 1239.

87. Waitkins, G. R.; Shutt, R. Inorg. Synth. **1946**, 2, 186.

88. Schrauzer, G. N. J. Am. Chem. Soc. **1959**, 81, 5310.

89. White, D. W.; Bertrand, R. D.; McKwen, G. K.; Verkade, J. G. J. Am. Chem. Soc. **1970**, 92, 7125.

90. Verkade, J. G.; Huttemann, T. J.; Fung, M.; King, R. W. Inorg. Chem. **1965**, 4, 83.

91. Kainosho, M.; Nakamura, A. Tetrahedron **1960**, 25, 4071.

92. Huttemann, T. J. Ph.D. Thesis, Iowa State University, Ames, Iowa, **1965.**

93. Lucas, H. J.; Mitchell, Jr., F. W.; Sculley, C. N. J. Am. Chem. Soc. **1950**, 72, 2491.

94. Denney, D. B.; Chang, L. L. J. Org. Chem. **1977**, 43, 782.

95. Bigorne, M. Bull. Soc. Chim. Fr. 1960, 1986.

96. Vinal, R. S.; Reynolds, L. T. Inorg. Chem. 1964, 3, 1062.

97. Levinson, J. J.; Robinson, S. D. Inorg. Synth. 1972, 13, 105.

98. Coskran, K. J.; Bertrand, R. D.; Verkade, J. G. J. Am. Chem. Soc. 1967 89, 4535.

99. White, D. W. Ph.D. Thesis, Iowa State University, Ames, Iowa, 1970.

100. Skoog, D. A.; West, D. M. "Analytical Chemistry, An Introduction"; Holt, Rinehart and Winston, New York, 1974.

101. Noller, C. C.; Pannell, C. E. J. Am. Chem. Soc. 1955, 77, 1862.

102. Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis", John Wiley and Sons: New York, 1967.

103. Main, P. M.; Woolfson, M. M.; Germain, G. "MULTAN: A Computer Program for the Automatic Determination of Crystal Structures", Dept. of Physics, University of York, England, 1971.

104. Baldwin, R. A.; Chang, M. T. J. Org. Chem. 1967, 32, 1572.

105. Baldwin, R. A.; Washburn, R. M. J. Org. Chem. 1965, 30, 3860.

106. Osborn, J. A.; Wilkinson, G. Inorg. Synth. 1967, 10, 67.

107. Snell, F. D. "Photometric and Fluorometric Methods of Analysis", John Wiley and Sons: New York, 1978.

108. Tolman, C. A.; Gosser, L. W. Inorg. Chem. 1970, 9, 2350.

109. Vande Griend, L. F. Ph.D. Thesis, Iowa State University, Ames, Iowa, 1975.

110. Vande Griend, L. F.; Verkade, J. G. Phosphorus 1973, 3, 13.

111. Weiss, R.; Vande Griend, L. F.; Verkade, J. G. J. Org. Chem. 1979, 44, 1860.

112. Angelici, R. "Synthesis and Technique in Inorganic Chemistry", 2nd Ed.; Saunders: Philadelphia, 1977; Appendix.

113. Harris, R. K.; Mann, B. E. "NMR and the Periodic Table", 1st ed.: Academic Press: New York, 1978, Chapter 9.

114. Epperlein, B. W.; Lutz, O. Z. Naturforsch. 1968, A(23), 1413.

115. Vriezen, W. H. H.; Jellinek, F. Rev. Trav. Chim. **1970**, <u>89</u>, 1306.

116. Cohen, B. M.; Smith, J. D. J. Chem. Soc. A **1969**, 2087.

117. Linke, W. F. "Solubilities of Inorganic and Metal-Organic Compounds", 4th ed., Van Nostrand, Princeton, 1958; p. 169.

118. O'Reilly, D. E. J. Chem. Phys. **1960**, <u>32</u>, 1007.

119. Cohen, B. M.; Cullingworth, A. R.; Smith, J. D. J. Chem. Soc. A **1969**, 2193.

120. Henderson, W. G.; Mooney, E. F. Ann. Review NMR Spect. **1969**, <u>2</u>, 219.

121. Kroger, C.; Tsay, Y. H. Cryst. Struct. Comm. **1974**, <u>3</u>, 455.

122. Pickardt, J.; Rosch, L.; Schummann, Z. Anorg. Allg. Chem. **1976**, <u>66</u>, 426.

123. Marriott, J. C.; Salthouse, J. A.; Ware, M. J.; Freeman, J. M. J. Chem. Soc. Chem. Comm. **1970**, 595.

124. Andreu, B.; Almengenmar, B. Acta Chem. Scand **1970**, <u>24</u>, 1599.

125. Milbrath, D. S.; Springer, J. P.; Clardy, J. C.; Verkade, J. G. Inorg. Chem. **1975**, <u>14</u>, 2665.

126. Dartiguenave, M.; Dartiguenave, Y.; Gleizes, A.; Saint-Joly, C.; Galy, J.; Meier, P.; Merbach, E. A. Inorg. Chem. **1978**, <u>17</u>, 3508.

127. Jacobson, R. J.; Karcher, B. A.; Montag, R. A.; Socol, S. M.; Vande Griend, L. J.; Verkade, J. G. Phosphorus and Sulfur **1981**, <u>11</u>, 27.

128. Schiff, D. E.; Richardson, J. W., Jr.; Jacobson, R. J.; Cowley, A. H.; Lasch, J.; Verkade, J. G. Unpublished paper, Department of Chemistry, Iowa State University, Ames, Iowa, 1983.

129. Cotton, F. A.; Wilkinson, G. "Basic Inorganic Chemistry", 1st Ed.: John Wiley and Sons, New York, 1976; Chapter 9.

130. Albanov, V.; Bellon, P. L., Scatturin, V. J. Chem. Soc. Chem. Commun. **1966**, 507.

131. Kabachnik, M. I.; Tsvetkov, E. N. Doklady Akademii SSSR **1960**, 135, 323.

132. Kosolopoff, K.; Maier, L. "Organic Phosphorus Compounds", 1st Ed., John Wiley and Sons, New York, 1967; Chapter 6.

133. Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. Top. Phos. Chem. 1967, 5, 267.

134. Carriatta, F.; Ugo, R.; Bonati, F. Inorg. Chem. 1966, 5, 1128.

135. Baizer, M. "Organic Electrochemistry", 1st Ed.; Marcel Dekker, New York, 1977.

136. Tolman, C. A. J. Am. Chem. Soc. 1970, 92, 6777.

137. Jenkins, J. M.; Huttemann, T. J.; Verkade, J. G. Adv. Chem. Ser. 1966, 62, 604.

138. Coskran, K. J.; Huttemann, T. J.; Verkade, J. G. Adv. Chem. Ser. 1966, 62, 590.

139. Verkade, J. G. U. S. Patent 4,267,195.

140. Published in catalogue of products, Alfa-Ventron Corporation, Beverly, Massachusetts, 1981.

141. Maryanoff, B. E.; Hutchins, R. O.; Maryanoff, C. A. "Topics in Stereochemistry", Allinger, N. L.; Eliel, E. L.; Eds., Vol. 11, John Wiley and Sons, Inc.: New York, 1979; p. 187.

142. Quin, L. D. "The Heterocyclic Chemistry of Phosphorus", John Wiley and Sons: New York; 1981.

143. Featherman, S. L.; Lee, S. O.; Quin, L. D. J. Org. Chem. 1974, 39, 2899.

144. Hudson, R. F.; Verkade, J. G. Tetrahedron Lett. 1975, 3231.

145. White, D. W.; Gibbs, D. E.; Verkade, J. G. J. Am. Chem. Soc. 1979, 101, 1937.

146. Ramirez, F.; Chow, Y. F.; Maracek, J. F.; Ugi, T. J. Am. Chem. Soc. 1974, 98, 2429.

147. Bentrude, W. G.; Johnson, W. D.; Khan, W. A. J. Org. Chem. 1972, 37, 642.

148. Howells, E. R.; Phillip, D. C.; Rodgers, D. Acta Cryst. 1950, 3, 210.

149. Tayosagawa, F.; Jacobson, R. A. Acta Cryst. 1978, B34, 213.

150. Wadsworth, W. S.; Larsen, S.; Horten, H. L. J. Org. Chem. 1973, 38, 256.

151. Hobbs, E.; Corbridge, D. E. C.; Rastrick, B. Acta Cryst. 1963, 6, 621.

152. Schlueter, A. W.; Jacobson, R. A. J. Am. Chem. Soc. 1966, 88, 2051.

153. Carpenter, L. E. II; Powell, D.; Jacobson, R. A.; Verkade, J. G. Phosphorus and Sulfur 1982, 12, 287.

154. Morris, E. D.; Nordman, C. E. Inorg. Chem. 1969, 8, 1673.

155. Romming, C.; Songstad, J. Acta Chem. Scand. 1979, A33, 187.

156. Romming, C.; Songstad, J. Acta Chem. Scand., 1978, A32, 688.

157. Socol, S. M.; Verkade, J. G. Submitted for publication to Inorg. Chem., 1983.

158. Fonti, P.; Damiana, D.; Favero, P. G. J. Am. Chem. Soc. 1973, 95, 756.

159. Brittain, A. H.; Smith, J. E.; Lee, P. L.; Cohn, K.; Schwendeman, R. H. J. Am. Chem. Soc. 1971, 93, 6772.

160. Clardy, J. C.; Kolpa, R. L.; Verkade, J. G. Phosphorus 1974, 4, 133.

161. Worley, S. D.; Hargis, J.; Chang, L.; Mattson, G. A.; Jennings, W. B. Chem. Phys. Lett. 1981, 79, 149.

162. Arshinova, R. P.; Zverev, V. V.; Villem, Y. Y.; Villem, N. V. J. Gen. Chem. USSR 1981, 51, 1503.

163. Arshinova, R. P. J. Gen. Chem. USSR 1978, 238, 47.

164. Leyden, D. E.; Cox, R. H. "Analytical Applications of NMR", John Wiley and Sons, New York, 1977.

165. Stanislowski, D. A.; Van Wazer, J. R. Anal. Chem. 1980, 52, 96.

166. Dale, S. W.; Hobbs, M. E. J. Phys. Chem. 1971, 75, 3537.

167. Gurley, T. W.; Ritchey, W. M. Anal. Chem. 1975, 47, 1444.

168. Kasler, F.; Tierney, M. Microchim. Acta 1978, 411.

169. McNair, H. M.; Bonelli, E. J. "Basic Gass Chromatography", Consolidated Printers: Berkeley, 1968.

170. Sleevi, P.; Glass, T. E.; Dorn, H. G. Anal. Chem. **1979**, _51_, 1931.

171. Schweighardt, F. K.; Retcofsky, H. L.; Friedman, S.; Hough, M. Anal. Chem. **1978**, _50_, 368.

172. Squires, T. G.; Venier, C. G.; Verkade, J. G.; progress report submitted to the U. S. Dept. of Energy, Ames Laboratory, Iowa State University, Ames, Iowa, July 1, 1980.

173. Squires, T. G.; Aida, T.; Chen, Y. Y.; Smith, B. F. Am. Chem. Soc. Div. Fuel Chem. Prepr. Pap. **1983**, _28_, 228.

174. Squires, T. G.; Venier, C. G.; Hunt, J. D.; Shei, J. C.; Smith, B. F. Fuel, 1982, _61_, 1170.

175. Squires, T. G.; Private communication, U. S. Department of Energy, Ames Laboratory, Iowa State University, Ames, Iowa.

176. Burgada, R.; Germa, H. Compt. Rend. Ser. C **1968**, _267_, 270.

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APPENDIX 1: STRUCTURE FACTORS FOR $Ni(\underline{6})_4$

K	L	FO	FC
-5	6	725	711
-5	8	1080	-1078
-5	10	575	572
-5	11	280	-292
-5	12	205	-229
-5	13	320	309
-5	14	288	-252
-5	15	184	-252
-5	16	166	172
-3	1	725	-734
-3	2	198	-84
-3	3	886	907
-3	4	636	582
-3	5	450	-332
-3	6	524	-599
-3	8	484	492
-3	10	797	-736
-3	11	491	492
-3	13	586	-548
-3	14	323	316
-3	15	245	237
-1	1	276	235
-1	2	637	-529
-1	3	305	238
-1	4	277	-237
-1	6	492	469
-1	7	201	-114
-1	9	486	509
-1	10	298	370
-1	11	770	-705
-1	13	269	256
-1	17	307	272
-1	19	206	-232
1	-9	397	67
3	-13	177	-197
5	-7	167	-130
5	-6	159	103
7	-16	161	218
9	-14	248	238
9	-9	161	174
11	-12	151	124
11	-11	148	122
11	-5	158	115
13	-13	160	-18
13	-8	172	-190
15	-9	152	100
15	-8	303	201

H = -6

K	L	FO	FC
-18	8	214	94
-18	9	241	28
-16	2	191	-61
-16	11	195	-109
-14	7	369	340
-14	9	444	-405
-12	1	194	215
-12	3	192	-176
-12	5	162	170
-12	7	252	-298
-12	8	246	270
-12	9	435	432
-12	11	274	-323
-12	13	197	165
-10	1	910	-967
-10	3	1007	1077
-10	5	686	-733
-10	6	200	134
-10	8	212	-176
-10	13	198	-127
-10	15	266	239
-8	1	893	879
-8	2	540	-507
-8	3	1090	-1075
-8	5	868	863
-8	6	137	-182
-8	7	335	-369
-8	8	293	200
-8	12	259	-270
-8	14	143	195
-8	15	210	-208
-8	17	221	232
-6	1	536	-501
-6	2	896	940
-6	3	1066	1129
-6	4	416	-394
-6	5	771	-804
-6	7	472	474
-6	8	235	-199
-6	12	147	147
-4	1	487	455
-4	2	955	-961
-4	3	768	-790
-4	4	682	616
-4	5	695	627
-4	6	234	176
-4	7	324	-468
-4	10	592	-582
-4	12	337	351
-4	14	487	-482
-4	15	288	266
-4	16	388	304
-4	18	152	-162
-2	2	789	844
-2	3	223	236
-2	4	589	-601
-2	5	609	-585
-2	7	228	217
-2	9	138	114
-2	10	1152	972
-2	12	857	-899
-2	14	207	309
-2	15	407	-355
-2	16	248	-236
-2	17	206	183
-2	18	242	247
0	0	156	180
0	2	323	329
0	4	319	-242
0	8	1092	926
0	10	1567	-1475
0	12	1234	1178
0	18	355	-329
2	-14	168	-144
8	-14	228	-200
8	-8	190	240
10	-2	205	-27
16	-7	265	-243

H = -5

K	L	FO	FC
-19	1	158	121
-17	9	205	-174
-15	3	152	210
-15	8	269	279
-15	11	236	-294
-13	1	287	257
-13	5	224	-228
-13	8	417	-376
-13	10	390	380
-13	11	169	149
-13	12	257	-298
-11	1	220	-197
-11	2	718	-723
-11	3	184	-168
-11	4	635	581
-11	5	262	232
-11	6	452	-417
-11	8	209	183
-11	10	158	-197
-11	12	249	257
-9	1	377	369
-9	2	1058	1084
-9	4	1030	-1077
-9	6	665	630
-9	7	339	-364
-9	11	274	246
-9	16	280	-192
-7	1	505	-571
-7	2	867	-904
-7	3	549	494
-7	4	984	969
-7	5	263	-222
-7	6	257	-244
-7	7	330	289
-7	8	274	-206
-7	9	171	-85
-7	11	276	-325
-7	13	185	203
-7	17	207	-237
-7	18	219	-266
-5	1	441	407
-5	2	221	195
-5	3	408	-369
-5	4	727	-704
-5	6	651	627
-5	7	315	250
-5	8	482	404
-5	9	335	250
-5	10	289	-294
-5	12	240	-239
-5	15	401	-408
-5	16	158	-104
-5	17	251	272
-5	18	208	213
-3	1	199	-99
-3	5	977	-911
-3	7	520	589
-3	8	292	-271
-3	9	310	-352
-3	11	580	556
-3	12	462	502
-3	13	381	-419
-3	15	633	587
-3	16	361	-354
-3	17	162	-235
-1	1	487	-478
-1	3	338	310
-1	4	185	-176
-1	6	218	-249
-1	7	2026	-1898
-1	9	1735	1643
-1	10	246	137
-1	11	1016	-997
-1	12	293	-279
-1	16	367	352
1	-17	209	184
3	-20	256	186
9	-15	203	-131
9	-3	134	123
11	-14	208	-150
17	-9	141	-73
17	-8	202	-120
17	-7	194	181

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-13	8	259	-251
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-11	5	712	781
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-3	13	208	-254
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 9 20   174   -73        2 14   708   681      12 12   258  -211       5  2  1694  1602      15  1   379  -373       6  1   918   827      -9-14   151   147
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13 16   222  -190        4 17   217  -301     -17 -1   204   164       7  4   692   679     -12 -3   139    77       8  9   566  -546       3  1   374   337
15  0   289   302        4 19   163   141     -15-11   190   214       7  5   525   530      -2-24   157   -64       8 11   646   576       3  2  1962 -1723
15  1   314  -310        6  1  1260  1222     -15-10   153  -152       7  6   374  -332       0  0   561   553      10  0   418  -372       3  3  1126 -1124
15  2   323  -301        6  2   473  -394     -11-16   178   154       7  7   413   424       0  2  1040  -939      10  1   732   737       3  4   165   227
15  3   249   229        6  3   130   -72     -11-15   207  -148       7  8   516   564       0  4   284   348      10  2   720   728       3  5   880   966
15  7   179  -151        6  4   967  -880     -11-11   150  -163       7  9   565   596       0  6   465  -530      10  3   450  -415       3  6   622   637
15  8   182  -172        6  5   995   962      -9-18   220   203       7 10   405  -393       0  8  1370  1383      10  4   511  -524       3  7   375  -418
15 12   159   132        6  6   754   641      -9-10   140  -109       7 11   384  -368       0 10   852  -843      10  7   193  -102       3  8   206  -203
17  1   203   172        6  7  1299 -1142      -7-20   179   108       7 13   167   156       0 12   325   361      10  8   517   456       3  9  1001   995
17  3   230  -237        6  8   666  -621      -1-16   169  -114       9  0   159  -172       0 14   306  -238      10  9   277   296       3 10   419   287
                         6  9   747   741      -1 -4   414    96       9  1   227  -208       0 16   167   179      10 10   518  -402       3 11   800  -783
     H = 2               6 10   639   641       1  0  1089   889       9  2   355   325       0 18   323  -333      10 11   394  -300       3 12   339  -408
 K  L   FO   FC          6 12   348  -340       1  1   350  -239       9  3   775   761       0 20   263   205      10 15   253  -207       3 16   268   248
-18 -7   200  -149       6 14   246   259       1  2   287   511       9  4   610  -596       2  0   197   266      12  0   452   452       3 17   175   124
-16 -6   186   156       8  0   170  -221       1  3   232  -205       9  5  1035  -970       2  1  1345  1255      12  1   455  -451       3 18   217  -236
-16 -3   415   385       8  2   376   320       1  4   425  -671       9  6   389   396       2  2  1001   916      12  2   784  -724       5  0   209  -180
-14 -7   149   -58       8  3   275   360       1  5   170   153       9  8   259  -251       2  3  1288 -1195                              5  1  1111 -1065
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K	L	FO	FC
5	3	467	406
5	4	339	-468
5	5	431	376
5	6	181	180
5	7	236	-227
5	8	292	-278
5	9	421	-446
5	11	870	876
5	12	278	265
5	13	419	-430
5	16	390	-356
5	18	223	222
7	0	925	864
7	1	498	487
7	2	548	-609
7	3	350	272
7	5	504	-456
7	6	206	230
7	10	269	-256
7	12	625	579
7	14	469	-425
7	17	186	124
9	0	983	-1000
9	1	136	-170
9	2	730	613
9	10	230	203
9	11	375	-352
9	12	557	-474
9	14	300	324
9	16	256	-173
9	17	167	-130
11	0	782	763
11	1	226	245
11	2	443	-471
11	4	371	302
11	6	309	-319
11	8	195	203
11	11	233	215
11	12	143	139
11	16	164	108
13	0	235	-176
13	1	225	-241
13	2	470	410
13	3	163	-105
13	4	545	-536
13	5	178	247
13	6	513	471
13	7	152	-108
13	8	341	-297
15	3	223	246
15	4	277	270
15	5	179	-224
15	6	358	-342
15	8	249	280
17	3	160	-182
17	5	295	253

H = 6

K	L	FD	FC
-14	-11	238	-250
-14	-10	164	-119
-12	-4	147	-98
-10	0	140	-45
-6	-16	150	-192
-2	-11	133	-141
0	2	2169	-1873
0	4	2326	2202
0	6	1138	-1190
0	8	1044	1038
0	10	203	-303
0	12	547	-536
0	14	350	373
2	0	576	-449
2	2	406	403
2	3	700	-641
2	4	737	-731
2	5	380	443
2	6	864	899
2	8	1168	-1188
2	10	612	562
2	11	198	-170
2	12	200	286
4	0	808	822
4	1	608	497
4	4	572	-431
4	5	707	-555
4	6	363	-305
4	7	243	184
4	8	589	540
4	9	255	-293
4	10	507	-442
4	11	277	241
4	12	394	395
4	14	281	-310
4	16	237	171
6	0	975	-931
6	1	132	-119
6	4	599	532
6	8	201	-216
6	11	524	-535
6	12	437	-431
6	13	628	564
6	14	395	390
6	15	314	-301
6	16	194	-178
6	17	156	193
8	0	459	451
8	1	566	-546
8	3	241	201
8	6	350	-330
8	7	172	-240
8	11	536	489
8	13	572	-581
8	15	198	285
8	16	225	163
10	1	460	432
10	6	147	130
10	11	247	-200
12	1	233	-284
12	3	267	298
12	4	172	-196
12	5	351	-365
12	7	307	302
12	9	210	-151
14	2	335	-301
14	4	364	342
14	5	383	425
14	6	197	-181
14	7	344	-380
16	4	220	-219
16	5	262	-269
16	8	203	-186

H = 7

K	L	FD	FC
-17	-7	209	-185
-13	-12	201	-137
-13	-4	146	131
-11	-17	163	-124
-11	-12	185	172
-9	-16	172	-209
-9	-14	212	188
-9	-10	172	129
-5	-19	214	122
-3	-20	244	27
-3	-17	228	194
-1	-14	156	-137
1	0	324	218
1	1	298	-315
1	2	234	127
1	3	816	792
1	4	623	-573
1	5	1711	-1753
1	6	338	385
1	7	895	1010
1	10	346	416
1	11	186	-154
1	12	250	-139
1	13	154	156
1	14	204	-180
3	0	406	-441
3	2	268	215
3	3	305	-368
3	4	693	623
3	5	665	624
3	6	670	-663
3	7	691	-661
3	8	642	625
3	10	826	-759
3	12	165	158
3	14	234	194
5	0	145	164
5	1	865	-826
5	2	167	165
5	3	225	307
5	4	390	-365
5	8	270	-306
5	10	459	433
5	12	321	-315
5	13	413	-370
5	14	237	195
5	15	312	298
5	16	193	-164
5	17	157	-129
7	0	569	581
7	1	524	536
7	2	357	-351
7	3	211	-200
7	5	278	203
7	6	400	359
7	7	258	-304
7	9	179	202
7	10	350	-368
7	12	510	501
7	13	241	211
7	14	311	-341
7	15	183	-245
9	0	468	-465
9	1	153	41
9	2	186	152
9	7	340	336
9	10	272	287
9	12	228	-297
11	1	316	-311
11	2	149	-66
11	3	312	349
11	4	230	174
11	6	306	-266
11	8	302	263
13	1	411	401
13	2	164	203
13	3	603	-588
13	4	350	-377
13	5	266	271
13	6	392	318
15	3	214	249
15	4	332	215
15	6	293	-296
15	7	179	156
17	2	257	214
17	3	263	-54

H = 8

K	L	FD	FC
-16	-6	157	170
-16	-1	146	-186
-14	-9	197	87
-10	-15	195	-184
-2	-15	173	-53
0	0	531	478
0	2	793	-866
0	4	1024	1019
0	6	440	-454
0	8	175	-157

APPENDIX 2: STRUCTURE FACTORS FOR 30

L = -4

H	K	FO	FC
0	0	2401	2625
0	-18	93	-105
0	-15	163	-178
0	-14	85	83
0	-13	186	179
0	-12	269	268
0	-9	439	407
0	-8	276	-263
0	-7	360	-349
0	-6	88	77
0	-5	212	-203
0	-4	313	-298
0	-3	390	-369
0	-2	858	831
0	-1	319	-313
1	15	103	66
1	-16	98	88
1	-10	88	51
1	-8	168	-171
1	-7	364	-332
1	-6	480	457
1	-4	725	697
1	-3	218	201
1	-2	473	468
1	-1	229	-230
2	0	1214	-1340
2	-17	86	-81
2	-14	121	128
2	-13	93	-56
2	-12	102	89
2	-11	137	136
2	-10	103	-86
2	-8	88	-61
2	-6	650	-627
2	-5	481	-444
2	-4	375	-346
2	-3	117	-115
2	-2	585	589
2	-1	475	-482
3	-16	118	124
3	-15	111	122
3	-14	217	201
3	-13	174	171
3	-11	77	-60
3	-10	287	-273
3	-8	192	-186
3	-7	266	-261
3	-6	910	860
3	-5	246	-221
3	-4	1031	1069
3	-3	229	186
3	-2	219	230
3	-1	439	-457
4	0	516	556
4	-13	269	-244
4	-11	249	-230
4	-10	137	-123
4	-9	193	-163
4	-8	503	440
4	-7	230	-216
4	-6	235	239
4	-5	917	-822
4	-4	292	-262
4	-3	881	-837
4	-2	321	-315
4	-1	737	739
5	1	645	661
5	2	635	-627
5	3	676	663
5	4	429	-416
5	5	181	-167
5	6	123	-126
5	7	110	-101
5	8	407	389
5	10	183	189
5	12	94	94
5	16	115	-136
6	0	595	-583
6	2	179	-159
6	3	757	-749
6	4	140	149
6	5	159	135
6	6	662	629
6	8	258	231
6	10	173	-174
6	11	106	-116
6	12	188	-177
7	1	599	-557
7	2	78	-53
7	3	391	366
7	4	273	257
7	6	152	-142
7	7	236	-251
7	8	164	146
7	10	140	172
7	12	116	121
7	15	85	84
7	16	78	-105
8	0	169	-152
8	1	263	-261
8	2	144	-159
8	3	132	-146
8	4	275	261
8	6	300	294
8	8	254	261
8	11	154	187
8	12	148	-142
8	14	94	-153
9	1	363	-341
9	3	99	-109
9	7	115	-142
9	8	114	-87
9	10	160	-176
10	0	283	-290
10	1	205	-173
10	2	262	-273
10	6	228	216
10	7	100	-67
10	10	116	154
11	1	237	-208
11	2	96	83
11	4	301	306
12	0	229	-227
12	2	208	-204
12	3	102	98
12	5	108	-111
12	6	103	-98
13	1	101	-77
13	2	273	258
13	4	113	120
14	0	266	256
15	1	118	-130

L = -3

H	K	FO	FC
1	-18	79	84
1	-16	133	157
1	-11	135	120
1	-10	326	-295
1	-9	86	99
1	-8	121	-114
1	-7	342	-335
1	-6	251	247
1	-5	173	-344
1	-4	375	399
1	-3	231	266
1	-2	586	-483
1	-1	562	-625
2	0	547	-601
2	-15	146	154
2	-14	180	-169
2	-13	165	-141
2	-9	321	-330
2	-8	387	354
2	-7	123	118
2	-6	296	344
2	-5	136	138
2	-4	491	-503
2	-3	459	-450
2	-2	481	413
2	-1	1035	1169
3	-14	147	167
3	-12	103	-88
3	-11	81	84
3	-10	88	-78
3	-9	197	196
3	-7	119	-130
3	-6	507	-507
3	-5	634	596
3	-4	405	416
3	-3	543	593
3	-2	581	603
3	-1	431	460
4	0	465	-467
4	-14	230	-245
4	-12	95	-78
4	-11	273	-256
4	-10	140	-139
4	-9	121	-155
4	-7	80	83
4	-6	1201	1176
4	-4	119	139
4	-2	857	-945
4	-1	274	-288
5	1	210	-217
5	2	542	553
5	3	516	524
5	4	349	337
5	5	610	605
5	6	65	51
5	7	571	-556
5	8	192	206
5	9	217	211
5	10	251	-255
5	11	86	125
5	13	163	-169
5	14	99	76
5	15	96	-139
6	1	985	963
6	3	406	-420
6	4	550	555
6	5	333	-328
6	6	679	662
6	8	418	414
6	9	74	65
6	10	219	-220
6	11	193	175
6	12	134	-158
6	13	213	-293
6	14	137	-139
6	15	80	62
6	16	98	-110
7	1	191	-190
7	2	543	528
7	3	412	391
7	4	385	375
7	5	453	433
7	7	192	162
7	8	434	-426
7	9	98	90
7	10	517	-557
7	11	111	124
7	12	110	-122
8	0	326	308
8	1	319	268
8	3	323	304
8	4	178	153
8	5	142	154
8	6	132	120
8	8	104	-104
8	9	243	271
8	11	189	215
8	12	93	106
8	14	103	-124
9	2	428	393
9	3	136	146
9	4	126	144
9	7	228	218
9	8	228	-238
9	9	83	-86
9	10	292	-309
9	12	191	-248
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10	1	120	74
10	2	251	245
10	3	247	222
10	4	239	-224
10	5	145	-124
10	6	137	-154
10	7	85	106
10	8	118	-131
10	9	171	202
10	12	115	128
11	4	98	103
11	7	119	122
12	0	237	225
12	1	90	76
12	2	93	100
12	3	108	125
12	4	103	-93
12	8	145	-163
13	7	91	-92
14	0	294	285
14	2	125	141
14	3	80	-74
15	1	93	-91
15	2	252	-264
15	6	96	-86

L = -2

H	K	FO	FC
0	0	1111	-1237
0	-18	114	125
0	-15	224	223
0	-14	130	-120
0	-13	137	-128
0	-12	253	-239
0	-11	136	136
0	-9	282	-255
0	-8	918	898
0	-6	725	696
0	-4	917	-888
0	-3	895	-941
0	-2	383	-305
0	-1	1177	1347
1	-16	159	-163
1	-11	138	-114
1	-10	96	92
1	-9	71	52
1	-8	501	466
1	-7	300	-258
1	-6	944	-938
1	-5	172	165
1	-4	286	-267
1	-3	155	144
1	-2	181	258
1	-1	588	-647
2	0	543	-650
2	-14	184	-187
2	-10	301	-273
2	-8	249	-230
2	-7	228	198
2	-6	526	474
2	-5	476	427
2	-4	508	-548
2	-3	736	-779
2	-2	2403	-2694
2	-1	290	318
3	-18	75	-54
3	-16	104	-127
3	-14	107	-87
3	-12	118	113
3	-11	114	-111
3	-10	178	156
3	-9	263	241
3	-8	158	128
3	-7	477	-459
3	-6	140	-157
3	-5	292	285
3	-4	639	-628
3	-3	320	-376
3	-2	2125	-2176
3	-1	939	-1019
4	0	926	923
4	-16	100	-127
4	-14	111	125
4	-13	99	96
4	-12	75	-36
4	-10	111	-111
4	-7	501	497
4	-6	227	207
4	-5	152	-161
4	-4	613	-578
4	-3	89	-118
4	-2	979	991
4	-1	1121	-1200
5	2	332	330
5	3	245	242
5	4	520	539
5	6	371	-357
5	7	181	-179
5	8	255	-238
5	9	385	376
5	10	423	-407
5	12	162	-173
5	13	161	-190
5	14	90	76
5	16	83	69
6	0	328	319
6	1	308	-206
6	2	171	166
6	4	95	-88
6	5	118	-106
6	6	463	-470
6	7	248	-244
6	8	179	-190
6	9	112	-104
6	11	172	-183
6	12	278	301
6	13	196	-255
6	14	91	92
7	1	95	-86
7	2	104	92
7	3	105	-71
7	4	276	255
7	5	68	56
7	7	258	256
7	8	129	-123
7	10	78	-89
7	11	101	-98
8	0	207	197
8	1	117	-113
8	2	201	206
8	3	373	371
8	4	325	-284
8	5	186	186
8	6	311	-305
8	8	372	-382
8	14	110	125
9	1	223	203
9	2	343	-320
9	3	120	122
9	7	119	122
9	9	99	111
9	10	107	113
9	11	115	-149
10	0	428	414
10	3	115	120
10	4	196	202
10	5	169	186
10	6	184	-201
10	9	142	-161
10	10	103	-121
10	11	87	97
11	1	199	191
11	2	99	-103
11	3	112	120
11	4	178	-173
11	5	80	86
11	7	89	-100
11	9	176	214
11	10	167	190
11	12	101	194
12	0	85	81
12	1	130	121
12	2	134	136
12	3	163	-150
12	5	131	122
13	2	326	-318
13	4	167	-175
13	6	202	-215

H	K	FO	FC
14	0	182	-162
14	6	109	87
14	8	126	170
15	1	88	-75
15	2	151	-143
16	0	181	-179
16	2	94	-94

L = -1

H	K	FO	FC
1-18		74	-117
1-16		236	-245
1-13		176	-167
1-12		84	75
1	-9	86	70
1	-7	112	-113
1	-6	506	-485
1	-5	1042	-1005
1	-4	658	-734
1	-3	1152	1326
1	-2	1676	-1984
1	-1	422	-649
2	0	1793	2368
2-14		214	199
2	-9	185	-156
2	-8	367	-317
2	-7	194	170
2	-6	339	354
2	-5	449	437
2	-4	474	-567
2	-3	1097	-1129
2	-2	538	-519
2	-1	133	-80
3	15	84	86
3-14		99	-127
3-12		320	309
3-10		405	381
3	-9	488	454
3	-8	153	160
3	-7	221	-213
3	-6	375	327
3	-5	220	-225
3	-3	498	513
3	-2	793	-816
3	-1	720	694
4	0	1044	-1060
4-16		111	123
4-14		272	267
4-12		297	279
4-10		249	-226
4	-9	75	-72
4	-8	298	-277
4	-7	135	123
4	-6	947	-921
4	-4	788	-858
4	-3	554	-547
4	-2	136	112
4	-1	273	300
5	1	333	-321

H	K	FO	FC
5	2	128	130
5	3	184	-186
5	4	341	-339
5	5	382	-375
5	6	75	-59
5	7	516	-505
5	8	290	-264
5	9	76	74
5	10	77	81
5	11	78	-79
5	12	137	177
5	14	98	-91
6	1	151	156
6	2	269	-267
6	3	140	-140
6	4	1032	-1019
6	5	262	-257
6	6	339	-345
6	7	194	-172
6	8	413	-405
6	10	120	-110
6	11	173	-186
6	12	337	374
6	16	107	154
7	1	222	-206
7	2	351	-334
7	3	139	-119
7	4	339	-347
7	8	341	339
7	9	147	-166
7	10	394	421
7	12	221	261
7	13	107	130
7	15	84	94
7	16	82	-108
8	0	106	-114
8	1	238	246
8	2	79	75
8	3	258	260
8	4	102	-105
8	5	195	171
8	6	79	-81
8	8	142	160
8	9	77	-78
8	13	111	183
9	1	119	103
9	2	165	-158
9	3	253	251
9	4	360	-353
9	5	205	-210
9	6	137	-150
9	7	205	-192
9	8	457	433
9	10	264	278
9	11	104	123
10	2	239	-238
10	3	104	-118
10	4	193	178
10	5	280	-286

H	K	FO	FC
10	6	425	410
10	8	176	199
10	11	143	-210
10	12	121	-179
11	4	94	-85
11	5	129	128
11	6	105	-99
11	8	101	82
12	0	319	-503
12	2	186	-180
12	3	108	88
12	5	151	-169
12	6	245	241
12	7	85	82
12	8	168	185
13	2	103	80
13	4	240	250
13	5	105	102
14	1	117	100
14	2	126	-118
14	4	139	-143
14	6	93	71
14	8	90	74
15	2	125	111
16	1	113	133

L = 0

H	K	FO	FC
0-18		111	-136
0-16		181	-169
0-14		319	315
0-12		113	106
0-10		94	84
0	-8	181	159
0	-6	993	974
0	-2	594	471
1-16		137	159
1-12		211	197
1-10		218	186
1	-8	107	105
1	-6	185	-179
1	-4	1550	1489
1	-2	1336	1470
2	0	1318	1295
2-14		333	313
2-12		132	89
2-10		169	-164
2	-8	409	-419
2	-6	146	-120
2	-4	873	-839
2	-2	708	736
3-18		98	104
3-16		147	159
3-14		160	129
3-12		157	-140
3-10		681	-642
3	-8	263	250
3	-6	405	-406
3	-4	1307	1343

H	K	FO	FC
4	0	495	524
4-16		164	170
4-14		136	-151
4-12		270	244
4-10		359	-323
4	-8	241	246
4	-6	515	514
4	-4	956	-979
5	2	292	-316
5	4	209	-230
5	6	478	454
5	8	134	157
5	10	324	352
5	12	396	423
6	0	554	-519
6	2	58	38
6	4	153	-144
6	6	513	497
6	12	113	-94
7	4	317	301
7	6	246	-236
7	8	259	255
7	10	88	101
8	0	453	402
8	2	475	-412
8	4	487	495
8	6	74	75
8	8	319	324
8	12	228	-252
9	2	98	-72
9	4	214	-215
9	8	338	-352
9	10	217	-250
9	12	112	-129
10	0	507	-479
10	2	259	-238
10	6	339	326
10	8	139	165
11	4	570	555
11	6	388	409
11	8	341	-407
12	0	209	-187
12	2	163	157
12	4	141	-130
12	6	117	-116
12	8	98	144
12	10	94	-115
13	2	91	86
13	4	267	257
13	6	262	298
13	8	123	-139
14	0	159	165
14	2	243	242
14	8	92	-134
15	2	141	-152
15	4	218	229

L = 1

H	K	FO	FC
7	6	74	-42
11	3	81	-51
15	4	99	-93

L = 2

H	K	FO	FC
0	17	96	-83
4	8	64	-26
7	14	78	-105
7	15	83	-136
8	12	93	88

L = 3

H	K	FO	FC
9	1	67	-61

L = 4

H	K	FO	FC
2-15		78	46
8	5	67	-32
9	4	92	-58

L = 5

H	K	FO	FC
1	-2	59	-16
12	3	82	-67
14	4	86	-80
15	3	76	78

L = 6

H	K	FO	FC
6	12	87	68
14	0	97	-91
14	2	85	-85

L = 7

H	K	FO	FC
2	-8	79	-78

L = 8

H	K	FO	FC
1	-6	88	-77
7	2	76	54
8	2	85	-87

L = 9

H	K	FO	FC
3	2	75	43
4-14		90	-95

L = 10

H	K	FO	FC
4-13		86	105
8	3	85	-57
9	10	78	85
10	0	98	59

L = 11

H	K	FO	FC
1	1	78	72
3	2	84	-52
3	3	78	54
4	-1	92	70
7	2	79	-32
9	3	74	-62

L = 12

H	K	FO	FC
0	-1	105	139
2	-5	91	60
9	7	69	-68
10	2	76	-88

L = 13

H	K	FO	FC
4	-9	90	69

L = 14

H	K	FO	FC
3	-8	80	100
4	0	89	-90
4	2	87	-64
4	-7	81	-92
5	3	74	72

APPENDIX 3: STRUCTURE FACTORS FOR 20

1	-7	80	83
1	-6	99	-93
1	-5	46	-45
1	-4	61	65
1	0	42	39
1	3	32	26
2	-7	63	59
2	-6	32	-31
2	-4	53	51
2	-1	40	42
2	1	37	-39
3	-6	31	-36
3	-5	37	31
3	-3	47	-44
3	-1	63	61
3	1	57	-55

L = 6

H	K	FO	FC
-3	2	30	-31
-1	4	43	38
0	-2	57	-58
0	3	31	20
1	-9	39	-48
1	-8	49	51
1	-5	69	-72
1	-4	33	31
1	-3	81	84
1	-2	66	-62
1	0	108	102
1	2	96	-88
1	4	29	25
2	-8	51	42
2	-6	44	-42
2	-3	88	81
2	-2	29	-24
2	-1	68	-65
2	0	42	40
2	1	37	-37
2	2	34	-30
2	3	47	44
2	5	48	-46
3	-9	37	-34
3	-8	58	58
3	-6	39	-35
3	-3	48	-48
3	0	39	-31
3	1	51	-54
3	2	29	24
3	3	72	75
3	4	42	-38
3	5	53	-48
4	-8	37	42
4	-7	35	-35
4	-6	42	-47
4	-5	39	44
4	-3	75	-71
4	-2	41	-37
4	-1	117	110
4	1	110	-103
4	2	55	50
4	3	77	75
4	4	46	-43
5	-5	79	87
5	-3	55	-60
5	-2	32	-32
5	-1	50	49
5	0	43	43
5	1	56	-55

L = 7

H	K	FO	FC
-1	1	41	38
0	-2	63	-65
1	-8	38	32

APPENDIX 4: STRUCTURE FACTORS FOR <u>21</u>

H = -9

K	L	FO	FC
-3	9	48	-2
-1	7	59	-48

H = -8

K	L	FO	FC
-6	0	68	80
-5	6	75	7
-2	20	65	-83
-1.	2	48	27

H = -7

K	L	FO	FC
-5	11	59	52
-5	17	92	-71
-2	1	53	-41
-2	3	47	-40
-1	18	77	61
0	23	52	13

H = -6

K	L	FO	FC
-8	1	49	-65
-8	6	116	-122
-8	12	79	90
-6	2	58	-43
-6	3	50	59
-6	19	67	-79
-5	4	80	-80
-5	9	60	-60
-4	2	68	73
-4	4	57	68
-4	13	57	49
-4	21	58	-51
-3	20	70	52
-2	26	78	-78
-1	3	57	80
-1	7	72	81
-1	9	62	63
0	24	62	-67

H = -5

K	L	FO	FC
-10	2	50	29
-9	5	67	57
-8	1	44	40
-7	9	78	80
-7	10	65	-56
-6	9	53	53
-5	15	62	41
-5	22	60	50
-4	4	52	30
-3	5	51	56
-3	9	62	-26
-3	11	73	55
-3	15	53	29
-3	25	61	-48
-2	10	65	58
-2	24	57	-69
-1	15	60	-48
-1	26	70	-61

H = -4

K	L	FO	FC
-10	7	52	56
-9	0	62	-43
-9	1	59	66
-9	5	59	-48
-8	2	71	-43
-8	4	134	133
-8	6	184	174
-8	10	158	-169
-8	12	104	-123
-8	18	76	74
-8	19	53	-31
-7	4	104	133
-7	5	56	14
-7	6	122	-115
-7	10	68	53
-7	15	64	93
-6	1	155	143
-6	14	75	73
-6	16	63	-65
-6	21	76	-83
-5	1	82	-82
-5	2	71	-120
-5	6	54	-99
-5	12	54	-45
-5	13	84	-114
-5	18	62	89
-5	20	57	-58
-4	12	55	-52
-4	26	82	51
-3	3	44	54
-3	10	53	45
-3	12	55	60
-3	14	92	-56
-3	24	72	10
-2	30	67	58
-1	4	42	-17
-1	10	49	31
-1	15	60	-56
0	20	57	-90

H = -3

K	L	FO	FC
-9	18	88	77
-8	13	65	-25
-7	18	66	86
-6	3	63	-57
-6	5	73	75
-6	9	72	-77
-6	12	63	-77
-5	7	68	-78
-5	27	98	-98
-4	2	66	-60
-4	6	80	104

H = -2

K	L	FO	FC
-10	5	83	73
-9	1	96	-69
-9	9	59	68
-8	21	55	62
-7	17	85	79
-7	19	69	-40
-6	19	63	39
-6	21	70	55
-6	24	63	-92
-6	27	90	-95
-5	9	95	-88
-5	13	52	52
-5	19	81	73
-3	20	66	-48
-3	28	52	-12
-2	2	57	72
-2	27	103	-48
-2	32	59	67
-1	11	49	-41
-1	28	59	52

H = -1

K	L	FO	FC
-11	5	108	-103
-7	6	56	78
-7	18	74	54
-6	19	58	29
-4	18	71	-72
-4	20	64	70
-4	21	70	45
-3	18	55	72
-2	1	43	35
-2	15	55	-42
-2	26	56	20
-1	19	81	-20

H = 0

K	L	FO	FC
-8	8	64	-76
-8	11	74	39
-8	23	76	102
-6	14	51	-27
-4	25	68	-51
0	2	491	279
0	4	2011	-1852
0	6	2121	-2116
0	8	625	-711
0	10	536	573
0	12	771	773
0	14	73	109
0	16	528	-515
0	18	508	-511
0	22	627	597
0	24	279	-278
0	26	98	-123
0	28	85	-91
0	32	205	216
2	0	378	397
2	1	476	-507
2	2	444	-519
2	3	171	310
2	4	598	703
2	5	288	306
2	6	754	647
2	7	401	518
2	8	338	317
2	9	440	-380
2	10	1590	-1623
2	11	755	-654
2	12	575	-595
2	13	68	-125
2	14	799	695
2	15	478	-482
2	16	680	707
2	17	73	61
2	18	269	240
2	19	462	462
2	20	434	-430
2	21	459	457
2	22	419	-438
2	24	175	-140
2	25	198	-196
2	26	260	237
2	27	187	-184
2	28	204	207
2	31	149	151
2	32	114	-111
4	0	685	-481
4	1	782	547
4	2	49	-21
4	3	86	47
4	4	363	-337
4	5	532	398
4	6	516	-506
4	7	369	371
4	8	355	373
4	9	744	-794
4	10	382	349
4	11	759	-696
4	12	385	338
4	13	81	38
4	14	58	-107
4	15	262	295
4	16	124	-99
4	17	249	226
4	19	146	-120
4	20	115	94
4	21	193	-228
4	22	101	-120
4	23	167	192
4	26	66	56
4	27	92	124
4	31	141	-126
6	1	550	430
6	2	74	-58
6	5	62	-31
6	6	489	-464
6	7	322	-292
6	8	138	-143
6	9	258	247
6	10	442	482
6	11	62	48
6	12	398	401
6	15	318	315
6	16	284	-286
6	17	270	-276
6	18	200	-159
6	19	129	-154
6	22	216	230
6	23	156	173
6	24	140	146
6	25	144	-152
6	27	74	-94
6	28	164	-184
8	0	303	-304
8	1	234	-217
8	2	101	-62
8	3	444	-417
8	4	374	368
8	5	137	-139
8	6	206	203
8	7	219	213
8	9	638	646
8	10	403	-386
8	12	217	-240
8	13	320	-312
8	14	172	172
8	15	125	94
8	16	163	149
8	18	192	205
8	20	118	-111
8	22	151	-141
8	24	86	-85
10	0	326	311
10	1	273	281
10	2	147	185
10	3	396	382
10	4	91	-95
10	5	119	111
10	6	150	-119
10	7	222	-218
10	8	191	-209
10	9	304	-338
10	12	120	97
10	13	263	282
10	15	135	140

H = 1

K	L	FO	FC
0	3	223	-274
0	5	372	380
0	7	295	-330
0	9	282	288
0	11	49	-70
0	15	177	-187
0	17	170	177
0	19	53	-41
0	21	86	-83
0	27	103	108
1	1	1503	1648
1	2	345	532
1	3	655	-627
1	4	1939	-1944
1	5	1254	-1310
1	6	224	-270
1	7	1277	-1207
1	8	253	-193
1	9	461	487
1	10	113	168
1	11	977	928
1	12	230	-229
1	13	527	497
1	14	602	567
1	15	260	-260
1	16	94	84
1	17	576	-540
1	18	271	-277
1	20	504	-512
1	21	467	449
1	22	213	215
1	23	229	240
1	24	341	330
1	25	198	-192
1	27	192	-186
1	28	126	113
1	29	146	-146
1	31	98	84
1	32	75	-83
1	33	112	95
2	2	181	220
2	4	165	-190
2	5	138	151
2	6	92	-68
2	7	258	-281
2	8	70	82
2	10	244	-254
2	11	107	109
2	12	228	217
2	13	137	118
2	14	66	-54
2	18	108	120
2	19	139	-138
2	20	69	-67
2	23	75	68
2	29	61	-30
3	1	799	-583
3	2	894	-812
3	3	429	377
3	4	88	-163
3	5	215	190
3	7	166	-103
3	8	660	650
3	9	509	-437
3	10	716	640
3	11	609	-558
3	12	257	-253
3	13	469	404
3	14	156	-168
3	15	594	577
3	16	391	-367
3	17	139	132
3	19	99	139
3	20	312	345
3	21	151	-139
3	22	188	187
3	23	140	-112
3	24	196	-200
3	25	88	-100
3	26	155	-144
3	28	85	-80
3	29	86	88
3	30	153	153
3	32	80	86
4	1	74	-76
4	3	88	91
4	5	77	-83
4	6	43	24
4	7	113	99
4	8	106	-84
4	10	51	-50
4	11	70	-56
4	13	89	-96
4	14	81	111
4	16	47	12
4	17	57	39
4	19	62	60
4	22	69	-50
4	23	61	-63
5	1	531	-494
5	2	62	42
5	3	528	527
5	4	456	459
5	5	43	33
5	6	436	383
5	8	118	-118
5	9	330	-310
5	10	115	-112
5	12	156	156
5	13	144	-171
5	14	147	148
5	15	111	101
5	17	130	138
5	18	58	-52
5	19	125	178
5	20	174	-130

K/H	L	FO	FC
5	21	145	-165
5	22	63	-83
5	23	122	-120
5	26	194	190
5	29	172	172
5	30	172	-181
6	3	70	98
6	6	62	57
6	8	83	-92
6	10	160	166
6	11	119	-140
6	13	77	66
6	16	92	-110
7	1	236	257
7	2	179	210
7	3	136	138
7	4	105	98
7	5	210	-176
7	7	433	-428
7	8	279	-280
7	10	164	170
7	11	785	783
7	12	168	180
7	13	161	-173
7	14	127	105
7	15	284	-302
7	16	136	-125
7	17	265	-250
7	19	165	-145
7	21	131	119
7	23	203	201
8	6	55	56
8	12	63	-36
9	1	197	-199
9	2	354	-351
9	3	131	129
9	4	402	-408
9	5	256	238
9	6	66	-103
9	7	76	90
9	8	285	297
9	9	95	-54
9	10	311	286
9	11	105	-118
9	12	111	-118
9	13	126	-134
9	14	225	-253
9	16	79	-70
9	17	134	133
9	18	158	149
9	20	142	165
9	21	152	-171
11	1	69	64
11	2	227	210
11	4	74	64
11	6	124	-128
11	8	206	-186
11	10	122	-149

H = 2

K	L	FO	FC
0	0	3499	-3177
0	2	177	235
0	4	943	907
0	6	168	221
0	8	261	-179
0	10	54	-66
0	12	175	-174
0	14	153	-137
0	16	300	284
0	18	560	576
0	20	97	118
0	22	457	-438
0	26	65	-44
0	28	87	91
0	30	107	114
0	32	71	-89
1	0	202	-226
1	1	517	516
1	3	684	-593
1	4	63	64
1	5	389	409
1	6	287	-285
1	7	69	-75
1	8	400	392
1	9	64	-67
1	12	148	-160
1	14	106	117
1	15	85	-104
1	16	125	-130
1	17	103	-95
1	18	177	181
1	19	173	177
1	21	109	-103
1	22	113	-116
1	23	106	101
2	0	711	-564
2	1	998	934
2	3	1337	1188
2	4	192	152
2	5	342	289
2	6	135	-84
2	7	347	-367
2	8	605	-534
2	9	176	-195
2	10	563	503
2	11	149	166
2	12	329	320
2	13	246	257
2	14	278	-206
2	15	341	330
2	16	146	-157
2	18	154	-128
2	19	371	-353
2	20	117	125
2	21	283	-268
2	22	208	210
2	23	102	93
2	24	147	134
2	25	166	143
2	26	127	-105
2	28	145	-148
2	29	83	-88
2	30	63	-58
2	31	145	-136
3	0	160	-141
3	1	47	42
3	2	58	39
3	6	201	-208
3	7	94	-116
3	8	59	72
3	11	67	62
3	12	63	61
3	13	55	55
3	14	257	259
3	15	98	-123
3	16	162	-139
3	18	68	-70
3	24	77	86
3	25	49	-29
3	26	55	34
3	31	59	37
4	0	342	318
4	1	623	-532
4	3	388	-375
4	4	163	-126
4	5	200	-184
4	6	159	153
4	7	385	337
4	8	134	112
4	9	861	818
4	10	160	128
4	11	206	180
4	12	87	-56
4	13	547	-499
4	14	205	-172
4	15	395	-406
4	16	258	-261
4	17	72	88
4	18	162	-186
4	19	412	415
4	20	90	102
4	21	183	195
4	22	223	232
4	23	267	-260
4	25	160	-166
4	26	83	-72
4	27	99	-98
4	29	71	69
5	0	63	-50
5	1	139	-160
5	2	132	116
5	3	73	78
5	4	240	-237
5	5	88	98
5	6	159	160
5	7	140	-145
5	11	93	-77
5	14	83	-84
5	15	144	155
5	16	82	68
5	20	75	106
5	23	68	-73
6	0	443	-438
6	1	84	-69
6	2	152	-159
6	3	256	233
6	4	186	187
6	6	662	639
6	7	256	-253
6	8	379	388
6	9	446	-449
6	10	356	-416
6	11	204	176
6	12	485	-478
6	13	356	347
6	14	69	-71
6	15	107	-98
6	16	163	171
6	18	151	137
6	22	171	-179
6	25	170	182
7	2	65	82
7	4	116	-116
7	6	152	136
7	7	93	-97
7	9	107	103
7	10	67	-67
7	16	66	66
8	0	298	299
8	1	55	-65
8	2	81	68
8	4	257	-244
8	6	179	-190
8	7	77	-76
8	9	301	-285
8	10	267	258
8	11	106	89
8	12	109	185
8	13	191	168
8	15	87	-81
8	16	119	-104
8	18	144	-150
8	20	70	56
8	22	107	126
9	0	69	73
9	7	71	81
10	0	56	-70
10	1	181	-190
10	2	53	-61
10	3	210	-224
10	7	117	119
10	8	79	86
10	9	232	240
10	13	165	-180
10	15	106	-117

H = 3

K	L	FO	FC
0	3	62	72
0	5	398	-385
0	7	478	479
0	9	320	-308
0	11	75	80
0	13	48	-26
0	15	241	262
0	17	220	-226
0	27	97	-84
1	1	467	416
1	2	730	-680
1	3	363	334
1	4	177	-173
1	5	249	-225
1	6	196	229
1	7	130	-105
1	8	249	217
1	9	133	121
1	10	277	290
1	11	230	-238
1	12	244	235
1	13	256	-237
1	14	261	-256
1	15	99	-104
1	16	190	-187
1	17	266	251
1	18	217	241
1	19	249	246
1	20	206	208
1	21	185	-191
1	22	253	-260
1	23	243	-237
1	24	240	-231
1	27	72	72
1	29	158	156
1	30	62	48
2	2	226	-239
2	4	220	208
2	5	287	-244
2	7	295	262
2	9	51	-38
2	10	248	244
2	12	274	-263
2	13	58	-35
2	14	107	88
2	15	73	75
2	17	98	-94
2	18	117	-142
2	19	124	120
2	20	101	110
3	1	291	279
3	2	1444	1273
3	3	350	296
3	4	944	912
3	5	279	276
3	6	230	-200
3	7	164	-158
3	8	946	-897
3	9	282	-297
3	10	596	-594
3	11	288	-318
3	12	394	346
3	13	92	-65
3	14	411	417
3	15	176	191
3	16	198	213
3	17	208	183
3	18	149	-139
3	19	122	-115
3	20	288	-290
3	21	207	-219
3	23	61	-53
3	24	207	207
3	25	70	85
3	26	121	129
3	30	151	-155
4	3	67	-84
4	4	67	98
4	6	116	148
4	9	74	-69
4	12	73	95
4	18	92	-121
4	22	61	30
4	23	75	64
4	27	86	67
5	1	573	531
5	2	360	-407
5	3	308	-346
5	4	192	-214
5	6	499	-503
5	6	184	202
5	8	574	591
5	9	316	301
5	11	277	273
5	12	738	-770
5	13	108	121
5	14	613	-511
5	15	171	-142
5	16	137	139
5	17	234	-270
5	18	403	405
5	20	363	342
5	21	183	190
5	23	113	130
5	24	184	-172
5	26	166	-182
6	6	116	-128
6	8	190	211
6	10	157	-180
6	11	180	200
6	13	92	-110
6	16	90	131
7	1	441	-457
7	2	297	279
7	3	235	-241
7	4	243	246
7	5	297	292
7	6	74	-48
7	7	599	618
7	8	236	-227
7	9	105	81
7	10	196	-207
7	11	432	-444
7	13	91	-89
7	14	110	131
7	15	103	126
7	16	61	54
7	17	145	136
7	19	84	95
7	23	107	-102
8	3	69	88
8	4	70	-69
8	6	67	-87
8	8	79	67
9	3	153	-132
9	6	99	93
9	8	69	-70
9	10	115	-116
9	12	71	83
9	13	60	57
9	14	162	166
9	16	64	72
9	17	116	-123
10	10	58	-26
10	13	59	48
11	1	72	81
11	2	144	-143
11	4	84	-94
11	6	57	-55

H = 4

K	L	FO	FC
0	0	398	414
0	2	130	117
0	4	415	-409
0	6	186	178
0	8	196	206
0	10	75	-107
0	12	109	62
0	14	216	215
0	16	190	-170
0	18	509	-633
0	22	183	176
0	24	214	222
0	26	71	74
0	28	71	-84
0	30	97	-113
1	0	110	125
1	1	141	-133
1	2	62	-63
1	3	286	284
1	5	214	-209
1	6	174	155
1	7	73	90