1977

Spectroscopic implications of sigma-pi effects in some aminophosphine compounds

Robert Douglas Kroshefsky
Iowa State University

Recommended Citation

Kroshefsky, Robert Douglas, "Spectroscopic implications of sigma-pi effects in some aminophosphine compounds " (1977). *Retrospective Theses and Dissertations*. 6078.
https://lib.dr.iastate.edu/rtd/6078

INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.
2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.
4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.
5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

University Microfilms International
300 North Zeeb Road
Ann Arbor, Michigan 48106 USA
St. John's Road, Tyler's Green
High Wycombe, Bucks, England HP10 8HR

78-5943

KROSHEFSKY, Robert Douglas, 1951-
SPECTROSCOPIC IMPLICATIONS OF SIGMA-PI EFFECTS IN SOME AMINOPHOSPHINE COMPOUNDS.

Iowa State University,
Ph.D., 1977
Chemistry, inorganic

University Microfilms International, Ann Arbor, Michigan 48106

Spectroscopic implications of sigma-pi effects in some aminophosphine compounds

by

Robert Douglas Kroshefsky

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1977

TABLE OF CONTENTS

PREFACE

The primary thrust of the research discussed in this thesis is directed towards the three aminophosphines 1, 2, and 3.

$P(NMe_2)_3$ $P(NMeCH_2)_3CMe$ $P(NMeNMe)_3P$

1 2 3

In particular the Lewis basicity and pi acidity of these compounds are of interest because they are the nitrogen structural analogs of some phosphite esters which display unusual properties.

In the first part, the properties of various organophosphorus derivatives of 1, 2, and 3 will be discussed with particular attention devoted to those derivatives resulting from reactions with organic azides, chalconides and borane.

In the second part, the coordination complexes of 1 and 2 with metals will be discussed as well as the results of experiments which utilize the unique ligating ability of 2 and its derivatives.

I. ORGANOPHOSPHORUS COMPOUNDS

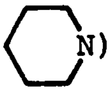
INTRODUCTION

Staudinger Reactions of Aminophosphines

The Staudinger reaction shown in equation 1 involves the interaction of a trivalent phosphorus compound and an organic azide to give nitrogen gas and a phosphinimine.

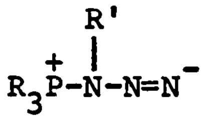
$$1. \quad R_3P + N_3R' \rightarrow R_3P{=}NR' + N_2$$

These monomeric compounds were first prepared by Staudinger and Meyer (1, 2) in 1919. Additional synthetic methods giving phosphinimines have been devised since that time and a general review of these compounds has been presented by Singh and Zimmer (3). Reaction 1 proceeds via the formation of an intermediate adduct, a phosphazide, $R_3P{=}N_3R'$, which decomposes at low to moderate temperature depending on the nature of the substituents on both phosphorus and the azide. In particular, it was found that phosphazide adduct stability increases when R' is electron withdrawing (4, 5) while Mosby and Silva (6) found that the electron donating ability of R was also important. They discovered that the rate of reaction for different R_3P compounds with the same azide was

()$_3$P > Ph_3P > $(MeO)_3P$ > $(PhO)_3P$ >> Cl_3P

where PCl_3 did not react at temperatures below 35°. There has been some controversy about the structure of the phosphazides also. Staudinger preferred to use a linear structure (2), but later Horner wrote a branched structure for them (4).

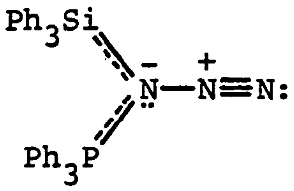
$R_3P{=}N{-}N{=}N{-}R'$



$R_3\overset{+}{P}{-}\overset{\overset{R'}{|}}{N}{-}N{=}N^{-}$

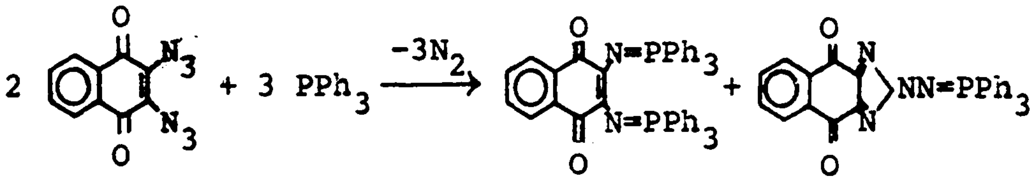
linear branched

Leffler et al. (7) favored a linear structure for the phosphazide of Ph_3P and Ph_3CN_3 (which would not decompose to the phosphinimine) on the basis of steric hinderance to the formation of a transition state with a branched structure. In conformity with a linear structure the solid state spectrum did not show an asymmetric stretching band near 2100 cm^{-1} (characteristic of an azide group). Such a band was observed in solution spectra, however, but was ascribed to dissociation of the complex with liberation of free Ph_3CN_3. Unlike the above complex, Thayer and West (8) observed a band at 2018 cm^{-1} in both the solid state and solution spectra of the phosphazide of Ph_3P and Ph_3SiN_3 which they attributed to a branched structure where pi electron delocalization between P, N, and Si would give a net weakening of the azide N-N bonds and lower the asymmetric stretching frequency.



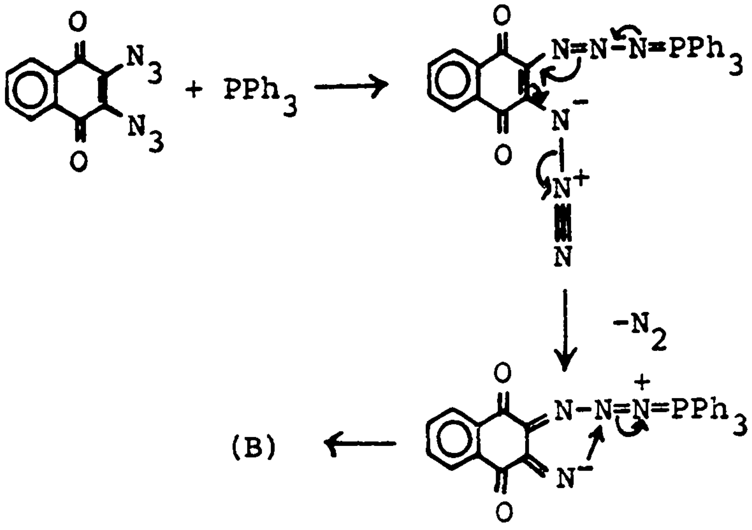
They also examined models which suggest that the branched structure is possible for the Ph_3SiN_3 compound but unlikely for the more sterically hindered Ph_3CN_3 compound.

Chemical evidence for the linear structure came from Mosby and Silva (6) who showed that one of the products obtained from the reaction of Ph_3P and 2,3-bisazidonaphthaquinone (shown below) could only be rationalized by a linear structure for the phosphazide. The formation of

2.


(A) (B)

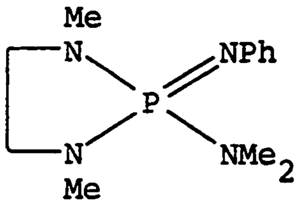
product (B) was thought to arise from the following mechanism.

3.


While the structure of the phosphazides has been a matter of contention, the mechanism of their decomposition was established by Bock and Schnöller (9) in a very elegant experiment wherein they analysed the product nitrogen gas evolved in the reaction of Ph_3P and ^{15}N-labelled p-$MeC_6H_4SO_2N_3$ using mass spectrometry. A four-membered cyclic transition state was consistent with the experimental results although it could arise from either a linear or non-linear adduct. The infrared spectrum of the phosphazide lead them to favor a linear structure.

The modern day use of tris(dialkylamino)phosphines for Staudinger reactions began in 1959 with a patent application by Malz to use the phosphazide intermediates of some morpholino-, piperidino- and dialkylaminophosphines as pesticides (10). These phosphazides were produced by reaction of the aminophosphines with aromatic azides at or below room temperature in ether solution. Vetter and Nöth reported the Staudinger synthesis of $(Me_2N)_3P{=}NPh$, 8 in 1963 (11) in a paper on addition and substitution reactions of 1. They were not interested in the intermediate phosphazide so the reaction mixture was heated to 120° to give 8.

Gutmann and coworkers (12, 13) reported the syntheses of $(Et_2N)_3P{=}NPh$ and



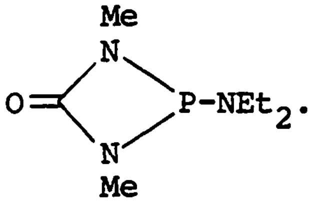
in 1965 via the Staudinger reactions of PhN_3 with the trivalent aminophosphines.

The reaction of organotin azides with 1 was described in 1967 by Lorberth *et al.* who then investigated the effect of the tin moiety on the reactivity of the P=N bond (14).

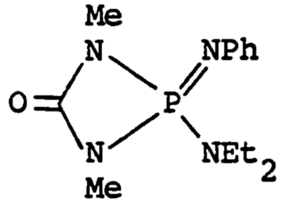
Russian workers, directed by Derkach (15-18), prepared Staudinger reaction products of 1, $P(NEt_2)_3$ and P(N)$_3$ with alkyl azido formates and phosphinyl azides in studies directed toward investigating the insecticidal activity of the phosphinimines produced.

Pilgram, Görgen and Pollard (19) isolated the phosphazides produced by the reaction of morpholino-, piperidino- and diethylaminophosphines with benzoyl azide and phenylazidoformate. These phosphazides were then decomposed by heating in toluene solution. Decomposition was noticed to occur from 30 to 90° depending on the compound. The benzoylphosphazides decomposed at the lower temperatures as would be expected from the inductive effect of R' on the phosphazide stabilities (4, 6).

Work by Bermann and Van Wazer (20), published in 1973, concerned the reactions of the unusual 4-membered ring system



The compound would not give characterizable products from reactions with air, sulfur or BMe_3 but did undergo the Staudinger reaction with PhN_3 in benzene at room temperature to give an 86% yield of the expected product



.

Later in 1973, Bermann and Van Wazer published a note on the kinetics of the reaction of phenyl azide with the adamantane-like molecule $P_4(NMe)_6$ (21) where the phosphorus atoms in the cage could be successively reacted to produce the mono, bis, tris or tetrakis phenylimido compounds as observed by ^{31}P-NMR. While the mono and tetrakis products were crystalline solids, the bis and tris species were non-crystallizable oils. The various rates of formation for the four products were determined by curve fitting the experimental data (^{31}P-NMR peak areas), assuming first order kinetics, to the four equations for product formation.

4. $(PhN)_nP_4(NMe)_6 + PhN_3 \xrightarrow{k_{n+1}} (PhN)_{n+1}P_4(NMe)_6 + N_2;\ n = 0\text{-}3$

The k values are the following: $k_1 \geq 50$, $k_2 = 7$, $k_3 = 1.0$, and $k_4 = 0.3\ M^{-1}\ hr^{-1}$. They concluded that the rate constants favored formation of the essentially pure products having one or four PhN groups and that the presence of more than one species was responsible for the inability to crystallize the bis and tris products.

Bermann and Van Wazer then extended their study of aminophosphine Staudinger reactions to include compound 3 (22), which was reacted with both phenyl azide and diphenylphosphinyl azide, $Ph_2P(O)N_3$. Interestingly enough, they were not able to produce the monosubstituted product 10 from phenyl azide and 3, but always isolated the disubstituted product 11 no matter what ratio of phenyl azide to 3 they employed.

$P(NMeNMe)_3P{=}NPh$ 10 $PhN{=}P(NMeNMe)_3P{=}NPh$ 11

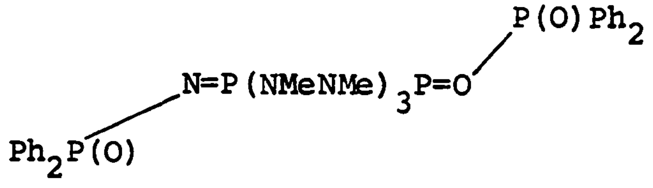
Another point of interest was the proton-decoupled ^{31}P-NMR of compound 17 which exhibited eight peaks as com-

$Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$

17

pared to the single peak seen for 11 under similar conditions. The eight peaks were assigned to two sets of two doublets with a P-P coupling constant of 10.7 Hz. The four chemically nonequivalent phosphorus nuclei were thought to arise from rotational isomerism around the P=N bond in 17 as illustrated below.

isomer A



isomer B

The peculiar cage structure was then responsible for the transmission of the configurational information from one phosphorus to the other. However, such a mechanism would render extremely fortuitous the equal peak areas seen in the ^{31}P-NMR spectrum.

Lorberth (23) attempted to prepare $MeHgN{=}P(NMe_2)_3$ via the Staudinger reaction of $MeHgN_3$ and 1 but failed. Instead of the usual products expected from reaction 1, the conditions of the reaction (sealed tube under vacuum, and high temperatures) caused the organometallic azide to decompose to elemental mercury and other uncharacterized products. The desired mercury compound was finally synthesized by the reaction of methylmercury halide with the Staudinger reaction product of Me_3SiN_3 and 1, *i.e.* $Me_3SiN{=}P(NMe_2)_3$.

Haasemann and Goubeau (24) prepared $MeN{=}P(NMe_2)_3$ via the Staudinger reaction of 1 and MeN_3 and assigned vibrational modes of the phosphinimine. In particular they assigned ν(P=N) at 1284 cm^{-1}.

The insecticidal activity of the phosphazides of 1 with a variety of substituted phenyl azides was studied by Petrenko *et al.* (25) in 1974. They were found to be effective on houseflies having LD_{50} values in the range of 0.1-1.52 mg/insect while the LD_{50} values for white mice were 49-550 mg/kg.

Very recently Goldwhite _et al_. (26, 27) reported the results of Staudinger reactions of _1_ with both alkyl and aryl azides and used infrared, ultraviolet and NMR spectroscopy to help in assigning structures to the phosphazides and phosphinimines produced.

When Bermann and Van Wazer put forth their explanation for the ^{31}P-NMR spectrum of _17_ (22), we attempted to observe a similar effect in $PhN{=}P(NMeCH_2)_3CMe$, _9_, but to no avail. This finding, coupled with a similar failure by Goldwhite _et al_. to observe this phenomenon in acyclic phenylphosphinimines (27) prompted us to reinvestigate the previous work on _17_. It was also of interest to us to compare the Staudinger reaction of _1_, _2_, and _3_ with respect to the phosphazide stabilities since Goetze _et al_. (28) reported an apparent decrease in phosphorus basicity on going from _1_ to _3_ upon synthesis of the chalconide derivatives of these two aminophosphines.

New Derivatives of $P(NMeNMe)_3P$

During the course of the present work on the Staudinger reaction of _3_ we were able to produce the monosubstituted derivative _10_ (29). Its isolation opened up a new area of exploration involving the bonding in _3_ and its derivatives.

$$P(NMeNMe)_3P{=}NPh$$

_10_

When the synthesis of 3 and some of its cage derivatives was first reported by Payne, Nöth and Henniger (30) in 1965, it was noted that the ^{1}H-NMR spectrum consists of a pseudo-triplet which was tentatively explained by postulating additional phosphorus-proton coupling. That is, in addition to the "normal" three bond P-H coupling there also exists a four bond "across the cage" P-H coupling which gives the appearance of a triplet to the methyl proton resonances in 3 and its cage derivatives. This type of spectrum has been observed for all the cage derivatives of 3 until the isolation of 10 and $P(NMeNMe)_3P{=}N{-}N{=}NPh$.(29). The possibility of phosphorus-phosphorus coupling in the cage system was first mentioned by Spangenberg and Sisler (31) when they synthesized the bis(triethylalane) derivative of 3. Molecular models indicated that the phosphorus nuclei of 3 and $Ph_2P(NMeNMe)PPh_2$, which also give triplet patterns in the ^{1}H-NMR spectrum, were or could be in close proximity and therefore P-P coupling could occur *via* a "through space" mechanism as well as through the bonds. The ^{1}H-NMR spectra of $PhP(NMeNMe)_2PPh$ (31) and $ClP(NMeNMe)_2PCl$ (28) consist of simple doublets and in the former this was ascribed to the fact that the bond angles may not be appropriate to allow coupling of the protons with both ^{31}P nuclei (through-bond). For the latter compound Finer and Harris (32) suggested that the presumed chair conformation of the ring would not allow the back lobes of the phosphorus sp^3 hybridized lone pair orbitals to have a suitable orientation for partial overlap (through-space) whereas the cage structure of <u>3</u> would allow orientation for overlap.

Crystal structure determinations have given results which support the ideas of both groups. The crystal structures of <u>3</u> (33), its dioxide $O{=}P(NMeNMe)_3P{=}O$, <u>25</u> (34) and bis(phenylimide) $PhN{=}P(NMeNMe)_3P{=}NPh$, <u>11</u> (35) have been determined. They all show that the P-P distance is well within the sum of the van der Waals radii for phosphorus which is 3.8 Å (36), but much larger than the normal P-P single bond length of 2.3 Å (36). In particular the P-P distances found were 2.99 Å in <u>3</u> (33), 2.82 Å in <u>25</u> (34) and 2.844 Å in <u>11</u> (35); distances which are consistent with the partial overlap hypotheses put forward. It is interesting to note that in <u>3</u> the P-N-N-P linkages are planar while in <u>11</u> and <u>25</u> the linkages are twisted to give dihedral angles of 20° and 18.6° respectively. Since the P-N and N-N distances in all three cages are essentially equal, the twisting results in the shorter P-P distances seen in the latter two compounds. The cause of the twisting may well be the opening of the cage NPN angles in <u>11</u> and <u>25</u> (103° and 103.6°) compared to <u>3</u> (100°) brought about by oxidation and subsequent rehybridization of the bridgehead phosphorus atoms. Such rehybridization is observed in the opening of the OPO angle of $P(OCH_2)_3CCH_2Br$ (100.1°) (37) to $O{=}P(OCH_2)_3CMe$ (103.7°) (38).

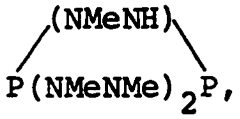
The crystal structure of $ClP(NMeNMe)_2PCl$ (39) shows that the ring does indeed exist as the chair form with the P-Cl bonds equatorially directed and therefore the P lone pairs are in axial positions. This result gives credence to the argument of Finer and Harris (32).

These findings bring up the question of through-bond *versus* through-space mechanisms for orbital interactions between atoms in the same molecule. Recent investigations of the PES spectrum of $N(CH_2CH_2)_3N$ (40) coupled with theoretical calculations of orbital splitting patterns and energy level orderings (41, 42) has led to the conclusion that the through-bond mechanism is much more important than any through-space interaction for the bicyclic amine. Because of a similar phosphorus lone pair energy ordering observed in the PES spectrum of 3, the through-bond mechanism was favored (43).

Bertrand *et al*. (44) concluded that it was not necessary to invoke through-space effects to explain the trends in JPH and JPP for derivatives of $P(OCH_2)_3P$. The PES spectrum of $P(OCH_2)_3P$ did not allow a determination of whether through-bond or through-space effects dominated, however (43).

If through-bond effects are important in compounds of 3 then the P-P coupling constants should be sensitive indicators of these interactions as they appear to be in derivatives of $P(OCH_2)_3P$. However, except for 7, 10, 17 and $(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$, 14 (29) all the derivatives of 3 possess phosphorus nuclei which are chemically as well as magnetically equivalent in their ^{31}P-NMR spectra with proton decoupling. Under these conditions the observation of any P-P coupling is impossible.

Nöth and Ullmann (45) were able to detect JPP in



$$\overset{\text{(NMeNH)}}{P(NMeNMe)_2P},$$

a compound very closely related to 3 and then satisfactorially solved the ^{1}H-NMR spectrum of 3 using that value of JPP in the calculations.

However, with the synthesis of 10 we were able to prepare unsymmetrically disubstituted derivatives of 3 wherein P-P coupling could be directly observed from the proton-decoupled ^{31}P-NMR spectrum. The novel synthesis of the monoxide of 3, $P(NMeNMe)_3P{=}O$, 24 gave a second compound from which unsymmetrical cages can be made. These systems also permit comparisons of the effect of the exocyclic group on P-P and P-H couplings.

Selenophosphoryl Compounds

In the period since the first instances of phosphorus-selenium couplings were reported in 1969 (46, 47), there has been a steady growth in data on these systems and in

Table 1. Chemical shifts and coupling constants for compounds containing a $\geqq$P=Se group

$\geqq$P=Se Species	Coupling Constant $^{1}J_{PSe}$[a]	^{31}P Chemical Shift δP[b]	Solvent	Reference
SeP(C_6H_5)(t-C_4H_9)H	656 ± 6	- 37.9	C_6H_6	48
SeP(C_6H_5)$_2$H	740 ± 10	- 5.6	CH_2Cl_2	49, 50
SeP(CH_3)$_3$	684 ± 2	- 8.0	CH_2Cl_2	49, 50
SeP(C_2H_5)$_3$	705 ± 6	- 44.2	C_6H_6	48
SeP(n-C_4H_9)$_3$	693 ± 6	- 36.4	neat	48
SeP(t-C_4H_9)$_3$	712	- 92.5	C_6D_6	51
SeP(C_6H_5)(CH_3)$_2$	710 ± 10	- 15.1	neat	50
SeP(C_6H_5)(C_2H_5)(CH_3)	693 ± 6	- 29.8	C_6H_6	48
SeP(C_6H_5)(C_2H_5)$_2$	650 ± 6	- 44.3	CF_3COOH	48
	693 ± 6	- 43.8	CH_3COOH	48
	705 ± 6	- 44.6	neat	48
SeP(C_6H_5)(n-C_3H_7)(CH_3)	704 ± 6	- 26.1	C_6H_6	48
SeP(C_6H_5)(t-C_4H_9)(CH_3)	702 ± 6	- 47.7	$CHCl_3$	48
SeP(C_6H_5)$_2$(CH_3)	725 ± 10	- 22.3	CH_2Cl_2	50

$SeP(C_6H_5)_2(C_2H_5)$	722 ± 6	- 37.4	C_6H_6	48
$SeP(C_6H_5)_3$	735.4	- 36.1	$CHCl_3$	52
	738 ± 6	- 36.1	DMF	48
$SeP(C_6H_4\text{-}\underline{p}\text{-}CH_3)_3$	723.5	- 34.5	$CHCl_3$	52
$SeP(C_6H_4\text{-}\underline{m}\text{-}CH_3)_3$	726.3	- 36.3	$CHCl_3$	52
$SeP(C_6H_4\text{-}\underline{o}\text{-}CH_3)_3$	708.0	- 28.5	$CHCl_3$	52
$SeP(C_6H_4\text{-}\underline{p}\text{-}OCH_3)_3$	719.3	- 32.3	$CHCl_3$	52
$SeP(C_6H_4\text{-}\underline{p}\text{-}Cl)_3$	752.8	- 33.9	$CHCl_3$	52
$SeP(C_6H_5)(\underline{t}\text{-}C_4H_9)(SeH)\cdot N(C_2H_5)_3$	604 ± 6	- 58.0	CH_3OH	48
$SeP(C_6H_5)(t\text{-}C_4H_9)(SeCH_3)$	753 ± 6	- 81.3	CH_3OH	48
$SeP(CH_3)_2[N(CH_3)_2]$	720 ± 10	- 59.0	CH_2Cl_2	50
$SeP(C_2H_5)_2[N(C_2H_5)_2]$	728 ± 6	- 79.0	neat	48
$SeP(C_6H_5)_2[N(CH_3)_2]$	760 ± 10	- 71.6	CH_2Cl_2	50
$SeP(C_6H_5)_2[N(C_2H_5)_2]$	753 ± 6	- 66.7	C_6H_6	48
$SeP(C_6H_5)(C_2H_5)Cl$	840	-[c]	-[c]	53
$SeP(C_2H_5)_2Cl$	884 ± 10	- 86.9	neat	54

---

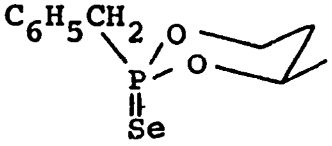
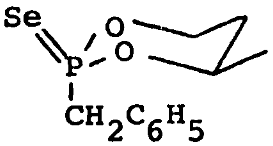
[a] In Hz, uncertainties are indicated if reported.

[b] In ppm relative to 85% H_3PO_4.

[c] Not reported.

Table 1. (continued)

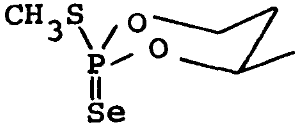
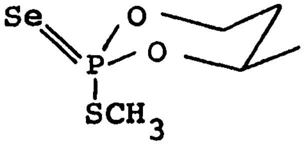
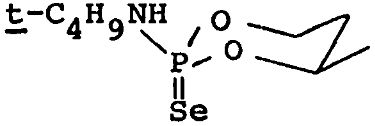
$\geqslant$P=Se Species	Coupling Constant $^1J_{PSe}$[a]	^{31}P Chemical Shift δP[b]	Solvent	Reference
$SeP(CH_3)_2(OCH_3)$	768 ± 2	- 90.2	CH_3OH	50
$SeP(C_2H_5)_2(OC_2H_5)$	755 ± 6	-107.5	neat	48
$SeP(C_6H_5)(\underline{t}\text{-}C_4H_9)(OH)\cdot N(C_2H_5)_3$	632 ± 6	- 74.8	CH_3OH	48
$SeP(C_6H_5)_2(OCH_3)$	810 ± 10	- 86.8	CH_2Cl_2	50
$SeP(C_6H_5)_2(OC_2H_5)$	795 ± 6	- 84.1	C_6H_6	48
$SeP(CH_3)[N(CH_3)_2]_2$	767 ± 4	- 80.5	neat	50
	789 ± 10	- 82.5	neat	54
$SeP(C_2H_5)[N(C_2H_5)_2]_2$	748 ± 6	- 85.7	neat	48
$SeP(C_6H_5)[N(CH_3)_2]_2$	790 ± 10	- 84.0	neat	50
$SeP(C_6H_5)[N(C_2H_5)_2]_2$	766 ± 6	- 77.2	neat	48
$SeP(CH_3)Cl_2$	955 ± 2	- 55.1	-[c]	55
$SeP(C_2H_5)Cl_2$	920	-[c]	-[c]	53
	921 ± 10	- 75.5	neat	54
$SeP[N(CH_3)_2]_3$	794 ± 6	- 83.4	neat	48

	805 ± 2	- 81.8	CH_2Cl_2	49, 50
	815	–[c]	–[c]	56
$SeP[N(C_2H_5)_2]_3$	790 ± 6	- 77.3	neat	48
$SeP(OC_2H_5)_2H$	860 ± 10	- 70.4	neat	50
	883 ± 3	- 96.9	C_6H_6	57, 58
	909 ± 3	- 92.0	C_6H_6	57, 58
$SeP(CH_3)(OCH_3)_2$	861.0 ± 0.5	-102.3	neat	50
$SeP(C_2H_5)(OC_2H_5)_2$	837 ± 6	-107.0	neat	48
$SeP(C_6H_5)(OCH_3)_2$	876 ± 4	- 97.5	neat	50
$SeP(C_6H_5)(OC_2H_5)_2$	850 ± 6	- 92.2	neat	48
(ℓ)-$SeP(CH_3)(OCH_3)(OH)$	783[d]	- 95	–[c]	59
$(d\ell)$-$SeP(CH_3)(OCH_3)(OH)$	790[d]	- 95	–[c]	59
(d)-$SeP(CH_3)(OCH_3)(OH)$	793[d]	- 96	–[c]	59
$SeP(OC_2H_5)_2(SeH)$	822 ± 6	- 61.5	neat	48

---

[d] Theoretically there should be no difference in $^1J_{PSe}$ for enantiomers or racemates. The differences reported here are probably due to experimental error.

Table 1. (continued)

≡P=Se Species	Coupling Constant $^1J_{PSe}$[a]	^{31}P Chemical Shift δP[b]	Solvent	Reference
$SeP(OC_2H_5)_2(SeC_2H_5)$	882 ± 6	- 73.5	neat	48
$SeP(OC_2H_5)_2(SH)\cdot N(C_2H_5)_3$	732 ± 6	-100.3	CH_3OH	48
$SeP(OC_2H_5)_2(SH)$	777 ± 6	- 84.7	neat	48
$SeP(OC_2H_5)_2(SCH_3)$	887 ± 6	- 94.0	neat	48
	895 ± 3	- 94.0	C_6H_6	58, 60
	960 ± 3	- 88.5	C_6H_6	58, 60
$SeP(CH_3)ClF$	1020 ± 5	- 98.1	–[c]	55
$SeP(OC_2H_5)_2[N(CH_2CH_2)_2O]$	920 ± 10	- 80	neat	54
	900 ± 3	- 66.5	C_6D_6	58, 61

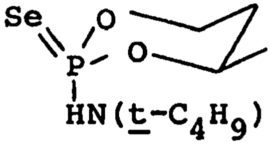
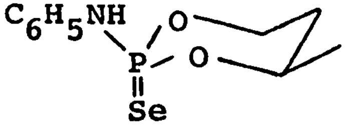
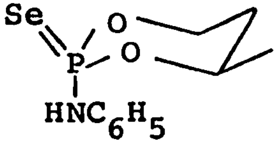
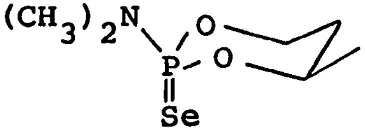
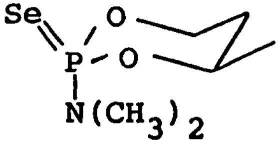
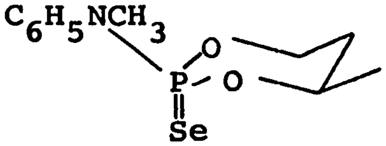
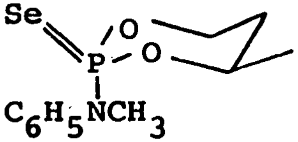
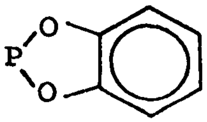
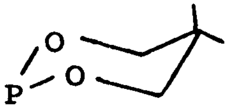
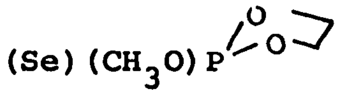
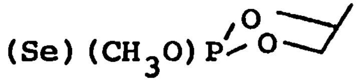
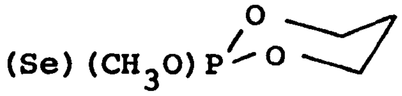
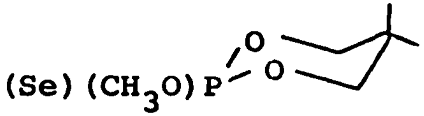
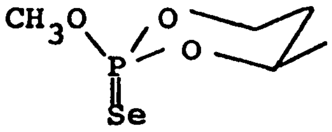
	916 ± 3	- 58.7	C_6D_6	58, 61
	887 ± 3	- 62.5	$O(CH_2CH_2)_2O$	58, 62
	942 ± 3	- 60.0	$O(CH_2CH_2)_2O$	58, 62
	930 ± 3	- 79.0	C_6H_6	58, 63
	960 ± 3	- 79.8	C_6H_6	58, 63
	925 ± 3	- 72.5	C_6H_6	58
	941 ± 3	- 65.2	C_6H_6	58

Table 1. (continued)

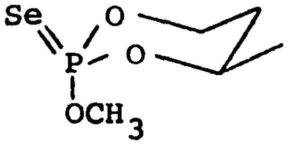
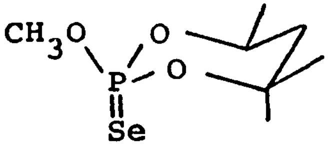
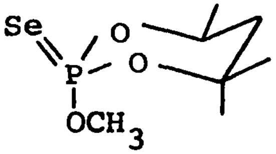
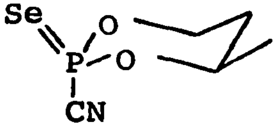
$\equiv$P=Se Species	Coupling Constant $^1J_{PSe}$[a]	^{31}P Chemical Shift δP[b]	Solvent	Reference
$[SeP(OC_4H_9)]_2NCH_3$[e]	946 ± 10	- 75.6	neat	54
$SeP(O\text{-}\underline{i}\text{-}C_4H_9)_2Cl$	1030	- 63.0	-[c]	64
Cl(Se)P 	1130 ± 10	- 65.6	neat	54
$SePF_2H$	1046	- 74.2	-[c]	65
$SeP(OC_2H_5)_2(OH) \cdot N(C_2H_5)_3$	772 ± 3	- 50.2	CH_3OH	48
$SeP(OC_2H_5)_2(OH)$	881 ± 6	- 62.3	C_2H_5OH	48
	894 ± 6	- 63.4	neat	48
(Se)(HO)P 	882 ± 6	- 55.3	CH_3OH	66
$SeP(OCH_3)_3$	945 ± 6	- 78.4	neat	48
	936.0 ± 0.5	- 77.5	neat	49, 50
$SeP(OCH_3)_2(OC_2H_5)$	940 ± 6	- 76.4	neat	48

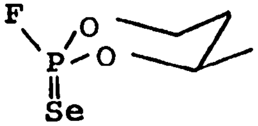
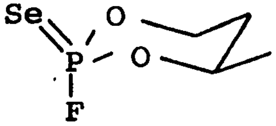
$SeP(OCH_3)(OC_2H_5)_2$	935 ± 6	- 73.8	neat	48
$SeP(OC_2H_5)_3$	935 ± 6	- 71.8	neat	48
$SeP(OC_2H_4Cl)_3$	955 ± 6	- 72.8	neat	48
$SeP(O\text{-}\underline{n}\text{-}C_3H_7)_3$	933 ± 6	- 72.4	neat	48
$SeP(O\text{-}\underline{i}\text{-}C_3H_7)_3$	912 ± 6	- 67.7	neat	48
$SeP(OC_4H_9)_3{}^{e}$	952 ± 10	- 73	neat	54
	948 ± 6	- 77.0	$-^{c}$	66
	989 ± 6	- 83.3	$-^{c}$	66
	989 ± 6	- 84.3	$-^{c}$	66
	968 ± 6	- 68.0	CH_3OH	66
	961 ± 6	- 66.7	CH_3OH	66
	941 ± 6	- 68.5	neat	66

---

[e] The structure of the C_4H_9 group was not specified.

Table 1. (continued)

⩾P=Se Species	Coupling Constant $^{1}J_{PSe}$[a]	^{31}P Chemical Shift δP[b]	Solvent	Reference
	978 ± 6	- 67.2	neat	66
	975 ± 6	- 62.5	neat	66
	984 ± 6	- 64.0	neat	66
	1040	- 28.2	–[c]	67
$SeP(CH_3)F_2$	1040 ± 5	-112.5	–[c]	55
$SeP[NHSi(CH_3)_3]F_2$	1075	- 68.3	–[c]	55

	1110 ± 3	- 60.8	C_6H_6	68
	1122 ± 3	- 60.8	C_6H_6	68

particular those compounds which contain the P=Se bond. These pentavalent species can now easily be observed by ^{31}P- and ^{77}Se FT-NMR techniques. In the absence of additional couplings, both the coupled ^{31}P and ^{77}Se resonances for Se=P$\leqq$ compounds are doublets owing to a spin value of 1/2 for each of these nuclei. The coupled ^{31}P resonance appears as "wing" peaks symmetrically disposed around the single resonance for the Se=P$\leqq$ species which contain non-NMR active Se hereafter referred to as ^{0}Se. As the natural abundance of ^{77}Se is only 7.58% the central peak is very intense compared to the "wing" peaks. All of the previously reported P=Se coupling constants are listed in Table 1 along with the ^{31}P chemical shifts of the pentavalent species. It should be noted that ^{1}JPSe coupling constants have also been reported for singly bonded species but these values are not included in the table.

In 1971, Cree reported the first P=Se bond ^{1}JPSe value (56). The 815 Hz coupling for <u>29</u> was contained in a general report on some work concerning couplings of low abundance nuclei. Other compounds with different substituents on phosphorus were said to exhibit ^{1}JPSe values from 745 to 1035 Hz but were never mentioned specifically.

Shortly thereafter values of ^{1}JPSe for selenophosphoryl compounds were reported by Nuretdinov and Loginova (53). Although their investigation included acid chlorides, esters and amides of selenophosphoric acid, only two specific values of $^1J_{PSe}$ were quoted (i.e., 920 Hz for $EtP(Se)Cl_2$ and 840 Hz for EtPhP(Se)Cl). Mention was made that the range of $^1J_{PSe}$ values observed was 900-1100 Hz and depended upon the nature of the substituents on phosphorus. The structure of selenium-containing organophosphorus compounds could also be determined from $^1J_{PSe}$, presumably because the coupling constant for P-Se bonds is smaller than for P=Se bonds, e.g. $^1J_{PSe}$ for $Me_2P(S)SeMe$ is -341 ± 4 Hz (46) compared to the range 900-1100 Hz for P=Se bonds quoted (53).

Prompted by these early reports, Stec et al. published values of $^1J_{PSe}$ they had observed for many different types of selenium-phosphorus compounds (48). They extended the lower limit of $^1J_{PSe}$ for the P=Se bond in covalent compounds to 656 Hz for a secondary phosphine selenide and also showed how the smaller $^1J_{PSe}$ value for P-Se bonds could be useful in elucidating the structure of isomers, e.g. $(EtO)_3PSe$ (935 Hz) as compared to $(EtO)_2P(O)(SeEt)$ (468 Hz). The magnitude of $^1J_{PSe}$ can also be used to determine the ratio of tautomers in equilibrium situations as in equation 5,

$$5.\quad (EtO)_2P(Se)OH \rightleftarrows (EtO)_2P(O)SeH$$

where the P=Se form dominates. A similar situation prevails for the equilibrium of $(EtO)_2P(Se)(SH)$.

The increase of ^1JPSe in the order $R_3PSe < (R_2N)_3PSe < (RO)_3PSe$ was interpreted as showing the decrease in s-character of the phosphorus-substituent bonds on going from carbon to nitrogen to oxygen with a concomitant increase in the s-character of the P=Se bond and hence larger values of the coupling constant (48). The effect of charge on the coupling was demonstrated by making the triethylammonium salts of the acids $(EtO)_2P(Se)OH$ and $(EtO)_2P(Se)SH$. In both instances ^1JPSe decreased as the phosphorus gained negative charge upon reaction with the amine. A decrease of 122 Hz occurred in the former and 45 Hz in the latter which may be indicative of the acid strength.

By performing heteronuclear triple resonance NMR experiments, McFarlane and Rycroft (49, 50) concluded that the sign of ^1JPSe is negative and that the P=Se bond is best represented as a resonance hybrid of the canonical forms shown below.

$$\underset{\text{non-polar}}{R_3P{=}Se} \qquad \underset{\text{dipolar}}{R_3\overset{+}{P}{-}\overset{-}{Se}}$$

Previous studies (69) had shown that the ^{77}Se chemical shift, δSe, moved to lower field (more negative values) as the amount of electronic charge withdrawal from selenium increased. The only substantially high field shifted examples of δSe are in alkyl selenide anions RSe^-, MeSeH and H_2Se. The observation that organophosphorus selenides also have very high field δSe values (Table 2) strongly suggested that the dipolar form makes a major contribution to the resonance hybrid.

However, the changes in δSe do not parallel substituent electronegativities and in fact are opposite to the expected trend. For example, on simple electronegativity grounds, Me_3PSe would be expected to have a δSe significantly to high field of δSe in $(MeO)_3PSe$ whereas the contrary is observed. This behavior was rationalized by assuming that the non-polar form makes some contribution to the hybrid and the extent of this depends upon the pi bonding abilities of the phosphorus substituents. The Me groups in Me_3PSe do not compete for the phosphorus 3d orbitals and so the non-polar contribution may be quite large. As the Me groups are replaced by better pi bonding groups the phosphorus 3d orbitals will be less readily available to overlap with the selenium 4p orbitals and, as a consequence, the importance of the non-polar form will decrease and the dipolar form will increase. The selenium atom will then become more shielded and δSe will move to a higher field. However, this change will be offset to some extent by the greater electronegativity of the pi bonding groups relative to a Me group; especially MeO, and this could account for δSe of $Me_2(MeO)PSe$ being downfield from that of Me_3PSe.

Table 2. Selenium chemical shifts and coupling constants for organophosphorus selenides

Compound[a]	^{77}Se Chemical Shift δSe[b]	Coupling Constant $^{1}J_{PSe}$[c]
F_2HPSe[d]	170	-1046
$Me_2(MeO)PSe$	218.6 ± 0.5	-768 ± 2
Me_3PSe	234.9 ± 0.5	-684 ± 2
$(EtO)_2HPSe$	257.5 ± 0.5	-860 ± 10
$Me(MeO)_2PSe$	268.9 ± 0.5	-861.0 ± 0.5
Me_2PhPSe	271.7 ± 0.5	-710 ± 10
$(MeO)Ph_2PSe$	276.3 ± 0.9	-810 ± 10
$MePh_2PSe$	277.0 ± 0.9	-725 ± 10
$Me_2(Me_2N)PSe$	279.4 ± 0.5	-720 ± 10
$(MeO)_2PhPSe$	320.4 ± 0.3	-876 ± 4
$Me(Me_2N)_2PSe$	327.0 ± 0.9	-767 ± 4
Ph_2HPSe	348.7 ± 0.5	-740 ± 10
$(Me_2N)_3PSe$	365.8 ± 0.5	-805 ± 2
$(Me_2N)_2PhPSe$	370.0 ± 0.5	-790 ± 10
$(Me_2N)Ph_2PSe$	384.8 ± 0.5	-760 ± 10
$(MeO)_3PSe$	396.1 ± 0.2	-963.0 ± 0.5

[a] All compounds from reference 50 unless noted.

[b] In ppm relative to Me_2Se.

[c] In Hz.

[d] Reference 65.

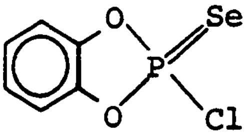
The variations in ^{1}JPSe were discussed by McFarlane and Rycroft (50) in terms of the Pople-Santry molecular orbital treatment (70) of nuclear spin-spin couplings. The nature of this treatment will be described later.

It was possible to predict ^{1}JPSe to ±10 Hz using additive substituent parameters which paralleled the known inductive effects of the groups studied (50). Similar arguments have been made for the behavior of the coupling constants ^{1}JCH, ^{1}JCF, ^{1}JPH and ^{1}JPF (71-75). In this manner ^{1}JPSe could be used to assess the effective electronegativity of the substituents on the phosphorus atom in R_3PSe molecules. This is supported by the much narrower spread of ^{1}JPSe observed by Pinnell et al. (52) in a series of triarylphosphine selenides. Here, the value of ^{1}JPSe correlated very well with the Hammet sigma parameters for the substituent groups studied except in the case of tris(o-tolyl)phosphine selenide (see Table 1) which was attributed to steric effects.

The effect of halogen substituents was demonstrated by Roesky and Kloker (55) by substituting fluorine atoms for chlorine atoms to give compounds of the type RP(Se)Cl_2, RP(Se)ClF and RP(Se)F_2. Primarily their interest was directed towards changes in vibrational spectra but the ^{1}JPSe data they included showed the coupling constant increased as the fluorine content of the molecules increased.

Such findings are to be expected on inductive grounds as seen before (50). Anderson et al. (65) performed a total NMR study of the molecule F_2HPSe (where all the atoms are NMR active) and determined the coupling signs. Again, ^1JPSe was determined to be negative.

Loginova, Nuretdinov and Petrov (54) reported P-Se coupling constants for some acyclic compounds as well as the first report of ^1JPSe for a cyclic organophosphorus selenide, ortho phenylene phosphorochloroselenoate,



,

which has the largest ^1JPSe value yet reported (1130 Hz). It had been observed that the trend in one bond reduced coupling constants, ^1K, related to the observed coupling constant ^1J by the equation

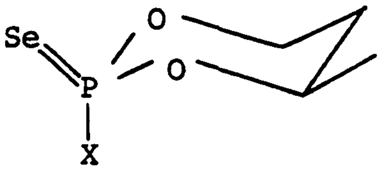
$$6. \quad {}^1K_{NN'} = \frac{2\pi}{\hbar\gamma_N\gamma_{N'}} \cdot {}^1J_{NN'}$$

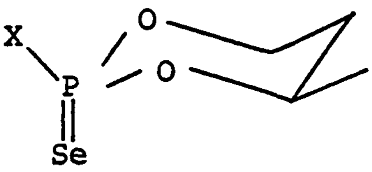
where γ_N is the magnetogyric ratio of atom N, was from predominantly positive signs in XH systems to predominantly negative signs in XF systems, viz., the sign changed from positive to negative upon moving across the periodic table from left to right. The magnitude of the couplings increased as one moved down the table. A model for predicting the signs and, in some cases the magnitudes, of such couplings had been proposed by Jameson and Gutowsky (76, 77). The borderline cases seemed to occur in groups V and VI. The sign changes were attributed to nuclear spin-electron spin contact contributions, $@_N$, for atom N, composed of two parts

$$7.\quad @_N = @_N(s) + @_N(\text{core pol})$$

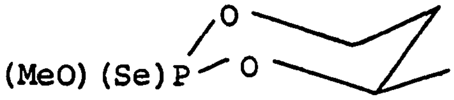
where $@_N(s)$ is the direct Fermi contact term caused by the s density of the bonding electrons at the nucleus and $@_N$(core pol) is an indirect Fermi contact interaction due to polarization of the s electrons in the core. If the atom uses primarily ns orbitals in the bond, $@_N(s)$, which is positive, would dominate but if the bonding used primarily p orbitals, $@_N$(core pol) would dominate and the sign would probably be negative (40). While both mechanisms $@_N(s)$ and $@_N$(core pol) would be in operation in every case, the sign of the coupling constant is determined by the dominant nuclear spin-electron spin interactions for N and N', since ${}^1K_{NN'} \propto @_N @_{N'}$. Loginova *et al*. (54) argued that the dominant term for P^V was $@_P(s)$ (positive) based upon the signs of ^{1}KPC and that the dominant term for Se was $@_{Se}$(core pol) (negative) based upon the signs of ^{1}KCSe. Thus the sign of ^{1}KPSe should be negative. This prediction was in agreement with earlier sign determinations of ^{1}KPSe (46, 50, 65) which had shown it to be negative both for P-Se and P=Se bonds.

Most recently Stec and coworkers have used ^{1}JPSe as a probe of the configuration of phosphorus in monocyclic selenophosphorinanes. Most of the work has been directed towards isomers of the ring compounds below where X has been

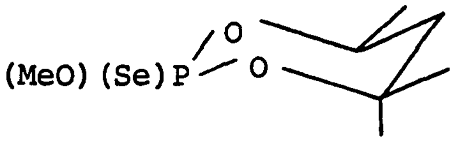




benzyl (57), methylanilino (58), methylthio (60), tertiary butylamino (61), anilino (62), dimethylamino (63), methoxy (66), cyano (67), and fluoro (68). In all cases studied ^{1}JPSe for the equatorial Se isomer was found to be from 12 to 65 Hz larger than the axial Se isomer. Extensive methyl substitution on the ring had the effect of lowering the difference between ^{1}JPSe for the two isomers, e.g. Δ^1JPSe for



is 37 Hz (66) while Δ^1JPSe for



is 9 Hz (66). Non-locked ring compounds for 5 and 6 membered rings were also studied (66).

An investigation of ^{1}JPSe values for various acyclic and cyclic selenophosphates seemed to be warranted based upon (1) the unusually large values of $^{1}J_{PSe}$ reported for monocyclic selenophosphorinanes as compared to the acyclic analogs (see Table 1) considering the equivalent electronegativities of the substituents around phosphorus and (2) the finding of Vande Griend *et al*. (78-80) that the protonated species of monocyclic and bicyclic phosphites displayed larger $^{1}J_{PH}$ values than acyclic phosphites. A comparison of $^{1}J_{PSe}$ for acyclic and bicyclic aminophosphine selenides was also sought as an extention of previous work (29).

EXPERIMENTAL

Techniques

Precautions

All compounds were regarded as being moisture sensitive and were always handled under a dry nitrogen atmosphere either in Schlenk apparatus, gas-tight syringes, or glove bags.

Materials

All general solvents were reagent grade or better and were stored over 4A molecular sieves. Before use they were saturated with dry nitrogen. Benzene, toluene, THF and ether were additionally dried by refluxing with and distilling from $LiAlH_4$ and/or Red-Al (sodium bis(2-methoxyethoxy)aluminum hydride). Acetonitrile was dried by refluxing with and distilling from CaH_2. Acetonitrile so obtained had a resistance of about 1.5×10^6 ohms.

Elemental reagent grade bromine was purchased from Fisher Scientific Co. and used as received. Triethylamine was purified by distillation from dry BaO under nitrogen. Tris(dimethylamino)phosphine (TDP, 1), diphenylphosphoryl azide - $(PhO)_2P(O)N_3$, diphenylphosphinyl azide - $Ph_2P(O)N_3$ and 1,2-dimethylhydrazine dihydrochloride were purchased from Aldrich Chemical Co. and used as received. Trimethyl phosphite, 46, was purchased from Aldrich Chemical Co. and distilled twice under nitrogen.

Infrared and ultraviolet spectra

Infrared spectra were recorded on a Beckman IR 4250 Spectrophotometer as indicated in the text and calibrated using a polystyrene standard. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer using THF or ether solutions and were analyzed with the program LOGFIT (81).

Mass spectra

Mass spectra were obtained on an AEI MS902 high-resolution mass spectrometer. Exact masses were obtained by peak matching.

Conductivity measurements

Conductivities were measured on about 10^{-2} molar solutions in acetonitrile at room temperature using an Industrial Instruments RC-1632 conductivity bridge operated at a bridge frequency of 1000 Hz. The cell was standardized using about 0.1 M KCl solution.

Dipole moment measurements

Dielectric measurements were determined with the heterodyne beat apparatus described by Vandenbroucke *et al.* (82) and refractive index measurements were made on a Bausch and Lomb "Abbe-56" Refractometer. The solutions used were generally in the range of about 10^{-3} to 10^{-2} mole fraction in toluene prepared under nitrogen. Solutions were thermostatically maintained at 25.00 ± 0.05° during all measurements. Dipole moments were calculated using the Debye equation by the program LSDP (83).

NMR spectroscopy

Proton NMR spectra were obtained on a Varian HA-100 spectrometer using $CDCl_3$ or CD_3CN solutions. TMS was used as an internal standard and the spectrometer was locked on the resonance of either TMS or $CHCl_3$ depending on the chemical shifts of the compound resonances.

^{31}P-NMR spectra were obtained on solutions in 10-mm tubes with a Bruker HX-90 spectrometer operating at 36.434 MHz in the Fourier transform (FT) mode locked on the ^{2}H resonance of the deuterated solvent. The external standard was 85% H_3PO_4 contained in a 1-mm capillary tube held coaxially in the sample tube by a Teflon vortex plug. The spectrometer was interfaced with a Nicolet Instruments 1080 minicomputer system. Negative shifts are those downfield of H_3PO_4.

^{31}P-NMR spectral calculations were executed on the 1080 computer with ITRCAL (84), an implementation of the well-known LAOCN3 algorithm for a minicomputer. It allows for the laboratory real-time iterative analysis of experimentally obtained spectra for systems up to six nuclei of spin 1/2 and uses the method of Castellano and Bothner-By (85).

^{13}C-NMR spectra were obtained on the Bruker HX-90 spectrometer operating at 22.63 MHz in the FT mode locked on the solvent ^{2}H resonances. The solvent carbons were references.

Preparations

Red selenium was prepared from the grey form of the element by the method of Campbell and McCullough (86). Triphenylmethyl fluoroborate was prepared by the method of Dauben et al. (87) from triphenylcarbinol and fluoroboric acid in acetic anhydride. Phenyl azide was prepared by the method of Lindsay and Allen (88) and stored at 5° in the dark under nitrogen.

Reaction products

$P(NMeCH_2)_3CMe$, 2 Although the preparation of this compound, formally named 1-phospha-2,6,7-triaza-2,4,6,7-tetramethyl-bicyclo[2.2.2]octane, has been reported previously (89, 90), the preparation in this work is a combination of the earlier methods along with some modifications which improve the yield. The preparative route is shown below.

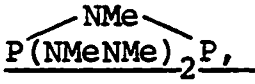
8. $(HOCH_2)_3CMe \rightarrow (PhSO_3CH_2)_3CMe \rightarrow (BrCH_2)_3CMe \rightarrow$
$(HNMeCH_2)_3CMe \rightarrow P(NMeCH_2)_3CMe$

The tribromide precursor to 2 was prepared from 1,1,1-tris(hydroxymethyl)ethane (Aldrich Chemical Co.) via the tris (benzenesulfonate) ester as described earlier (90). 1,1,1-Tris(methylaminomethyl)ethane was prepared and isolated in over 95% yield, compared to 80% (89) and 22% (90) yields, by the following method. A 93.0 g (0.301 moles) sample of tribromide (b_3 = 100°) was dissolved in 300 ml of absolute ethanol in a 500 ml flask. A magnetic stirring bar was added and the flask was cooled in an ice bath. A dry ice condenser was fitted to the flask and approximately 150 ml of methylamine (Matheson Gas Products) was condensed into the alcoholic solution. This solution was poured into a Berghof/America 500 ml Teflon-lined autoclave and heated with vigorous stirring to 190° for at least 24 hours. The autoclave was then cooled, the excess methylamine allowed to evaporate and the ethanol removed from the clear colorless reaction mixture using a rotary evaporator. After 400 ml of benzene had been added to the white solid residue, the mixture was mechanically stirred and refluxed for 9 hours under nitrogen. During the first hour, 100 g of 86% KOH was added in small portions to neutralize the amine hydrobromide salts. The mixture was cooled to room temperature and filtered under nitrogen. The benzene was removed on a rotary evaporator to leave a clear yellow oil. This was distilled (b_4 = 72°) to give 46.0 g (96%) of the pure triamine as a clear colorless liquid.

The bicyclic aminophosphine 2 was then prepared as described (89) and distilled (b_{10} = 70°) to give a clear colorless liquid in 85% yield (lit. 90%, b_{10} = 82-86°).

$P(NMeNMe)_3P$, 3 This compound was prepared from 1 and 1,2-dimethylhydrazine dihydrochloride (Aldrich Chemical Co.)

in refluxing benzene following the method of Goetze, Nöth and Payne (28). It was purified by repeated vacuum sublimations at 50° (0.01 torr) until there was no yellowish residue remaining. The proton and phosphorus NMR spectral parameters matched those previously reported (28).



$\overset{NMe}{P(NMeNMe)_2P}$, 4 This compound was prepared according to the method of Nöth and Ullmann (91). The present work scaled the reaction up by a factor of nine with no appreciable decrease in isolated yield, (68%; lit. 72%). Proton, carbon and phosphorus spectra always indicated the presence of small amounts of 3 which is a known decomposition product of 4 (91). Decomposition was moderate at room temperature but could be totally arrested by freezing at -10°.

$(Me_2N)_3P{=}N{-}N{=}NPh$, 5 To a solution of 0.68 ml (6.2 mmoles) of phenyl azide in 25 ml of hexane at 0° was added dropwise 1.00 ml (6.15 mmoles) of 1. A bright yellow precipitate formed immediately upon adding each drop. The mixture was cooled to -78° and the solid was filtered, washed twice with cold hexane, and dried *in vacuo* yielding 1.42 g (82%) of the product (m.p. = 91-92°; *m/e* for P^+: 254.1659 ± 0.0013, experimental; 254.1660, calculated).

$MeC(CH_2NMe)_3P{=}N{-}N{=}NPh$, 6 To a solution of 1.00 ml (5.60 mmoles) of 2 in 25 ml of pentane at 0° was added dropwise 0.62 ml (5.6 mmoles) of phenyl azide. The solution became turbid but cleared after 5 minutes. The solvent was removed under vacuum at 0° and the remaining yellow liquid was cooled at -10° for 4 days. During this time, a bright yellow solid formed which was washed with cold pentane, filtered and dried in vacuo at 0° yielding 1.09 g (64%) of product (m.p. = 82-83° (decomposition)). The compound was unstable in the mass spectrometer, decomposing on the heated probe (60°) to give nitrogen gas and compound 9.

$P(NMeNMe)_3P=N-N=NPh$, 7 To a solution of 0.70 g (3.0 mmoles) of 3 in 25 ml of ether at 0° was added dropwise 0.65 ml (5.9 mmoles) of phenyl azide. The solution was kept at -5° for 14 hours and filtered while cold. The solvent was removed at 0° under vacuum leaving a light yellow residue which was washed with cold hexane, filtered and dried in vacuo to give 0.57 g of solid. Proton NMR indicated only the presence of 7 for a yield of 54% (m.p. = 83-85° (decomposition)). The same stoichiometries of reactants in either hexane or acetonitrile gave only 7 in yields of 27% and 95%, respectively. This compound was also unstable in the mass spectrometer, decomposing to give nitrogen and 10.

$(Me_2N)_3P=NPh$, 8 This compound was prepared as reported by Vetter and Nöth (11) and was obtained as a clear yellow oil ($b_{0.07}$ = 104°; lit. $b_{0.4}$ = 127°) in 63% yield (lit. 92%).

$\underline{\text{MeC(CH}_2\text{NMe)}_3\text{P=NPh, }\underline{\underline{9}}}$ The solution formed by adding 1.00 ml (5.60 mmoles) of $\underline{2}$ and 0.61 ml (5.6 mmoles) of phenyl azide to 10 ml of toluene at room temperature was heated to 80° for 2 hours. After cooling the solution to room temperature and removal of the solvent under vacuum, 15 ml of heptane was added to the light yellow solid residue. The mixture was heated to reflux to dissolve the solid and then cooled to room temperature. Addition of 15 ml of pentane caused precipitation of a pale yellow solid which was filtered, washed twice with pentane and dried in vacuo yielding 1.20 g (78%) of the product (m.p. = 68-69°; m/e for P^+: 278.1663 ± 0.0014, experimental; 278.1660, calculated). For dipole moment measurements the compound was sublimed twice at 80° (0.01 torr).

$\underline{\text{P(NMeNMe)}_3\text{P=NPh, }\underline{\underline{10}}}$ A solution of 1.06 g (4.50 mmoles) of $\underline{3}$ and 0.49 ml (4.5 mmoles) of phenyl azide in 10 ml of benzene was heated to exactly 40° for 2 hours and then cooled to room temperature. Filtering the solution and removing the solvent under vacuum gave a white solid residue. Sublimation at 65° (0.01 torr) removed any unreacted $\underline{3}$ and some product in a ratio of 2:1 $\underline{10}$:$\underline{3}$ as determined by ^{1}H-NMR examination of the sublimate. The pure product could be obtained by continued sublimation at 100° (0.01 torr) which removed all the desired product and left any $\underline{11}$ behind as residue. In this manner 1.16 g of product (79%) was isolated even though the total yield of product was 86% as determined by ^{1}H-NMR integration of the sublimates and residue (m.p. = 123-125°; m/e for P^+: 327.1486 ± 0.0017, experimental; 327.1490, calculated).

$PhN{=}P(NMeNMe)_3P{=}NPh$, 11 This compound was prepared as described by Bermann and Van Wazer (22). It was recrystallized from boiling benzene in 50% yield (m.p. = 253°; lit., 76% yield, m.p. = 243-244° with decomposition).

$(Me_2N)_3P{=}NP(O)(OPh)_2$, 12 A solution of 1.90 ml (8.82 mmoles) of diphenylphosphoryl azide in 10 ml of toluene was added in 1 ml increments over 20 minutes to a solution of 1.63 ml (10.0 mmoles) of 1 in 10 ml of toluene at room temperature. Each addition to the colorless solution was accompanied by a yellow coloration and vigorous gas evolution. The solution became colorless as the gas evolution subsided. During the reaction period the solution temperature rose noticeably. After the addition was complete, the solvent was removed under vacuum leaving a clear yellow oil which changed to a white solid after being triturated with pentane and cooled to -78°. Recrystallization from a boiling 3:1 hexane-benzene solution yielded 2.19 g (60%) of the product (m.p. = 44-46°; m/e for P^+: 410.1621 ± 0.0021, experimental; 410.1637, calculated).

$MeC(CH_2NMe)_3P{=}NP(O)(OPh)_2$, 13 A solution composed of 1.00 ml (5.60 mmoles) of 2, 1.21 ml (5.61 mmoles) of diphenylphosphoryl azide and 10 ml of toluene was heated to 80° for 1 hour. After cooling the solution to room temperature, the addition of 30 ml of hexane caused precipitation of a white solid. The mixture was heated to dissolve the solid and then slowly cooled to -78°. The white solid was filtered, washed twice with pentane and dried *in vacuo* to yield 2.35 g (97%) of the product (m.p. = 99-101°; *m/e* for P^+: 434.1622 ± 0.0022, experimental; 434.1637, calculated).

$(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$, **14** A solution of 1.18 g (5.00 mmoles) of **3** and 2.16 ml (10.0 mmoles) of diphenylphosphoryl azide in 15 ml of toluene was heated to 80° for 2 hours. Cooling the solution to room temperature and then to -78° caused a white solid to precipitate. Recrystallization from ethyl acetate followed by several washings with hexane and drying *in vacuo* yielded 2.90 g (80%) of the product (m.p. = 118-119°; *m/e* for P^+: 730.1856 ± 0.0037, experimental; 730.1873, calculated).

$(Me_2N)_3P{=}NP(O)Ph_2$, **15** The solution formed by adding 0.81 ml (5.0 mmoles) of **1** and 0.98 ml (5.0 mmoles) of diphenylphosphinyl azide to 20 ml of benzene at room temperature was refluxed for 3 hours even though gas evolution, which began upon heating, subsided after about 5 minutes. The clear solution was cooled to room temperature and the solvent was removed under vacuum. After adding 30 ml of heptane to the yellow oil remaining, the mixture was refluxed for 1 minute. Upon cooling to 0° the white crystalline product (0.64 g, 35% yield) precipitated from the solution (m.p. = 77-78°; m/e for P^+: 378.1742 ± 0.0019, experimental; 378.1738, calculated).

$MeC(CH_2NMe)_3P{=}NP(O)Ph_2$, 16 A solution composed of 0.89 ml (5.0 mmoles) of 2, 0.98 ml (5.0 mmoles) of diphenylphosphinyl azide and 15 ml of toluene was heated to 80° for 3 hours. The precipitate obtained by slowly cooling the solution to -78° was collected and recrystallized by cooling a boiling 10:1 pentane-toluene solution to -10°. The off-white solid was filtered, washed with pentane and dried *in vacuo* to yield 1.69 g (85%) of the product (m.p. = 136-138°; m/e for P^+: 402.1741 ± 0.0020, experimental; 402.1738, calculated).

$Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$, 17 This compound was prepared using the method of Bermann and Van Wazer (22) and was recrystallized in 59% yield from a boiling 2:1 toluene-ethyl acetate solution (m.p. = 283° (decomposition); lit., 69% yield, m.p. = 285-286° with decomposition (22)).

$(Me_2N)_3P{:}BH_3$, 18 This compound was a gift from Mr. R. L. Kolpa who prepared it by the method of Reetz and Katlafsky (92).

$MeC(CH_2NMe)P{:}BH_3$, 19 While this compound was first reported by Laube *et al.* (89) by reacting 2 and B_2H_6 at low temperatures in ether solution, the present work took advantage of the ready availability of THF:BH_3 as a convenient source of BH_3.

To a solution of 0.54 ml (3.0 mmoles) of 2 in 25 ml of ether was added 3.0 ml of a 1.0 *M* THF:BH_3 solution dropwise at room temperature. The clear colorless solution became turbid and was stirred for 10 hours after which the volatiles were removed and the residue dried *in vacuo*. Sublimation at 80° (0.01 torr) gave 0.52 g (87%) of the white solid (m.p. = 76-77°). The compound was further characterized by its ^1H- and ^{31}P-NMR spectra.

$H_3B{:}P(NMeNMe)_3P{:}BH_3$, 20 This compound was synthesized by the method of Goetze *et al.* (28) from 3 and B_2H_6 in toluene at -78°.

$H_3B{:}P\overset{NMe}{\overbrace{(NMeNMe)_2}}P{:}BH_3$, 21 In the same manner described above for 20, 0.37 ml (2.0 mmoles) of 4 was dissolved in 5 ml of toluene which had been flash distilled from Red-Al and the solution was outgassed. Excess diborane was condensed onto the sample at -196° and the mixture was equilibrated at -78° for 20 minutes. The volatiles were then removed under vacuum and the white solid was collected and characterized by ^1H- and ^{31}P-NMR spectroscopy.

$MeC(CH_2NMe)_3P{=}O$, 23 This compound was synthesized by treating 3.60 ml (20.2 mmoles) of the triamine precursor of 2 and 8.43 ml (60.5 mmoles) of NEt_3 in 40 ml of dry ether at 0°

with a solution of 1.84 ml (20.0 mmoles) of $POCl_3$ in 20 ml of dry ether. After addition, the mixture was stirred for 6 hours at room temperature and then filtered to remove amine hydrochloride. The clear filtrate was evaporated to a white residue which was sublimed at 60° (0.01 torr) to give 1.95 g (48%) of product. This compound was synthesized by Laube et al. (89) in 26% yield without the presence of NEt_3 in the reaction.

$P(NMeNMe)_3P{=}O$, 24 A solution of 2.50 g (10.6 mmoles) of 3 in 40 ml of freshly dried acetonitrile was made up under nitrogen at room temperature. This was then cooled in a carbon tetrachloride/dry ice bath which caused considerable precipitation. With vigorous stirring, 543 µl (10.6 mmoles) of Br_2 was added dropwise to the solution over a period of 30 minutes. Each drop of bromine produced a bright yellow precipitate which dissolved in the acetonitrile. The mixture was then stirred at -23° for 15 minutes after all the bromine had been added. Quickly adding 191 µl of twice distilled water to the flask via syringe caused the yellow coloration to disappear. Four minutes after adding the water, 2.95 ml (21.2 mmoles) of triethylamine was added which caused the precipitation of a copious amount of white solid.

The mixture was warmed to room temperature, filtered and the volatiles were removed in vacuo. The solid residue was then sublimed at 110° (0.01 torr) for 12 hours and this white sublimate, a mixture of the product and some triethylammonium bromide, was resublimed at 70° (0.01 torr) for 6 hours.

The white sublimate so isolated gave 0.80 g (30%) of 24 (m.p. = 210-213°; m/e for P^+: 252.1018 ± 0.0013, experimental; 252.1018, calculated).

$O=P(NMeNMe)_3P=O$, 25 This compound was prepared by alcoholic H_2O_2 oxidation of 3 using the method of Goetze *et al.* (28).

$MeC(CH_2NMe)_3P=S$, 27 This compound was prepared by the method of Laube *et al.* (89).

$(Me_2N)_3P=Se$, 29 This compound was prepared by the method of Räuchle *et al.* (93).

$MeC(CH_2NMe)_3P=Se$, 30 A mixture of 1.00 ml (5.60 mmoles) of 2 and 0.94 g (12 mg-atoms) of red selenium in 30 ml of benzene was heated at 70° for 10 hours. The mixture was then cooled to room temperature and filtered to remove unreacted selenium. The solvent was removed from the filtrate under vacuum and the residue was sublimed at 60° (0.01 torr) to give 1.14 g (77%) of product (m.p. = 118-120°; m/e for P^+: 267.0404 ± 0.0017, experimental; 267.0403, calculated).

$Se=P(NMeNMe)_3P=Se$, 31 This compound was prepared from 3 and red selenium in refluxing benzene by the method of Goetze *et al.* (28). It was quantitatively isolated in pure form by Soxhlet extraction of the reaction residue for

16 hours with $CHCl_3$ under a nitrogen atmosphere. The product precipitated out of the solvent flask as fine white crystals.

$(Me_2N)_3P{\cdot}Br_2$, 32 This compound was prepared from 1 and Br_2 by the method of Nöth and Vetter (94).

$MeC(CH_2NMe)_3P{\cdot}Br_2$, 33 A solution of 1.00 ml (5.60 mmoles) of 2 in 20 ml of CCl_4 was cooled in an ice bath and 5.6 ml of a 1.0 M Br_2/CCl_4 solution (5.6 mmoles Br_2) was added dropwise with vigorous stirring. The bromine color was immediately discharged and a light yellow precipitate formed. After stirring for 10 minutes following the addition the solid was filtered off, washed twice with cold ether and dried *in vacuo* to give 1.92 g (100%) of cream colored product (m.p. = 163° (decomposition)). The product was further characterized by ^1H- and ^{31}P-NMR spectroscopy.

$P(NMeNMe)_3P{\cdot}Br_2$, 34 To a solution of 1.49 g (6.29 mmoles) of 3 in 25 ml of CCl_4 was added 6.2 ml of a 1.0 M Br_2/CCl_4 solution (6.2 mmoles Br_2) at 0°. As each drop of bromine solution was added its color was discharged and a bright yellow solid formed. The mixture was stirred for 10 minutes after all the bromine had been added and then the solid was filtered off, washed three times with cold ether and dried *in vacuo*. The cream colored solid weighed 2.35 g (96%) and was characterized by its ^1H- and ^{31}P-NMR spectra.

$[(Me_2N)_3P\text{-}CPh_3]BF_4$, 35 This phosphonium salt was prepared by the method of Dimroth and Nürrenbach (95).

$[MeC(CH_2NMe)_3P\text{-}CPh_3]BF_4$, 36 To a solution of 1.54 g (4.65 mmoles) of triphenylmethyl fluoroborate in 20 ml of CH_2Cl_2 was added 0.83 ml (4.7 mmoles) of 2 dropwise at room temperature. The initially dark turbid solution became a clear golden color. After stirring for 1/2 hour addition of 50 ml of ether caused precipitation of a tan solid. This was filtered, washed three times with ether and dried *in vacuo* to give 2.09 g (87%) of product which was characterized by its ^1H- and ^{31}P-NMR spectra.

$O{=}P(NMeNMe)_3P{=}NPh$, 37 A solution of 0.58 g (1.8 mmoles) of 10 in 15 ml of absolute ethanol was treated with 2 ml of 30% aqueous H_2O_2 at room temperature. After stirring for 20 minutes the flask was cooled to -10° which caused white crystals to form. These were recrystallized in 49% yield from hexane (m.p. = 222°; *m/e* for P^+: 343.1433 ± 0.0017, experimental; 343.1439, calculated).

$S{=}P(NMeNMe)_3P{=}NPh$, 38 A mixture of 0.475 g (1.45 mmoles) of 10 and 0.070 g (2.2 mg-atoms, 50% excess) of sublimed sulfur in 15 ml of toluene was heated to reflux for 3 hours. The hot solution was decanted off of the rubbery unreacted sulfur and cooled to room temperature whereupon 50 ml of pentane was added to cause precipitation. The precipitate was recrystallized from hexane to give 0.275 g (53%) of the white product (m.p. = 224°; *m/e* for P^+: 359.1198 ± 0.0018, experimental; 359.1211, calculated).

<u>$Se{=}P(NMeNMe)_3P{=}NPh$, 39</u> A mixture of 0.7036 g (2.151 mmoles) of <u>10</u> and 0.18 g (2.3 mg-atoms) of red selenium in 10 ml of dry benzene was refluxed for 17 hours and then filtered while hot. Upon cooling, a solid crystallized out which was washed with ether and dried *in vacuo* to give 0.6652 g (76%) of product (m.p. = 228-230°; *m/e* for P^+: 407.0585 ± 0.0017, experimental; 407.0655, calculated).

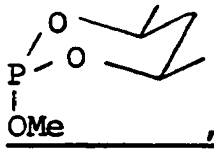
<u>$H_3B{:}P(NMeNMe)_3P{=}NPh$, 40</u> To a solution of 0.615 g (1.88 mmoles) of <u>10</u> in 25 ml of tetrahydrofuran was added 3.0 ml of 1 *M* $THF{:}BH_3$ solution *via* syringe. After stirring for 1 hour at room temperature, all volatiles were removed *in vacuo* to leave a white residue. This was taken up in 25 ml of fresh THF and filtered into 150 ml of pentane which caused a white solid to precipitate. This mixture was cooled to -78° and the solid was filtered off and dried *in vacuo* to give 0.370 g (58%) of white product (m.p. = 148-150° (decomposition); *m/e* for P^+: 341.1822 ± 0.0017, experimental; 341.1818, calculated).

<u>$S{=}P(NMeNMe)_3P{=}O$, 41</u> A mixture of 0.198 g (0.784 mmoles) of <u>24</u> and 0.0467 g (1.46 mg-atoms) of sublimed sulfur in 10 ml of toluene was refluxed for 8 hours. The solution was decanted off of the unreacted sulfur and cooled to room temperature whereupon 50 ml of pentane was added to cause precipitation. After cooling the mixture to -78°, the solid was filtered, washed with pentane and dried *in vacuo* to give

0.1247 g (56%) of pure white product subliming at 260° without melting (m/e for P$^+$: 284.0745 ± 0.0014, experimental; 284.0738, calculated).

Se=P(NMeNMe)$_3$P=O, 42   A mixture composed of 0.46 g (1.8 mmoles) of 24 and 0.20 g (2.6 mg-atoms) of red selenium in 15 ml of toluene was heated to 80° for 24 hours. The hot mixture was filtered and the residue was extracted with 10 ml of $CHCl_3$ and filtered. White crystals formed in the toluene filtrate as it cooled and the $CHCl_3$ was removed under vacuum to give a white residue. The two solids were combined and recrystallized from 15 ml of boiling toluene at -78° to give 0.47 g (83%) of the white product which sublimed at 255° without melting (m/e for P$^+$: 332.006 ± 0.020, experimental; 332.0182, calculated).

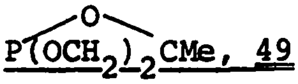
H_3B:P(NMeNMe)$_3$P=O, 43   The mixture formed by adding 1 ml of 1 M THF:BH_3 to a solution of 0.100 g (0.400 mmoles) of 24 in 10 ml of THF was stirred at room temperature for 1 hour. All volatiles were then removed *in vacuo*, 10 ml of fresh THF added and the solution filtered into 50 ml of pentane. This was cooled to -78° and the precipitate obtained was dried *in vacuo* to give 0.0810 g (76%) of the white product (m.p. = 237° (decomposition); m/e for P$^+$: 266.1344 ± 0.0013, experimental; 266.1345, calculated).



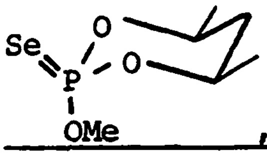
, 47   This monocyclic phosphite was

prepared by the method of White et al. (96).

$MeC(CH_2O)_3P$, 48 This bicyclic compound was synthesized by the method of Verkade et al. (97).

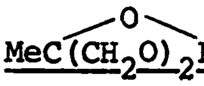

$\overset{O}{P(OCH_2)_2CMe}$, 49 This bicyclic compound was made using the method of Vande Griend et al. (80).

$(MeO)_3P{=}Se$, 50 This compound was synthesized from 46 and red selenium by the method of Nuretdinov and Grechkin (98).



, 51 A mixture of 2.00 g (12.2 mmoles) of phosphite 47 and 1.60 g (20.3 mg-atoms) of red selenium in 15 ml of toluene was heated to 80° for 18 hours. The hot mixture was filtered, cooled to room temperature and the solvent removed under vacuum. The residue was recrystallized from hexane at -78° to give 2.46 g (83%) of product (m.p. = 68-70°; m/e for P^+: 243.1019 ± 0.0016, experimental; 243.1025, calculated).

$MeC(CH_2O)_3P{=}Se$, 52 A mixture of 4.74 g (32.0 mmoles) of freshly sublimed 48 and 3.80 g (47.0 mg-atoms) of red selenium in 25 ml of toluene was heated at 80° for 10 hours. The hot mixture was filtered and the solid residue was extracted with 150 ml of toluene in a Soxhlet apparatus for 2 days under nitrogen. The solid which precipitated upon cooling to room temperature was recrystallized from 300 ml of boiling toluene, washed with two 30 ml portions of hexane and dried *in vacuo* to give 6.36 g (88%) of white product (m.p. = 246-248°; *m/e* for P^+: 227.9454 ± 0.0014, experimental; 227.9454, calculated).


$\mathrm{MeC(CH_2O)_2P{=}Se}$, 53 A mixture of 0.60 ml (5.8 mmoles) of 49 and 0.86 g (11 mg-atoms) of red selenium in 15 ml of toluene was heated at 75° for 10 hours. The mixture was then cooled to room temperature and filtered. The filtrate was cooled to -78° and the product crystallized to give 0.78 g (63%) of white solid (m.p. = 74-76°). This compound is very unstable to atmospheric moisture and also decomposed slowly at room temperature under nitrogen, both processes giving red selenium as a product (*m/e* for P^+: 213.9289 ± 0.0014, experimental; 213.9297, calculated).

RESULTS AND DISCUSSION

Due to the large number of compounds discussed in this thesis, Table 3 has been included so the reader may have ready access to structural formulae. The various compounds have been grouped to keep common functional derivatives (1-4, 46-49, etc.) and structurally similar compounds (37-43) together as much as possible.

Staudinger Reactions of Aminophosphines

The question of rotational isomerism

As stated in the Introduction, it was of interest to reinvestigate the ^{31}P-NMR spectrum of 17 in order to determine whether the geometrical isomerization hypothesized by Bermann and Van Wazer (22) could be substantiated and to see what effect the apparent basicity differences of 1, 2 and 3 would have on their behavior in the Staudinger reaction.

One way to test the geometrical isomerization hypothesis was to study a simpler analogue wherein the effect of rotational restriction about the P=N bond could be readily detected. Compound 9 was chosen because its rigid cage structure (90) would show non-equivalence of the NMe groups in the proton NMR spectrum if the P=N bond rotation could be sufficiently slowed. The proton NMR spectra of 2 and its derivatives consist of two doublets and a singlet. The NMe

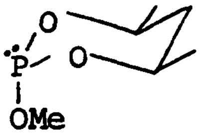
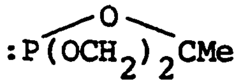
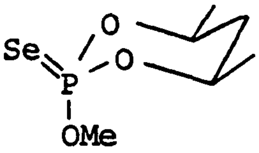
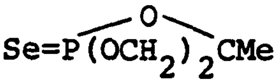
Table 3. A listing of the organophosphorus and organoarsenic compounds discussed in this work

Compound	Number
$(Me_2N)_3P:$	1
$MeC(CH_2NMe)_3P:$	2
$:P(NMeNMe)_3P:$	3
 $:\overbrace{P(NMeNMe)_2P}^{NMe}:$	4
$(Me_2N)_3P{=}N{-}N{=}NPh$	5
$MeC(CH_2NMe)_3P{=}N{-}N{=}NPh$	6
$:P(NMeNMe)_3P{=}N{-}N{=}NPh$	7
$(Me_2N)_3P{=}NPh$	8
$MeC(CH_2NMe)_3P{=}NPh$	9
$:P(NMeNMe)_3P{=}NPh$	10
$PhN{=}P(NMeNMe)_3P{=}NPh$	11
$(Me_2N)_3P{=}NP(O)(OPh)_2$	12
$MeC(CH_2NMe)_3P{=}NP(O)(OPh)_2$	13
$(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$	14
$(Me_2N)_3P{=}NP(O)Ph_2$	15
$MeC(CH_2NMe)_3P{=}NP(O)Ph_2$	16
$Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$	17
$(Me_2N)_3P{-}BH_3$	18
$MeC(CH_2NMe)_3P{-}BH_3$	19

Table 3. (continued)

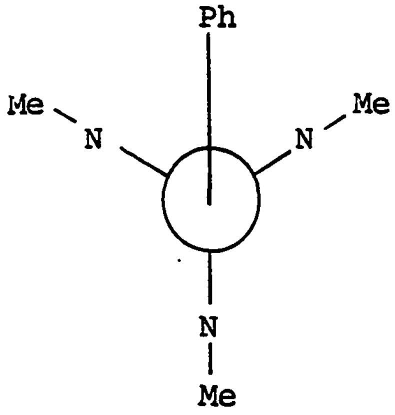
Compound	Number
$H_3B\text{-}P(NMeNMe)_3P\text{-}BH_3$	20
 $H_3B\text{-}\overbrace{P(NMeNMe)_2P}^{NMe}\text{-}BH_3$	21
$(Me_2N)_3P{=}O$	22
$MeC(CH_2NMe)_3P{=}O$	23
$:P(NMeNMe)_3P{=}O$	24
$O{=}P(NMeNMe)_3P{=}O$	25
$(Me_2N)_3P{=}S$	26
$MeC(CH_2NMe)_3P{=}S$	27
$S{=}P(NMeNMe)_3P{=}S$	28
$(Me_2N)_3P{=}Se$	29
$MeC(CH_2NMe)_3P{=}Se$	30
$Se{=}P(NMeNMe)_3P{=}Se$	31
$[(Me_2N)_3P\text{-}Br]Br$	32
$[MeC(CH_2NMe)_3P\text{-}Br]Br$	33
$[:P(NMeNMe)_3P\text{-}Br]Br$	34
$[(Me_2N)_3P\text{-}CPh_3]BF_4$	35
$[MeC(CH_2NMe)_3P\text{-}CPh_3]BF_4$	36
$O{=}P(NMeNMe)_3P{=}NPh$	37
$S{=}P(NMeNMe)_3P{=}NPh$	38
$Se{=}P(NMeNMe)_3P{=}NPh$	39
$H_3B\text{-}P(NMeNMe)_3P{=}NPh$	40

Table 3. (continued)

Compound	Number
$S{=}P(NMeNMe)_3P{=}O$	41
$Se{=}P(NMeNMe)_3P{=}O$	42
$H_3B{-}P(NMeNMe)_3P{=}O$	43
$[Br{-}P(NMeNMe)_3P{=}NPh]Br$	44
$[Br{-}P(NMeNMe)_3P{=}O]Br$	45
$:P(OMe)_3$	46
	47
$:P(OCH_2)_3CMe$	48
 $:P(OCH_2)_2(O)CMe$	49
$Se{=}P(OMe)_3$	50
	51
$Se{=}P(OCH_2)_3CMe$	52
 $Se{=}P(OCH_2)_2(O)CMe$	53
$:As(NMe_2)_3$	54
$:As(NMeCH_2)_3CMe$	55

and NCH_2 protons each appear as doublets caused by ^3JPNCH coupling, the magnitude of which depends on the exocyclic group on phosphorus. In room temperature spectra all of the NMe groups are equivalent as are all the NCH_2 groups. The bridgehead methyl group is too far away from phosphorus to show any coupling effect and appears as a singlet.

If the P=N bond rotation were stopped or sufficiently slowed, the expected lowest energy conformation would most likely contain the phenyl group in one of the three-fold symmetry planes of the cage so as to bisect the angle between two NMe groups and thus be trans to the third NMe group. Such an orientation (shown below) would cause the NMe groups to become nonequivalent on the NMR time scale. While this would not necessarily lead to different values of ^3JPNCH it almost certainly would cause a profound effect in the NMe group chemical shifts as two would now be in close proximity to the shielding cone of the phenyl group and should appear upfield relative to the remaining NMe group. Two sets of



doublets in a 2 to 1 ratio would then be observed for the NMe resonances.

A sample of 9 was prepared in $CFCl_3$ and the variable temperature proton NMR spectra for the temperature range +30 to -100° were recorded. Although the peaks broadened considerably at low temperature there was never any indication of NMe nonequivalence. After this experiment was performed, a similar result obtained by Goldwhite et al. (26) came to our attention. Their variable temperature study was done on a number of acyclic $\geqslant$P=NMe derivatives in which the decreased steric bulk of the Me group and the lack of a shielding cone associated with this group could account for the inability of Goldwhite et al. to observe nonequivalence in the other substituents on phosphorus. The possibility that these substituents could rotate out of the way of the =NMe group might also be a factor. Clearly these two effects can not be operative in 9.

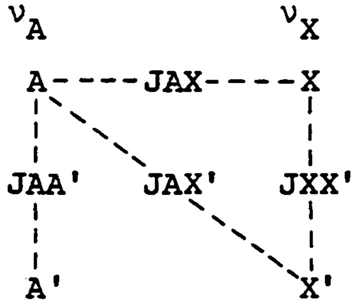
Because the steric interaction of the phenyl group in 9 with the cage NMe groups might be similar to that of the $Ph_2P=O$ groups in 17, the geometrical isomerism hypothesis seemed unlikely. Assuming this to be true, an attractive alternate explanation of the observed ^{31}P-NMR spectrum of 17 was to describe it as an example of an AA'XX' spectrum (99, 100). Such a system is characterized by the four coupling constants JAA', JXX', JAX and JAX' (JAX = JA'X' and

JAX' = JA'X) as depicted below. In such a system all four

$Ph_2(O)P{-}N{=}P(NMeNMe)_3P{=}N{-}P(O)Ph_2$

X A A' X'

nuclei are magnetically nonequivalent and form two pairs of chemically equivalent nuclei separated from each other by a chemical shift which is large compared with the associated coupling constants. If the chemical shifts are represented as ν_A and ν_X then the system can be represented diagrammatically as shown.



9. K = JXX' + JAA'

10. L = JAX - JAX'

11. M = JXX' - JAA'

12. N = JAX + JAX'

The quantities K, L, M and N are useful in calculating the transition energies of the spectrum. After appropriate factorization of the symmetrized spin functions for the system (99) the frequencies of the allowed transitions and their relative intensities can be calculated and the explicit expressions for these are shown in Table 4. One needs only to consider the A transitions (Figure 1) since the X part of

Table 4. Transition energies for the A branch of an AA'XX' system relative to ν_A

Transition Number[a]	Transition energy[b]	Relative Intensity[c]
1 2	$1/2\,N$	2
3 4	$-1/2\,N$	2
5	$1/2K + 1/2(K^2 + L^2)^{1/2}$	$\sin^2 \Theta_s$
6	$-1/2K + 1/2(K^2 + L^2)^{1/2}$	$\cos^2 \Theta_s$
7	$1/2K - 1/2(K^2 + L^2)^{1/2}$	$\cos^2 \Theta_s$
8	$-1/2K - 1/2(K^2 + L^2)^{1/2}$	$\sin^2 \Theta_s$
9	$1/2M + 1/2(M^2 + L^2)^{1/2}$	$\sin^2 \Theta_a$
10	$-1/2M + 1/2(M^2 + L^2)^{1/2}$	$\cos^2 \Theta_a$
11	$1/2M - 1/2(M^2 + L^2)^{1/2}$	$\cos^2 \Theta_a$
12	$-1/2M - 1/2(M^2 + L^2)^{1/2}$	$\sin^2 \Theta_a$

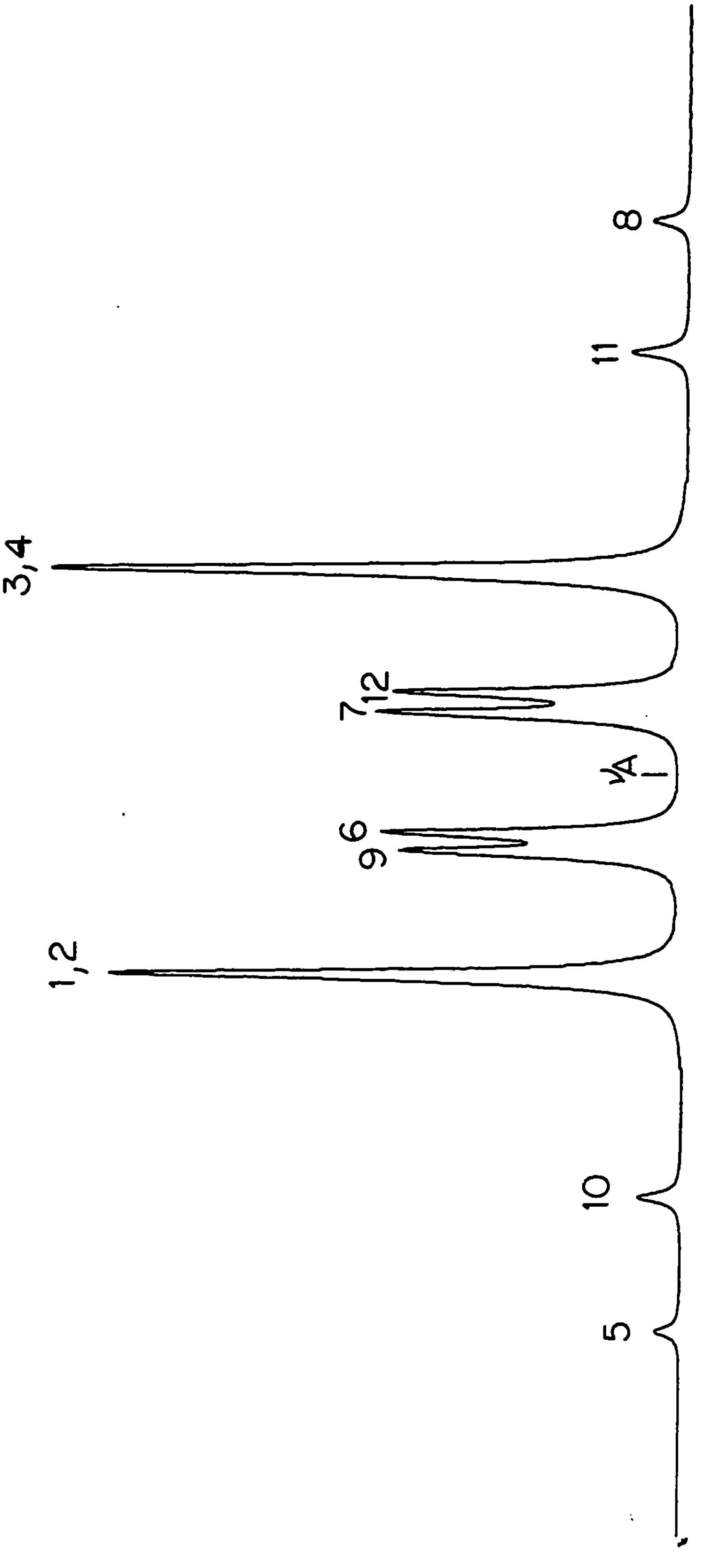
[a] Refer to Figure 1.

[b] See text for definitions of K, L, M and N.

[c] $\cos 2\Theta_s : \sin 2\Theta_s : 1 = K : L : (K^2 + L^2)^{1/2}$

$\cos 2\Theta_a : \sin 2\Theta_a : 1 = M : L : (M^2 + L^2)^{1/2}$

Figure 1. The A branch of an AA'XX' spectrum having JAA' = 110 Hz, JAX = JA'X' = 100 Hz, JA'X = JAX' = 5 Hz and JXX' = 20 Hz. The spectrum was generated using the program ITRCAL.


8
11
3,4
7,12
ν_A
9,6
1,2
10
5

the spectrum is identical. In each branch of the spectrum there are 12 possible transitions, but four of them form two doubly degenerate sets (1, 2 and 3, 4) so that only 10 distinct transitions can ever be observed. Each part of the spectrum is characterized by the presence of two strong absorption bands (transitions 1, 2 and 3, 4) separated by N = JAX + JAX' and centered about the resonance frequency ν_A and two pairs of symmetrical quartets (transitions 5, 6, 7, 8 and 10, 9, 12, 11) centered about ν_A with the components of each increasing in intensity toward ν_A.

Through the use of modern computer programs it is now possible to generate theoretical spectra and match them to experimentally obtained spectra. The particular program used in this work is ITRCAL (84) which was described in the Experimental section. Using this program one can iteratively fit calculated spectra to experimental spectra using a least squares criterion for systems up to six nuclei of spin 1/2 while simultaneously monitoring an oscilloscope trace of the spectra. One need only input reasonably accurate values of the chemical shifts and coupling constants. To obtain reasonable values of the P-P coupling constants in <u>17</u>, various derivatives of <u>1</u> and <u>2</u> were synthesized and their ^{31}P-NMR are reported in Table 5 along with other derivatives synthesized for comparison.

Table 5. ^{31}P-NMR chemical shifts and P-P coupling constants for some derivatives of $P(NMe_2)_3$ and $P(NMeCH_2)_3CMe$

Compound		^{31}P Chemical Shifts[a]		Coupling Constant[b]
		$\delta(P(N<)_3)$	$\delta(P(O)N)$	$^2J_{PP}$
<u>1</u>	$(Me_2N)_3P$	-122.0		
<u>22</u>	$(Me_2N)_3P=O$	- 24.8		
<u>5</u>	$(Me_2N)_3P=N_3Ph$	-42.8(-41.2)[c]		
<u>8</u>	$(Me_2N)_3P=NPh$	- 19.5		
<u>12</u>	$(Me_2N)_3P=NP(O)(OPh)_2$	- 23.5	+11.3	64.5
<u>15</u>	$(Me_2N)_3P=NP(O)(Ph_2)$	- 25.1	- 9.2	22.2
<u>2</u>	$MeC(CH_2NMe)_3P$	- 83.5		
<u>23</u>	$MeC(CH_2NMe)_3P=O$	- 18.2		
<u>6</u>	$MeC(CH_2NMe)_3P=N_3Ph$	- 33.7		
<u>9</u>	$MeC(CH_2NMe)_3P=NPh$	- 11.5		

13	$MeC(CH_2NMe)_3P{=}NP(O)(OPh)_2$	-13.8	+12.0	74.4
16	$Me(CH_2NMe)_3P{=}NP(O)(Ph_2)$	-14.6	-10.9	24.4

---

[a] In ppm relative to 85% H_3PO_4.

[b] Values precise to ±1.1 Hz.

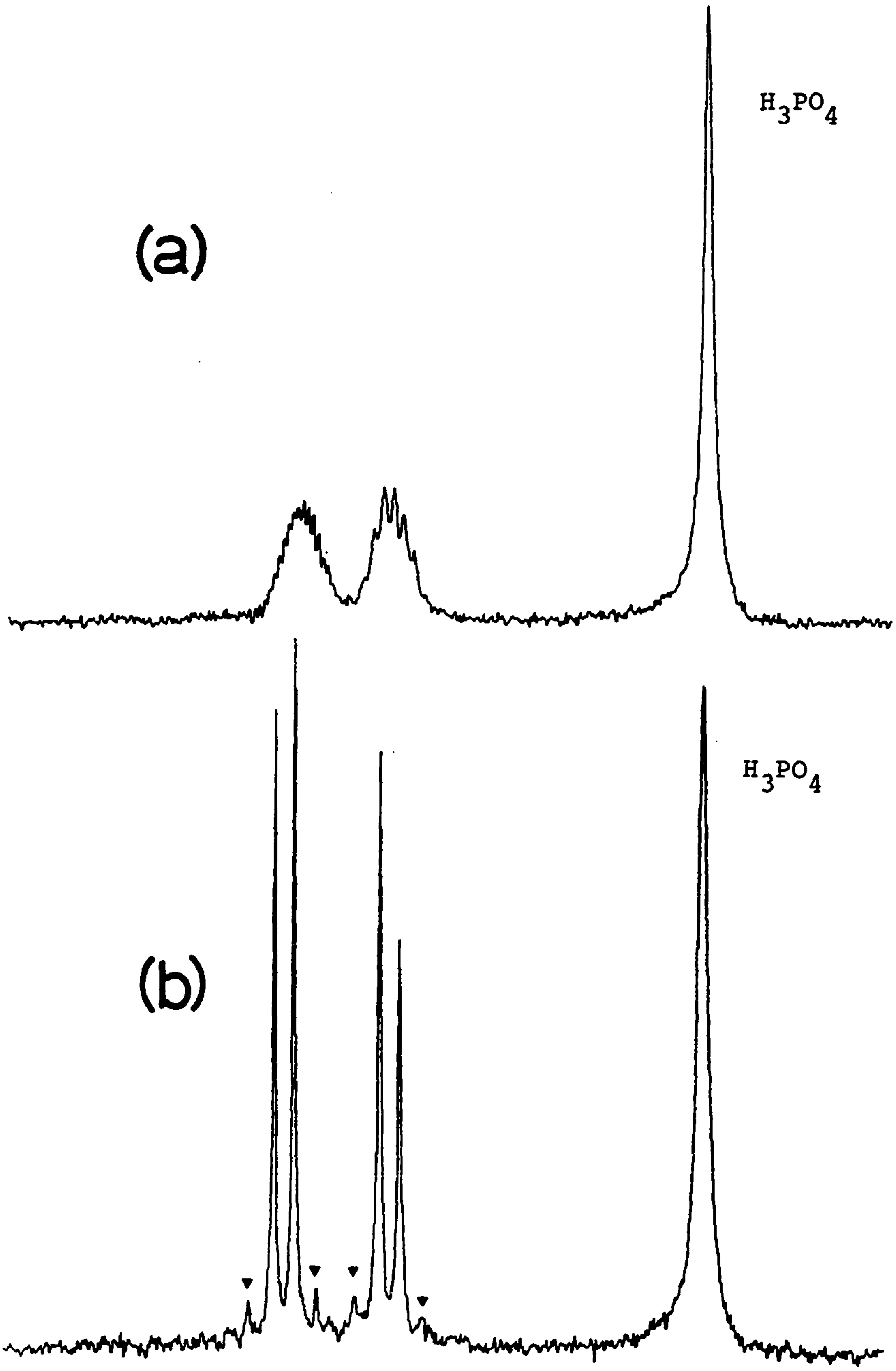
[c] Reference 27.

The upfield shift of the ^{31}P resonances from the aminophosphines 1 and 2 to the corresponding aminophosphine oxides is also seen in the phosphinimines produced by the Staudinger reaction and this is expected upon oxidation of phosphorus. The assignments of chemical shifts in 12, 13, 15 and 16 were based mainly on the fewer proton couplings expected in the proton-undecoupled ^{31}P-NMR spectra of the $\geq$P(O)N phosphorus (there being at most only four protons within a distance of three bonds) compared to those of the $(\geq N)_3P$ phosphorus (which in all cases is only three bonds removed from at least nine equivalent protons). Figure 2a is illustrative of this point. The higher field multiplet obviously has fewer couplings than the lower field multiplet and so is assigned to the $\geq$P(O)N phosphorus. The proton decoupled spectrum shown in Figure 2b readily affords ^{2}JPP by inspection.

The expected constancy of δP for the $\geq$P(O)N phosphorus in the free azides and the phosphinimines was of aid in verifying the assignments as was the expectation that $\delta(P(N\leq)_3)$ would not change appreciably among the various phosphinimine derivatives for a given aminophosphine. These two expectations are reasonably fulfilled in that $\delta(\geq P(O)N)$ remains very close to the +10.2 ppm resonance of $(PhO)_2P(O)N_3$ in its phosphinimines. However, $\delta(\geq P(O)N)$ is shifted upfield by about 20 ppm from the -30.0 ppm resonance of

Figure 2a. Proton undecoupled ^{31}P-NMR spectrum of $MeC(CH_2NMe)_3P{=}NP(O)Ph_2$.

Figure 2b. Proton decoupled ^{31}P-NMR spectrum of $MeC(CH_2NMe)_3P{=}NP(O)Ph_2$. The peaks marked with ▼ are spinning sidebands.


(a)
H_3PO_4
(b)
H_3PO_4

$Ph_2P(O)N_3$ in its phosphinimines. Fortunately in the latter compounds, the constancy of $\delta(P(N\equiv)_3)$ in the phosphinimines (regardless of the exocyclic group) enabled ready assignment of the resonances.

The magnitude of ^2JPP for 15 and 16 (22.2 and 24.4 Hz) was inconsistent with the ^2JPP value of 10.7 Hz proposed for compound 17 on the basis of geometrical isomerization (22). Thus armed with a value for JAX (=JA'X') it is now necessary to consider JAX' (=JA'X), JAA' and JXX'. It was expected that JXX' (a seven bond coupling) and JAX' (=JA'X) (a five bond coupling) would be nonobserved (i.e. set equal to zero in the calculation) owing to the distances involved. The value of JAA' is a different matter as it is only a three bond coupling and must be appreciable in order to give the more complex spectra seen in Figures 3a and 4a compared to the first order spectrum in Figure 2b. Moreover, the shape of the proton spectra for derivatives of 3 has been interpreted to be indicative of substantial coupling between the two phosphorus nuclei (31, 32). The 140 Hz coupling observed earlier by Bertrand et al. (44) for $O{=}P(OCH_2)_3P{=}O$ was taken to approximate JAA' in the calculation.

The results of the calculations for compounds 14 and 17 are given in Table 6 along with some parameters from other derivatives of 3. The calculated and experimental spectra for 14 and 17 are shown in Figures 3a, b and 4a, b, respectively.

Figure 3a. Experimentally obtained proton decoupled ^{31}P-NMR spectrum of $(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$. The peaks marked with ▼ are spinning sidebands.

Figure 3b. Calculated proton decoupled ^{31}P-NMR spectrum of $(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$. This spectrum was generated using ITRCAL.

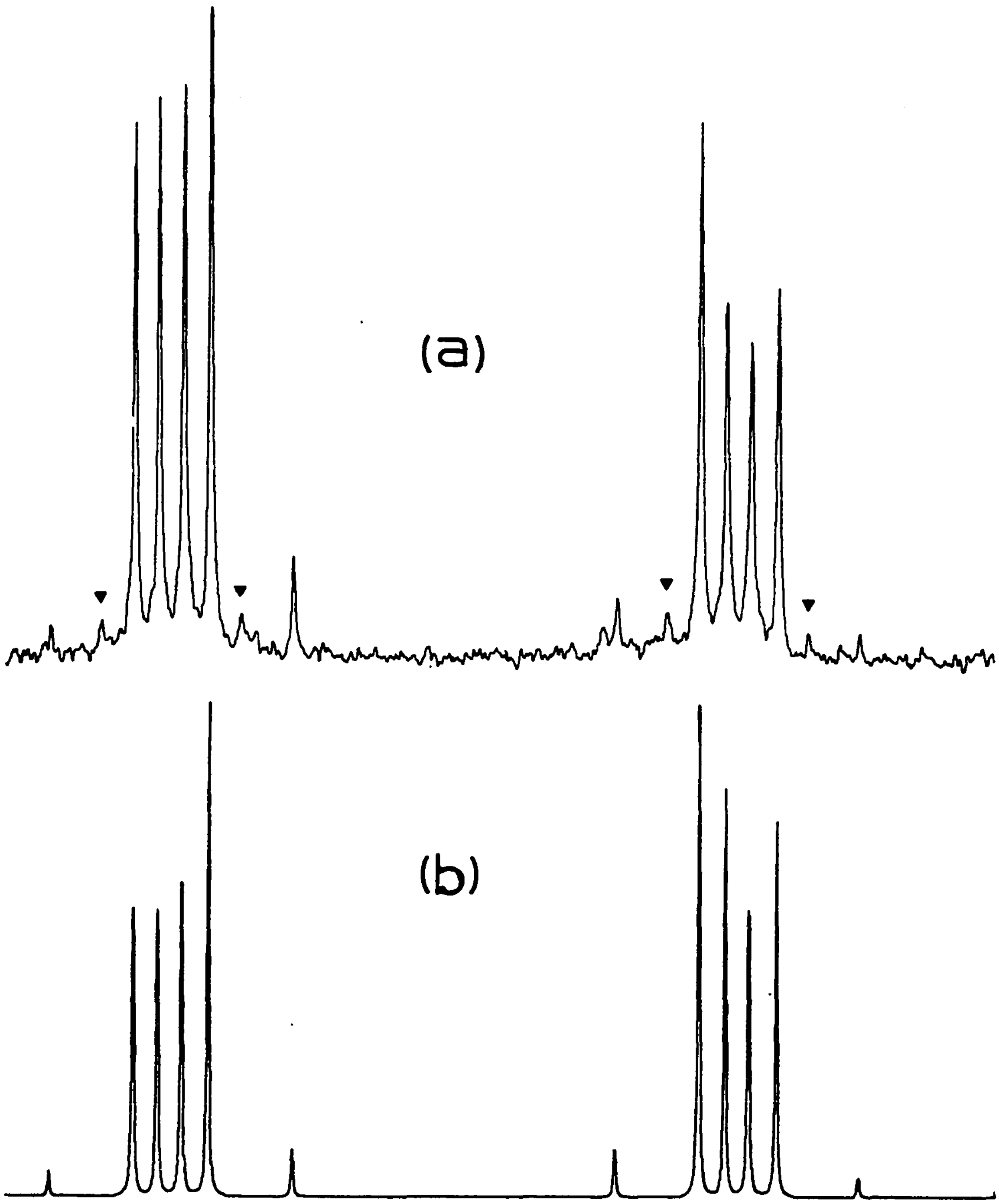
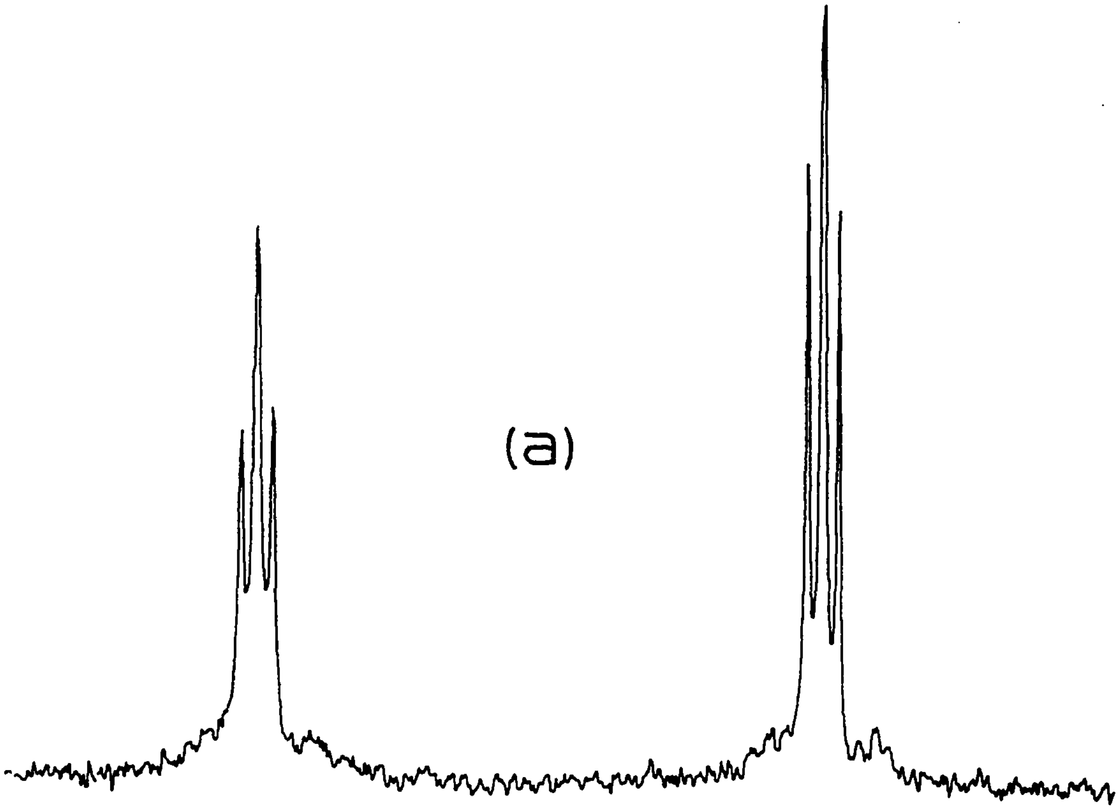

(a)
(b)

Figure 4a. Experimentally obtained proton decoupled ^{31}P-NMR spectrum of $Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$.

Figure 4b. ITRCAL-generated proton decoupled ^{31}P-NMR spectrum of $Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$. Note the very weak innermost peaks.


(a)

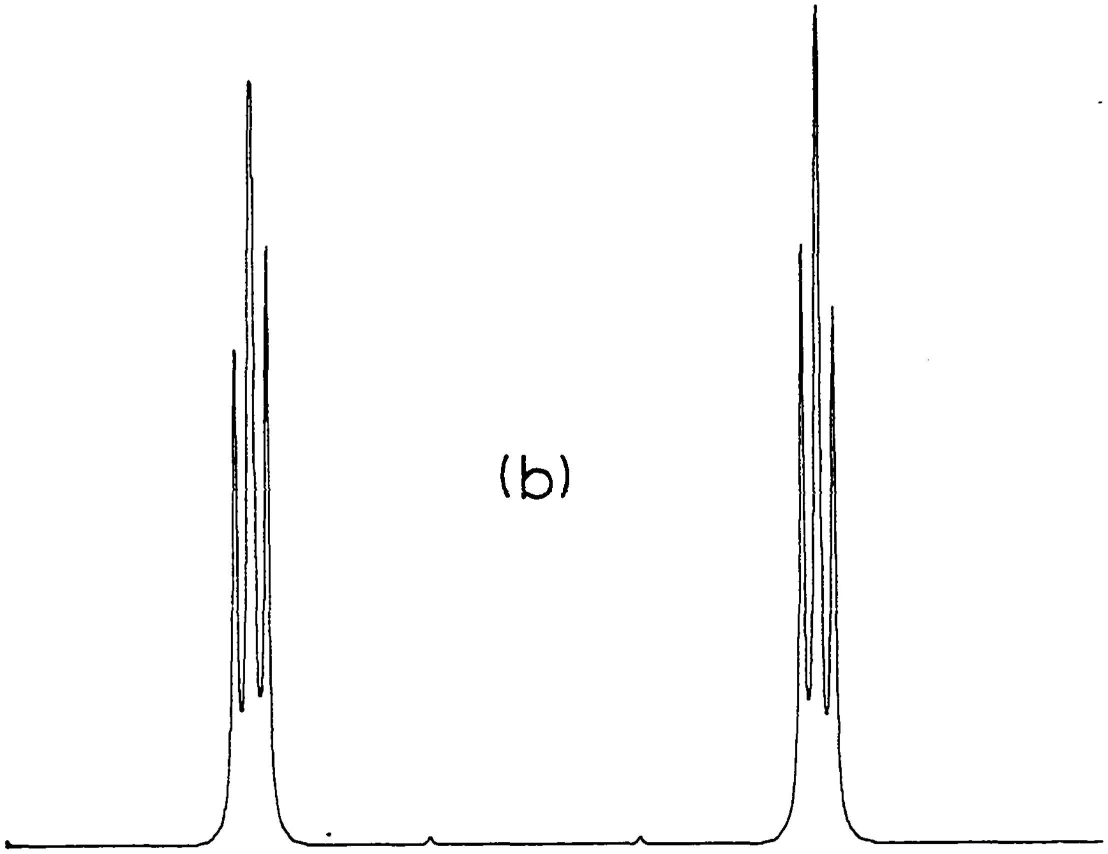

(b)

Table 6. ^{31}P-NMR chemical shifts and P-P coupling constants for some derivatives of $P(NMeNMe)_3P$

	Compound	Chemical shift[a]		Coupling constant[b]	
		$\delta(P(N<)_3)$	$\delta(P(O)N)$	$^2J_{PP}$	$^3J_{PP}$
<u>3</u>	$:P(NMeNMe)_3P:$	-107.4	-	-	32.0[c]
<u>7</u>	$:P(NMeNMe)_3P{=}N_3Ph$	-[d]	-	-	74.4
<u>25</u>	$O{=}P(NMeNMe)_3P{=}O$	- 8.6	-	-	-
<u>10</u>	$:P(NMeNMe)_3P{=}NPh$	-[e]	-	-	78.2
<u>11</u>	$PhN{=}P(NMeNMe)_3P{=}NPh$	+6.0(+6.6)	-	-	-
<u>14</u>	$(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$[f]	- 1.0	+13.9	74.0	107.5
<u>17</u>	$Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$[f]	- 2.5	-12.2	19.0	110.5
<u>31</u>	$Se{=}P(NMeNMe)_3P{=}Se$[f]	- 66.2	-	-	113.6

[a] In ppm relative to 85% H_3PO_4.

[b] Values precise to ±1.1 Hz.

[c] Reference 45, all others this work.

[d] $\delta(P^{111})$ - 102.0 ppm, $\delta(P^{V})$ - 25.4 ppm.

[e] $\delta(P^{111})$ - 96.8 ppm, $\delta(P^{V})$ + 1.8 ppm.

[f] All parameters determined using ITRCAL (see text).

The agreement between the observed and calculated transition frequencies is expressed as the RMS error in units of Hz. The errors for 14 and 17 of 0.30 Hz and 0.63 Hz, respectively, represent excellent agreements since the frequencies are only accurate to ±1.1 Hz.

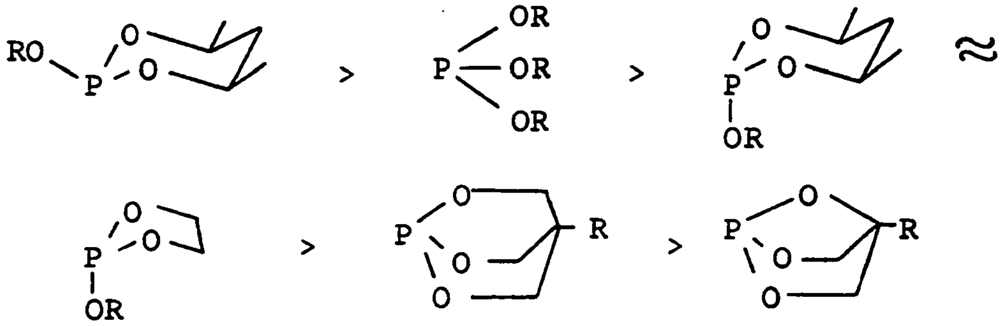
The great difference between the two spectra is due to the magnitude of JAX for compound 14 and 17 (74.0 Hz and 19.9 Hz, respectively). To see why this is so one needs to look at the expressions for the transition energies in Table 1. Because JXX' and JAX' are zero, a simplification occurs which results in the energy equivalence of the transition pairs (5, 10), (1, 2), (6, 9), (7, 2), (3, 4) and (8, 11) thus giving a maximum of six distinct lines in each branch of the spectrum. For compound 14 the separation of the outermost lines is 238.0 Hz (intensity 0.089) while for the innermost lines the separation is 23.0 Hz (intensity 0.911). For compound 17 the same separations and intensities are 222.8 Hz (0.008) and 1.8 Hz (0.992). Clearly, in the former the separations and intensities are large enough so all six lines are observed. In the latter the intensities of the outermost lines are so slight that they are submerged in spectrum noise. In fact, they are barely visible in the calculated spectrum. The separation of the innermost lines is just slightly greater than the accuracy of the spectrometer and line broadening causes them to be unresolvable.

Undoubtedly the non-observance of the outermost lines by Bermann and Van Wazer led them to the erroneous hypothesis of geometrical isomers (22).

The ^1H-NMR spectra of the Staudinger reaction products are included in Table 7 for completeness. The spectra of derivatives of 3 will be discussed in the next section.

Phosphazide stabilities

As noted before, another interesting feature of the Staudinger reaction concerns the correlation of the stability of phosphazide intermediates to the basicity of the trivalent phosphorus precursor. It has been shown that the order of lone pair basicity to a Lewis acid such as BH_3 decreases in the sequence:



for phosphites. This was determined by observation of the B-H stretching frequency, ν(B-H), for the borane adducts of many phosphites (79, 101, 102) as well as equilibrium studies of BH_3 exchange (101). Although the same trends were suspected to hold true for aminophosphines, the borane adducts

Table 7. ^{1}H-NMR chemical shifts and JPH values for some Staudinger reaction products[a]

Compound		Chemical Shifts[b]	Coupling Constants[c]
1	$(Me_2N)_3P$	2.48^{d}	9.0^{e}
5	$(Me_2N)_3P{=}N{-}N{=}NPh$	2.75^{d} 7.30^{f}	9.0^{e}
8	$(Me_2N)_3P{=}NPh$	2.67^{d} 6.86^{f}	9.5^{e}
12	$(Me_2N)_3P{=}NP(O)(OPh)_2$	2.60^{d} 7.10^{f}	10.0^{e}
15	$(Me_2N)_3P{=}NP(O)Ph_2$	2.62^{d} $7.86, 7.32^{g}$	10.0^{e}
2	$MeC(CH_2NMe)_3P$	2.52^{d} 2.56^{h} 0.83^{i}	17.0^{e} 3.5^{j}
6	$MeC(CH_2NMe)_3P{=}N{-}N{=}NPh$	2.69^{d} 3.14^{h} 0.96^{i} 7.34^{f}	12.0^{e} 7.0^{j}
9	$MeC(CH_2NMe)_3P{=}NPh$	2.62^{d} 3.08^{h} 0.91^{i} 6.90^{f}	12.0^{e} 7.0^{j}
13	$MeC(CH_2NMe)_3P{=}NP(O)(OPh)_2$	2.59^{d} 3.01^{h} 0.87^{i} 7.16^{f}	13.0^{e} 7.0^{j}
16	$MeC(CH_2NMe)_3P{=}NP(O)Ph_2$	2.63^{d} 3.04^{h} 0.88^{i} $7.85, 7.32^{g}$	13.5^{e} 7.0^{j}
3	$P(NMeNMe)_3P$	2.83^{k}	15.0^{l}
11	$PhN{=}P(NMeNMe)_3P{=}NPh$	2.98^{k} 7.05^{f}	11.0^{l}

14	$(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$	2.85[k]	7.24	12.0[l]
17	$Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$	2.92[k]	7.78,7.38[g]	12.0[l]

[a] $CDCl_3$ solvent, probe temperature 34°.

[b] In ppm downfield from internal TMS.

[c] Values precise to ±0.2 Hz.

[d] NMe protons, doublet.

[e] $^3JPNCH_3$.

[f] Phenyl protons, multiplet.

[g] Phenyl protons, two multiplets because of P-H couplings.

[h] NCH_2 protons, doublet.

[i] CMe protons, singlet.

[j] $^3JPNCH_2$.

[k] NMe protons, pseudotriplet.

[l] $|{}^3JPNCH + {}^4JPNNCH|$.

of 1, 2, 3 and several additional aminophosphines were synthesized and studied by infrared spectroscopy (Table 8).

The isovalent hybridization rule of Bent (103) predicts that the B-H bond strength should be proportional to the s character of boron in that bond. It is reasonable that this should be true for the B-H stretch since the C-H stretching force constants are similarly dependent on the hybridization of the carbon orbitals (104). A decrease in electron density donated from phosphorus to boron can cause the hybridization at boron to vary from sp^3 (strong donor) toward sp^2 (weak donor). Measurement of ν(B-H) for all the adducts was made using the nonpolar solvent CCl_4 so that comparison of values could be made in the absence of substantial solvent effects.

Since the BH_3 group has effective C_{3v} symmetry when coordinated to a donor, the infrared spectrum shows bands due to the symmetric (A_1 mode) and antisymmetric (E mode) B-H stretch. The higher energy band has been assigned to the antisymmetric B-H stretch (105, 106). The weighted averages of the symmetric and antisymmetric stretch (ν(B-H) = 1/3 ($\nu_{symm} + 2\nu_{asymm}$)) (107) are given in Table 8 in order of increasing magnitude. As already discussed, the general increase in ν(BH) reflects the decreased capability of the aminophosphine to act as a Lewis base and the basicity ordering obtained is: $\underline{1} \gg \underline{2} \geq \underline{3} \approx \underline{4}$.

The rationale for the basicity order of the parent aminophosphines will be discussed shortly.

As previously mentioned, the stability of the phosphazide intermediates is enhanced when the phosphorus substituents are electron donating (6). Such groups would tend to enhance the basicity of the phosphorus lone pair and so adduct stability should be a good measure of lone pair basicity. It was found by Goetze et al. (28) that 3 is a poorer nucleophile than 1 in that while the latter readily reacts with selenium and tellurium, the former needs more drastic conditions to effect reaction with selenium and would not react with tellurium at all. The poorer donating ability of 3 relative to 1 is borne out by the results of ν(B-H) studies above and it is seen that 2 is just a slightly better donor than 3. On this basis it would seem likely that the phosphazide stabilities should follow the same order as basicity.

To test the validity of this supposition, solutions of the phenylazide adducts 5, 6 and 7 were prepared and their decomposition rates monitored at 34° by observing proton NMR spectral changes immediately upon dissolution in $CDCl_3$. While solutions of 5 and 7 indicated only the presence of the adducts, 6 already displayed traces of its phosphinimine, 9. The spectra were recorded at 30 minute intervals thereafter. Compounds 6 and 7 showed a steady rate of decomposition to their respective phosphinimines, but 5 never showed any indication of decomposition. After 6.5 hours both 6 and 7 had decomposed completely to 9 and 10, respectively. It would therefore seem that the phosphorus basicity does indeed play an important role in the phosphazide stability. It is interesting that of all the phosphazides isolated so far, most of them have been adducts of aminophosphines (2, 10, 19, 27, 29) and a few of phosphines (4-6, 108). This is in accord with Mosby and Silva's order of stabilities (6) in which aminophosphines and phosphines give the most stable adducts.

It has also been found that increased electron withdrawal on the azide moiety increases the adduct stability (4, 5) and this is confirmed by the findings of Pilgram *et al.* (19) where aminophosphine adducts of the type $R_3P{=}N{-}N{=}N{-}C(O){-}(O)_n{-}Ph$ decomposed at lower temperatures when $n = 0$ than when $n = 1$. The relatively greater electron withdrawing power of a phenoxy compared to a phenyl group is probably responsible for the rate difference.

Phosphazide structures

To this point, the structures of all the phosphazides discussed have been represented by the linear, rather than branched, structure. Goldwhite *et al.* (27) argued on the basis of the ^{1}H-NMR spectrum of $(Me_2N)_3P{=}N{-}N{=}NMe$ (which shows no P-H coupling for the azido methyl but does show $^3J_{PNCH}$ =

Table 8. Infrared spectroscopic data for aminophosphine boranes

Compound	Bonds in the ν(B-H) region[a]			
	Asymm.	Symm.	Weighted Average	Solvent
18 $H_3B{:}P(NMe_2)_3$	2372.0	2334.5	2359.5	CCl_4
19 $H_3B{:}P(NMeCH_2)_3CMe$	2396.5	2350.5	2381.2	CCl_4
43 $H_3B{:}P(NMeNMe)_3P{=}O$	2408.0	2352.5	2389.5	CCl_4
40 $H_3B{:}P(NMeNMe)_3P{=}NPh$	2411.0	2357.0	2393.0	CCl_4
21  $H_3B{:}\overset{NMe}{P(NMeNMe)_2P}{:}BH_3$	2411.0	2358.5	2393.5	CCl_4
20 $H_3B{:}P(NMeNMe)_3P{:}BH_3$	2412.5	2360.0	2395.0	CCl_4
	2415	2350	2393	Nujol[b]
$H_3B{:}CO$[c]	2434	2380	2416	solid glass

[a] Frequencies measured in this work are precise to ±0.5 cm^{-1}.

[b] Reference 28.

[c] Reference 109.

9.6 Hz for the NMe_2 groups) that the structure must be linear. ^{3}JPNCH for the imido Me group in $(Me_2N)_3P{=}NMe$ is 23.3 Hz. The closeness of δP for $(Me_2N)_3P{=}N_3Me$ (-40.7 ppm) and 5 (-41.2 ppm; -42.8 ppm in this work) to δP for $(Me_2N)_3P{=}NMe$ (-32.6 ppm) was taken to indicate a similarity of structure for all three compounds and thereby indicated a linear structure. The appearance of new intense longer wavelength bands in the UV spectrum of 5 (300 and 310 nm) compared to PhN_3 suggested that the phosphazide had a more extended pi system than PhN_3 itself. This is consistent with a linear structure and the lack of an asymmetric azide stretch near 2100 cm^{-1} in either the solid state or in solution seems to bolster this conclusion.

With the linear structure of 5 reasonably established, phosphazides 6 and 7 were also assigned linear structures on the basis of their similar δP values to 5 (see Tables 5 and 6). In the three phosphazides 5, 6 and 7, δP of the formally P^V nucleus occurs about 20 ppm to lower field than δP of the corresponding phosphinimines 8, 9 and 10. Goldwhite's suggestion of an extended pi system in 5 (27) makes it interesting to speculate that this factor is responsible for the observed lower field δP values of the phosphazides relative to the phosphinimines.

Phosphorus lone pair basicity

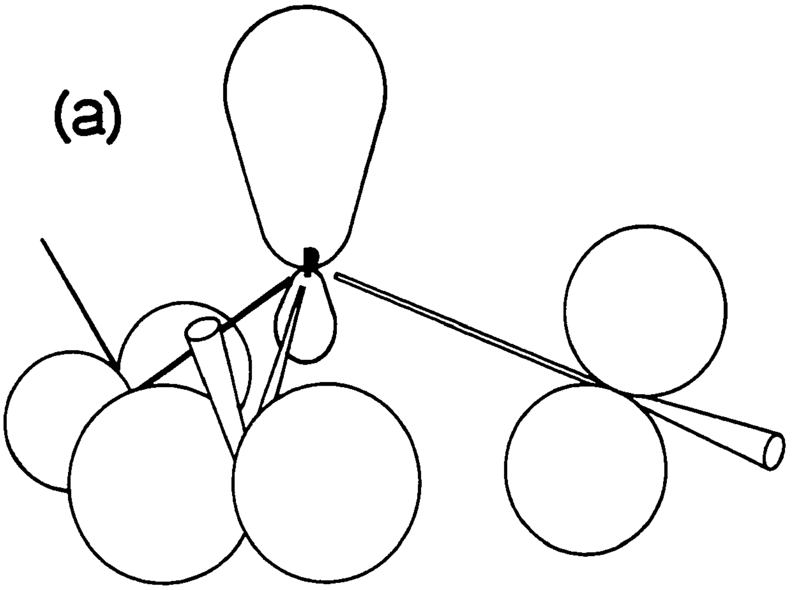
The differences in basicity of the aminophosphines 1,

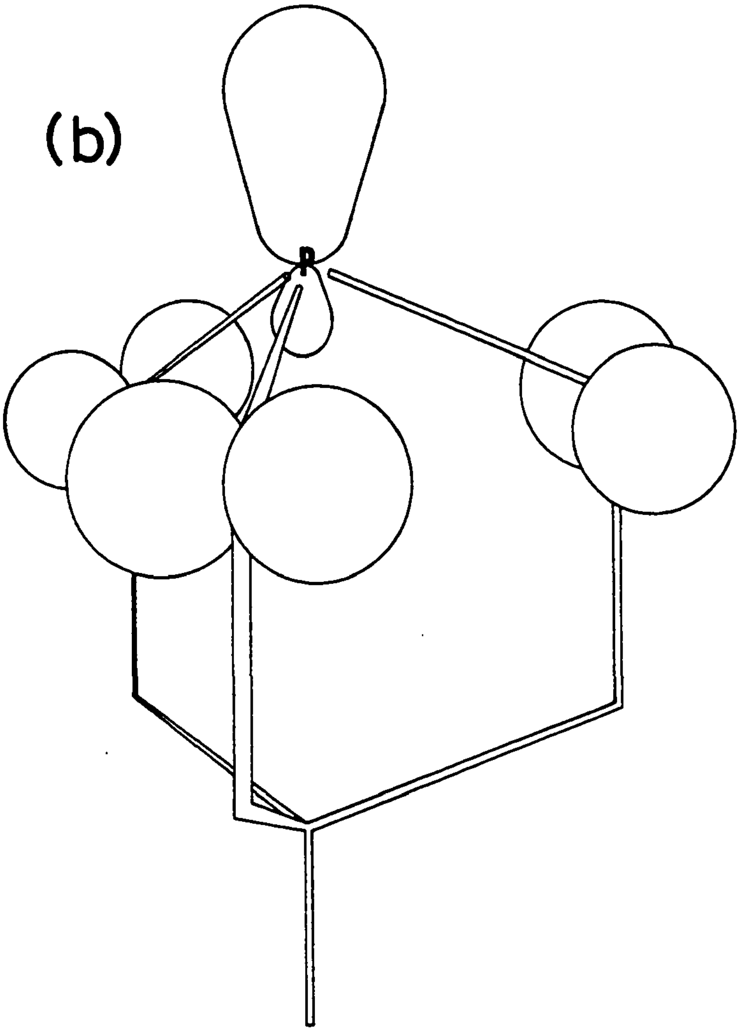
2 and **3** can be ascribed to "hinge" (109, 110) and "orbital repulsion" (111, 112) effects. These effects have been suggested to be operative in phosphites and they account for the decreasing basicity order shown on page 77. As shown in this work the acyclic aminophosphine **1** is more basic than either **2** or **3** and this can be accounted for in terms of an orbital repulsion effect.

The spatial arrangements of the almost purely p character lone pairs on each nitrogen in **1** are very probably different from those on **2** and **3**. Molecular structures have been obtained by x-ray diffraction methods for two derivatives of **2** (90) and several derivatives of **3** (33-35). The structures all indicate that the nitrogen lone pairs in **2** and **3** are constrained from free rotation about the P-N bond by the cage structures and that they are orthogonal to the phosphorus lone pair or P=Y bond present. In contrast, **1** has the possibility of free P-N bond rotation and so at least one of the nitrogen lone pairs could orient itself in the manner shown in Figure 5. Indeed, this is the orientation found in the solid state structure of $(PhO)_3P$ (113) and it is also consistent with the photoelectron spectrum of **1** (43, 114).

By symmetry, the nitrogen lone pair in **1** that is non-orthogonal to the phosphorus lone pair is capable of interacting with the phosphorus lone pair in a repulsive manner which would raise the energy of the phosphorus lone pair and

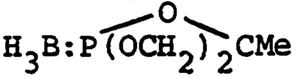
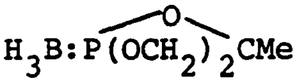
Figure 5. Lone pair orientations for (a) acyclic and (b) bicyclic aminophosphines.

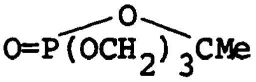

(a)
P


(b)
P

render it more basic. Such an enhancement of the lone pair basicity is not possible in 2 or 3 and consequently they are weaker bases than 1.

Between 2 and 3 the difference in nitrogen lone pair hybridization might be thought to cause different orbital repulsions but the slight change in hybridization (as determined by the sum of the bond angles around nitrogen in 23 (90) and 25 (34)) is probably negligible as in each case the lone pairs are still orthogonal to the phosphorus lone pair.

The fact that ν(BH) measurements yield little difference in the P^{III} basicities of 20, 40 and 43 indicates that the P^{V} of 40 and 43 and the presence of two BH_3 groups in 20 has little influence on the basicity of the BH_3-bearing phosphorus. However, the very slight increase in ν(BH) observed for the three compounds is in the expected direction based upon electronegativities of the exocyclic groups (O > NPh > BH_3). The relationship of 3 and 4 is deserving of comment because the "hinge" effect would predict 3 to be more basic than 4 based upon ν(BH) of $H_3B{:}P(OCH_2)_3CMe$ (2402.2 cm^{-1}) and  $H_3B{:}\overset{O}{\overbrace{P(OCH_2)_2}}CMe$ (2410.2 cm^{-1}) (80). In the phosphite compounds there is a change in hybridization of the oxygens upon constraint from sp^2 in the former to sp^3 in the latter. As a result there could be less pi donation to phosphorus in  $H_3B{:}\overset{O}{\overbrace{P(OCH_2)_2}}CMe$ and hence a lower phosphorus basicity. While the same sort of hybridization change must occur in 4, the ^{1}H-NMR spectra of both 4 and 21 give no indication that the NMeNMe groups are non-equivalent as would be expected if the sp^3 nature of the NMe group directed the Me group over one NMeNMe linkage and the N lone pair over the other. The possibility of rapid inversion can not be ruled out, however.

The great strain in 4 manifests itself in facile cage opening and subsequent disproportionation to 3 and polymer (45). The structurally similar phosphate  $O{=}\overbrace{P(OCH_2)_3C}^{O}Me$ shows its strain with an average POC angle of 102° and an average OPO angle of 99.9° (37). It is interesting to note that the stability towards polymerization of the three compounds  $\overbrace{P(NMeNMe)_3P}^{X}$ (X = NMe, O, S) is in the order S > NMe > O (45). The more diffuse nature of the bonding orbitals and longer P-X bond lengths for X = S may allow release of cage strain thus accounting for the observed greater stability. The reason why the cage is more stable when X = NMe than when X = O is not readily apparent.

An interesting basicity effect was noted early on in this work and has been utilized to explore another aspect of amino phosphorus chemistry. While monitoring the reaction of a 2:1 mixture of PhN_3 and 3 in $CDCl_3$ at 34° by proton NMR spectroscopy, it was noticed that there were absorptions in addition to those due to 3 and the expected product, 11. These additional signals were later found to arise from 7 and 10 in the reaction mixture. When a 1:1 mixture of PhN_3 and 3 was monitored under the same conditions only signals from 3, 7 and 10 were seen. The same ratio at 34° in C_6D_6 gave identical results. No 11 was observed in either case. This is in marked contrast to previous findings (22) wherein only 3 and 11 were reported to exist in a one to one ratio. A large scale preparative reaction was carried out in benzene with a 1:1 mixture in which the reaction temperature was maintained near 35° and allowed to go no higher than 40°. Upon working up the reaction mixture, an 86% yield of pure 10 was realized. The same reaction carried out at 50° lead to a great increase in the amount of 11 at the expense of 10. It is now believed that the earlier workers performed their experiment just above a certain "critical" temperature (>40°) which favored the production of 11 over 10. Above this temperature the formation of 7 is followed by decomposition to 10 which further reacts with a molecule of PhN_3 to give the very unstable adduct $PhN{=}P(NMeNMe)_3P{=}N_3Ph$. Rapid decomposition of this adduct produces 11.

That a "critical" temperature for the formation of 11 exists was shown by monitoring a 1:1 mixture of PhN_3 and 10 in $CDCl_3$ at 34°. No evidence for the formation of 11 was seen and this agrees with the above mentioned findings for the 2:1 mixture of PhN_3 and 3.

Why only one phosphorus atom of 3 should react with PhN_3 under these conditions now became a matter of interest. A decreased basicity of the unoxidized phosphorus due to the oxidation of the other end of the cage was proposed by us earlier (29). However, the ν(B-H) study described above suggests that the trivalent phosphorus in 10 is at least as basic as in 3. Steric effects could not be important due to the diametrically opposed phosphorus lone pair orientations on the cage. Another alternative is a decreased nucleophilicity of the phosphorus lone pair in 10 as compared to 3. Such an effect could arise from the direction of the dipole moment in 10 if it placed the lone pair at the positive end of the dipole. By symmetry, there can be no net dipole moment in 3. The dipole moments of 2, 9, 10 and 23 were determined in toluene at 25° and the results, along with those of other researchers, are shown in Table 9. To a close approximation, the magnitude and direction of the dipole moment of 10, $\vec{\mu}(\underline{10})$, should be obtained by the vector equation

$$13. \quad \vec{\mu}(\underline{10}) = \vec{\mu}(\underline{9}) - \vec{\mu}(\underline{2}).$$

Using the values obtained in this work a value of $\mu(\underline{10})$ = 3.23 D is calculated. By using the value of $\mu(\underline{2})$ obtained by Besserre and Troquet (115), $\mu(\underline{10})$ = 2.96 D; clearly in excellent agreement with the experimental results. The positive terminus of the molecular dipole in 10 is clearly near the lone pair and this could account for its diminished

Table 9. Dipole moments of aminophosphine compounds[a]

Compound	$\delta\varepsilon/\delta\chi$	$\delta\eta/\delta\chi$	P_o	μ^b	solvent	reference
1 $(Me_2N)_3P$	1.915		29.94	1.21	C_6H_{12}	116
				1.46	C_6H_6	115
				1.56	C_6H_6	117
2 $MeC(CH_2NMe)_3P$	3.430		53.62	1.62	C_6H_{12}	116
	3.486	0.020	57.12	1.67	$C_6H_5CH_3$	this work
			55.13	1.94	C_6H_6	115
9 $MeC(CH_2NMe)_3P{=}NPh$	29.95	0.172	490.5	4.90	$C_6H_5CH_3$	this work
10 $P(NMeNMe)_3P{=}NPh$	11.56	0.261	179.7	2.96	$C_6H_5CH_3$	this work
22 $(Me_2N)_3P{=}O$	17.36		271.3	3.64	C_6H_{12}	116
				4.27	C_6H_6	115
				4.30	C_6H_6	117
				4.31	C_6H_6	118
				5.54	C_6H_6	119
23 $MeC(CH_2NMe)_3P{=}O$	24.52		383.2	4.33	C_6H_{12}	116
	28.01	0.033	465.2	3.77	$C_6H_5CH_3$	this work

[a] All measurements made at 25.00 ± 0.05°.

[b] In Debyes, values for this work and reference 116 are precise to ±0.05 D.

reactivity towards PhN_3 as compared to 3. A similar dipole moment argument has been invoked to rationalize the reactivity of $P(OCH_2)_3P$ towards Lewis acids (120). The difference between the dipole moment values of Laube (116) and this work for μ(2) are not significant as the experimental error is estimated to be ±0.05 D. The differences for μ(23) are marked and the present value is felt to be more accurate due to stringent sample purification and the inclusion of refractive index slope measurements (which Laube assumed to be zero) in the calculation of the polarization orientation *via* the Cohen-Henriquez equation (82).

14. $$P_o = [3M/d(\varepsilon_o + 2)^2][(\delta\varepsilon/\delta\chi) - 2\eta_\infty(\delta\eta_\infty/\delta\chi)].$$

In this equation M, d and ε_o are the molecular weight, density and dielectric constant of the pure solvent, η_∞ is the refractive index of a particular solution (for a given mole fraction, χ) extrapolated to infinite wavelength and $\delta\varepsilon/\delta\chi$ and $\delta\eta_\infty/\delta\chi$ are the slopes of the straight lines representing the changes in solution dielectric constant and refractive index with changing solute mole fraction, respectively.

An explanation for the difference in μ(2) calculated in the present work and μ(2) of Besserre and Troquet (115) is not obvious. Sample purity is not the reason (at least in this work) as the sample of 2 used was distilled in a 40 cm long spinning bond column and shown to be pure on the basis of ^1H- and ^{31}P-NMR. The French workers used the approximation of Halverstadt and Kumler (121) to eliminate solvent polarization errors while these errors are assumed to be compensated for by the measurement of $\delta\eta/\delta\chi$ in the present work. As experimental errors in μ values are usually in the neighborhood of 0.05-0.1 D (115), it may be that the difference in μ(2) values is not significant.

It is interesting to note that the difference in the dipole moments, $\Delta\mu$, of 22 and 1, according to values obtained by Besserre and Troquet, is 2.85 D which is almost the same difference between the value of μ(23) (4.77 D) obtained in this work and their value of μ(2) (1.94 D) ($\Delta\mu$ = 2.83 D). On the other hand, $\Delta\mu$ for 23 and 2 using values obtained in this work is 3.10 D. The significance of the differences in the two sets of measurements is not clear.

Phosphorus pi acidity

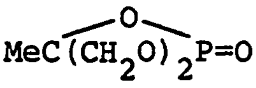
The question of phosphorus lone pair basicity has as a corollary the question of phosphorus pi acidity. The low lying empty 3d orbitals on phosphorus are capable of accepting electron density *via* pi-type bonds from donor atom orbitals. In this manner phosphorus and the heavier elements in Group V are able to expand their octets.

In the present study the P=N bond could involve pi overlap of empty phosphorus 3d orbitals with the nitrogen lone pair in concert with phosphorus lone pair donation in a sigma bond. Due to the diffuse nature of the phosphorus 3d orbitals, there is no restricted rotation about this bond and this has been demonstrated both in this work and by others (26). Even though this is true, the P=N bond does have appreciable double bond character which has recently been estimated for a number of phosphinimines using a ^{31}P-NMR chemical shift method developed by Tarasevich and Egorov (122-124).

By extending the Letcher-Van Wazer semi-empirical theory of ^{31}P chemical shifts (125) to include the polarizing effect of the valence sigma and pi bonds primarily from the nitrogen atom of an =NR group, they express δP as a function of the effective electronegativity of the =NR group. Once this was accomplished a comparison of =NR electronegativities against groups of known electronegativity (e.g. O or S) allowed an estimation of the occupation of the d orbitals on phosphorus and hence, the amount of pi bonding in the PN link.

From their calculations (123), the pi bond orders ranged from 0.34 for $Cl(CCl_3)_2P{=}N(\underline{i}\text{-}Pr)$ to 0.97 for $Cl_3P{=}NC(O)Ph$ (123). Of particular interest is the value of 0.53 found for 8 (123) which is intermediate to the values of 0.89 and 0.46 found for 22 and 26, respectively, from vibrational analysis by Räuchle *et al.* (93). This result indicates that there is also considerable PN pi overlap in the polycyclic phosphinimines discussed in the present work. From P=O stretching frequencies and phenol shift experiments (79, 80, 109) it was

Table 10. Phosphoryl group stretching frequencies for some aminophosphine oxides and phosphates

Compound	$\nu(P=O)^a$	Solvent	Reference
22 $(Me_2N)_3P=O$	1210	-[b]	93
23 $MeC(CH_2NMe)_3P=O$	1285.4	CCl_4	this work
24 $P(NMeNMe)_3P=O$	1283.0	CCl_4	this work
	1274	-[c]	this work
25 $O=P(NMeNMe)_3P=O$	1287.6, 1278.6	CCl_4	this work
	1274	-[d]	28
$(MeO)_3P=O$	1290, 1274	CCl_4	126
$RC(CH_2O)_3P=O^e$	1327	$CHCl_3$	80
 $\overset{O}{\overbrace{MeC(CH_2O)_2P}}=O$	1346, 1354	CH_2Cl_2	80

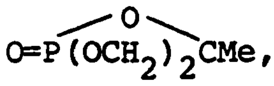
[a] Frequencies obtained for solutions in this work are precise to ±0.5 cm^{-1}.

[b] Solvent not specified (probably neat since it is a liquid).

[c] 2% KBr pellet.

[d] Nujol mull.

[e] $R = \underline{n}\text{-}C_5H_{11}$.

found that the amount of P=O pi bonding in phosphates increased in the order acyclic < monocyclic < bicyclic. To discover if the same order would hold true for aminophosphine oxides, measurements of $\nu(P{=}O)$ for a number of these compounds have been carried out and the results are displayed in Table 10. The increase of 75 cm^{-1} in $\nu(P{=}O)$ on going from acyclic 22 to bicyclic 23 is much greater than the 45 cm^{-1} increase for the corresponding phosphates. Not surprisingly, $\nu(P{=}O)$ for 23, 24 and 25 are almost the same as might be expected from their similar cage structures. The seemingly low $\nu(P{=}O)$ values for the KBr pellet spectrum of 24 and the Nujol mull spectrum of 25 are probably due to intermolecular forces which occur in the solid state, but which are absent in dilute solutions. As is found in the spectra of $O{=}P(OMe)_3$ and  $O{=}P(OCH_2)_2CMe$, the $\nu(P{=}O)$ region of the spectrum of 25 contains two absorptions. The acyclic phosphate is thought to exist in two rotameric forms thus giving rise to two independent P=O stretches (127). A similar argument cannot be used in the cases of the bicyclic phosphate and 25 owing to the rigidity of their bicyclic structures. The value of $\nu(P{=}O)$ of 25 in the solid state (1274 cm^{-1}) suggests that the 1278 cm^{-1} bond in solution should be assigned to this vibration. However, such an assignment would be inconsistent with the spectra of 23 and 24 in solution and so the 1287 cm^{-1} bond of 25 is assigned to $\nu(P{=}O)$. Since it was seen that lone pair basicities, (and hence sigma bonding) decrease in the order 1 > 2 ≈ 3, the observed increase in ν(P=O) is consistent with an increase in P=O pi bonding in the bicyclics due to greater pi acidity of the phosphorus 3d orbitals.

The ultraviolet spectra of compounds 5 and 8-11 are tabulated in Table 11. Band shape analysis was performed using the computer program LOGFIT (81). The hypsochromic shift observed for 9, 10 and 11 relative to 8 is similar to that found for the anilinium ion relative to aniline (128). In the latter case the high energy shift was ascribed to the absence of nitrogen lone pair interaction with the aromatic pi system in the ion. In particular the E_2 band was shifted from 230 to 203 nm and the B band from 280 to 254 nm. In the phosphinimines studied the E_2 band was partially hidden by solvent cutoffs. Upon progressing from 8 to 9-11, a small but distinct decrease of ca. 10 nm is seen to occur in all absorptions. This trend undoubtedly reflects the increased pi acidity of 2 and 3 relative to 1 and the similar size of the shift for 9, 10 and 11 is consistent with the very similar ν(P=O) values of 23, 24 and 25.

That the phosphorus-nitrogen interaction affects the phenyl pi cloud is supported by the crystal structure of 11 (35). The PNCC dihedral angles for the exocyclic groups in 11 were calculated from the atomic positional parameters to be 174.5 and 8.1° to the ortho carbons which are trans and

Table 11. Ultraviolet spectroscopic data for some Staudinger reaction products and derivatives

Compound	Solvent	λ_{max}[a]	ε_{max}[b]
5 $(Me_2N)_3P=N-N=NPh$	Et_2O	224(223)[c]	11500(12400)[c]
		259	4200
		286(290)	6000(13400)
		298(300)	5900(14900)
		318(310)	12500(14200)
8 $(Me_2N)_3P=NPh$	Et_2O	256(257)[c]	18600(16900)[c]
		266	1400
		284(290)	1600(2060)
		296	1300
		307	800
9 $MeC(CH_2NMe)P=NPh$	Et_2O	249	20300
		255	1800
		278	1800
		288	1400
		297	1300
10 $P(NMeNMe)_3P=NPh$	THF	248	19500
		258	3100
		276	1300
		287	1200
		296	500
11 $PhN=P(NMeNMe)_3P=NPh$	THF	249	38900
		255	11900
		263	2300
		274	3100
		285	2300
		293	1300

---

[a] Values precise to ±0.5 nm.

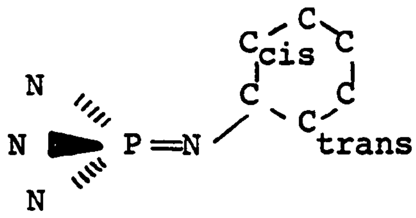
[b] Values precise to ±50 l $mole^{-1}$ cm^{-1}.

[c] Parenthetical values are from reference 26.

Table 11. continued

Compound	Solvent	λ_{max}	ε_{max}
<u>37</u> $O{=}P(NMeNMe)_3P{=}NPh$	THF	245	17900
		254	1700
		277	400
		278	1000
		286	800
		296	500
<u>38</u> $S{=}P(NMeNMe)_3P{=}NPh$	THF	245	16000
		255	2600
		278	900
		287	700
		296	400

cis to the P=N bond respectively. The PNC bond angle of 134.3° is indicative of nitrogen sp^2 hybridization which would



place the lone pair in a predominantly p orbital, conducive to maximum interactions with both the phosphorus and phenyl group in the planar arrangement. Similar geometries are expected to exist for 8, 9 and 10 as the aminophosphine cone angles (129) should not present any greater steric hinderance than in 11.

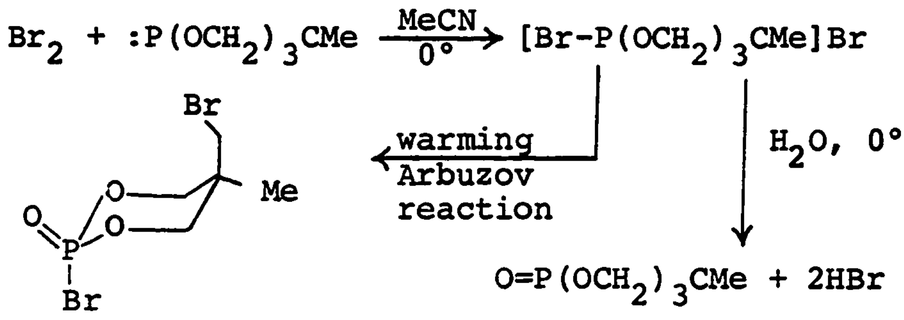
The similarity in the UV spectra of 10 and 11 would indicate that there is no inductive effect from one end of the cage to the other. This assumption is borne out by the UV spectra of 37 and 38 which display their major absorptions in about the same positions as 10 and 11.

New Derivatives of $P(NMeNMe)_3P$

Synthesis and characterization

Prior to the isolation of 7 and 10 (29), all of the derivatives of 3 had been symmetrical with respect to the exocyclic groups on the phosphorus. The trivalent phosphorus in 7 and 10 offered the possibility of obtaining additional unsymmetrical cages having two pentavalent phosphorus atoms. The ready decomposition of 7 to 10 made it unsuitable for further synthetic work and so only the mono phenylimido cage compound <u>10</u> was used. A short while after the serendipitous synthesis of <u>10</u>, the monoxide, <u>24</u>, was synthesized deliberately to make another unsymmetrical cage of <u>3</u>. The synthetic method used to make <u>24</u> was based on the accidental discovery (130) that $O{=}P(OCH_2)_3CMe$ was obtained at low temperature from an equimolar CH_3CN solution of Br_2 and <u>48</u> if there were traces of water present. The reaction was thought to proceed <u>via</u> the hydrolysis of the bromonium salt compound $[Br{-}P(OCH_2)_3{-}CMe]Br$ which could be isolated at low temperature but upon warming underwent the Arbuzov reaction as shown in equation 15. The reaction method used to synthesize <u>24</u> is shown in

15.



equation 16. While it was fairly easy to isolate <u>24</u>, the

$$\begin{tikzcd}
16. \quad Br_2 + \underset{\underline{3}}{:P(NMeNMe)_3P:} \arrow[r, "MeCN", "-21°"'] & \underset{\underline{34}}{[Br{-}P(NMeNMe)_3P:]Br} \arrow[dl, "\begin{array}{l}1.\ H_2O,\ -21° \\ 2.\ NEt_3\end{array}"] \\
\underset{\underline{24}}{O{=}P(NMeNMe)_3P:} + 2NEt_3\cdot HBr &
\end{tikzcd}$$

identical reaction using <u>2</u> never led to the preparation of <u>23</u> but rather to a viscous oil that may have been the result of cage opening by HBr produced in the hydrolysis step. Decomposition at that point is supported by the fact that the salt 33 could be made very easily from Br_2 and 2.

Solutions of 33 were reasonably stable with time, giving spectra indicative of a cage structure over a period of days. No evidence of an Arbuzov-type reaction was observed. Unlike the synthesis of $O{=}P(OCH_2)_3CMe$, it is absolutely necessary to have a suitable Lewis base present in the preparation of 24 as free mineral acid has been shown to readily attack and destroy the cage (28) and an attempted base-free preparation of 24 lead to a yellow oil similar to that obtained upon attempted synthesis of 23. Many organic tertiary amines were tried but NEt_3 was judged the best. The procedure is not straight-forward, however, since if the base is added prior to the hydrolysis of 34, it is likely that there is ready formation of $NEt_3{\cdot}Br_2$ (in a manner similar to $C_5H_5N{\cdot}Br_2$ (131)) at the expense of 34. Evidence for this comes from the hydrolytic workup of such a reaction which yields $NEt_3{\cdot}HBr$ and unreacted 3. The production of $NEt_3{\cdot}Br_2$ is probably due to the more basic nitrogen lone pair on NEt_3 (pK_a 11.01) compared to the phosphorus lone pairs of 3. Two equally undesirable procedural choices were then considered. Adding the base before the water would remove intermediate 34 while adding water before base would invite destruction of the cage from the HBr produced. While both methods were investigated, the latter procedure was chosen as it was hoped that the low reaction temperature would tend to slow the detrimental HBr/cage reaction. The isolated yields of <u>24</u> varied from 0 to 30% and this range reflects variations in technique. In the many preparations attempted with the water/NEt_3 method, the addition timing was found to profoundly affect the yield. If base was added immediately after water, a very low yield of <u>24</u> was obtained. On the other hand, if base addition was delayed more than 6 minutes, no <u>24</u> was obtained. The greatest yield (30%) was realized with a 4 minute delay in adding base.

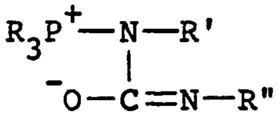
Compound <u>24</u> had been previously synthesized by careful N_2O_4 oxidation of <u>3</u> in CCl_4 at 0° by Kolpa (132) and although the method was attempted in this work with particular attention to his experimental detail no <u>24</u> was ever isolated. Oxidation of <u>3</u> with stoichiometric amounts of $m\text{-}ClC_6H_4C(O)OOH$ and $Me_3N\rightarrow O$ were also unsuccessful, giving uncharacterized oils upon workup. Reaction of phosphinimines with oxygen-containing organic species are known to yield phosphoryl compounds as illustrated by the reactions

17. $R_3P{=}NR' + R''_2C{=}O \rightarrow R_3P{=}O + R''_2C{=}NR'$

18. $R_3P{=}NR' + R''NCO \rightarrow R_3P{=}O + R''NCNR'$

as well as reaction with H_2O, CO_2, SO_2 and NOCl (3, 133). In all these reactions $R_3P{=}O$ is a product. Reaction of <u>10</u> with either 3-pentanone or PhNCO in refluxing Bu_2O (140°)

did not produce 24. Unreacted 10 was recovered from the former reaction while decomposition occurred in the latter. The nonreactivity of 10 observed may be due to steric problems since a four-membered cyclic intermediate is postulated



$$\begin{array}{lllll} R_3P^{+} & — & N & — & R' \\ & & | & & \\ {}^{-}O & — & C & = & N—R'' \end{array}$$

(134) for the reaction of isocyanates, R'NCO, with catalytic amounts of $R_3P{=}O$ compounds (through the initial formation of $R_3P{=}NR'$) to produce carbodimides, R'NCNR', and the same is to be expected for reactions of $R_3P{=}NR'$ with R"NCO as in equation 17. The steric bulk of the NMe groups held rigid in the cage of 10 could preclude formation of the intermediate. Such a likelihood is supported by the ready reaction of the nonrigid compounds 22 and $(PhNH)_3P{=}O$ (134. However, the two molecules are electronically different and the role of this effect is presently unknown.

It is interesting to note that while 33, 34 and the compound $P(NMeNMe)_3P \cdot 2Br_2$ (28) are very moisture sensitive, compound 32, while hygroscopic, is extremely stable towards hydrolysis. The bromide ion can even be gravimetrically determined by precipitation as AgBr from aqueous solutions of 32 (94). It is tempting to ascribe this behavior to the enhanced basicity of the phosphorus atom in 1.

While 32, along with the Cl_2 and I_2 adducts of 1, have been shown to be ionic in nitrobenzene solution by conductivity measurements (94), the nature of 32, 33 and 34 in acetonitrile was of interest because of the formulation of $[Br-P(OCH_2)_3CMe]Br$ as a 1:1 electrolyte in acetonitrile (130). The conductivities of 32, 33 and 34 were measured in acetonitrile at 0° and found to be in the correct range for 1:1 electrolytes having specific conductance values of 140, 125 and 152 mhos cm^{-1} l $mole^{-1}$ respectively as compared to a specific conductance of 145 mhos cm^{-1} l $mole^{-1}$ for Et_4NI in acetonitrile.

The ^{31}P-NMR spectra of the Br_2 adducts were recorded and the relevant parameters are shown in Table 12. Comparison of the chemical shifts for the two sets of compounds 32, 35 and 33, 36 reinforce the ionic formulation of the Br_2 adducts. The trityl compounds 35 and 36 must be totally ionic species in solution because BF_4^- is a noncoordinating ion. Metathesis of 32 and 33 to their respective BF_4^- salts by reaction with $AgBF_4$ gave products which had ^{31}P chemical shifts of -47.2 and -52.8 ppm respectively. Metathesis of 32 was reported previously by Nöth and Vetter (94) who made the BPh_4^- salt by reaction of 32 with $NaBPh_4$ and by Castro and Dormoy (135) who made the PF_6^- salt of 32.

Compounds 44 and 45 were never isolated but their compositions were inferred from the ^{31}P-NMR spectra produced from

Table 12. ^{31}P-NMR chemical shifts for aminophosphine salts and their precursors[a]

Compound	Chemical shift[b]		
	δP^{111}	δP^{+}	δP^{V}
1 $(Me_2N)_3P$:	-120.9		
32 $[(Me_2N)_3P\text{-}Br]Br$		-47.0	
35 $[(Me_2N)_3P\text{-}CPh_3]BF_4$		-52.4	
2 $MeC(CH_2NMe)_3P$:	- 84.0		
33 $[MeC(CH_2NMe)_3P\text{-}Br]Br$		-53.1	
36 $[MeC(CH_2NMe)_3P\text{-}CPh_3]BF_4$		-43.6	
3 :P$(NMeNMe)_3P$:	-106.9		
34 [:P$(NMeNMe)_3P\text{-}Br]Br$	-113.7	-14.4	
10 :P$(NMeNMe)_3P{=}NPh$	- 95.9		+ 3.1
44 $[Br\text{-}P(NMeNMe)_3P{=}NPh]Br$		-23.1[c]	+16.2[c]
24 :P$(NMeNMe)_3P{=}O$	- 94.9		- 9.8
45 $[Br\text{-}P(NMeNMe)_3P{=}O]Br$		-26.1	- 7.3
48 $MeC(CH_2O)_3P$:	-91.9		
$[MeC(CH_2O)_3P\text{-}Br]Br$		-36.5[d]	

[a] Recorded in CD_3CN at 0° unless noted.

[b] In ppm relative to 85% H_3PO_4.

[c] $CDCl_3$ solvent at 0°.

[d] This work and reference 130.

1:1 mixtures of Br_2 with 10 and 24, respectively, in both CD_3CN and $CDCl_3$ at 0°. They will be discussed in more detail shortly.

Bonding considerations in derivatives of $P(NMeCH_2)_3CMe$

The syntheses of 33 and 36 made it possible to study the behavior of ^3JPNCH in the aminophosphine cage similar to the work performed on derivatives of 48 regarding ^3JPOCH (97, 120). In those works it was found that proton chemical shifts and ^3JPOCH correlated linearly over a range of sigma bonding Lewis acids such as borane, trimethylborane and ethyl carbonium, triphenylmethyl carbonium and bromonium ions. A separate correlation was found for species which could pi bond to the phosphorus such as chalconides and metal carbonyl moieties (136). The ^1H-NMR parameters for various derivatives of 2 are listed in Table 13 and plotted in Figure 6.

While in derivatives of 48 there is coupling only to the methylene protons, in derivatives of 2 couplings to the NMe protons and the NCH_2 protons are observed. Inspection of Figure 6 reveals the existence of a correlation between ^3JPNCH and δNCH_2 for the sigma bonding groups (i.e. lone pair, BH_3, Ph_3C^+ and Br^+) having a correlation coefficient of 0.986 as well as a correlation between ^3JPNCH and δNMe for the pi bonding groups (i.e. O, NPh, S and Se) also having a correlation coefficient of 0.986. It appears, however, that

Table. 13. ^{1}H-NMR parameters for derivatives of $P(NMeCH_2)_3CMe$ in CD_3CN solution

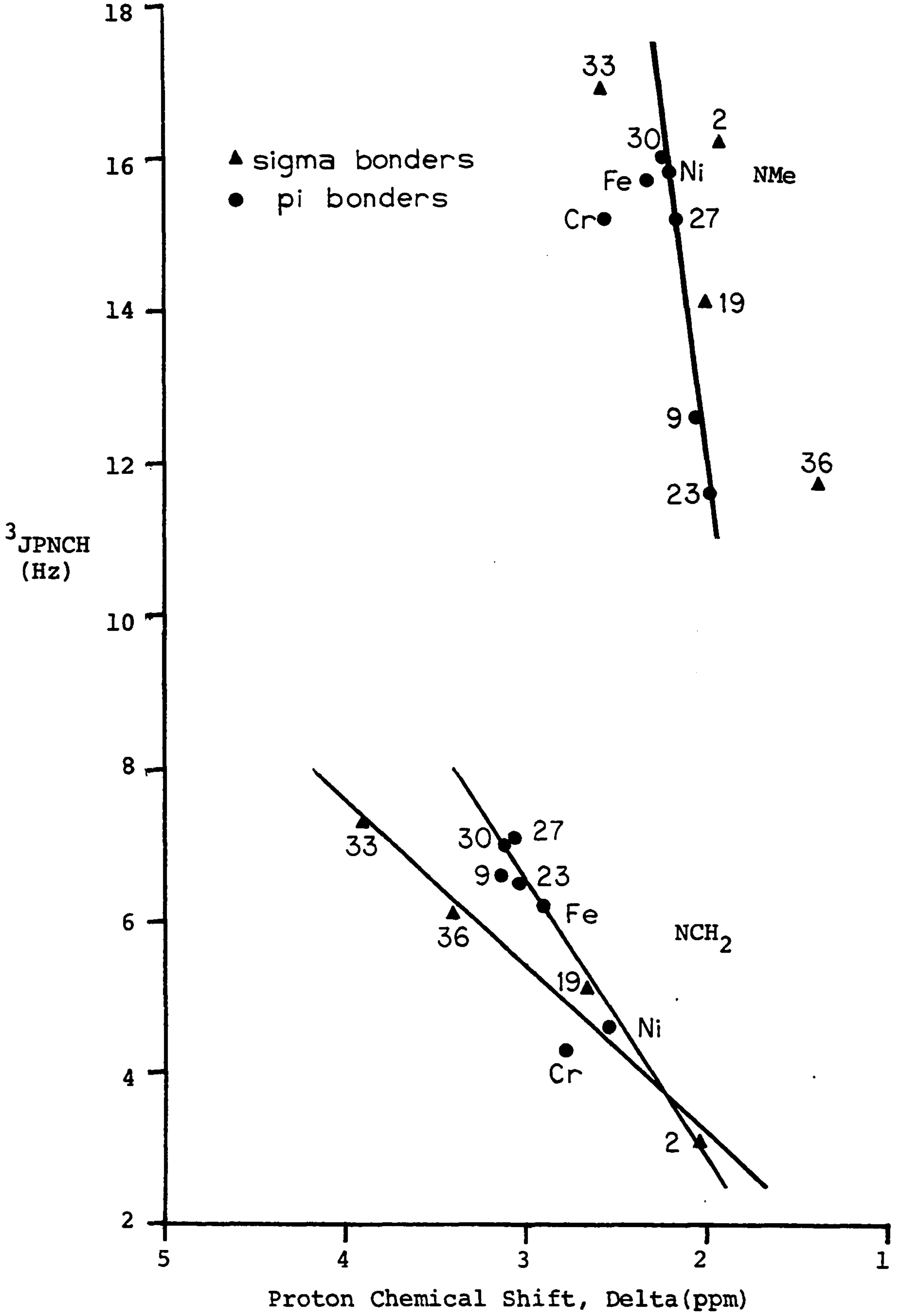
Compound $MeC(CH_2NMe)_3P$-Y	δNMe[a]	$^3J_{PNCH_3}$[b]	δNCH_2[a]	$^3J_{PNCH_2}$[b]	δCMe[a]
2 Y = lone pair	2.46	16.2	2.52	3.1	0.80
9 Y = NPh	2.53	12.6	3.07	6.6	0.88
19 Y = BH_3	2.50	14.1	2.83	5.1	0.86
23 Y = 0	2.49	11.6	3.02	6.5	0.82
27 Y = S	2.58	15.2	3.03	7.1	0.87
30 Y = Se	2.62	16.0	3.06	7.0	0.89
33 Y = Br^+ (Br^-)[c]	2.79	16.9	3.45	7.3	1.00
36 Y = CPh_3^+ (BF_4^-)[c]	2.19	11.7	3.20	6.1	0.94
Y = $Cr(CO)_5$	2.78	15.2	2.89	4.3	0.83
Y = $Fe(CO)_4$	2.66	15.7	2.95	6.2	0.88
Y = $Ni(CO)_2(2)_2$	2.60	15.8	2.77	4.6	0.84

[a] In ppm downfield relative to TMS.

[b] Values precise to ±0.1 Hz.

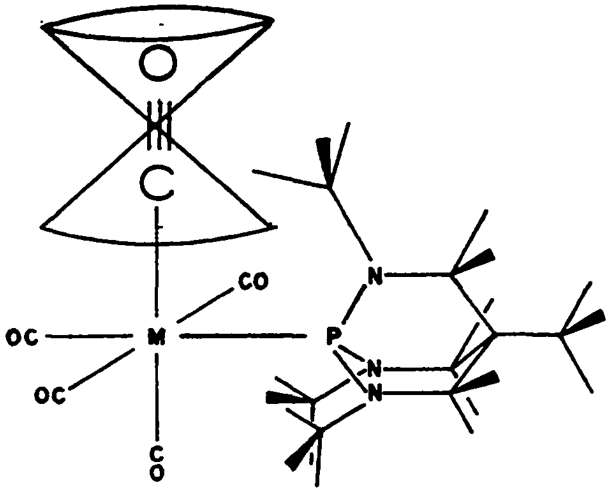
[c] Counterion.

Figure 6. Plot of ^{3}JPNCH for derivatives of P(NMeCH$_2$)$_3$CMe *versus* proton chemical shift in CD$_3$CN solution. The uppermost line is for the NMe groups and the lower lines are for the NCH$_2$ groups as described in the text.


▲ sigma bonders
● pi bonders
NMe
NCH$_2$
^{3}JPNCH (Hz)
Proton Chemical Shift, Delta(ppm)
18
16
14
12
10
8
6
4
2
5
4
3
2
1
33
2
30
Ni
Fe
Cr
27
19
9
23
36
33
30
27
9
23
Fe
36
19
Ni
Cr
2

there is no correlation of ^3JPNCH with δNCH_2 for the four pi bonding groups and the same is true for ^3JPNCH and δNMe for the four sigma bonding moieties. However, if the points for some transition metal carbonyls of 2 are included, a situation similar to that previously observed (136) in derivatives of 48 is seen in the NCH_2 region. Thus, a correlation for pi bonding groups can be obtained (correlation coefficient = 0.930) by including these data. While the points for axial-$Fe(CO)_4(\underline{2})$ and $Ni(CO)_2(\underline{2})_2$ appear to obey the pi bonding correlation in the NMe region (lowering the correlation coefficient to 0.924) and provide a pi bonding correlation in the NCH_2 region (correlation coefficient = 0.985), the point for $Cr(CO)_5(\underline{2})$ in both regions seems to be anomalously shifted downfield considering its ^3JPNCH values. In the NMe region a $^3JPNCH_3$ value of >20 Hz would be necessary to place the point near the established correlation line.

The inclusion of all three metal carbonyl points causes the correlation in the NCH_2 region to decrease from 0.985 to 0.931 and it totally destroys the correlation in the NMe region (correlation coefficient = 0.669). It is likely that the deshielding torus of each magnetically anisotropic CO group on the metal carbonyl moiety strongly influences the chemical shifts of the protons on the ligand 2. From the relative proximities of the NCH_2 and NMe protons as shown, this effect is expected to manifest itself most strongly in the NMe resonances. It can be seen that the NCH_3 protons of $Cr(CO)_5$(2), which has four perpendicular CO groups, are



shifted downfield more than those of axial-$Fe(CO)_4$(2) (which has only three perpendicular CO groups) from the least squares line generated by the points for 9, 23, 27 and 30. On the other hand, $Ni(CO)_2(2)_2$ (whose CO groups are tetrahedrally disposed) is almost on the least squares line. It is expected that the NCH_2 protons will not be affected as much as the NMe protons owing to their greater distance and this appears to be the case in axial-$Fe(CO)_4$(2) although $^3JPNCH_2$ seems to be high compared to that of the other two metal complexes. The downfield NCH_2 proton shift of $Cr(CO)_5$(2) might then reflect the attenuation of the carbonyl anisotropy effect. As in the derivatives of 48, the point for the BH_3 adduct 19 falls very close to the line drawn for the pi bonding Lewis acids (without $Cr(CO)_5$(2)) even though the

BH_3 group is often considered to be primarily sigma bonding. The idea of hyperconjugation of the BH_3 molecular orbitals with the phosphorus 3d orbitals has been put forward (137), however, and in fact, inclusion of this point does not alter the correlation of ^3JPH with δNCH_2 for the pi bonders (without $Cr(CO)_5$(2)). It remains at 0.985 in both cases.
The anomaly of $H_3B-P(OCH_2)_3CMe$ could be a coincidence due to the intersection of the sigma and pi correlation plots near this point. It is interesting to note that while the range of ^3JPH for the NCH_2 protons of compounds 9, 23, 27 and 30 is very small (0.6 Hz) the range for the NMe protons is larger (4.4 Hz) and increases as the effective electronegativity of the exocyclic group decreases O > NPh > S > Se (122). The metal carbonyl complexes fall near the low electronegativity end of the range yielding high ^3JPH values for NMe protons. A similar coupling trend is not observed for the NCH_2 protons in adducts containing pi bonding groups. By analogy with the metal carbonyl complexes of 48, the points for metal carbonyls of 2 give the lower ^3JPH values for NCH_2 protons with Fe > Ni $\geq$ Cr. This was ascribed to the ability of the chalcogens to polarize the predominantly s lone pair on 48 (i.e., raise ^3JPOCH) more so than the metal carbonyl groups (120). It seems reasonable in the present derivatives of 2 to invoke the same rationale. However, the trend is clearly reversed in the correlation of ^3JPH with NMe

proton chemical shifts. In this case, the more polarizing the exocyclic group, the smaller the value of ^{3}JPH. Why such a reversal in coupling trends is seen for the NMe and NCH_2 protons in derivatives of 2 is unknown.

P-P coupling interactions

Compounds 7, 10, 24, 34 and 37-45 constitute the first derivatives of 3 where the exocyclic substitution on the phosphorus atoms is not symmetric. The resultant nonequivalence of the ^{31}P nuclei in these systems made the direct observation of JPP possible. Nöth and Ullmann (45) were able to observe ^{3}JPP directly in a very close analog of 3 wherein they replaced a NMeNMe bridging group with a NMeNH group to give two chemically nonequivalent phosphorus nuclei. The ^{31}P-NMR parameters of the above compounds and also 14 and 17 are tabulated in Table 14. The proton decoupled spectra for the unsymmetrical compounds appear as two sets of doublets. The separation in each doublet is JPP and the chemical shifts are represented by the midpoint of each doublet as all the compounds are examples of AX systems. In the cases of 20, 40 and 43 the quadrupole moment of the boron atom broadened the ^{31}P signal for the adducted phosphorus into a hump and the chemical shifts were taken as the centers. ^{3}JPP in the latter two compounds was determined from the P=NPh and P=O resonances, respectively.

Table 14. Tabulation of ^{31}P-NMR parameters for derivatives of P(NMeNMe)$_3$P^a

Compound	Chemical shifts^b	^{3}JPP^c
3 :P(NMeNMe)$_3$P:	-107.4^d(-109)^e	32.0^f
4  $:\overset{NMe}{P(NMeNMe)_2P}:$	-100.5^d(-101.8)^g	-
7 :P(NMeNMe)$_3$P=N-N=NPh	-102.0 -25.4	74.4
10 :P(NMeNMe)$_3$P=NPh	- 96.8 +1.8	78.2
11 PhN=P(NMeNMe)$_3$P=NPh	+6.0 (+6.6)^h	-
14 (PhO)$_2$P(O)N=P(NMeNMe)$_3$P=NP(O)(OPh)$_2$	-1.0^i +13.9^j	107.5^k
17 Ph$_2$P(O)N=P(NMeNMe)$_3$P=NP(O)Ph$_2$	-2.5^i -12.2^j	110.5^k
20 H$_3$B:P(NMeNMe)$_3$P:BH$_3$	-103.7(-101.5)^e	-

---

[a] Recorded in CDCl$_3$ unless noted.

[b] In ppm relative to 85% H$_3$PO$_4$.

[c] Values precise to ±1.1 Hz.

[d] C$_6$H$_6$ solution.

[e] Reference 28, in C$_6$H$_6$.

[f] Reference 45.

[g] Reference 91, in C$_6$H$_6$.

[h] Reference 22, in CHCl$_3$.

[i] Bridgehead phosphorus.

[j] Exocyclic phosphorus.

[k] Obtained from ITRCAL-analyzed spectrum.

Table 14. continued

Compound	Chemical shifts^b		$^3J_{PP}$^{c}
21  $H_3B{:}\overset{NMe}{P(NMeNMe)_2P}{:}BH_3$	-112.8		-
24 $:P(NMeNMe)_3P{=}O$	-96.1	-5.6	84.3
25 $O{=}P(NMeNMe)_3P{=}O$	-8.9	(-8.6)[1]	-
28 $S{=}P(NMeNMe)_3P{=}S$	(-66.5)[1]		-
31 $Se{=}P(NMeNMe)_3P{=}Se$	-67.0		113.6^k
34 $[:P(NMeNMe)_3P{-}Br]Br$	-112.7	-16.1	132.1
37 $O{=}P(NMeNMe)_3P{=}NPh$	-9.0	+6.8	102.0
38 $S{=}P(NMeNMe)_3P{=}NPh$	-65.6	+6.7	106.5
39 $Se{=}P(NMeNMe)_3P{=}NPh$	-67.0	+7.3	107.6
40 $H_3B{:}P(NMeNMe)_3P{=}NPh$	-98.6	+6.1	99.9
41 $S{=}P(NMeNMe)_3P{=}O$	-66.2	-8.8	105.3
42 $Se{=}P(NMeNMe)_3P{=}O$	-67.3	-8.0	107.6
43 $H_3B{:}P(NMeNMe)_3P{=}O$	-100.1	-9.5	101.0
44 $[Br{-}P(NMeNMe)_3P{=}NPh]Br$	-23.1	+16.2	109.8
45 $[Br{-}P(NMeNMe)_3P{=}O]Br$	-23.6	-6.9	110.4

[1] CH_2Cl_2 solution.

Comparison of the chemical shifts of the unsymmetrical cages with the appropriate symmetrical cages makes the peak assignments straight-forward. Thus the high field signals in 10, 37-40 and 44 are assigned to the $(>\mathrm{N})_3\mathrm{P{=}NPh}$ phosphorus, in 24, 41-43 and 45 to the $(>\mathrm{N})_3\mathrm{P{=}O}$ phosphorus and in 34 to the ionic phosphorus atoms.

There is a trend in $^3J_{PP}$ for derivatives of 3 similar to one observed in derivatives of $\mathrm{P(OCH_2)_3P}$ (44, 120). A comparison of the two systems can be made by inspection of Table 15. It is seen that in both systems, the value of $^3J_{PP}$ increases in magnitude as one progresses from the presence of two $\mathrm{P^{III}}$ atoms in the molecules to systems with a $\mathrm{P^{III}}$ and a $\mathrm{P^{V}}$ present and the coupling reaches its greatest value when both phosphorus atoms are $\mathrm{P^{V}}$. The derivatives of $\mathrm{P(OCH_2)_3P}$ show that $^3J_{PP}$ is more sensitive to oxidation of the phosphine phosphorus than the phosphite phosphorus and this was ascribed to the greater polarizability of a more basic phosphine lone pair compared to a phosphite lone pair (44). While the $^3J_{PP}$ value for 3 has never been measured it was estimated to be about 80 Hz by Finer and Harris (138) based upon a lineshape analysis of the ^{1}H-NMR spectrum of 3. However, Nöth and Ullmann (45) were able to directly measure $^3J_{PP}$ as 32.0 Hz in the bicyclic compound  $\overbrace{\mathrm{P(NMeNMe)_2P}}^{\mathrm{(NMeNH)}}$. Because of the great similarity of 3 and the above hydrazinobisphosphine the 32.0 Hz value is assumed to be valid in 3. They

Table 15. ^{3}JPP values for selected derivatives of $P(OCH_2)_3P$ and $P(NMeNMe)_3P$

$P(OCH_2)_3P$ Compound	^{3}JPP[a]	$P(NMeNMe)_3P$ Compound	^{3}JPP[b]
$P(OCH_2)_3P$	- 37.2	$P(NMeNMe)_3P$, 3	32.0[c]
$O{=}P(OCH_2)_3P$	+ 65	$P(NMeNMe)_3P{=}O$, 24	84.3
$P(OCH_2)_3P{=}O$	+140		
$S{=}P(OCH_2)_3P$	+ 48.1	$P(NMeNMe)_3P{=}NPh$, 10	78.2
$P(OCH_2)_3P{=}S$	+118		
$O{=}P(OCH_2)_3P{=}O$	+139.1	$O{=}P(NMeNMe)_3P{=}NPh$, 37	102.0
$S{=}P(OCH_2)_3P{=}S$	+150	$Se{=}P(NMeNMe)_3P{=}Se$, 31	113.6
$S{=}P(OCH_2)_3P{=}O$	+151.3	$S{=}P(NMeNMe)_3P{=}O$, 42	105.3

[a] Values from references 44 and 120.

[b] Values from this work unless noted. Precise to ±1.1 Hz.

[c] Reference 45.

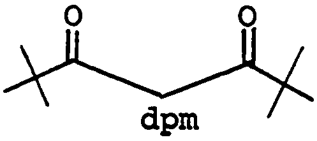
then used this value to obtain a "best fit" for the ^{1}H-NMR spectrum of 3.

The trend in ^{3}JPP would seem to indicate that sign reversal also occurs on going from 3 to any of its derivatives. Since aminophosphines are more basic than phosphites (as evidenced by comparison of ν(BH) frequencies presented earlier) it would stand to reason that ^{3}JPP for 24 (84.3 Hz) is larger than in $O=P(OCH_2)_3P$ (+65 Hz) on the basis of lone pair polarizabilities.

The polarization hypothesis is also consistent with the increase in ^{3}JPP upon reaction of the P^{III} in 10 and 24 with BH_3 to give 40 and 43, respectively. The value of ^{3}JPP increases from 78.2 Hz to 99.9 Hz in the couple 10, 40 and from 84.3 Hz to 101.0 Hz for the couple 24, 43. These approximately 20 Hz increases upon P^{III} adduction with BH_3 are not out of line considering the almost 50 Hz increase in ^{3}JPP in progressing from $P(OCH_2)_3P$ to $H_3B-P(OCH_2)_3P$ (120). Interestingly, when P^{III} in 10 or 24 is converted to a P^+ species, ^{3}JPP increases by 35.4 and 32.2 Hz, respectively, while converting a P^{III} in 3 to a P^+ in 34 increases ^{3}JPP by a comparatively large 100.1 Hz. These two results do not appear to be consistent with the finding that P^V species give larger JPP values than P^{III} species. ^{3}JPP in 44 and 45 would be expected to be much larger than is observed based upon the results in 34, or the results in 34 are anomalously large compared to 44 and 45.

Further discussions of coupling interactions necessitate the use of ^{1}H-NMR spectral parameters which are collected in Tables 16 and 17.

The assignment of ^{1}H-NMR spectral absorptions for unsymmetrical derivatives of 3 was accomplished in part through the use of lanthanide shift reagents (LSR's). It has been found that addition of LSR to solutions of organophosphorus compounds produces dramatic changes in the spectra depending upon the distance of the proton from the LSR binding site (139-142). While LSR's were found to complex both P^{III} and P^{V} compounds, a definite preference for the latter was shown (142), especially when it was contained in a phosphoryl group. Incremental addition of either Eu(dpm)$_3$ or Pr(dpm)$_3$ to a CCl$_4$ solution of 23 produced shifts in all the proton resonances with the NMe groups showing twice as large a shift as the NCH$_2$ groups up to the line broadening limit which occurs because of the paramagnetic nature of the LSR metal ion. This larger shift is expected from the close proximity of the NMe groups of 23 to the LSR coordinated on the phosphoryl oxygen. Upon addition of LSR to a CCl$_4$ solution of 24 similar shifts are seen for the NMe groups and are shown in



dpm

Table 16. ^{1}H-NMR spectral data for symmetrical derivatives of hydrazinobiphosphines

Compound	Chemical shifts[b]			Coupling constants[c]		Reference
	δNMe[d]		δPh[e]			
<u>3</u> $P(NMeNMe)_3P$	2.83			15.0		this work
	2.78[f]			15.2		45
<u>4</u>  $\overset{\text{NMe}}{\overbrace{\text{P(NMeNMe)}_2\text{P}}}$	2.59[f]	2.77[f,g]		15.0[h]	13.2[i]	this work
	2.57[f]	2.79[f,g]				45
<u>11</u> $PhN{=}P(NMeNMe)_3P{=}NPh$	2.98		7.05	11.0		this work
	2.98		6.93	11.0		22
<u>14</u> $(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$	2.85		7.24	12.0		this work
<u>17</u> $Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$	2.92		-[j]	12.0		this work
	2.93		-[k]	12.0		22
<u>20</u> $H_3B{:}P(NMeNMe)_3P{:}BH_3$[l]	2.87[f]			12.6		28
<u>21</u>  $H_3B{:}\overset{\text{NMe}}{\overbrace{\text{P(NMeNMe)}_2\text{P}}}{:}BH_3$[l]	2.74	2.96[g]		13.7[h]	11.6[i]	this work
<u>25</u> $O{=}P(NMeNMe)_3P{=}O$	2.88[m]			11.0		28
<u>28</u> $S{=}P(NMeNMe)_3P{=}S$	2.96[m]			12.8		28
<u>31</u> $Se{=}P(NMeNMe)_3P{=}Se$	2.95[m]			12.8		28

[a] Recorded in $CDCl_3$ solution except where noted.

[b] In ppm downfield from TMS.

[c] $|{}^{3}JPH + {}^{4}JPH|$ for the pseudotriplet except as noted. Values for this work are precise to ±0.2 Hz.

[d] For NMeNMe protons except as noted.

[e] Resonances were multiplets with centers reported.

[f] In C_6H_6 solution.

[g] For NMe protons.

[h] Simple doublet.

[i] Simple triplet.

[j] Two multiplets centered at 7.38 and 7.78 ppm.

[k] Three multiplets centered at 7.35, 7.68 and 7.83 ppm.

[l] The BH_3 protons where not observed.

[m] In CH_2Cl_2.

Table 17. ^{1}H-NMR spectral data for unsymmetrical derivatives of the compounds $(X)P_a(NMe_aNMe_b)_3P_b(Y)$[a]

Compounds			Chemical shifts[b]		Coupling constants[c]			
	X	Y	δMe_a	δMe_b	$^3JP_aH_a$	$^3JP_bH_b$	$^4JP_aH_b$	$^4JP_bH_a$
34	lone pair	Br^{+}[d]	3.30	3.12	10.3	12.6	0	2.8
24	lone pair	O[e]	2.77	2.73	15.1	9.7	0	1.7
7	lone pair	N_3Ph	2.90	2.94	14.5	10.3	0	1.5
10	lone pair	NPh	2.86	2.85	14.8	10.4	0	1.6
37	O	NPh	2.95	2.92	9.5	10.1	1.6	1.6
38	S	NPh	3.01	2.92	11.4	9.8	1.6	1.6
39	Se	NPh	3.05	2.95	12.0	9.6	1.5	1.6
40	H_3B	NPh	2.93	2.90	12.1	9.8	0	1.6
41	S	O	2.97	2.91	11.0	9.1	1.4	1.5
42	Se	O	3.03	2.94	12.0	9.1	1.5	1.7
43	H_3B	O	2.91	2.88	11.9	9.4	0	1.6

[a] Recorded in $CDCl_3$ unless noted.

[b] In ppm downfield relative to internal TMS. For assignments, see text.

[c] Values precise to ±0.2 Hz.

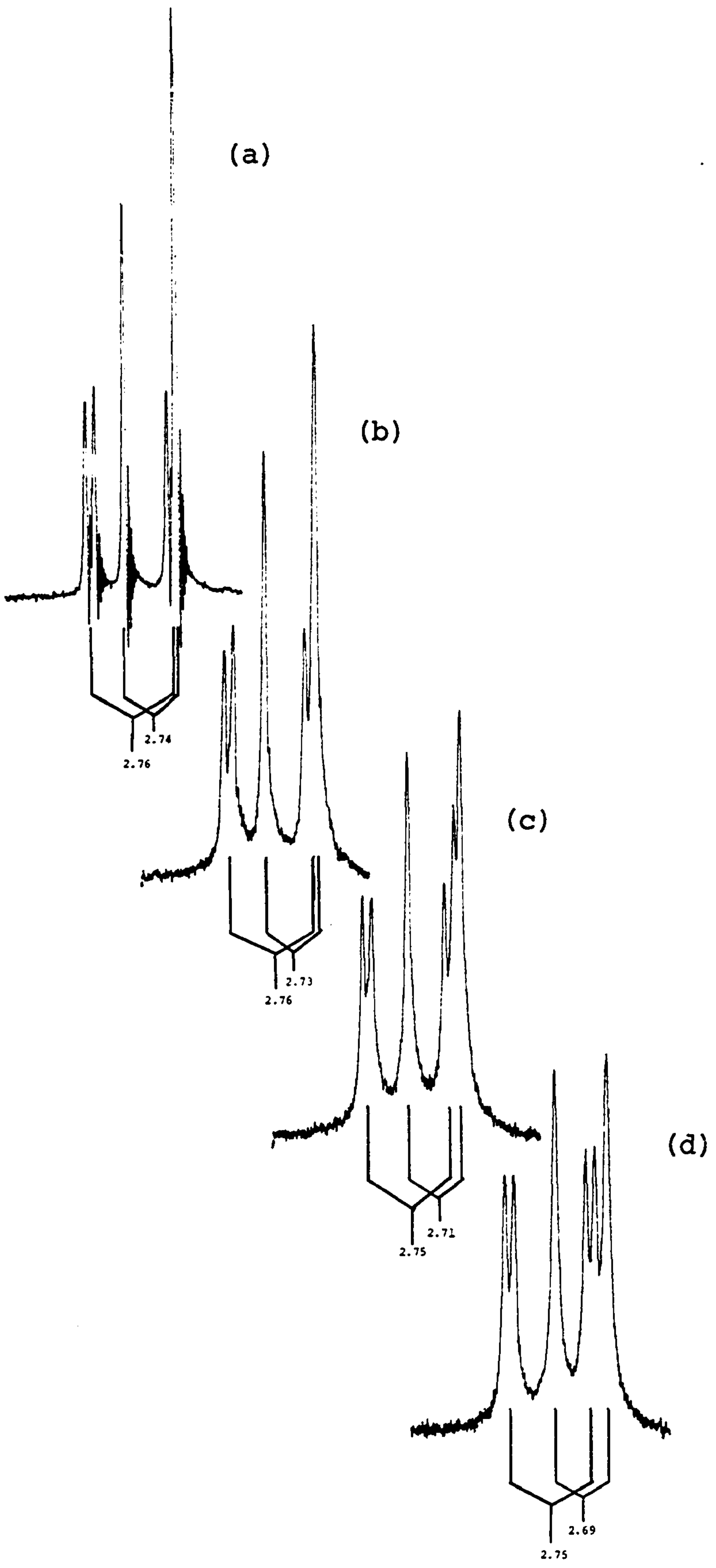
[d] Counterion is Br^-.

[e] In CCl_4.

Figure 7. As the large doublet in each case undergoes the greatest shift, it was assigned to the NMe group closest to the phosphoryl group. It is seen that while both phosphorus nuclei couple to the NMe groups nearest them, the P^V nucleus also gives rise to a noticeable four-bond coupling while the P^{III} nucleus does not. The values of JPH obtained from 24 show very good agreement with the information obtained from 3 and 25. In both of the latter cases a pseudo-triplet appears in the ^{1}H-NMR spectra. The separation of the outermost peaks is represented by the absolute value of the sum of the three- and four-bond P-H couplings, *i.e.*, $|{}^3JPH + {}^4JPH|$. In 3 the value obtained in this work is 15.0 Hz, in excellent agreement with the 15.1 Hz found for ^3JPH of the P^{III} in 24 assuming that ^4JPH is zero (*i.e.* in 3, $|{}^3JPH + {}^4JPH| = |{}^3JPH|$). Nöth and Ullmann (45) found that the "best fit" for the ^{1}H-NMR spectrum of 3 occurred when $^3JPH = 12.8$ Hz and $^4JPH = 2.4$ Hz (using the assumption that $^3JPP = 32.0$ Hz). Such a large value of ^4JPH for P^{III} in a derivative of 3 would appear to be contradicted by the results of this work. Unfortunately, they did not specify what the "best fit" criterion was and we were not able to perform calculations on an $AX_9X'_9A'$ system.

In 24 excellent agreement is again seen when the sum of ^3JPH (9.7 Hz) and ^4JPH (1.7 Hz) for P^V (11.4 Hz) is compared to the 11.0 Hz observed in 25. The last case also indicates

Figure 7. LSR effects on the proton spectrum of $P(NMeNMe)_3P=O$ upon addition of incremental amounts of the upfield shift reagent $Pr(dpm)_3$ progressing from (a) containing no LSR to (d). Note the broadening of the resonances and the greater upfield shift of the large doublet.

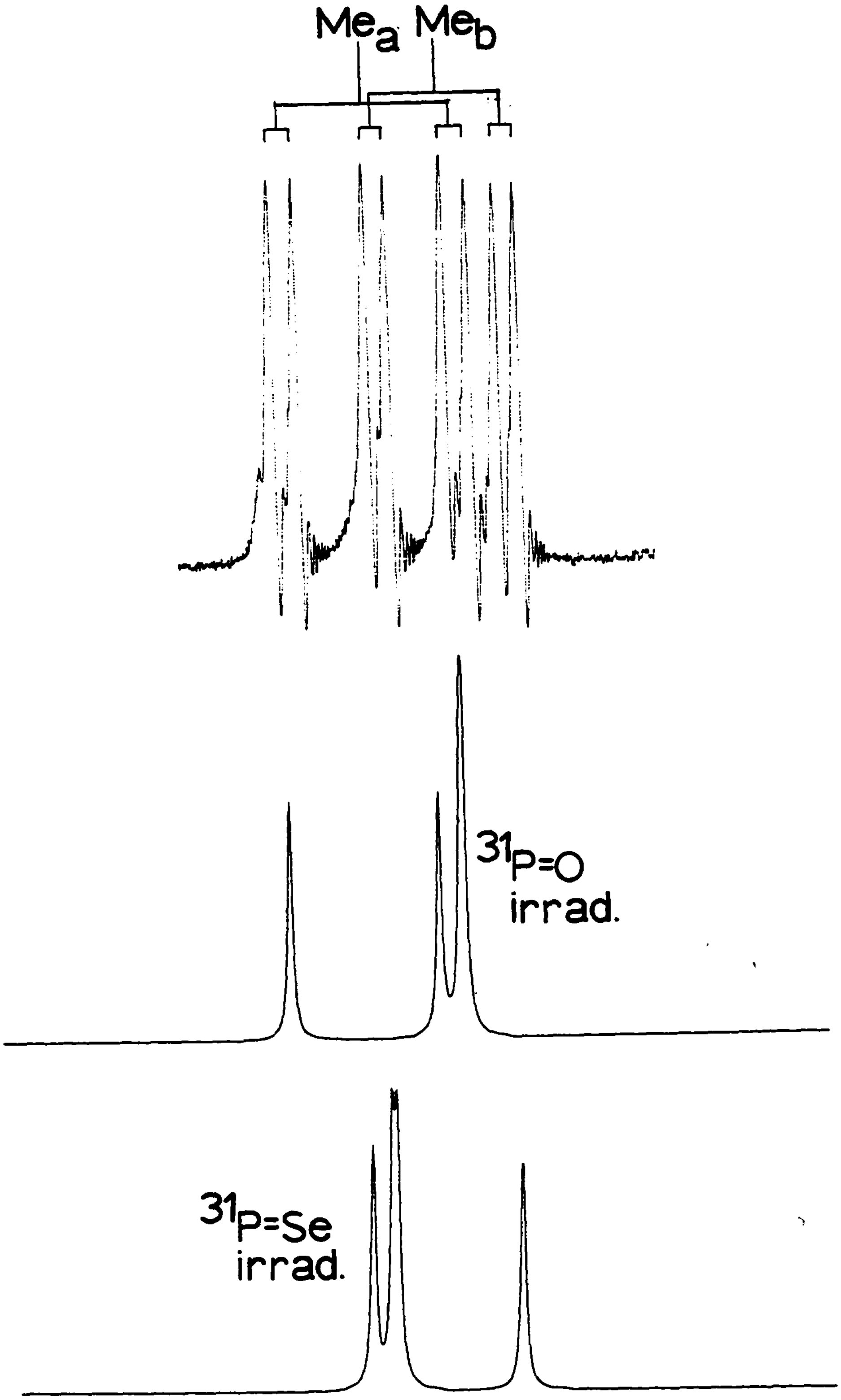

(a)
2.74
2.76
(b)
2.73
2.76
(c)
2.71
2.75
(d)
2.69
2.75

that both ^{3}JPH and ^{4}JPH are of the same sign so that the magnitude of their sum is larger than the individual couplings whereas if they were of opposite sign their sum would be about 8 Hz. A similar analysis of **10** would predict values for $|^{3}\text{JPH} + {}^{4}\text{JPH}|$ of 14.8 Hz for **3** and 12.0 Hz for **11** as compared to the 15.0 Hz and 12.0 Hz observed. Clearly, the excellent agreement between observed values of P-H couplings for the symmetrical species **3**, **11** and **25** tends to confirm the correctness of the ^{1}H-NMR assignments in **10** and **24**.

From the results obtained for **10** and **24** with regard to P^{III} and P^{V} four-bond proton coupling, the ^{1}H-NMR spectra of their BH$_3$ adducts **40** and **43** were assigned assuming that the adducted phosphorus atoms would closely resemble P^{III} in the parent compound (*i.e.* the adducted phosphorus would not show a ^{4}JPH coupling). By similar reasoning, the couplings in **7** were thought to be analogous to those in **10** and the spectrum was assigned in this manner.

Assignments for the bis P^{V} derivatives of **3** were arrived at with more difficulty. It was originally thought that the ^{1}H-NMR spectra could be greatly simplified by selective irradiation of each phosphorus nucleus while observing the ^{1}H-NMR spectra as shown in Figure **8** for compound **42**. Except for **37**, all the unsymmetrical derivatives of **3** had ^{31}P-NMR resonances sufficiently far apart to make this a viable

Figure 8. The expected collapse of the proton spectrum of $Se{=}P(NMe_aNMe_b)_3P{=}O$ upon selective irradiation of the two phosphorus nuclei. The irradiated spectra were generated by ITRCAL.


Me$_a$
Me$_b$
^{31}P=O irrad.
^{31}P=Se irrad.

technique. However, difficulties with the phosphorus decoupling generator on the Bruker HX-90 spectrometer and operator nonfamiliarity with the technique combined to give spectra of doubtful scientific validity although broadband ^{31}P decoupling did allow determination of the two different chemical shifts for the Me groups which could be used to check assignment accuracies. Certain trends in both ^{3}JPH and ^{4}JPH were noticed upon careful examination of the spectra and were used in assignments as described below.

The spectral assignments for the two groups <u>37</u>-<u>40</u> and <u>41</u>-<u>43</u> shown in Table 17 appear to bring consistency to the data. The range of ^{3}JPH for the P=NPh phosphorus is 9.6-10.4 Hz for compounds <u>10</u> and <u>37</u>-<u>40</u> and ^{4}JPH remains at 1.6 Hz. Also the chemical shifts of the NMe groups nearest the P=NPh ends of the molecules are quite similar for <u>37</u>-<u>39</u>. This would be expected if the solvent orientation around these three compounds was very similar. The electronic similarity of O, S and Se on one end of the molecule and the presence of the NPh group on the other end (which probably dominates solvent orientation) could account for the identical shift of 2.92 ppm for the NMe groups in <u>37</u> and <u>38</u> and the nearly identical shift of 2.95 ppm for <u>39</u>. The chemical shift of the NMe groups at the other end of the molecule in <u>37</u>-<u>39</u> show a monotonic decrease to low field in the order O, 2.95 ppm; S, 3.01 ppm and Se, 3.05 ppm. This could be a consequence of solvent effects and/or systematic electronic variations in the chalconides. The latter effect is suggested by the increase in ^{3}JPH for the P=Ch nuclei (9.5, 11.4 and 12.0 Hz for O, S and Se, respectively).

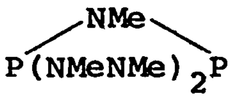
Similar trends are shown for 37, 41 and 42 where P=O is the common functional group. While chemical shift comparisons are not evident for the P=O end there is again a correlation of movement to lower field concomitant with an increase in ^{3}JPH for the other end of the molecule in going from NPh to S to Se (δ: 2.92, 2.97, 3.03 ppm, respectively and ^{3}JPH: 10.1, 11.0, 12.0 Hz, respectively). That O and NPh have almost the same electronic effects could be ascribed to their similar electronegativities as it might reasonably be expected that the presence of an electron withdrawing Ph group on nitrogen could raise the total NPh group electronegativity to a value comparable to an O atom. Tarasevich and Egerov (122) have calculated the group electronegativity of NPh to be 3.24 when O is assigned a value of 3.55. Thus the two groups could have nearly equal inductive effects on phosphorus and therefore lead to the similar coupling magnitudes for ^{3}JPH, ^{4}JPH and ^{3}JPP seen in the two groups 37-39 and 37, 41, 42.

Why ^{3}JPH is larger for P^{III} than for P^{V} while the reverse is true for ^{4}JPH in derivatives of 3 is not clear.

Undoubtedly, P-H coupling depends greatly upon geometrical considerations which could be substantially different for P^{III} and P^{V} nuclei.

Gray and Albright (143) have observed ^{1}JPN to become increasingly negative in the series of compounds <u>1</u> (+59.1 Hz), <u>26</u> (-6.0 Hz) and <u>22</u> (-26.9 Hz) while $^{2}JPNC$ decreases in the same series (+19.15, +3.3, +3.4 Hz, respectively). In this work $^{2}JPNC$ was determined to be 3.9 ± 0.5 Hz for compound <u>29</u> and it was assumed to have a positive sign. Tables 18 and 19 list ^{13}C-NMR data for various aminophosphine systems of interest. From CNDO/2-FPT calculations on $P(NH_2)_3$, $S{=}P(NH_2)_3$ and $O{=}P(NH_2)_3$ it was found that the phosphorus 3s- nitrogen 2s bond order (P_{SPSN}) increased in the above series (0.1271, 0.2473 and 0.2651, respectively) and by analogy it can be assumed that a similar trend obtains in the series <u>1</u>, <u>26</u> and <u>22</u> (143). Although the s bond order appears to increase upon oxidation of the phosphorus, Räuchle and coworkers (93) found that the P-N total bond order decreased from 1.18 in <u>1</u> to 1.12 in <u>26</u> to 1.10 in <u>22</u> to 1.06 in <u>29</u>. To rationalize these two trends one could consider P-N pi bonding to decrease as the phosphorus is oxidized. Since all the chalcogens can pi bond with phosphorus it is not too surprising that P-N pi bonding could decrease as P=X pi bonding increases. The total P=X bond orders calculated (93) are 1.46 in <u>26</u>, 1.88 in <u>22</u> and 2.02 in

Table 18. ^{13}C-NMR spectral data for derivatives of $P(NMe_2)_3$ and $P(NMeNMe)_3P$

Compound	Chemical shifts[a] $\delta^{13}C$	Coupling constants	Solvent
1 $(Me_2N)_3P$	------	+19.15 ± 0.05[b]	neat
22 $(Me_2N)_3P{=}O$	------	+ 3.4 ± 0.1[b]	neat
26 $(Me_2N)_3P{=}S$	------	+ 3.3 ± 0.05[b]	neat
29 $(Me_2N)_3P{=}Se$	-36.6	3.9 ± 0.5[b]	$CDCl_3$
3 $P(NMeNMe)_3P$	-37.7	12.8 ± 1.0[c]	C_6D_6
11 $PhN{=}P(NMeNMe)_3P{=}NPh$	-37.0	4.4 ± 0.5[c]	$CDCl_3$
25 $O{=}P(NMeNMe)_3P{=}O$	-36.3	4.4 ± 0.5[c]	$CDCl_3$
4  $P(NMe)(NMeNMe)_2P$	-35.3[d] -28.8[e]	15.9 ± 1.2[c] 22.6 ± 1.2[f]	C_6D_6

[a] Referenced relative to TMS.

[b] Doublet.

[c] Pseudotriplet. Coupling reported is separation of outermost peaks.

[d] NMeNMe carbons.

[e] NMe carbon.

[f] Triplet.

Table 18. continued

Compound	Chemical shifts ^{13}C	Coupling constants	Solvent
10 $P(NMeNMe)_3P=NPh$	-37.8^{g}	9.8 ± 1.0^{b}	$CDCl_3$
	-35.5^{h}	3.9 ± 1.0^{b}	
24 $P(NMeNMe)_3P=O$	-37.9^{g}	9.8 ± 1.0^{b}	$CDCl_3$
	-36.3^{h}	2.9 ± 1.0^{b}	

[g] Carbons closest to P^{III}.

[h] Carbons closest to P^{V}.

Table 19. ^{13}C-NMR spectral data for derivatives of $P(NMeCH_2)_3CMe$

Compound	NMe carbon[b]		NCH_2 carbon[b]		Bridgehead carbon[b]		Methyl carbon[b]
	$\delta^{13}C$	^2JPNC	$\delta^{13}C$	^2JPNC	$\delta^{13}C$	^3JPNCC	$\delta^{13}C$
2 $P(NMeCH_2)_3CMe$	-34.8	-[c]	-61.2	3.9	-40.0	25.9	-22.7[d]
23 $O{=}P(NMeCH_2)_3CMe$	-35.3	-[c]	-62.9	-[c]	-33.5	30.8	-20.4
27 $S{=}P(NMeCH_2)_3CMe$	-37.3	-[c]	-62.5	2.9	-33.3	25.4	-21.2
30 $Se{=}P(NMeCH_2)_3CMe$	-38.6	-[c]	-62.4	3.9	-34.1	24.4	-21.5

[a] The solvent was $CDCl_3$ except for 2 where it was C_6D_6. Chemical shifts are referenced relative to TMS. Coupling constants are precise to ±0.5 Hz.

[b] Assignments were based on the gated decoupled spectrum of 2.

[c] Insufficient resolution. Coupling probably near zero.

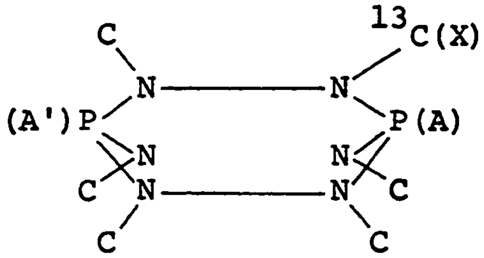
[d] There is no ^4JPNCCC coupling observed.

29. The two bond order trends show that P-N and P=X bonding are evidently inversely related. The N-C bond order remains constant at 1.03 or 1.04 for the entire series 1, 22, 26, and 29.

The postulated lessening of nitrogen pi donation to phosphorus and the apparent increase in sigma bonding upon phosphorus oxidation might allow a change in nitrogen MO's which could markedly affect the transmission of spin couplings through nitrogen and lead to the large change in ^{2}JPC observed upon phosphorus oxidation.

Coupling of phosphorus to protons in derivatives of 1 also changes upon oxidation. In the series 1, 18, 22, 26, 29 and $Te{=}P(NMe_2)_3$ the value of ^{3}JPH increases in the order 9.0, 9.5, 9.5, 11.3, 11.7, 11.9 Hz (28) and it has already been seen that ^{2}JPNC and ^{1}JPN become more negative in the same series. Due to free rotation about the P-N bond the values of ^{2}JPC and ^{3}JPH for derivatives of 1 are necessarily averages of many conformations but low temperature studies of P^{III} compounds have shown that ^{2}JPC is large/positive and small/negative for carbons cis and trans to the lone pair, respectively (144). It seems that all the couplings to phosphorus become more negative (less positive) upon oxidation of the phosphorus. McFarlane has determined (145) that ^{2}JPCC and ^{2}JPOC become more negative upon phosphorus oxidation and the smaller positive values of ^{2}JPNC observed for oxidized derivatives of 1 as compared to 1 itself are in accord with these findings. In 2 and its derivatives no cis P-C coupling is observed and the trans couplings show no apparent trend. A large ^3JPNCC to the bridgehead carbon is observed, however. Similar couplings are seen in bicyclic phosphites, phosphates and phosphine oxides (79, 146).

The rise in magnitude of JPC from 2 to 3 may be indicative of a change in the ability of nitrogen to transmit spin information when an N-N bridge is present in a molecule like 3 rather than the N-C bridge in 2. The ^{13}C-NMR spectrum of 3 is a pseudotriplet which can be solved by ITRCAL (84) as the X part of an AA'X system using the value of $^3JPP = 32.0$ Hz determined previously (45). The value of



^2JPNC one obtains is then 12.8 Hz which is the separation of the two outermost peaks of the pseudotriplet. Implicit in this analysis is the assumption that ^3JPNNC is zero or at least very small so that $|^2JPNC + {}^3JPNCC| \cong |^2JPNC|$. Such an assumption appears to be borne out by the ^{13}C-NMR spectra of 10 and 24 which consist of two doublets; one due to each chemically non-equivalent carbon nucleus split by its nearest neighbor phosphorus. From chemical shift comparisons of the spectra of 3, 10, 11, 24 and 25, it was determined that ^{2}JPNC for P^{III} was 9.8 Hz in 10 and 24 while for P^{V} the values were 3.9 and 2.9 Hz, respectively. ITRCAL solutions for 11 and 25 gave ^{2}JPNC values of 4.4 Hz in each case. ^{3}JPP was estimated at 100 Hz for the two compounds. In all the systems, reasonable solutions could be obtained by assigning ^{3}JPNNC = 0 Hz. It is very interesting to observe that in derivatives of 3 there is appreciable ^{2}JPNC coupling for carbons _cis_ to the phosphorus lone pair or P=X bond (as is also observed in low temperature spectra of acyclic aminophosphines (116)) but there is no such coupling observed in derivatives of 2. Whether this ^{2}JPNC phenomenon arises from the hydrazine backbone of 3 is a matter of speculation. However, if so, it hardly makes a difference in ^{3}JPNCH couplings of 2 or 3.

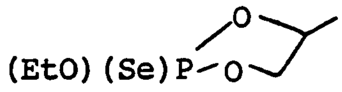
The extremely large ^{3}JPNCC coupling for derivatives of 2 may have a great bearing on the P-P interaction in compounds of 3 because it seems to show that the cisoid vicinal coupling over three bonds is a very favored pathway in bicyclics.

Selenophosphoryl Compounds

Syntheses

The syntheses of 29 (93), 31 (28) and 50 (98) have been previously reported in the literature. An earlier preparation (147) of the ethyl analog of 52 did not come to attention until well after the present work was completed. It is interesting to note that Chang did not observe any reaction between the bicyclic phosphite and Se in refluxing benzene after one hour while in this work an almost quantitative reaction of Se and 48 proceeded in toluene at 80° over 10 hours. The addition of a small amount of Na_2Se catalysed his reaction which then proceeded quickly. Other compounds used in this work were synthesized by methods routinely used in the literature.

While most of the compounds were stable, an exception was 53 which decomposed to give red selenium either upon standing under N_2 or in solution at room temperature. In solution the decomposition was rapid, being noticeable after about 2 hours whereas in the solid state decomposition occurred over a period of days. Such behavior was found for the cyclic compound

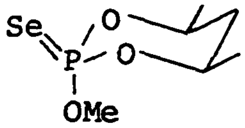
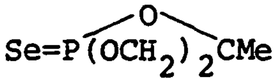


by Arbuzov and Razumova (148) and both can be rationalized on the basis of strain in the five-membered rings in each compound.

^{31}P-NMR spectra

^{31}P-NMR data is compiled in Table 20 for the selenophosphoryl compounds studied in this work. Spectroscopic

Table 20. ^{31}P-NMR chemical shifts and ^{1}JPSe values for some organophosphorus compounds^{a}

Compound	δP^{b}	$^{1}JPSe^{c}$
29 $Se{=}P(NMe_2)_3$	-82.5	783.5
30 $Se{=}P(NMeCH_2)_3CMe$	-77.7	854.5
31 $Se{=}P(NMeNMe)_3P{=}Se$	-66.2	922.9
39 $Se{=}P(NMeNMe)_3P{=}NPh$	$-67.0^{d}(+7.3)^{e}$	918.3
42 $Se{=}P(NMeNMe)_3P{=}O$	$-67.3^{d}(-8.0)^{f}$	925.5
50 $Se{=}P(OMe)_3$	-78.0	954.4
51 	-66.8	996.5
52 $Se{=}P(OCH_2)_3CMe$	-60.1	1053.1
53  $Se{=}P(OCH_2)_2CMe$	-81.4	1098.6

^{a}CDCl$_3$ solutions.

^{b}In ppm relative to 85% H_3PO_4.

^{c}Values are precise to ±1.1 Hz.

^{d}P=Se.

^{e}P=NPh.

^{f}P=O.

parameters for the compounds 30, 31, 39, 42, 51, 52 and 53 are reported for the first time.

The peaks giving rise to ^{1}JPSe values are symmetrically disposed about a main peak which is due to non-NMR active Se atoms. These "wing" peaks have 7.58% as much total area as the central peak due to the natural abundance of ^{77}Se and their separation is usually the value of ^{1}JPSe. Additionally, other couplings not involving hydrogen may manifest themselves in the proton decoupled ^{31}P-NMR spectra. A straightforward example is the spectrum of 39 shown in Figure 9. The broad upfield peak is the signal of the reference, 85% H_3PO_4. The large upfield doublet belongs to the phenylimido phosphorus while the downfield doublet is associated with the phosphorus bearing the non-NMR active selenium. The separation in the doublets is ^{3}JPP (107.6 Hz) listed previously in Table 14. Two much smaller doublets are symmetrically placed about this latter doublet and these arise from the ^{31}P-^{77}Se coupling. The separation in each of these smaller doublets is due to ^{3}JPP while the separation of the centers of the smaller doublets is ^{1}JPSe (918.3 Hz).

A unique case involving the manifestation of other couplings appears in the ^{31}P-NMR spectrum of 31 shown in Figure 10. It was thought at first that all the small peaks surrounding the central peak were spinning side-bands which arose due to bad tuning of the spectrometer shims. The

Figure 9. Proton decoupled ^{31}P-NMR spectrum of Se=P(NMeNMe)$_3$P=NPh. Note the set of "wing" doublets centered about δPSe. The peak marked with ▼ is the reference H_3PO_4.

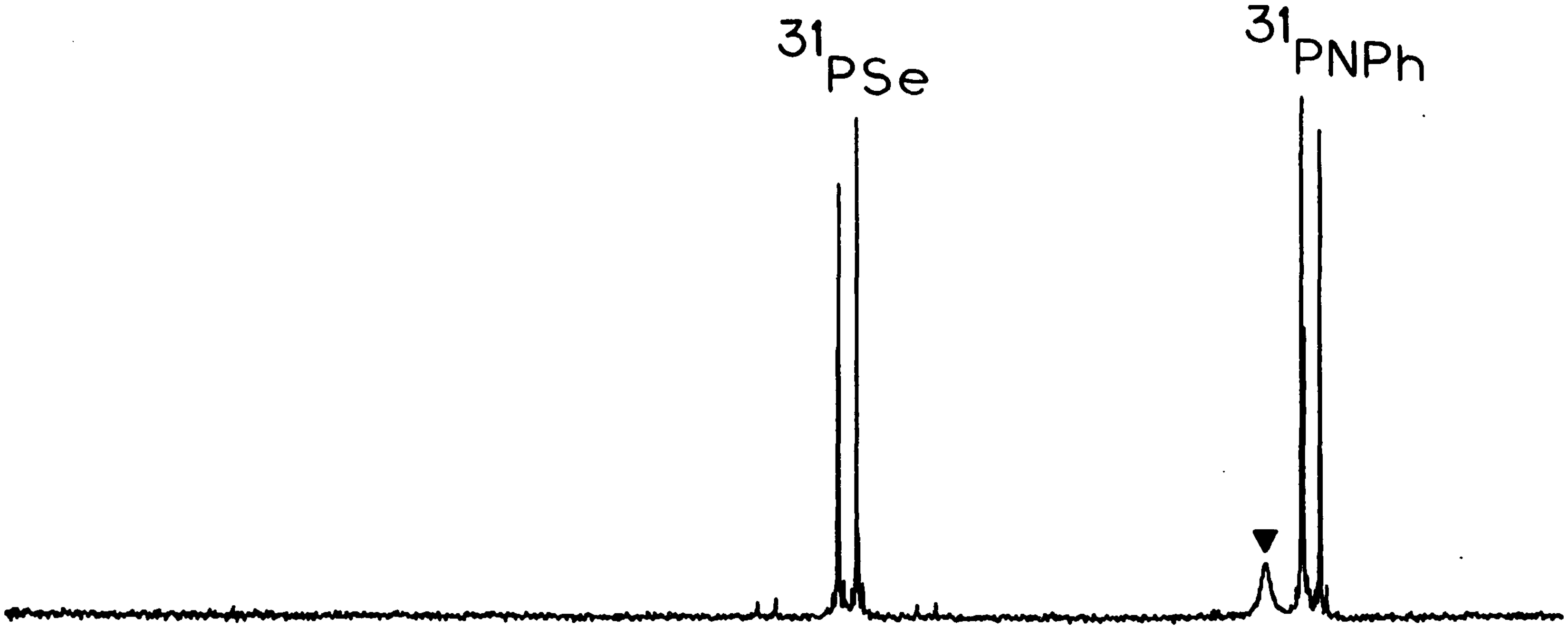
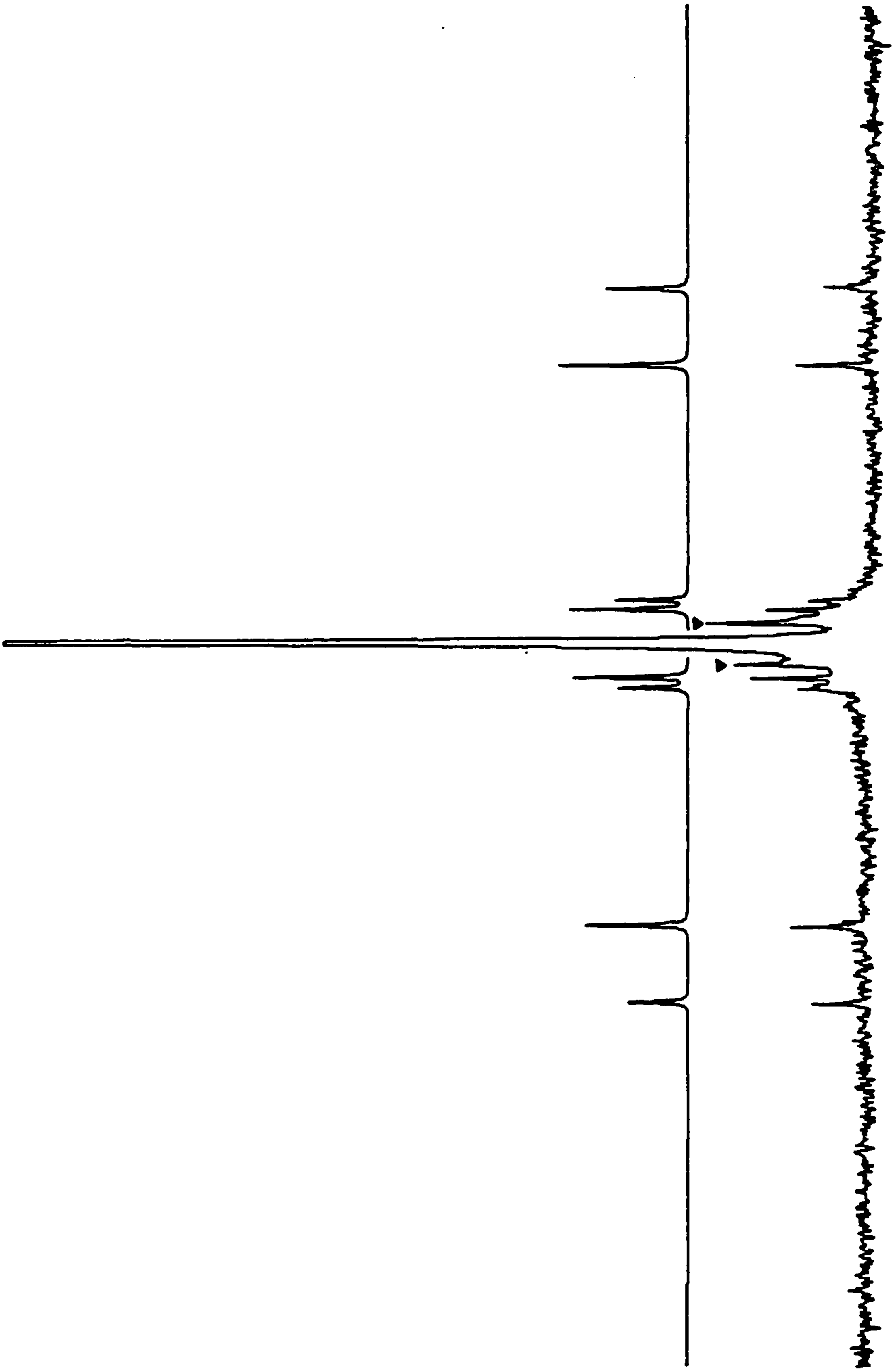
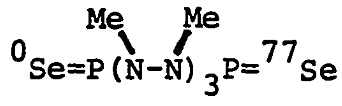

$^{31}P_{Se}$
$^{31}P_{NPh}$
▼

Figure 10. Proton decoupled ^{31}P-NMR spectrum of $Se{=}P(NMeNMe)_3P{=}Se$. The ITRCAL generated spectrum illustrating the effect of ^3JPP coupling is displayed above the experimental spectrum. The peaks marked with ▼ are spinning sidebands.



spectrum obtained after careful retuning of the instrument was very similar whereupon it was realized that most of these peaks were due to a non-first order spectrum which was superimposed on the central peak. That the ^{31}P-NMR spectrum of 31 was even obtained is due only to the advent of Fourier transform (FT) NMR spectrometers. Using continuous wave (CW) techniques, earlier workers (28) were not able to obtain even δ^{31}P for 31 owing to its great insolubility. Since FT allows one to "collect" a great many spectra and "add" them together to get a composite spectrum, solubility problems are minimized.

Using ITRCAL it was possible to analyse the ^{31}P-NMR spectrum of 31 as an example of the A branch of an AA'X system superimposed on an A_2 system. Since the natural abundance of ^{77}Se is only 7.58% the chances of having a molecule of 31 containing two ^{77}Se atoms is 0.58%. Similarly, the chances of having one ^{77}Se atom is 14.01% and no ^{77}Se atoms is 85.41%. In the first and third case the ^{31}P-NMR spectrum is an A_2 singlet even though there may be substantial A-A coupling. The second case gives rise to an AA'X system as shown below



$$^{0}\mathrm{Se{=}P(\overset{Me}{N}{-}\overset{Me}{N})_3P{=}^{77}Se}$$

where A is the phosphorus with the non-NMR active Se atom (^{0}Se), A' is the phosphorus with the ^{77}Se atom and X is the

^{77}Se atom itself. The A and A' designations arise because the phosphorus atoms are chemically but not magnetically equivalent because of the presence of an NMR active and an NMR nonactive Se atom in the molecule.

The spectrum for this system as calculated by ITRCAL is shown in Figure 10 slightly above the real spectrum on about the same intensity scale. The "fit" of the real and calculated spectra is expressed by the RMS error in the ITRCAL program which is a measure of the iterative least squares convergence; the smaller the RMS error, the better the "fit." Usually acceptable values of the RMS error are 0.01-0.1. For compound 31 the RMS error was 9.3×10^{-4}. The values of $^{1}J_{PSe}$ and $^{3}J_{PP}$ are 922.9 and 113.6 Hz, respectively. These values are somewhat different from the values measured directly from the experimental spectrum (936.6 and 113.2 Hz) due to its nonfirst order nature.

A very interesting result from the ITRCAL analysis concerns the chemical shifts of the phosphorus atoms bound to ^{0}Se and ^{77}Se. The excellent fit of the two spectra arises when the chemical shifts of the phosphorus atoms are not identical, *i.e.* compound 31 is actually an ABX system and not an AA'X system. The chemical shifts are -66.187 and -66.972 ppm for the ^{77}Se and ^{0}Se phosphorus atoms, respectively, and represent the influence of isotopic species of Se. To be sure, the chemical shift for ^{0}Se phosphorus is a composite of the many Se isotopes comprising it which include ^{74}Se (0.87%), ^{76}Se (9.02%), ^{78}Se (23.52%), ^{80}Se (49.82%) and ^{82}Se (9.19%). Such isotopic differences have been reported for some phosphorus compounds of Cu (149), Cd (150) and Sn (150) but were not resolvable for Mo (151).

Inspection of Table 20 shows that ^{1}JPSe for aminophosphine selenides rises from the smallest value in <u>29</u> (783.5 Hz) to the largest value for <u>42</u> (925.5 Hz) an increase of over 140 Hz. Similarly for selenophosphates ^{1}JPSe rises from <u>50</u> (954.4 Hz) to <u>53</u> (1098.6 Hz); an increase again of about 140 Hz.

<u>Phosphorus - selenium coupling constants</u> As mentioned in the Introduction, the variations in ^{1}JPSe were discussed by McFarlane and Rycroft (50) in terms of the Pople-Santry treatment of nuclear spin-spin couplings (70) and are related to s electron density and effective nuclear charge. For directly bound atoms, Ramsey (152) and later Pople and Santry (70) found that coupling due to the Fermi contact interaction is the most important. McFarlane and Rycroft (50) were able to express the reduced coupling ^{1}KPSe, which is related to the coupling constant ^{1}JPSe by the expression

$$19. \quad {}^1\mathrm{KPSe} = (2\pi/h\gamma_P\gamma_{Se})\,{}^1\mathrm{JPSe}.$$

In this equation γ_P and γ_{Se} are the magnetogyric ratios of ^{31}P and ^{77}Se, respectively. Their expression for ^{1}KPSe was

20. $^{1}K_{PSe} \propto \Psi^2_{3s(0)P} \cdot \Psi^2_{4s(0)Se} \cdot \alpha^2_P \alpha^2_{Se} \cdot \pi_{PSe}$

In the above equation the Ψ^2 terms are the electron densities of the valence s orbitals of P and Se evaluated at the nucleus (an effective nuclear charge term), the α^2 terms are quantitative measures of the s orbital character (76) in the hybrid bonding orbital from ^{31}P and ^{77}Se (an s character term) and π_{PSe} is the mutual polarizability of the valence s orbitals of ^{31}P and ^{77}Se and depends upon the amount of s overlap in the P=Se bond (153). Since the Ψ^2 and α^2 terms must be positive, it is the π term that determines the sign of $^{1}K_{PSe}$ ($^{1}J_{PSe}$). However, McFarlane states that any variations in π_{PSe} are unimportant if $^{1}K_{PSe}$ ($^{1}J_{PSe}$) is large (70). Such is the case with $^{1}J_{PSe}$ as it ranges from 604 to 1130 Hz (cf. Table 1). The coupling constant is then dependent not only upon the square of the s character in the bond but also upon the cube of the effective nuclear charge of either atom as shown by Schoolery (154) and also by Grant and Litchman (155). The latter effect was supported experimentally for $^{1}J_{CH}$ (155) and $^{1}J_{PH}$ (80).

It was noted that $^{1}K_{PSe}$ increases as the electronegativity of the phosphorus substituents increase (50) and this is illustrated in Table 21 and Figure 11 for the compounds studied in that work and in Table 22 and Figure 12 for those compounds studied by Stec *et al*. (48). In the two figures the value of $^{1}J_{PSe}$ is plotted *versus* the average

Table 21. Tabulation of ^{1}JPSe(Hz) values and average Sanderson electronegativities for compounds in reference 50

Letter	Compound	^{1}JPSe^a	$\chi_{average}$^{b,c}
A	$SePMe_3$	684	2.47
B	$SeP(Ph)Me_2$	710	2.47
C	$SeP(Ph)_2Me$	725	2.47
D	$SeP(NMe_2)Me_2$	720	2.62
E	$SeP(NMe_2)Ph_2$	760	2.62
F	$SeP(OMe)Me_2$	768	2.80
G	$SeP(OMe)Ph_2$	810	2.80
H	$SeP(NMe_2)_2Me$	767	2.78
I	$SeP(NMe)_2Ph$	790	2.78
J	$SeP(NMe_2)_3$ <u>29</u>	805	2.93
K	$SeP(OMe)_2Me$	861	3.13
L	$SeP(OMe)_2Ph$	876	3.13
M	$SeP(OMe)_3$ <u>50</u>	963	3.46

[a] ^{1}JPSe accuracies vary from ±0.5 to ±10 Hz (see Table 1) and were determined by heteronuclear triple resonance techniques.

[b] Obtained by using $\chi_{average} = (\chi_R + \chi_{R'} + \chi_{R''})/3$ for SePRR'R" compounds. χ_R is the χ value of the atom directly bound to phosphorus.

[c] $\chi_C = 2.47$, $\chi_N = 2.93$, $\chi_O = 3.46$ (reference 156).

Figure 11. Correlation plot of $^1J_{PSe}$ *versus* $\chi_{average}$ for compounds in reference 50. The correlation coefficient is 0.977.

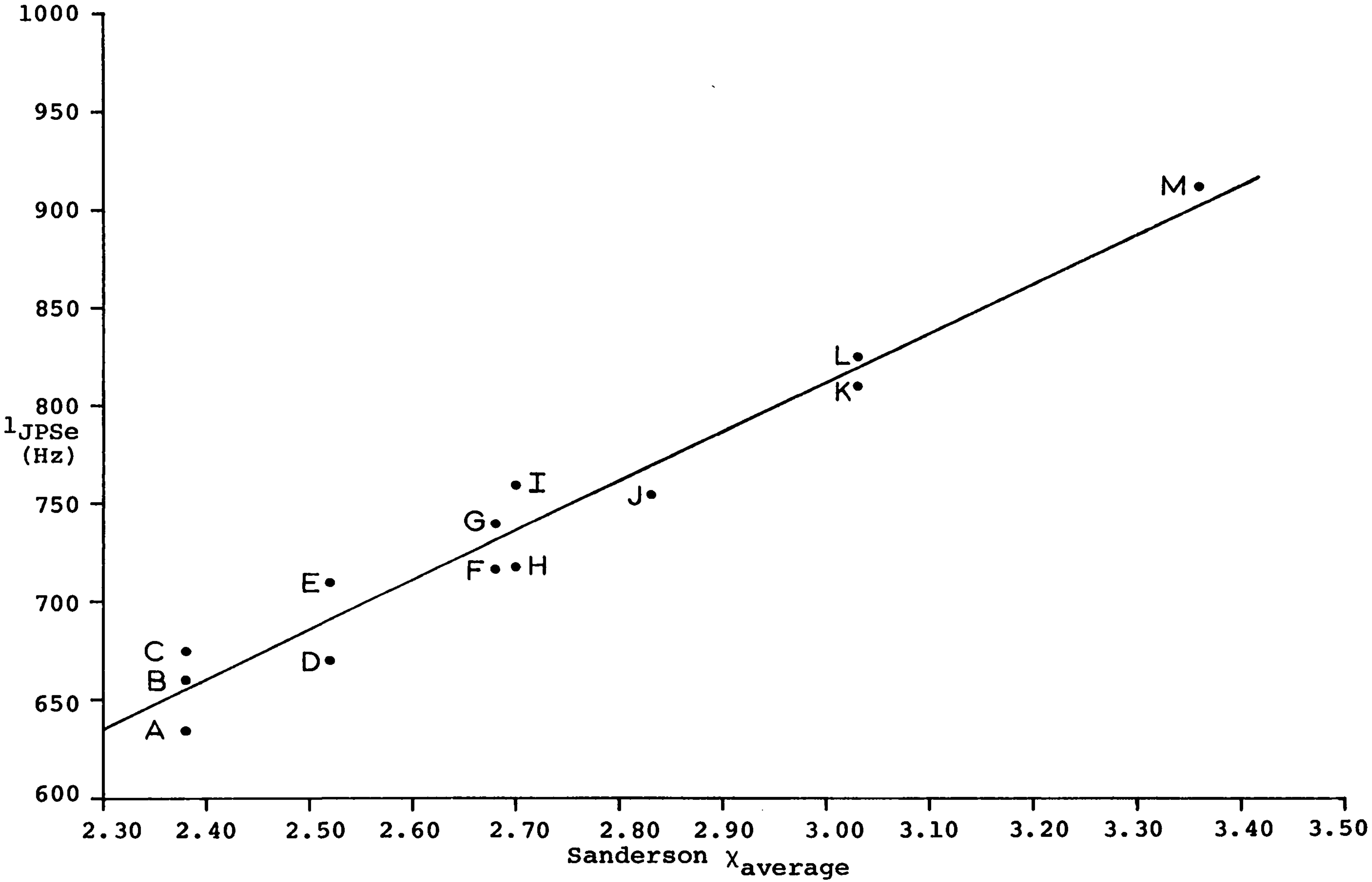

1000
950
900
850
800
750
700
650
600
$^{1}J_{PSe}$ (Hz)
2.30
2.40
2.50
2.60
2.70
2.80
2.90
3.00
3.10
3.20
3.30
3.40
3.50
Sanderson $\chi_{average}$
A
B
C
D
E
F
G
H
I
J
K
L
M

Table 22. Tabulation of ^{1}JPSe(Hz) values and average Sanderson electronegativities for compounds in reference 48

Letter	Compound	^{1}JPSe[a]	$\chi_{average}$[b,c]
A	SeP(Ph)(*t*-Bu)H	656	2.42
B	SeP(*n*-Bu)$_3$	693	2.47
C	SeP(Ph)(Et)(Me)	693	2.47
D	SeP(Ph)(*t*-Bu)(Me)	702	2.47
E	SeP(Ph)(*n*-Pr)(Me)	704	2.47
F	SeP(Ph)Et$_2$	705	2.47
G	SePEt$_3$	705	2.47
H	SeP(Ph)$_2$Et	722	2.47
I	SeP(Ph)$_3$	738	2.47
J	SeP(Ph)(*t*-Bu)(SeMe)	753	2.57
K	SeP(NEt$_2$)Et$_2$	728	2.62
L	SeP(NEt$_2$)Ph$_2$	753	2.62
M	SeP(NEt$_2$)$_2$Et	748	2.78
N	SeP(NEt$_2$)$_2$Ph	766	2.78
O	SeP(OEt)Et$_2$	755	2.80

[a] Values are accurate to ±6 Hz and were determined by CW-NMR techniques.

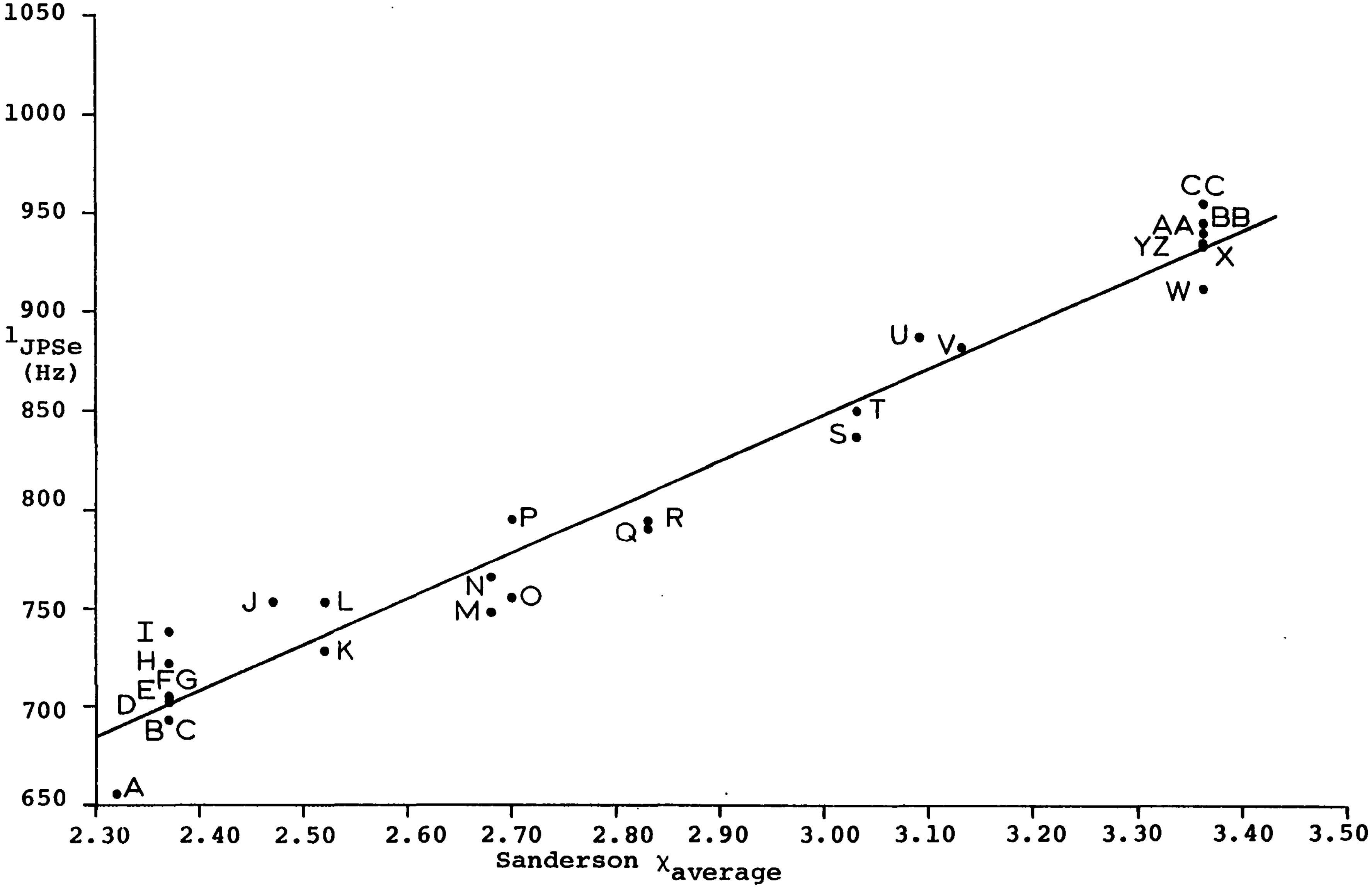
[b] Obtained by using $\chi_{average} = (\chi_R + \chi_{R'} + \chi_{R''})/3$ for SePRR'R" compounds. χ_R is the χ value of the atom directly bound to phosphorus.

[c] $\chi_H = 2.31$, $\chi_C = 2.47$, $\chi_S = 2.66$, $\chi_{Se} = 2.76$, $\chi_N = 2{,}93$ $\chi_O = 3.46$ (see reference 156).

Table 22. (continued)

Letter	Compound	$^{1}J_{PSe}$[a]	$\chi_{average}$[b,c]
V	$SeP(OEt)_2(SeEt)$	882	3.23
W	SeP(O-<u>i</u>-Pr)$_3$	912	3.46
X	SeP(O-<u>n</u>-Pr)$_3$	933	3.46
Y	$SeP(OEt)_3$	935	3.46
Z	$SeP(OEt)_2(OMe)$	935	3.46
AA	$SeP(OEt)(OMe)_2$	940	3.46
BB	$SeP(OMe)_3$ <u>50</u>	945	3.46
CC	$SeP(OCH_2CH_2Cl)_3$	955	3.46

Figure 12. Correlation plot of $^1J_{PSe}$ *versus* $\chi_{average}$ for compounds in reference 48. The correlation coefficient is 0.984.


1050
1000
950
900
850
800
750
700
650
$^1J_{PSe}$ (Hz)
2.30
2.40
2.50
2.60
2.70
2.80
2.90
3.00
3.10
3.20
3.30
3.40
3.50
Sanderson $\chi_{average}$
A
B
C
D
E
FG
H
I
J
K
L
M
N
O
P
Q
R
S
T
U
V
W
X
YZ
AA
BB
CC

Sanderson electronegativity (156) of the three atoms directly bound to the phosphorus. While considerable point scatter is obvious in both plots the overall correlation coefficients of 0.977 and 0.984 in Figures 11 and 12, respectively show that substituent electronegativities are indeed very important to $^{1}JPSe$. Plots were also constructed using the Pauling and Allred-Rochow electronegativity scales (156). These scales give correlation coefficients of 0.966 and 0.963, respectively, for compounds A-M in Table 21 and Figure 11, and 0.973 and 0.969, respectively, for compounds A-CC in Table 22 and Figure 12.

That such correlations are expected to exist can be seen from equation 20. A more electronegative substituent will tend to increase $\Psi^2_{3s(O)P}$ by inductive effects and also increase α^2_P according to Bent's (103) isovalent hybridization rule which states that p character will tend to concentrate in bonds towards more electronegative groups. Such a concentration of p character in the substituent bonds will cause a concomitant increase in the s character of the P=Se bond. In the two plots the effects of group electronegativities and steric problems are manifested by the point scatter mentioned above. In Figure 11 the greater group electronegativity of Ph groups compared to Me groups is shown in the positive displacement from the least squares line of $^{1}JPSe$ values for compounds containing one or two Ph groups. If it is reasonably assumed that Ph has a greater electronegativity than Me, the points labelled B, C, E, G, I, and L will be displaced to larger $\chi_{average}$ values. Points B, E and G should be displaced even more so due to the presence of two Ph groups. Such $\chi_{average}$ displacements would tend to bring these compounds closer to the correlation line. Both electronic and steric effects are manifested in the correlation plot of Figure 12. As before, the presence of Ph groups lead to upward displacements of ^1JPSe values from the least squares line. This is illustrated by the points labelled H, I, L and P which are very close to or outside one standard deviation. Steric effects are illustrated by the low ^1JPSe values of points A and W which contain bulky t-Bu or i-PrO groups, respectively. The bulk of these two groups would tend to cause the XPX angle in X_3PSe to increase and this would increase the s character in the P-X bond. The P=Se bond would then decrease in s character (α_P^2) and ^1JPSe is expected to decrease. The opposite effects of a Ph group and a t-Bu group would appear to negate one another in compound D and it falls very close to the correlation line. Compounds J and U possess unusually large ^1JPSe values which may be due to the presence of a divalent group V atom (Se and S, respectively). However, the additional presence of a t-Bu group in J would be expected to cause a lower ^1JPSe value for that compound. Perhaps the compound is in some way affected by its alcoholic environs (Table 1) giving rise to the large ^1JPSe value. Reasons for the low ^1JPSe values of M, O, Q and S are not obvious. Inductive effects by the $-CH_2CH_2Cl$ groups on CC could raise $\Psi^2_{3s(O)P}$ and α^2_P leading to its anomalously large ^1JPSe value.

Comparison of ^1JPSe values determined by different researchers is not quantitatively valid because the measuring techniques are different, *viz*. values determined in one work by off-resonance experiments for **29** (805±2 Hz) and **50** (963±0.5 Hz) (50) are different than those determined in this work by direct observation of the ^{31}P-NMR FT spectra of **29** (783.5±1.1 Hz) and **50** (954.4±1.1 Hz).

The selenophosphates in Table 20 differ among themselves mainly by the increased amount of constraint which the alkoxy moieties experience in the order **50** < **51** < **52** < **53** and an approximately monotonic 48 Hz increase in ^1JPSe from 954.4 to 1098.6 Hz reflects this trend. As discussed earlier (*vide ante*), the basicity order for the parent phosphites with the Lewis acid BH_3 is **46** > **47** > **48** > **49** and thus the decreasing basicity parallels the increase in ^1JPSe for the selenophosphates. A similar phenomenon was seen for ^1JPH in the analogous protonated phosphites (80) and was rationalized on the basis of orbital repulsion and "hinge" effects which imposed more positive nuclear charge on the phosphorus atom upon increased constraint and so led to an increase in ^1JPH.

Results of CNDO/2 calculations were used to support these arguments and a fair correlation (coefficient = 0.90) of ^{1}JPH with the cube of the net positive charge on phosphorus was obtained. Since the correlation existed, it appeared probable that the effective nuclear charge on phosphorus was dominant in the Fermi-contact mechanism, i.e., Ψ^2 terms dominate equation 20.

A plot of ^{1}JPSe versus ^{1}JPH in Figure 13 for the organophosphorus compounds appropriate to this work gives an excellent correlation of 0.996 with 0.5% standard deviation and this seems to indicate that the phosphorus charge factor which probably dominates ^{1}JPH also dominates ^{1}JPSe.

The CNDO/2 calculations (80) also indicate the validity of McFarlane's hypothesis concerning P=Se bonding as described in the Introduction. Table 23 contains parameters associated with the charges on the oxygens in the phosphates analogous to 50-53 and the precursor phosphites 46-49. In these latter compounds, progression from acyclic to monocyclic to bicyclic reveals an increase in negative charge on the alkoxy oxygens with concomitant buildup of positive charge on the phosphorus as predicted by the "hinge" effect (109, 110). This is due to the decreasing p-d pi bonding ability of the alkoxy oxygens upon constraint. The same increase in negative charge is experienced by the alkoxy oxygen atoms in the structurally similar phosphates. However, the phosphoryl

Figure 13. Correlation plot of $^{1}J_{PH}$ <u>versus</u> $^{1}J_{PSe}$ values for increasingly constrained organophosphorus compounds.

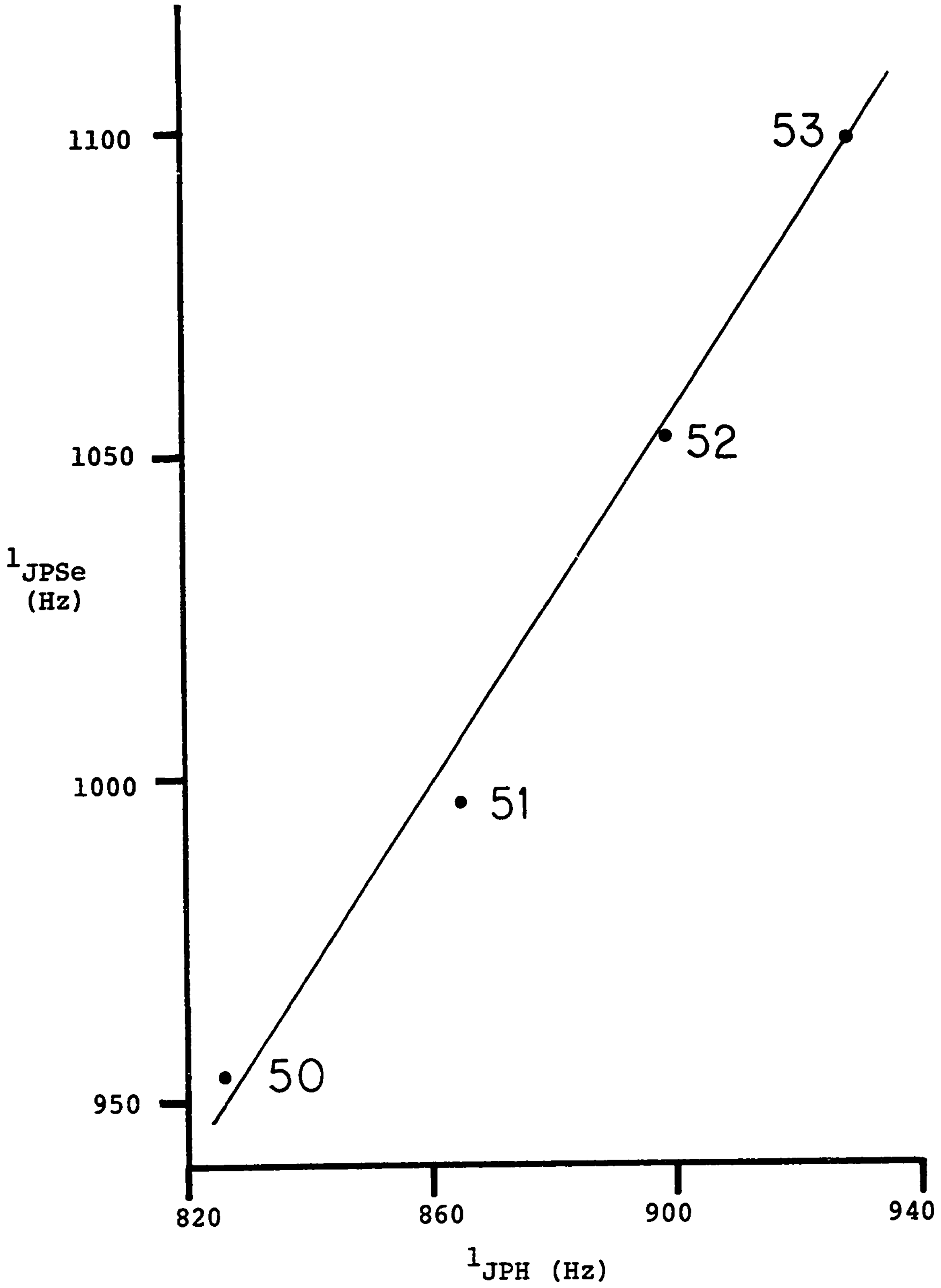
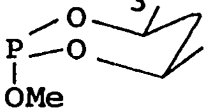
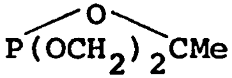
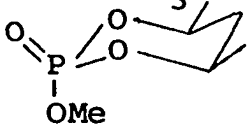
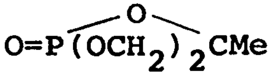

1100
1050
1000
950
$^1J_{PSe}$ (Hz)
820
860
900
940
$^1J_{PH}$ (Hz)
50
51
52
53

Table 23. CNDO/2 parameters for some phosphites and phosphates[a]

Compound	ρ_O	$\Sigma\rho_O$	ρ_P	ρ_P^3	$\rho_{=O}$	$^1J_{PSe}$[b]
46 $P(OMe)_3$	-0.246	-0.738	0.361	0.047		
47 	-0.264[c]	-0.774[d]	0.395	0.061		
48 $P(OCH_2)_3CMe$	-0.285	-0.855	0.409	0.068		
49  $P(OCH_2)_2CMe$	-0.276[e] -0.302[f]	-0.854[g]	0.477	0.109		
$O{=}P(OMe)_3$	-0.202	-0.606	–[h]		-0.431	954.4
	-0.232[c]	-0.666[i]	–[h]		-0.343	996.5
$O{=}P(OCH_2)_3CMe$	-0.245	-0.735	–[h]		-0.316	1053.1
 $O{=}P(OCH_2)_2CMe$	–[j]	-0.796[k]	–[j]		–[j]	1098.6

[a] Parameters ρ_O, ρ_P and $\rho_{=O}$ are taken from reference 80.

[b] For selenophosphoryl analogs. Values precise to ±1.1 Hz.

[c] Value for ring oxygen charge.

[d] 2(ρ_O for 47) + (ρ_O for 46).

[e] OCH_2 oxygen charge.

[f] Unique oxygen charge.

[g] $2(\rho_O$ for OCH_2 oxygens) + (ρ_O for unique oxygen).

[h] Parameter ρ_P not reported in reference 80.

[i] $2(\rho_O$ for ring oxygen in this phosphate) + (ρ_O for $O{=}P(OMe)_3$).

[j] Use of the structural parameters in reference 37 led to non-convergence.

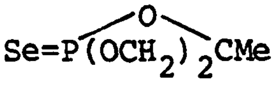
[k] Calculated from Figure 14 (see text).

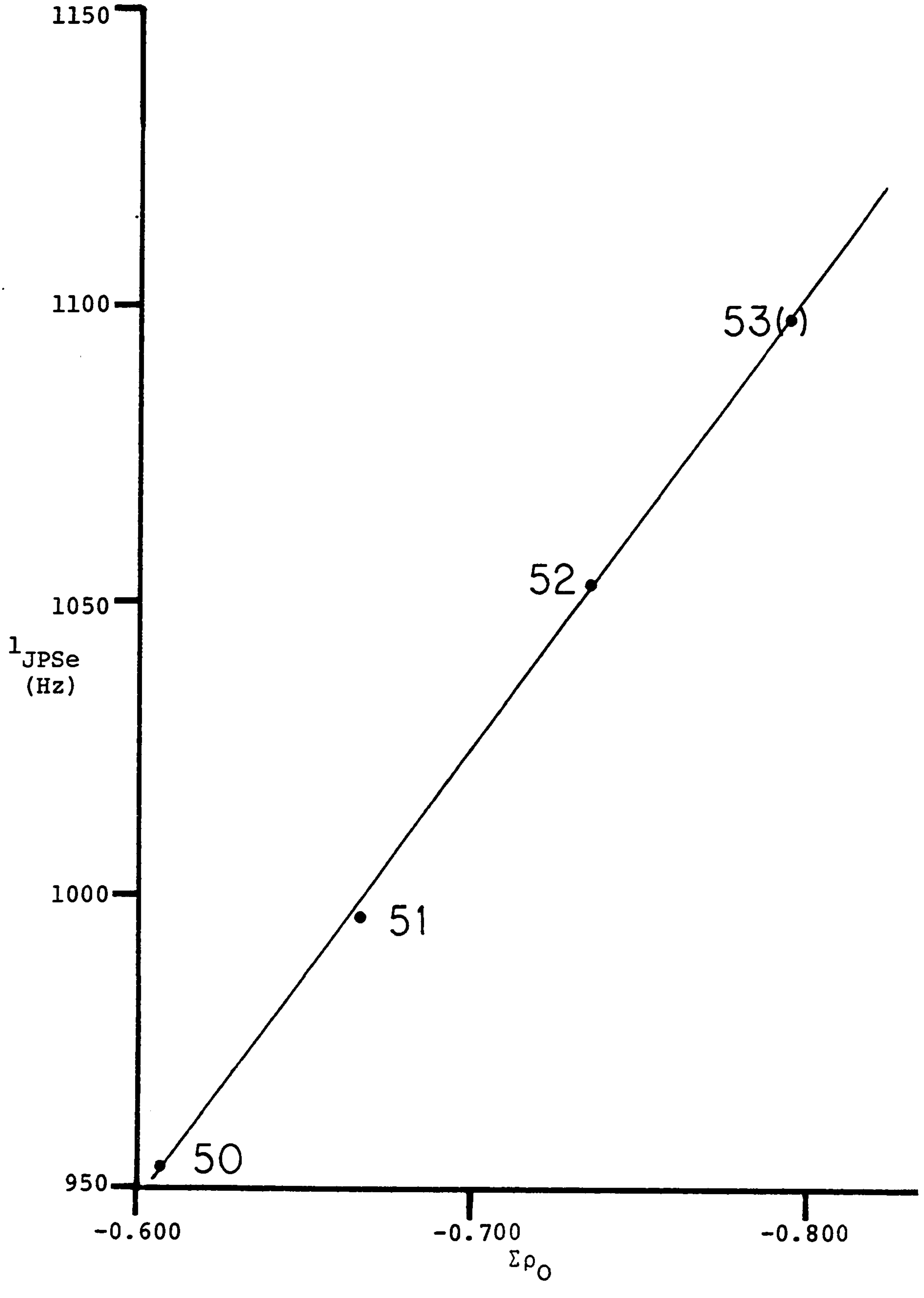
oxygen experiences a decrease in negative charge (an increase in positive charge) upon constraint, probably as a consequence of a rise in positive charge on phosphorus siphoning off electron charge. Unfortunately, the calculated charge on phosphorus for the series of phosphates is not available. These trends in phosphoryl oxygen and phosphorus charge suggest that constraint in the series of selenophosphates, 50-53, does not lead to an increase in the nonpolar contribution to the P=Se bond (and thus a decrease in the negative charge on selenium) as would follow from McFarlane's arguments concerning the pi bonding ability of the phosphorus substituents (50). Rather, the decrease in negative charge on ^{77}Se is simply due to an increasing charge imbalance between the phosphorus and its surrounding heteroatoms. As the alkoxy oxygens in 50-53 increase their negative charge, the phosphoryl oxygen (or in the present instance selenium) could decrease in negative charge to maintain overall electroneutrality.

The present hypothesis is then consistent with the increase in ^{1}JPSe observed upon constraint, whereas the dipolar/nonpolar argument of McFarlane would lead one to expect a decrease in ^{1}JPSe upon constraint. Thus the "hinge" effect predicts an increase in the $\Psi^2_{3s(O)P}$ and $\Psi^2_{4s(O)Se}$ terms of equation 20 (the $\Psi^2_{4s(O)Se}$ term is, however, an order-of-magnitude less important (71)). Constraint of the cage in progressing from 52 to 53 would also tend to increase the α_P^2 term in equation 20 and thus augment ^{1}JPSe even more.

In the absence of ρ_P values for the phosphates (which should correlate very well with ^{1}JPSe if, as hypothesized above, this coupling is dominated by phosphorus charge) it was decided to ascertain whether a correlation of the total alkoxy oxygen charge with ^{1}JPSe could be made. Such a plot would be analogous to the plots in Figure 11 and 12. Using the $\Sigma\rho_O$ values calculated from the phosphate data in Table 23, the correlation shown in Figure 14 was obtained. The three points for compounds 50, 51 and 52 give rise to a correlation coefficient of 0.999 with a 0.003 standard deviation in $\Sigma\rho_O$. This result strongly indicates that charge is the dominant factor influencing ^{1}JPSe. Locating the 1098.6 Hz ^{1}JPSe value obtained for 53 on the least squares line to calculate $\Sigma\rho_O$ for this compound gives a value of -0.796. If one assumes that the OCH_2 oxygens in 53 have about the same ρ_O value as in 52 (-0.245) then ρ_O for the unique oxygen would be -0.309 (a value similar to the -0.302 calculated (80) for the unique oxygen in 49) which is consistent with the buildup of negative charge on this oxygen due to its decreased pi bonding ability.

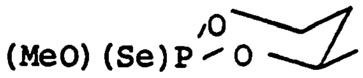
The excellent correlations of ^{1}JPSe in selenophosphates with charge related parameters of analogous phosphates (which

Figure 14. ^{1}JPSe for some selenophosphates *versus* $\Sigma\rho_{o}$ calculated from the analogous phosphates in reference 80. The point for  $Se{=}P\overset{O}{(OCH_2)_2}CMe$ was extrapolated from the least squares line of the former three compounds.

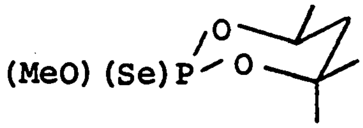

1150
1100
1050
1000
950
$^1J_{PSe}$ (Hz)
-0.600
-0.700
-0.800
$\Sigma\rho_O$
50
51
52
53(•)

supports the idea that ^1JPSe like ^1JPH (125) is dominated by the Ψ^2 terms in equation 20.

It was previously mentioned (see Introduction and Table 1) that Stec and coworkers had observed a difference in ^1JPSe values ($\Delta\ ^1JPSe$) for axial and equatorial P=Se bonds in conformationally stable selenophosphorinanes, with the larger ^1JPSe values occurring when the P=Se bond was equatorial. In particular, the compounds



and



show $\Delta\ ^1JPSe$ values of 37 and 9 Hz, respectively. In the absence of other effects, one would expect $\Delta\ ^1JPSe$ to be about equal for both sets of selenophosphates. The smaller difference in $\Delta\ ^1JPSe$ for the more extensively substituted ring compounds may be of steric origin in that 2,4-syn diaxial interactions in these two isomers could cause distortion of the ring away from a chair conformation and thereby lessen the electronic difference in the P=Se bonds between the two isomers.

The discussion will now center upon the results obtained for the aminophosphine selenides. The 71.0 Hz increase observed (Table 19) in ^1JPSe in proceeding from <u>29</u> to <u>30</u> is somewhat smaller than the 98.7 Hz increase seen between <u>50</u> and <u>52</u>. The larger ^1JPSe increase from <u>50</u> to <u>52</u> may be due to the greater electronegativity of oxygen as compared to nitrogen which could lead to greater charge separations affecting the Fermi contact term. In any event the increase is reasonably ascribed to the "hinge" and orbital repulsion effects in analogy to the selenophosphates discussed earlier.

The 68.4 Hz increase observed in ^{1}JPSe in proceeding from 30 to 31 is due to both electronic and steric effects which are interrelated. A "hinge" effect may be operative as the crystal structures of the analogous 23 and 25 show a decrease of over 2° between the endocyclic 115.9° PNC angle of the former (90) and the 113.6° PNN angle of the latter (34). This would increase the effective nuclear charge on the phosphorus ($\Psi^2_{3s(O)P}$) leading to greater coupling between this atom and selenium. As a consequence of the greater sp^3 character of the nitrogens in 31, one would expect even less p-d pi bonding to be possible in 31 than in 30 which would lead to a marginally greater positive charge on phosphorus. An electronegativity effect due to the replacement of an $NMeCH_2$ group with an NMeNMe group (45) would tend to augment the charge separations further. Thus there are two effects working in concert to cause the larger ^{1}JPSe value observed.

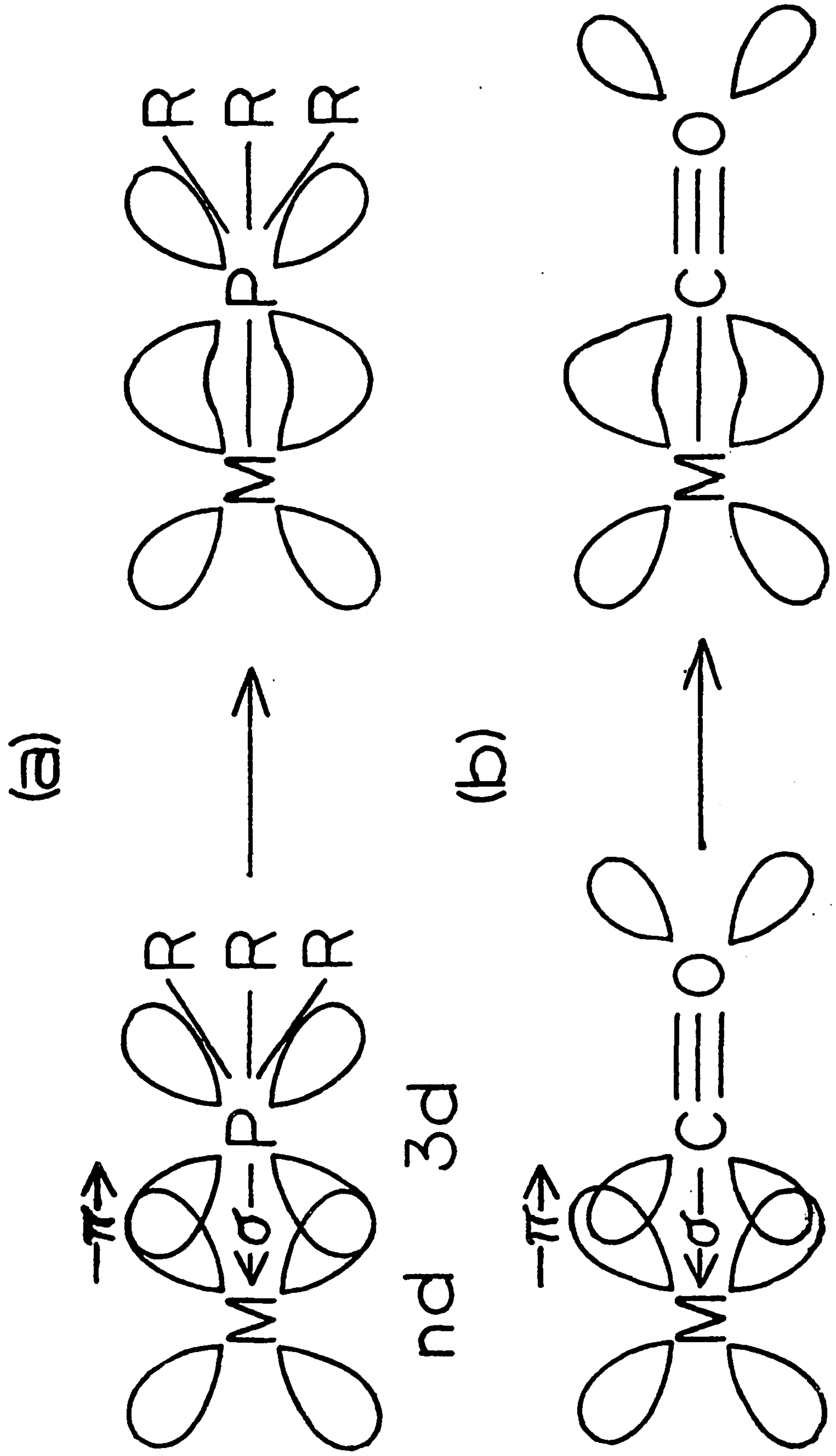
The inductive effect on ^{1}JPSe of a group at the other end of the cage is not very great as the coupling values for 31, 39 and 42 attest. Also, the ^{1}JPSe values do not increase in the same order as the effective electronegativity of the exocyclic group is expected to increase (Se < NPh < O) (122). It seems likely, therefore, that any inductive effects are so small as to be overshadowed by rehybridization effects resulting from structural changes. Similar conclusions were drawn based on the analysis of UV and ν(B-H) data (*vide ante*).

II. METAL COMPLEXES

INTRODUCTION

Metal complexes containing trivalent phosphorus ligands have been of continued interest for many years. In particular, the possibility that metal-phosphorus bonds may have appreciable double bond character has been intensively investigated ever since Chatt and Williams proposed (157) synergistic bonding to explain the stability of metal complexes of low oxidation states. According to MO theory, bonds with little, if any, transfer of negative charge from the donor atom of the ligand to the metal *via* a sigma bond can be accounted for by invoking pi back donation from the metal into energetically suitable empty orbitals of the ligand, giving a bond order greater than one. Such a hypothesis is illustrated in Figure 15 for metal-phosphorus and metal-carbonyl bonds. This type of bonding was in fact suggested in much simpler terms many years before the use of MO descriptions of complexes became general (158, 159). In the metal-phosphorus case, pi bonding occurs between the principal quantum level (nd) orbitals of the metal and the 3d orbitals of the phosphorus while for the metal-carbonyl bond pi bonding occurs between the metal nd orbitals and the lowest empty orbitals of CO, namely the antibonding 2π orbitals, which are localized mainly on the carbon atom (160).

Figure 15. Orbital overlap in (a) metal-phosphorus and (b) metal-carbonyl bonds.


(a)
M
P
R
R
R
σ
π
nd
3d
(b)
M
C
O
σ
π
nd
2π*

Experimental "proof" of the presence of pi bonding was indirect even after much research until 1974 (vide infra) and consisted of the following: (1) in zerovalent compounds the interatomic distances between metal and ligand are generally shorter than expected for a single bond and (2) bond moments are very low, as expected for nearly apolar bonds of the synergic type described above.

Evidence to support (and also discredit) the pi bonding hypothesis has been primarily spectroscopic, especially infrared spectra of the metal carbonyl CO stretching region. These spectra were first used to support the hypothesis by Abel et al. (161) and later by Horrocks and Taylor (162) while Cotton and Kraihanzel developed force field approximations to allow the ranking of ligands in terms of pi bonding ability (163-165). Bigorgne has argued that carbonyl stretching frequencies are merely a function of the inductive effects of the groups on a phosphorus ligand (166). However, Tolman showed this type of correlation to be weaker than first envisaged (167) and has since argued cogently that steric effects which alter the sigma and pi characteristics of ligands can be used to rationalize coordination geometrical properties of complexes, their oxidative-addition and dissociation-association reactions, and their spectroscopic properties (168). Angelici was able to show correlations between the pK_a or basicity of a ligand and $\nu(CO)$ (169, 170).

The analysis of NMR parameters, especially metal-phosphorus coupling constants, ^{1}JMP, has been used to probe the nature of the bonding in metal complexes. Nixon and Pidcock (171) reviewed this subject thoroughly in 1969 and concluded that synergism may occur to produce changes in ^{1}JMP but that changes in the metal s orbital arrangement are more important to the coupling than any subtle variation of phosphorus s orbitals.

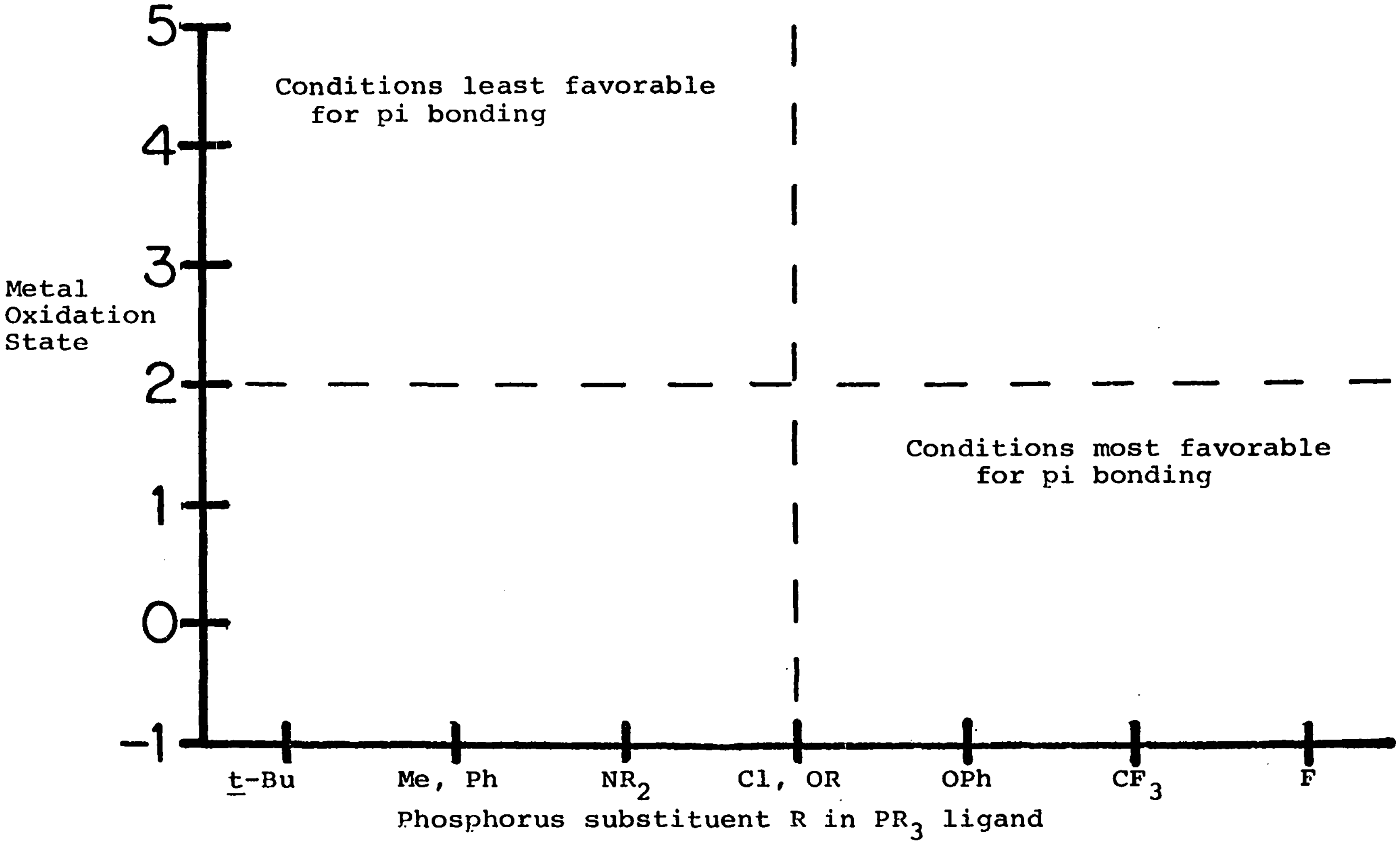
While carbonyl stretching spectra or metal-phosphorus coupling constants can be interpreted in terms of either sigma or synergistic effects, the same has not been true for crystal structures. In the absence of gross crystal packing effects the M-P bond distance should show whether pi bonding augments the sigma bond. The structures of $Cr(CO)_5PPh_3$, $Cr(CO)_5P(OPh)_3$ (172) and trans-$Cr(CO)_4[P(OPh)_3]_2$ (173) support the pi bonding hypothesis. If the bonding were purely sigma, the more basic ligand would have the stronger (and hence shorter) bond length. On this basis, PPh_3 would be expected to have stronger bonds than $P(OPh)_3$. In reality, the opposite is found in the $Cr(CO)_5L$ species. The M-P bond lengths are 2.422 Å and 2.309 Å for the PPh_3 and $P(OPh)_3$ complexes, respectively (172). This result was rationalized by postulating a transfer of metal orbital electron density back to the phosphorus. A bond strengthening mechanism could only occur *via* metal-phosphorus d-d orbitals, and pi bonding was believed thus to be demonstrated. The slight difference in M-C bond lengths for the CO group trans to the L group (1.844 Å for PPh_3 and 1.861 Å for $P(OPh)_3$) tend to show that the CO group is less successful in competing for pi electrons when trans to $P(OPh)_3$ than when trans to PPh_3. A further example of the pi bonding ability of $P(OPh)_3$ comes from the structure of trans-$Cr(CO)_4[P(OPh)_3]_2$ where the M-P distances are both 2.252 Å (173). The decrease in M-P bond length from 2.309 Å in $Cr(CO)_5P(OPh)_3$ is significant. It rules out steric factors as the reason why the M-P bond length in the $P(OPh)_3$ complex is shorter than in the PPh_3 complex. If the very good pi bonding trans CO group is replaced by a less effective pi bonding $P(OPh)_3$ group, the synergistic argument would predict a decrease in the M-P bond length and this is experimentally observed.

The existence of pi bonding in $Ni(PF_3)_4$ was established from its photoelectron spectrum by Green and coworkers (174). Interestingly, this research suggested that the pi system in $Ni(PF_3)_4$ was stronger than that in $Ni(CO)_4$, thus bearing out the observation that PF_3 is a better pi acid than CO (165).

The experimental results which have been obtained so far have led Pidcock (175) to conclude that the bonding is clear in two extremes: (1) metals in oxidation states of +2 or more form essentially pure sigma bonds with organophosphines and (2) metals in oxidation states of zero or lower form both sigma and pi (synergistic) bonds to PF_3, PCl_3 and $P(OPh)_3$ ligands. Between the extremes there is not enough information available to enable definite conclusions to be made. The possibility of pi bonding will be dependent upon both the ligand and the metal center. Diagrammatically, this is shown in Figure 16 (175). Obviously, there are no clearly defined boundary lines in the Figure but it is worthwhile noting that zerovalent aminophosphine metal complexes will probably be in a position to exhibit synergistic M-P bonding. This is especially true for complexes of **2** because of the apparently greater electronegativity of the cage structure as indicated by ^1JPSe measurements (*vide supra*). In connection with the influence of the metal center on pi bonding, Stelzer and Schmutzler (176), among others, have determined the relative "pi donor ability" of metal carbonyls to be $W(CO)_5 > Mo(CO)_5 > Cr(CO)_5 \geq Ni(CO)_3$ using the changes in ^3JPH and ^1JPF upon complexation of fluorophosphine ligands as a criterion.

The measurement of metal-phosphorus stretching frequencies have also been used to infer relative sigma and pi contributions in phosphite complexes (79, 177, 178). Bicyclic phosphites like **48** are readily amenable to this kind of study since ligand vibrations are absent in the

Figure 16. Metal oxidation state - phosphorus substituent coordinates for M-P pi bonding according to Pidcock.


Conditions least favorable for pi bonding
Conditions most favorable for pi bonding
Metal Oxidation State
5
4
3
2
1
0
−1
t-Bu
Me, Ph
NR2
Cl, OR
OPh
CF3
F
Phosphorus substituent R in PR3 ligand

lower infrared region where ν(MP) values are expected (ca. 98 to 463 cm^{-1} depending on the complex (109)). Phosphite ligands like 46 (178, 179) and 49 (79) give rise to more low energy bands due in part to their lower symmetries and the only reliable way to obtain ν(MP) would be through the relatively expensive technique of metal isotopic substitution (179, 180). However, if a large enough number of structurally related complexes of the same ligand are studied, systematic trends in the far infrared spectra might lead to reasonable assignments of ν(MP). This technique was used with complexes of 48 (177).

Chemical shifts of ^{31}P-NMR resonances do not reflect phosphorus electron density changes in a simple manner and this is especially so for metal complexes of phosphorus ligands. Problems with this simple approach have been reviewed by Nixon and Pidcock (171). The difficulties stem from the interplay of the diamagnetic and paramagnetic shielding terms in the Ramsey equation for chemical shifts (181). This is especially true when comparing $\delta^{31}P$ values in complexes which vary only in the metal in a periodic family. From the upfield trend in this shift observed in two series of FeL_5, CoL_5^{+1}, NiL_5^{+2} complexes (182), it appears that the paramagnetic term probably dominates.

In the semiempirical approach of Letcher and Van Wazer (125) the paramagnetically dominated ^{31}P chemical shift (relative to a particular standard) is given by equation 21.

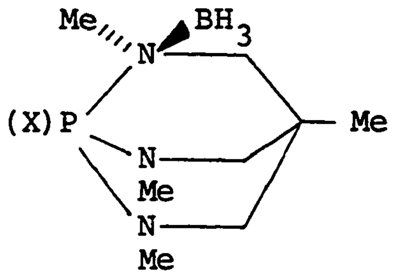
$$21. \quad \delta_P = -\frac{2}{3}\left[\frac{e^2h^2}{m^2c^2}\right]\left[\left\langle r^{-3}\right\rangle_p \zeta_1 + \left\langle r^{-3}\right\rangle_d \zeta_2\right]\cdot\frac{1}{\Delta E}$$

where ζ_1 and ζ_2 are dependent on the occupation of the phosphorus 3p and 3d orbitals, respectively. An assumption commonly made to simplify the equation is that the $\langle r^{-3}\rangle\cdot 1/\Delta E$ term is constant for a given coordination number of phosphorus. Thus, the chemical shift of phosphorus is dependent solely upon ζ_1 and ζ_2. Systematic changes in δ_P and the lowest energy e'→a' d-d transition for the two series FeL_5, CoL_5^{+1}, NiL_5^{+2} where L = 46 and $P(OCH_2)_3CEt$ lead to the conclusions that the pi acidity of the ligands dominates the ligand field parameter Dq for these systems (182) and that the bicyclic compound is a better pi acid than 46.

As part of the comparison of the ligand properties of 1 and 2, the zerovalent metal carbonyl complexes of the two aminophosphines were synthesized and studied by ν(CO) infrared, ^1H- and ^{31}P-NMR spectroscopy. The syntheses of these complexes included $Ni(CO)_{4-n}L_n$, $Fe(CO)_{5-n}L_n$ and $M(CO)_{6-n}L_n$ (M = Cr, Mo, W) where n = 1 or 2. Previously the complexes of 1 had been synthesized by Nöth and Vetter (183) and by King (184). Additional complexes of 1 and the analogous aminoarsine $As(NMe_2)_3$ 54, were made by King and Korenowski (185). Complexes of 2 have been used in studies of ^1JWP trends (186) and ASIS effects (187). The syntheses of complexes of 2 have never been published (188) but the procedures are based on those used to prepare the analogous complexes of 1 (184).

The primary purpose in making complexes of 2 was to react them with B_2H_6 and thereby hopefully make use of an unusual property of 2 discovered when it was first synthesized (89). Reaction 22, shown below, which does not occur with acyclic 1, is known to proceed when X is a lone pair, BH_3, O or S. Note that only one enantiomer of the adduct is

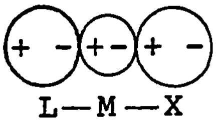
22. $(X)P(NMeCH_2)_3CMe + {}^{1}/2B_2H_6 \rightarrow$



shown. It was hoped that the same type of adduct could be synthesized with the more sterically demanding $M(CO)_x$ groups present on phosphorus and that changes in the electronic nature of the phosphorus in such new complexes would manifest themselves by changes in $\nu(CO)$ and $\nu(MP)$ as well as ^1H- and ^{31}P-NMR shifts. The results of these experiments on some metal carbonyl complexes of 2 as well as on the new organophosphorus compounds 9 and 30 are described in this section of the thesis.

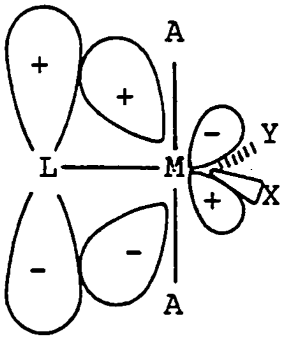
In addition to zerovalent metal carbonyl complexes of 1 and 2, their corresponding PtX_2L_2 (X = Cl, I) complexes were synthesized to see if the electronic differences of the ligands would cause noticeable changes in complex characteristics. Complexes of this type are square planar and therefore can form either *cis* or *trans* isomers. Considerable research has been conducted with complexes of this type, especially in the area of the *trans* effect; *i.e.*, the effect a ligand has on the rate of substitution of the ligand opposite itself. Many ligands have been investigated in this regard and the order of *trans* directing ability has been established as $CO \sim CN^- \sim NO \sim C_2H_4 > H^- \sim PR_3 > CH_3^- \sim SR_2 > O_2^- \sim I^- \sim SCN^- \sim C_6H_5^- > Br^- > Cl^- > C_5H_5N > RNH_2 \sim NH_3 > OH^- > H_2O$ (189). It is immediately seen that good pi bonding ligands tend to be strongly *trans* directing, which would indicate a causality relationship. However, the placement of such non-pi bonding groups as CH_3^- and H^- high in the above order would seem to indicate that pi bonding is not the only effect operative. The two principal theories put forward once again set the sigmaphiles and synergists at odds. All theorizing about the *trans* effect of ligands must take into account the fact that since it is a kinetic phenomenon, depending upon activation energies, the stabilities of both the ground state and activated complex are relevant. The activation energy can, in principle, be affected by changes in either one or both of the above configurations.

The polarization theory of Grinberg (190) is primarily concerned with effects in the ground state. The theory deals with a postulated charge distribution (shown below) where a strong dipole interaction between ligand L and the



metal M would tend to weaken the attachment of the *trans* group X by a mis-match of dipoles. The theory suggests that the magnitude of the *trans* effect of L should be monotonically related to its polarizability. For some ligands in the *trans* effect series, (*i.e.* $H^- > I^- > Br^- > Cl^- > OH^-$) this would appear to be the case.

The second theory is based on the expectation that *trans* ligands compete for the same metal d orbitals *via* pi bonding and it attributes their effectiveness in this regard on their ability to stabilize a five-coordinate transition state. This theory was developed with special consideration given to the ordering of non-ionic ligands (*e.g.* $CO > PR_3 > SR_2 > C_5H_5N > RNH_2 > H_2O$) and it is relevant only if the reactions are bimolecular. Fortunately, there is good evidence that this is so in the majority of cases. The ability of a ligand, L, to withdraw metal d electron density could enhance the stability of a species in which both the incoming group, Y, and the outgoing group, X, are simultaneously bound to the metal. This part of the theory would account for a labilizing effect to obtain a transition state. To account for *cis* or *trans* directing ability, a



ground state pi bonding effect is put forward where, in order to have maximal interaction with the metal, two pi bonding ligands would orient themselves cis. Thus, they would not have to share the same metal d orbital for pi bonding as they would if in a trans configuration. This sort of reasoning would indicate why the cis-$PtCl_2(PR_3)_2$ isomer is about 40 kJ $mole^{-1}$ thermodynamically more stable than the trans isomer (191).

However, bond length data tend to show that such pi bonding could be unimportant (at least in the ground state) because the Pt-Cl distance in trans-$PtClH(PEtPh_2)_2$ (2.422 Å) (192) is longer than in cis-$PtCl_2(PMe_3)_2$ (2.376 Å) (193) or trans-$PtCl_2(PEt_3)_2$ (2.298 Å) (194). The Pt-P bond distances, on the other hand, seem to show the presence of pi bonding as the trans compounds have longer bond lengths than the cis. The differences, however (2.268, 2.247 and 2.294 Å, respectively), are nowhere near as great as the Pt-Cl variations. Also, complexes of Pt(II) fall in the no man's land of pi bonding likelihood according to Pidcock (175) (Figure 16).

The present consensus of opinion among workers in the field is that both of the theories put forward may be involved to some extent depending on the ligand.

While complexes of 1 with platinum have been reported previously (195) no studies have been done on complexes of 2. In the course of this work these complexes were seen to have rather different properties in solution and a preliminary account of the findings will be given.

EXPERIMENTAL

Techniques

Precautions

Inert atmosphere techniques and nitrogen-saturated solvents were used for work with the metal derivatives of 1, 2, 3, 54 and 55.

Materials

Chromium, molybdenum and tungsten hexacarbonyls as well as di-iron nonacarbonyl were purchased from Pressure Chemical Company. Iron pentacarbonyl and silver tetrafluoroborate were purchased from Alfa Inorganics. Nickel carbonyl was purchased from Matheson Gas Products. Norbornadiene (NBD) was purchased from Aldrich Chemical Company and used as received.

Infrared Spectra

Carbonyl stretching frequencies were measured on a Perkin Elmer 337 grating infrared spectrophotometer using a Beckman 10-inch recorder for scale expansions. Absorption bands for the solutions were referenced using the 2147.0 cm^{-1} band of CO gas and are precise to ±0.5 cm^{-1}.

Far infrared spectra were recorded on Nujol mulls of the compounds using a Digilab FTS-18 Fourier transform infrared spectrophotometer located in the Chemistry department of the University of Wisconsin, Madison and the help of Professors E. M. Larsen and P. Bender is gratefully acknowledged.

Raman Spectra

Carbonyl modes were obtained from concentrated benzene solutions by Dr. J. M. Hayes on a Jarrel-Ash 25-400 laser Raman spectrophotometer using either the 5145 Å or 4880 Å line of an Ar^+ laser as the excitation wavelength.

NMR Spectra

Proton spectra were obtained from C_6D_6 solutions of the compounds on a Varian HA-100 spectrometer using TMS as an internal standard and trifluoroacetic acid as an external frequency lock. For very dilute solutions a Nicolet Instruments Corp. Model 535 signal averager was interfaced thus allowing computer averaging of transients (CAT) to improve the signal to noise ratio.

^{31}P-NMR spectra were obtained on a Bruker HX-90 spectrometer operating at 36.434 MHz in the FT-mode. Solutions were run in either C_6D_6 or d_8-toluene using the ^{2}H resonance of the solvent as a frequency lock. The reference used was external 0.2 $\underline{M}$ $P(OH)_4^+ ClO_4^-$ (196). Chemical shifts are reported as in Part I relative to 85% H_3PO_4.

^{31}P-NMR spectral calculations were performed using ITRCAL (84).

Preparations

All of the metal complexes described below were characterized by their ^{1}H- and ^{31}P-NMR spectra as well as ν(CO) spectra. The carbonyl species $Cr(CO)_5(\underline{2})$, $Mo(CO)_5(\underline{2})$, trans-$M(CO)_4(\underline{2})_2$ (where M = Cr, Mo, W) and trans-$Fe(CO)_3(\underline{2})_2$ have previously been synthesized in low yields by UV irradiation of methylcyclohexane solutions of the appropriate metal carbonyl and 2 at room temperature (188).

Reaction products

$Et_4N[M(CO)_5I]$; M = Cr, W These salts were synthesized from the appropriate Group VI hexacarbonyl and Et_4NI in diglyme using the method of Abel *et al.* (197).

$Fe_3(CO)_{12}$ This carbonyl was made from $Fe(CO)_5$ by the method of King and Stone (198).

cis-$Cr(CO)_4(NBD)$ and *cis*-$Mo(CO)_4(NBD)$ These organometallics were synthesized from the metal hexacarbonyls and norbornadiene using the methods described by King (199).

cis-$W(CO)_4(NBD)$ This compound was made by the method of King and Fronzaglia (200).

cis-$Pt(PhCN)_2Cl_2$ and *cis*-$Pt(PhCN)_2I_2$ These complexes were prepared by the method of Church and Mays (201).

$(Me_2N)_3As$, 54 This compound was prepared from Me_2NH and $AsCl_3$ by the method of Mödritzer (202).

$MeC(CH_2NMe)_3As$, 55 This compound was prepared from 54 and the triamine $MeC(CH_2NMeH)_3$ in an analogous manner to the preparation of 2 described by Laube *et al.* (89).

$Cr(CO)_5(1)$, $Mo(CO)_5(1)$, axial-$Fe(CO)_4(1)$, *trans*-$Fe(CO)_3(1)_2$, $Ni(CO)_2(1)_2$, *trans*-$Cr(CO)_4(1)_2$, *trans*-$Mo(CO)_4(1)_2$ and *trans*-$W(CO)_4(1)_2$ These complexes were prepared using the methods described by King (184).

$W(CO)_5$(1), $Cr(CO)_5$(54) and axial-$Fe(CO)_4$(54) These complexes were prepared by the method of King and Korenowski (185).

$Ni(CO)_3$(1) This complex was prepared by the method of Nöth and Vetter (183).

$Cr(CO)_5$(2) A mixture of 4.90 g (21.0 mmoles) of acetonitrile chromium pentacarbonyl and 4.00 ml (22.4 mmoles) of 2 in 60 ml of methylcyclohexane was heated to 80° for 3 hours. After cooling to room temperature and filtering, the solvent was removed under vacuum. The residue was sublimed for 3 hours at 55° (0.01 torr) to remove $Cr(CO)_6$. The sublimation was continued for 4 hours at 100° (0.01 torr) to give a yellowish sublimate which was resublimed to give 4.11 g (52%) of the desired product.

$Mo(CO)_5$(2) This compound was prepared in the following manner based upon an earlier preparation by McInerney (203).

A solution of 1.32 g (5.00 mmoles) of $Mo(CO)_6$, 0.90 ml (5.0 mmoles) of 2 and 25 ml of methylcyclohexane was refluxed for 4 hours. It was then cooled to room temperature and the solvent was removed under vacuum. The tan residue was extracted in a Soxhlet apparatus with 40 ml of pentane for 3 hours. Cooling the pentane solution to -78° precipitated an off-white solid which was sublimed at 90° (0.01 torr) to give 0.91 g (43%) of white product.

$W(CO)_5$(2) A mixture of 1.82 g (5.01 mmoles) of acetonitrile tungsten pentacarbonyl, 0.90 ml (5.0 mmoles) of

2 and 35 ml of methylcyclohexane was heated to 85° for 10 hours during which time the color went from clear yellow to colorless. The hot solution was filtered and cooled slowly to -78° causing precipitation of an off-white solid which was sublimed at 95° (0.01 torr) to give 1.35 g (69%) of the white product.

axial-$Fe(CO)_4(2)$ and *trans*-$Fe(CO)_3(2)_2$ These compounds were prepared simultaneously by reaction of 2 with $Fe_3(CO)_{12}$ as follows. A mixture of 1.90 g (3.80 mmoles) of $Fe_3(CO)_{12}$ and 4.00 ml (22.4 mmoles) of 2 in 50 ml of benzene was stirred at room temperature for 24 hours. The color gradually faded from a very dark green to clear amber. The mixture was filtered and the solvent removed under vacuum. The residue was extracted with 50 ml of pentane and filtered to give a clear amber filtrate and a tan solid which was dried *in vacuo*. The filtrate was cooled to -78° causing precipitation of a light yellow solid which was collected and dried. This solid and the tan residue were sublimed at 105° (0.01 torr) to give a total of 1.14 g (28%) of pale yellow axial-$Fe(CO)_4(2)$. The nonvolatile tan residue was then recrystallized from boiling methylcyclohexane at -78° to give 0.93 g (16%) of white *trans*-$Fe(CO)_3(2)_2$. Yields are based on the maximum 11.4 mmoles of iron-containing species possible from the reaction.

$Ni(CO)_3(2)$ Unlike the analogous complex of 1, this complex is a low melting solid that is unstable to heat and/or light. A solution of 0.80 ml (6.2 mmoles) of $Ni(CO)_4$ in 20 ml of hexane was treated dropwise with 1.00 ml (5.60 mmoles) of 2 at room temperature. Vigorous bubbling occurred at once and the clear colorless solution was stirred for 30 minutes during which time the gas evolution ceased and the solution became slightly yellow. Volatiles were removed under vacuum to leave the product as a clear colorless oil. Since there was no ^1H- or ^{31}P-NMR spectral evidence of unreacted 2 or infrared evidence for unreacted $Ni(CO)_4$, the reaction was assumed to be quantitative.

$Cr(CO)_5$(55) A mixture of 1.35 g (3.00 mmoles) of $Et_4N[Cr(CO)_5I]$ and 0.48 ml (3.0 mmoles) of 55 in 30 ml of CH_2Cl_2 was treated with 1.10 g (4.50 mmoles) of $AgNO_3$ at room temperature for 30 minutes at which time the solvent was removed under vacuum. The residue was then extracted with 40 ml of a 1:1 toluene-hexane solution. After filtration, removal of solvents from the filtrate and drying, the resultant residue was extracted twice with 30 ml portions of pentane. The extracts were stripped of solvent and the yellow residue was sublimed at 85° (0.01 torr) to give 0.25 g (20%) of the pale yellow product.

axial-$Fe(CO)_4$(55) A mixture of 1.82 g (5.00 mmoles) of $Fe_2(CO)_9$ and 1.60 ml (10.0 mmoles) of 55 in 50 ml of pentane was stirred at room temperature for 36 hours. The mixture was filtered and the filtrate was concentrated to 25 ml under vacuum. Cooling to -78° produced a solid which was filtered, washed twice with cold pentane and dried in vacuo. Sublimation at 80° (0.01 torr) produced 1.37 g (34%) of the pale yellow compound.

trans-$Cr(CO)_4(\underline{2})_2$ A mixture of 1.64 g (6.40 mmoles) of freshly sublimed $Cr(CO)_4$(norbornadiene) and 2.50 ml (14.0 mmoles) of 2 in 25 ml of methylcyclohexane was heated to 100° for 23 hours. After cooling to room temperature the mixture was filtered and the solid was washed twice with pentane. Recrystallization from 40 ml of a boiling 3:1 heptane-toluene solution gave 2.65 g (77%) of the white product.

trans-$Mo(CO)_4(\underline{2})_2$ A mixture of 3.05 g (10.2 mmoles) of fresh $Mo(CO)_4$(norbornadiene) and 4.00 ml (22.4 mmoles) of 2 in 30 ml of methylcyclohexane was heated to 50° for 22 hours. A few minutes after mixing, a large amount of precipitate formed in the flask. After cooling to room temperature the mixture was filtered and the solid was washed twice with pentane. Recrystallization from 40 ml of a boiling 3:1 heptane-toluene solution gave 4.35 g (73%) of the white product.

trans-$W(CO)_4(\underline{2})_2$ A mixture of 3.08 g (7.94 mmoles) of $W(CO)_4$(norbornadiene) and 3.10 ml (17.4 mmoles) of 2 in 30 ml methylcyclohexane was heated to 50° for 23 hours. After cooling to room temperature and filtering, the solid obtained was washed twice with pentane and recrystallized from 40 ml of a boiling 3:1 heptane-toluene solution to give 3.13 g (59%) of the white product.

$\underline{Ni(CO)_2(\underline{2})_2}$ A solution of 0.89 ml (5.0 mmoles) of $\underline{2}$ in 20 ml of benzene was treated with 0.32 ml (2.5 mmoles) of $Ni(CO)_4$ at room temperature. After gas evolution subsided the solution was heated to reflux for 1 hour. The benzene was removed under vacuum and the residue was recrystallized from 20 ml of pentane at -78°. The solid so produced was sublimed at 110° (0.01 torr) to give 0.59 g (48%) of the pure white product.

$\underline{(OC)_3Ni(\underline{3})Ni(CO)_3}$ A solution of 1.10 g (4.66 mmoles) of $\underline{3}$ in 10 ml of toluene was added dropwise to a solution of 1.21 ml (9.35 mmoles) of $Ni(CO)_4$ in 10 ml of toluene at room temperature over a period of 5 minutes. Gas evolution was vigorous and ceased after 15 minutes. The clear colorless solution was stirred for 1 hour and then cooled to -78° which caused a solid to precipitate. This was filtered, washed with cold pentane and dried in vacuo to give 1.94 g (79%) of the tan product.

$\underline{(OC)_5W(\underline{3})W(CO)_5}$ A mixture of 0.86 g (3.6 mmoles) of $\underline{3}$ and 4.25 g (7.31 mmoles) of $NEt_4[W(CO)_5I]$ suspended in 50 ml of CH_2Cl_2 was treated with a solution of 2.41 g (12.4 mmoles) of $AgBF_4$ in 20 ml of nitromethane at room temperature. The suspension immediately changed from bright yellow to dark brown. Stirring was continued for 3 hours and then the volatiles were removed under vacuum. The residue was extracted twice with 40 ml portions of boiling toluene. The toluene was removed under vacuum and the residue was extracted with 40 ml of heptane at 95° to give a clear yellow solution. Cooling this solution to -78° caused precipitation of 0.32 g (10%) of golden yellow solid which was only slightly soluble in common solvents.

trans-$PtCl_2(1)_2$ and trans-$PtI_2(1)_2$ These coordination complexes were synthesized by the method of Jenkins and Verkade (195).

trans-$PtCl_2(2)_2$ A solution composed of 1.02 g (2.16 mmoles) of cis-$PtCl_2(PhCN)_2$, 10 ml of benzene and 0.90 ml (5.0 mmoles) of 2 was stirred at room temperature for 28 hours. The precipitate that formed was filtered off and washed twice with benzene. Recrystallization from boiling toluene gave 0.58 g (42%) of the product as a white solid.

cis-$PtI_2(2)_2$ To a mixture of 1.73 g (2.65 mmoles) of cis-$PtI_2(PhCN)_2$ in 10 ml of benzene was added 1.00 ml (5.60 mmoles) of 2 at room temperature. The opaque yellow mixture turned a deep red color immediately and became brownish after 3 hours. After 6 hours the mixture was yellow again and the solid was filtered off and recrystallized from benzene to give 0.57 g (26%) of the product as a bright yellow solid.

Tensimetric Titrations

Diborane was synthesized by the method of Norman and Jolly (204) according to equation 23.

23. $KBH_4 + H_3PO_4 \rightarrow \frac{1}{2}B_2H_6 + H_2 + K^+ + H_2PO_4^-$

The general procedure consisted of placing about 40 ml of 85%

H_3PO_4 in a 250 ml round bottom flask and about 3 g of KBH_4 (Alfa Inorganics) in an addition arm attached to the flask by a standard taper joint. This assembly was then attached to a vacuum line and evacuated for about 15 minutes. A trap was then cooled to -78° and two additional traps were cooled to -196°. The addition arm was rotated slightly and tapped so that small amounts of KBH_4 fell onto the surface of the magnetically stirred acid. The stopcocks were adjusted so that the gases had to pass through all three traps before passing into the main trap. All water vapor from the acid was trapped out in the first trap while most of the B_2H_6 was isolated in the second. The hydrogen produced passed through all the traps and was expelled by the vacuum pump.

Addition of KBH_4 was accomplished over a two hour period after which the first trap was isolated from the system. The condensate in the second trap was purified by warming it to -126° using a methylcyclohexane slush bath and condensing the B_2H_6 in the third trap at -196°. The vapor pressure of B_2H_6 at -126° is 69 torr while the vapor pressures of any higher boranes formed by B_2H_6 decomposition are much lower (205).

The purified B_2H_6 was measured out for reaction by trapping a known pressure of gas (measured using the vacuum line manometer) in a known volume at a known temperature. The ideal gas law was used to calculate the amount of B_2H_6 contained in the bulb. The B_2H_6 was then condensed onto the frozen outgassed solution of substrate (-196°) in a tensimeter reaction tube. The solution was made by flash distilling dry solvent into the apparatus containing the substrate.

The frozen solution was then warmed to either -78° or -45° with agitation from a magnetically activated jump-stirring rod and allowed to equilibrate with the B_2H_6 for 20 minutes after which the pressure in the isolated tensimeter was measured with a manometer. The isolation-equilibration process was then repeated to obtain the data presented in Table 24 and illustrated in Figure 17 for $W(CO)_5(\underline{2})$, $Ni(CO)_3(\underline{2})$ and trans-$Fe(CO)_3(\underline{2})_2$.

After the titration was finished, the still cold solution was filtered under vacuum in an apparatus similar to one devised by Parry et al. (206) in order to remove any mercury that had condensed into the frozen solution at -196°. The volatiles were removed from the filtrate under vacuum to leave residues which were collected in a dry bag. The bis(borane) adducts of trans-$M(CO)_4(\underline{2})_2$ (M = Cr, Mo, W) were insoluble in toluene and were isolated from the filtering frit.

Table 24. Reaction conditions and results for tensimetric titrations of (X)P$(NMeCH_2)_3$CMe with B_2H_6

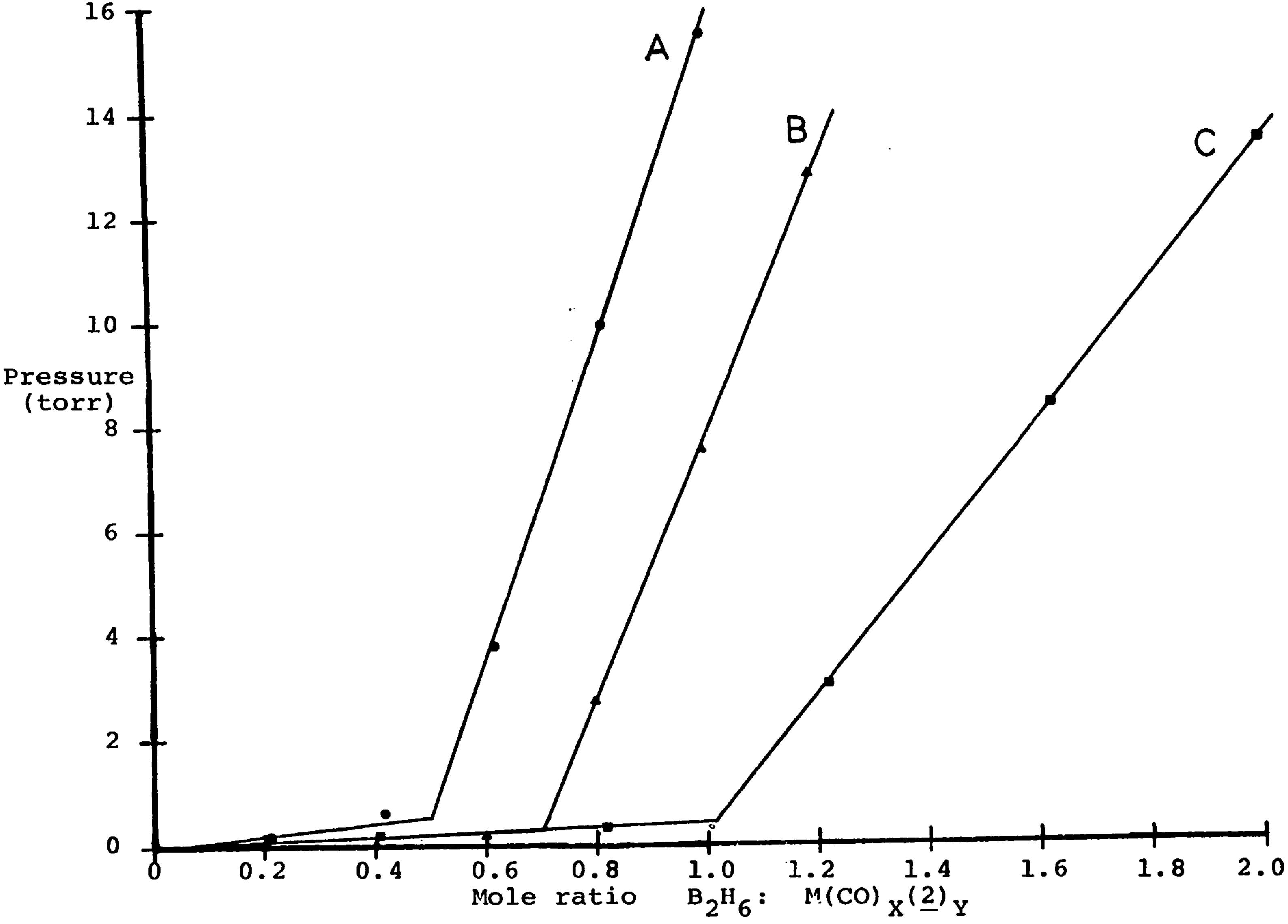
X		Solvent	Temperature[a]	Break point[b]
lone pair	2	Et_2O	-78°	1.03
PhN	9	$CHCl_3$	-45°	0.51
O	23	CH_2Cl_2	-78°	0.50
S	27	CH_2Cl_2	-78°	0.49
Se	30	$CHCl_3$	-45°	0.55
$(OC)_5Cr$		toluene	-78°	0.54
$(OC)_5W$		toluene	-78°	0.50
axial-$(OC)_4Fe$		toluene	-78°	0.53
$(OC)_3Ni$		toluene	-78°	0.70[c]
trans-(2)$(OC)_4W$		toluene	-78°	0.96
trans-(2)$(OC)_3Fe$		toluene	-78°	1.01
(2)$(OC)_2Ni$		toluene	-78°	0.99

[a] Equilibration temperature.

[b] Molar ratio of B_2H_6 to substrate at line intersection (see Figure 17).

[c] Discussed in text (*vide infra*).

Figure 17. Results of tensimetric diborane titrations of some metal carbonyl derivatives of 2. Curve A, $W(CO)_5(\underline{2})$; curve B, $Ni(CO)_3(\underline{2})$ and curve C, $Fe(CO)_3(\underline{2})_2$ are illustrative of the general results obtained.


A
B
C
16
14
12
10
8
6
4
2
0
Pressure (torr)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Mole ratio B2H6: M(CO)X(2)Y

RESULTS AND DISCUSSION

Synthesis and Stereochemistry

When the first metal carbonyl complexes of 1 were reported in 1963 (183, 184) it was noted that the ligand possessed two unusual properties. The first was the inability of 1 to replace more than two CO groups from a metal carbonyl and the second was the failure to isolate any cis disubstituted octahedral complexes of 1. It has since been found that 1 does form cis complexes but these rapidly rearrange to the trans isomers in solution (207). Also, 1 will displace olefins to give tris and tetrakis substituted complexes (which have been detected in reaction mixtures using infrared spectroscopy), but these complexes lose 1 to form only disubstituted species (185).

King originally proposed an electronic effect to be responsible for the poor ligating ability of 1 (184). The close proximity of the three nitrogen lone pairs to the phosphorus in 1 would lead to extensive P-N pi bonding which would make the phosphorus a good sigma donor but a very poor pi acceptor. As a consequence, any more than two molecules of 1 in a complex would place more negative charge on the metal atom than could be removed by synergistic bonding to 1 or CO.

A rationale for the apparent stability of the trans disubstituted complexes of 1 was put forward by King and

and Korenowski (185) based upon the steric interaction of the $-NMe_2$ groups of mutually *cis* **1** ligands. This argument also explained why the more extensively substituted complexes of **1** would rearrange to *trans* disubstituted complexes since tris or tetrakis complexes would always have at least one pair of *cis* **1** ligands.

Support for this steric interaction hypothesis comes from the cone angle measurements of Tolman (129). The cone angle of **1** (159°) would lead to substantial steric interaction in *cis* species thus favoring the *trans* forms. Steric factors alone, however, are not the only bases for the determination of stereochemistry. This point is demonstrated by *cis*-$Mo(CO)_4[P(NMePh)_3]_2$ which is very stable towards isomerization (208).

Complexes of **2** show very similar properties to complexes of **1**. The greatest degree of CO substitution is two and the *trans* isomers are most stable. However, it is possible to isolate *cis* $Mo(CO)_4(\underline{2})_2$ by reaction of *cis*-$Mo(CO)_4(NBD)$ and **2** (188). This compound isomerizes to the *trans* species very quickly in solution at room temperature.

While Group VI carbonyl complexes of **2** have been synthesized before from the hexacarbonyls (186, 188, 203), the yields were usually very low for both thermal and photolytic reactions. The one exception to this is the thermal preparation of $Mo(CO)_5(\underline{2})$ which proceeds in 43% yield. By and large, however, the yields of products were increased through the use of precursors such as $(MeCN)Cr(CO)_5$ and $Et_4N[Cr(CO)_5I]$. The former is made from the latter by Connor's method (209) as in reaction 24.

$$24.\quad Et_4N[Cr(CO)_5I] + MeCN + Et_3OBF_4 \xrightarrow[RT]{CH_2Cl_2} (MeCN)Cr(CO)_5 + Et_4NBF_4 + EtI + Et_2O$$

The advantages of this reaction are that it produces high yields (ca. 90%) and leads only to monosubstituted products. The MeCN group is easily displaced by 2 at moderate temperatures to give the desired $Cr(CO)_5(2)$. It was not possible to react 2 and the metal carbonyl salt directly because 2 and its complexes will react with halogenated solvents (probably giving phosphonium salts) and it appeared as though the Lewis acid Et_3OBF_4 also reacted with 2. When Et_3OBF_4 was reacted with either 1 or 2 in order to prepare the ethyl phosphonium salts, the products were always clear reddish amber oils which gave very complex ^{1}H-NMR spectra. Similar oily products were obtained when direct salt reactions were used to prepare carbonyl complexes. Use of $AgBF_4$ did give the metal complex but the yield was very low.

Reaction of 2 with the $M(CO)_4(NBD)$ complexes gave good yields of trans-$M(CO)_4(2)_2$ even though the cis isomers are probably initially formed as was shown for M=Mo (188). The greater stability of the trans isomers of 2 can also be rationalized on steric grounds as the cone angles of 1 and

2 should be quite similar. An unusual cis/trans isomerization is observed for the square planar Pt complexes of 1 and 2 and this will be discussed later.

The syntheses of Fe and Ni carbonyl complexes of 2 are very similar to analogous preparations involving 1 (183, 184). Of particular interest here is the unusual nature of $Ni(CO)_3(2)$. It appears as though this compound is a clear, colorless liquid at room temperature which is unstable towards heat and/or light. In contrast, $Ni(CO)_3(1)$ is a rose colored solid having a melting range from 103-113° (183). It was found that $Ni(CO)_3(1)$ is thermally unstable, decomposing to a dark brown oil upon standing at room temperature for a few days. Why these two compounds are so different remains obscure as the rigid cage of 2 would, a priori, lead one to anticipate facile crystallization. The purity of $Ni(CO)_3(2)$ was verified by both infrared and ^{31}P-NMR spectroscopy. This compound also yields unusual tensimetric diborane titration results and these will be discussed shortly.

The two metal carbonyl complexes of 3 were synthesized to assess its ligating properties relative to 1 and 2 and, in the case of the tungsten complex, to allow calculation of ^{3}JPP.

Tensimetric Titrations

As stated in the Introduction to this section, the main reason for synthesizing metal carbonyl complexes of 2 was to prepare the adducts which were expected to form upon tensimetric titration with B_2H_6. This unusual reaction of derivatives of 2 was discovered accidently during characterization of the new compound (89) and it was hoped that the adducts of metal carbonyl derivatives of 2 would give insight into the sigma-pi nature of metal-phosphorus bonding.

Results of the tensimetric titrations are reported in Table 24. While titrations were not performed for each metal complex, at least one from each group was titrated and the stoichiometries obtained. The other complexes in the group were simply reacted with an excess of B_2H_6 and their resulting compositions verified by comparison of their infrared and NMR spectra with those of a titrated compound. Except for $Ni(CO)_3(2)$, all of the compounds titrated gave the expected result that 0.50 mole of B_2H_6 was absorbed for every mole of 2 in the compound. In the case of 9, however, spectral data indicate that adduction occurs on the imido nitrogen and not on a ring nitrogen. While a search of the literature indicated that this is a general reaction of phosphinimines with Lewis acids (210), it is noteworthy that a ring nitrogen does not further react with an additional BH_3 group as does 2 (89). Only minimal steric problems are expected for the 1:1 adduct of 9 and so it becomes tempting to speculate that electron withdrawal from phosphorus resulting from adduction of the imido nitrogen lone pair could lead to increased P-N pi bonding in the cage and hence render the ring nitrogen lone pairs unavailable for BH_3 adduction. Interestingly the electronically similar compounds 23, 27 and 30 add BH_3 to a ring nitrogen to form very stable adducts. The origin of this contrasting behavior is presently obscure.

The results of B_2H_6 adduction with $Ni(CO)_3(2)$ are quite similar to those seen earlier with 22, which also gives a break at a ratio of 0.70 moles of B_2H_6 per mole of substrate (0.20 beyond theory). One great difficulty with the metal complex was its proclivity to decompose which prevented isolation of the pure compound. The compound was synthesized from a known amount of 2 and a 20 mole percent excess of $Ni(CO)_4$ in predried toluene. After a suitable reaction time this entire solution was outgassed and used in the titration apparatus. Initially, it was thought that the complex formation was incomplete and that uncomplexed 2 was absorbing B_2H_6 to give the unusual stoichiometry. However, both ^1H- and ^{31}P-NMR spectra of the reaction solution before and after B_2H_6 titration gave no indications of

2, 19 or $2 \cdot 2BH_3$. Consequently, an explanation for the phenomenon is not obvious. It is possible that association of BH_3 with a carbonyl oxygen is the cause of the anomalously large uptake of BH_3.

As mentioned earlier, all the metal complexes of 2 were reacted with B_2H_6 to give stoichiometrically adducted complexes. In addition, it was possible to limit the amount of B_2H_6 in the titration to obtain the 0.5:1 B_2H_6:metal complex adducts with the compounds *trans*-$M(CO)_4(2)_2$, *trans*-$Fe(CO)_3(2)_2$ and $Ni(CO)_2(2)_2$. Statistically, the resulting "product" should be a mixture of the non-adducted compound, the mono-and the bis-adducts. However, ^{31}P-NMR shows the mono-adducts clearly dominate the other two possible species and this was used to determine ^2JPMP values for the aforementioned five complexes.

The solution stability of the adducts can best be described as fair. Even in dry solvents the adducts decomposed with loss of gas and production of a floculent precipitate. Solutions in aromatic solvents were stable enough over a period of hours to permit useful data collection for the FT-NMR and computer averaging of transients (CAT) spectra although peaks arising from the parent compounds could be observed.

Carbonyl Frequencies

The ν(CO) frequencies of the metal carbonyl complexes of 1, 2, 2•BH_3 and 3 synthesized in this work are listed in Table 25. A comparison of the data for a particular metal carbonyl moiety shows that ν(CO) increases in the order 1 < 2 < 2•BH_3. The order of 1 and 2 (and also 3) is consistent with the sigma-pi orders for these ligands arrived at earlier in this work (*vide ante*). Since variations in ν(CO) can arise from changes in the sigma and/or pi character of the ligands, no firm conclusions as to a "dominant" effect can be made.

The placement of the ligand 2•BH_3 clearly shows, however, that it is a much weaker sigma donor and/or a much stronger pi acid than 2. Either one or both of these changes can be rationalized easily. In the case of sigma donation, the presence of the BH_3 group increases the electron withdrawal from phosphorus in the unique P-N bond by effectively increasing the electronegativity of the adducted nitrogen. Hence the phosphorus lone pair, being in one of the sp^3 sigma orbitals, becomes less basic. The alternative pi acid hypothesis requires that nitrogen adduction decreases the P-N pi bonding by utilizing the nitrogen lone pair in a $B \leftarrow N$ bond. The decrease in pi electron density about phosphorus will increase its acidity thereby leading to enhancement of M-P pi bonding. Of note here is that the two effects are *not* mutually exclusive, therefore synergism could also occur.

Table 25a. Carbonyl stretching frequencies of substituted metal carbonyl complexes

Compound	ν(CO)[a,b]					Solvent	Reference
	A_1^2	B_1[c]	A_1^1	E	E(^{13}C)		
$Cr(CO)_5(\underline{1})$	2060.6m	1975.4	1946.7sh	1938.0vs[d]	1912.8vw	C_6H_{12}	This work
	2064w	--[e]	1943s	1934vs	--[e]	C_6H_{12}	185
$Cr(CO)_5(\underline{2})$	2067.0m	1983.0	1951.0sh	1944.7vs	1915.0vw	C_6H_{12}	This work
	2066w	--[e]	1980w	1942vs	--[e]	$CHCl_3$	109, 188
$Cr(CO)_5(\underline{2}\cdot BH_3)$	2073.2m	1995.3w[f]	1962.1s	1949.4vs[g]	1914.5vw	C_6H_{12}	This work
$Mo(CO)_5(\underline{1})$	2070.6w	1985.1	1947.9sh	1945.6vs[h]	1910.2vw	C_6H_{12}	This work
	2073w	--[e]	1949s	1942s	--[e]	C_6H_{12}	185
$Mo(CO)_5(\underline{2})$	2075.4w	1992.9	1954.6sh	1951.1vs	1920.8vs	C_6H_{12}	This work
$Mo(CO)_5(\underline{2}\cdot BH_3)$	2081.6m	1999.8w[f]	1966.0s	1954.2vs[i]	1915.5vw	C_6H_{12}	This work
$W(CO)_5(\underline{1})$	2074.9w	1980.5	1943.4sh	1937.4vs[j]	1903.3vw	C_6H_{12}	This work
	2070.0	1971.0	--[e]	1936.0[k]	1902.6	C_6H_{12}	186
	2074w	--[e]	1940s	1932s	--[e]	C_6H_{12}	185
$W(CO)_5(\underline{2})$	2074.9w	1984.1	1949.7sh	1944.4vs	1914.4	C_6H_{12}	This work
	2071.5	--[e]	1949.0	1943.0	1914.0	C_6H_{12}	186[l]
$W(CO)_5(\underline{2}\cdot BH_3)$	2080.0w	1990.6w	1961.4s	1947.8vs[m]	--[e]	C_6H_{12}	This work

$(OC)_5W(\underline{3})W(CO)_5$	2076.7w	2019.4	1963.4m	1954.6vs	1920.6vw	C_6H_{12}	This work
$Cr(CO)_5(\underline{54})$	2074w	--[e]	1956s	1945s	--[e]	C_6H_{12}	185
$Cr(CO)_5(\underline{55})$	2072.2w	--[e]	1957.8sh	1954.4vs	--[e]	C_6H_{12}	This work

---

[a] Frequencies quoted in this work are accurate to ±0.5 cm^{-1}.

[b] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[c] Values quoted in this work for Raman-active modes were obtained in concentrated benzene solutions and are accurate to ±1.0 cm^{-1}.

[d] Average value of split E mode frequencies 1943.1 and 1933.0 cm^{-1}.

[e] Either not observed or not reported.

[f] Band observed in infrared spectrum.

[g] Average value of split E mode frequencies 1950.9 and 1947.8 cm^{-1}.

[h] Average value of split E mode frequencies 1949.7 and 1941.6 cm^{-1}.

[i] Average value of split E mode frequencies 1955.6 and 1952.8 cm^{-1}.

[j] Average value of split E mode frequencies 1941.6 and 1933.2 cm^{-1}.

[k] Average value of split E mode frequencies 1940.5 and 1931.5 cm^{-1}.

[l] The ligand was $P(NMeCH_2)_3CC_5H_{11}$.

[m] Average value of split E mode frequencies 1949.3 and 1946.3 cm^{-1}.

Table 25b. Carbonyl stretching frequencies of substituted metal carbonyl complexes

Compound	ν(CO)^{a,b}			Solvent	Reference
	A_{1g}^{c}	B_{1b}^{c}	E_u		
trans-Cr(CO)$_4$(1)$_2$	2004.5	1928.5	1883.7vs	C_6H_{12}	This work
	--^{d}	--^{d}	1880vs	C_6H_{12}	185
trans-Cr(CO)$_4$(2)$_2$	2019.0	1942.5	1899.8vs	C_6H_{12}	This work
	--^{d}	1938w	1887vs	$CHCl_3$	109, 188
	--^{d}	1931w	1876vs	Nujol	188
trans-Cr(CO)$_4$(2·BH$_3$)$_2$	2032.5w^e	1946.6w^e	1919.0vs, 1909.2vs	C_6H_{12}	This work
trans-Mo(CO)$_4$(1)$_2$	2019.5	1939.5	1892.7vs	C_6H_{12}	This work
	--^{d}	--^{d}	1891vs	C_6H_{12}	185
trans-Mo(CO)$_4$(2)$_2$	2032.0	1955.0	1909.2vs	C_6H_{12}	This work
	--^{d}	1949w	1905vs	$CHCl_3$	109, 188
trans-Mo(CO)$_4$(2·BH$_3$)$_2$	2044.6w^e	1951.6w^e	1926.6vs. 1920.7vs	C_6H_{12}	This work
trans-W(CO)$_4$(1)$_2$	2018.0	1935.0	1884.9vs	C_6H_{12}	This work
	--^{d}	--^{d}	1884vs	C_6H_{12}	185
trans-W(CO)$_4$(2)$_2$	2029.5	1949.5	1902.1vs	C_6H_{12}	This work
	--^{d}	1938w	1894vs	$CHCl_3$	109, 188
trans-W(CO)$_4$(2·BH$_3$)$_2$	2042.0w^e	--^{d}	1917.9vs, 1914.5vs	C_6H_{12}	This work

[a] Frequencies quoted in this work are accurate to ±0.5 cm^{-1}.

[b] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[c] Values quoted in this work for Raman-active modes were obtained in concentrated benzene solutions and are accurate to ±1.0 cm^{-1}.

[d] Either not observed or not reported.

[e] Band observed in infrared spectrum.

Table 25c. Carbonyl stretching frequencies of substituted metal carbonyl complexes

Compound	$\nu(CO)^{a,b}$			Solvent	Reference
	A_1^2	A_1^1	E		
$Fe(CO)_4$(1)	2047.8s	1973.3s	1936.2vs	C_6H_{12}	This work
	2053m	1975m	1937s	C_6H_{12}	185
$Fe(CO)_4$(2)	2058.0s	1985.3s	1951.4vs	C_6H_{12}	This work
	2053m	1976m	1942vs	$CHCl_3$	109, 188
$Fe(CO)_4(2 \cdot BH_3)$	2065.3s	1996.9s	1967.1vs	C_6H_{12}	This work
$Fe(CO)_4$(54)	2060m	1979m	1949s	C_6H_{12}	185
$Fe(CO)_4$(55)	2061.2s	1988.6s	1960.0vs	C_6H_{12}	This work

[a] Frequencies quoted in this work are accurate to ±0.5 cm^{-1}.

[b] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

Table 25d. Carbonyl stretching frequencies of substituted metal carbonyl complexes

Compound	$\nu(\mathrm{CO})^{a,b}$		Solvent	Reference
	$A_1'^{\,c}$	E'		
$\underline{\text{trans}}\text{-Fe(CO)}_3(\underline{1})_2$	1962.4	1878.1vs	C_6H_{12}	This work
	--[d]	1871vs	halocarbon	184
$\underline{\text{trans}}\text{-Fe(CO)}_3(\underline{2})_2$	1993.0	1905.2vs	C_6H_{12}	This work
	--[d]	1890vs[e]	$CHCl_3$	109, 188
$\underline{\text{trans}}\text{-Fe(CO)}_3(\underline{2}\cdot BH_3)_2$	--[d]	1922.5vs	C_6H_{12}	This work

[a] Frequencies quoted in this work are accurate to ±0.5 cm^{-1}.

[b] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[c] Values quoted in this work for Raman-active modes were obtained in concentrated benzene solutions and are accurate to ±1.0 cm^{-1}.

[d] Either not observed or not reported.

[e] Shoulder reported at 1931 cm^{-1}.

Table 25e. Carbonyl stretching frequencies of substituted metal carbonyl complexes

Compound	$\nu(CO)^{a,b}$		Solvent	Reference
	A_1	E		
Ni(CO)$_3$($\underline{1}$)	2064.6m	1991.5vs	C_6H_{12}	This work
	2066	1984	Nujol	183
Ni(CO)$_3$($\underline{2}$)	2075.7m	2003.4vs	C_6H_{12}	This work
	2079m	2004vs	$CHCl_3$	188
Ni(CO)$_3$($\underline{2}$•BH$_3$)	2085.8s	2023.5vs, 2005.0vs	C_6H_{12}	This work
(OC)$_3$Ni($\underline{3}$)Ni(CO)$_3$	2078.7m	2013.0s	C_6H_{12}	This work

[a] Frequencies quoted in this work are accurate to ±0.5 cm^{-1}.

[b] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

Table 25f. Carbonyl stretching frequencies of substituted metal carbonyl complexes

Compound	$\nu(CO)^{a,b}$		Solvent	Reference
	A_1	B_1		
$Ni(CO)_2(\underline{1})_2$	1997.0m	1938.1s	C_6H_{12}	This work
	1996	1938	Nujol	183
	1992vs	1929vs	halocarbon	184
$Ni(CO)_2(\underline{2})_2$	2016.3m	1960.1s	C_6H_{12}	This work

[a] Frequencies quoted in this work are accurate to ±0.5 cm^{-1}.

[b] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

One other effect which must be taken into account is steric in nature and arises from ligand cone angles (129). It is reasonable to expect that 2 and 3 should possess about the same cone angle as estimated for 1 because the rigid natures of 2 and 3 force methyl groups to point towards the phosphorus end of the molecule and free P-N rotation in 1 allows similar orientations. Therefore, steric interactions between any of these three ligands and any neighboring CO groups should be about the same and $\nu(CO)$ differences in analogous complexes of 1, 2 or 3 should be electronic in origin. That steric effects tangibly influence $\nu(CO)$ is demonstrated by the E mode splitting of the $M(CO)_5L$ species when L is 1 or $2 \cdot BH_3$ but not when L is 2 or 3. Such a phenomenon undoubtedly arises from the lowering of ligand symmetry which, in 1, can occur due to lone pair orientations as shown in Figure 5 (these being impossible for 2 and 3) and in $2 \cdot BH_3$, due to the adduction of a nitrogen by BH_3. This phenomenon has also been observed for $M(CO)_5L$ complexes of $P(o\text{-}MeC_6H_4)_3$ (211) and attributed to a distortion of the symmetry of the complex by the steric interaction of the bulky ligand (212). An estimated cone angle of 194° (129) for the tris-tolyl phosphine tends to support the hypothesis. While Keiter and Verkade first observed this behavior for $W(CO)_5(1)$ in C_6H_{12} solution (186) this effect went unnoticed by King and Korenowski (185) in the same solvent. The latter authors evidently mistook the split E mode bands as the A_1^1 and E modes (see Table 25a) for all the $M(CO)_5L$ complexes of <u>1</u>. From their description of the ν(CO) spectrum of $Cr(CO)_5$(<u>54</u>) it would appear the same error was made. Unfortunately, the author neglected to obtain a spectrum of $Cr(CO)_5$(<u>54</u>), synthesized in this work, so a comparison with the literature results cannot be made for this case.

The phenomenon of split E modes arises again in <u>trans</u>-$M(CO)_4L_2$ and $Ni(CO)_3L$ complexes of <u>2</u>$\cdot BH_3$ but not for <u>1</u> in contrast to the $M(CO)_5L$ complexes of both of these ligands. Strangely, however, no E mode splitting is observed in either $Fe(CO)_4L$ or <u>trans</u>-$Fe(CO)_3L_2$ complexes of either ligand. Why this phenomenon occurs in some complexes and not in others remains a mystery.

While the direct comparison of ν(CO) frequencies can be used to interpret ligand bonding abilities, a better comparison comes from the force constants derived from ν(CO) spectra. Using the Cotton-Kraihanzel method (CKM) to calculate the force constants for $M(CO)_5L$ species (163-165), the data displayed in Table 26 were obtained. The CKM can be used when only the A_1^1, A_1^2 and E modes are observed, by placing two constraints upon the system; (1) $k_{cis} > k_{trans}$ and (2) all CO cis interactions are about equal. A check on the validity of the CKM can be made by using the various force constants to calculate the B_1 mode frequency. In

Table 26. Force constants for some $M(CO)_5L$ species calculated by the Cotton-Kraihanzel method

Compound	k_{cis}[a]	k_{trans}[a]	B_{1calc}[b]	B_{1exp}[c]
$Cr(CO)_5(\underline{1})$	15.76	15.52	1975.3	1975.4
$Cr(CO)_5(\underline{2})$	15.86	15.58	1982.0	1983.0
$Cr(CO)_5(\underline{2}\cdot BH_3)$	15.94	15.77	1986.9	1995.3[d]
$Mo(CO)_5(\underline{1})$	15.89	15.53	1983.8	1985.1
$Mo(CO)_5(\underline{2})$	15.98	15.64	1989.1	1992.9
$Mo(CO)_5(\underline{2}\cdot BH_3)$	16.04	15.84	1992.8	1999.8[d]
$W(CO)_5(\underline{1})$	15.80	15.48	1977.8	1980.5
$W(CO)_5(\underline{2})$	15.90	15.57	1984.3	1984.1
$W(CO)_5(\underline{2}\cdot BH_3)$	15.96	15.77	1987.9	1990.6[d]
$(OC)_5W(\underline{3})W(CO)_5$	16.02	15.78	1991.7	2019.4

[a] Force constants are in units of millidynes/Angstrom.

[b] In cm^{-1}.

[c] Values measured by Raman spectroscopy accurate to ±1.0 cm^{-1}.

[d] Observed in infrared spectrum.

particular, $\nu(B_1) \propto k_{cis}$. Good agreement can usually be found, as is the case for all the complexes in this work where B_1 was determined by Raman spectroscopy. Braterman (213) has pointed out that this agreement does not vindicate the CKM because there is no unique solution to its quadratic equation.

While k_{cis} and k_{trans} both increase in the ligand order $\underline{1} < \underline{2} < \underline{2}\cdot BH_3$ for a given $M(CO)_5L$ complex, it is readily seen that k_{trans} is greatly increased by replacement of $\underline{2}$ with $\underline{2}\cdot BH_3$ in the complexes while k_{cis} is only slightly affected. Such effects are consistent with extensive M-P pi bonding but, as usual, sigma bonding changes cannot be ruled out.

Metal-Phosphorus Frequencies

Due to the highly symmetrical nature of phosphite $\underline{48}$ it has been possible to study the far infrared (FIR) spectra of its metal carbonyl complexes and deduce the position of metal-phosphorus stretching frequencies, $\nu(MP)$ (177, 178). In this manner, estimations regarding the relative sigma and pi contributions in metal-phosphorus bonds were made (177). The decreased ligand symmetry in $\underline{49}$ leads to an increase in the number of bands in the $\nu(MP)$ region of the FIR rendering definite $\nu(MP)$ assignments almost impossible (79).

It was hoped that the C_{3V} symmetry of $\underline{2}$ would also give rise to a small number of ligand bands so that $\nu(MP)$ could be reliably assigned. The FIR data for a number of metal complexes of $\underline{2}$ are listed in Table 27.

Table 27. Infrared bands observed in the FIR region for derivatives of $P(NMeCH_2)_3CMe$ and $As(NMeCH_2)_3CMe$

Compound	Frequency^{a,b}							
$\underline{2}$	308w				103m		62w	
$\underline{55}$	282s				100m		59w	
$Cr(CO)_5(\underline{2})$	245w		188w	152m^c	110s			164^d
$Cr(CO)_5(\underline{55})$	257m			131w^e	105m		57w	
$Mo(CO)_5(\underline{2})$		230w		162m^c	95m			195^d
$W(CO)_5(\underline{2})$	243w	228w	177w	151m^c	100m			180^d
$Fe(CO)_4(\underline{2})$	256s	228w	172w	152m^c	103s			169^d
$Fe(CO)_4(\underline{55})$	258w			142w^e	107s		59w	
$Cr(CO)_5(\underline{2}\cdot BH_3)$	280w	227m	154s^f		110s		63w	
$Mo(CO)_5(\underline{2}\cdot BH_3)$	273m	225s	153m^f	137w	98s			
$W(CO)_5(\underline{2}\cdot BH_3)$	257s	228m	147s^f	123w	102s			
$Fe(CO)_4(\underline{2}\cdot BH_3)$	258m	215w	160w^f	122s	113s	94s		

[a] Frequencies in cm^{-1} measured in Nujol mulls.

[b] w = weak, m = medium, s = strong.

[c] $\nu(MP)$ assignment based upon frequency for analogous complex where L = $\underline{48}$.

[d] $\nu(MP)$ for complex where L = $\underline{48}$ (from reference 177).

[e] $\nu(MAs)$ assignment from comparison of the analogous aminophosphine complex.

[f] $\nu(MP)$ assignment for adducted complex determined by spectral comparison.

Ligand 2 has only three significant absorptions in the region of interest and the same is true for the aminoarsine 55. Upon complexation, a great number of bands appear in the FIR in much the same manner as for complexes of 49 (79). All of the metal complexes of 2 show a medium band in the range from 103 to 110 cm^{-1} which can be attributed to the intraligand mode observed in 2 at 103 cm^{-1}. A similar shift can be seen for the complexes of 55.

Based upon the results with complexes of 48, it would appear that the most likely candidates for ν(MP) are the bands between 152-162 cm^{-1}. It is expected that, on the basis of mass differences alone, ν(MP) for complexes of 2 would be at lower frequencies than for complexes of 48. However, if the indicated assignments in Table 27 are correct, the ν(MP) frequencies for complexes of 2 do not follow the same frequency variation trend as shown by the complexes of 48. Comparison of the FIR frequencies for the analogous complexes of 2 and 55 (Cr and Fe) tends to confirm the assignments in the Table since ν(MP) is expected to be at higher frequency than ν(MAs).

Upon BH_3 adduction of the complexes of 2 the FIR spectra change and cast doubt upon the above assignments. Once again the intraligand mode shows up between 98 and 113 cm^{-1} and again there are bands in the previously assigned ν(MP) region, 147-160 cm^{-1}. If these bands are now assigned to ν(MP) for the adducts it would appear that the Cr and Fe species show the hoped for behavior and the Mo and W complexes do not. If pi bonding were the dominant effect ν(MP) would increase upon adduction and indeed, slight increases are shown for the Cr (152 to 154 cm^{-1}) and Fe (152 to 160 cm^{-1}) species upon adduction. However, the Mo and W species register decreases in their assigned ν(MP) frequencies from 162 to 153 cm^{-1} and 151 to 147 cm^{-1}, respectively. Even more unfortunate, the accuracy of band positions is no better than ±2 cm^{-1} which makes the smaller increases and decreases of uncertain validity. Thus the question of any clear cut sigma or pi dominance is still unsettled.

However, an interesting change is observed in the ν(P=O) frequency of <u>23</u> when it is adducted with BH_3. Compound <u>23</u> displays ν(P=O) at 1285.4 cm^{-1} (see Table 10) but compound <u>23</u>$\cdot BH_3$ shows its ν(P=O) at 1302.7 cm^{-1}. The increase of 17.3 cm^{-1} is experimentally significant and is apparently the result of an increased bond order in the P=O bond. Since the sigma donating ability of the phosphorus must decrease upon adduction, the obvious explanation is an increase in pi bonding. Some might argue that the P=O bond is better represented as $P^+ - O^-$ (50) and therefore adduction of the cage nitrogen will simply tend to increase the phosphorus positive charge and hence the bond polarity. The ν(P=O) frequency would then be expected to increase on electrostatic grounds. However, since a mechanism for charge transfer from "negative" oxygen to "positive" phosphorus exists (pi bonding), it is also to be expected that this would tend to counteract any such charge imbalance. This same argument was used to rationalize the ^1JPSe trends seen earlier (*vide* *ante*).

Thus, while pi bonding cannot be portrayed as dominant in the metal carbonyl complexes of 2, a strong argument can be put forth for its dominance in 23, 23$\cdot$BH$_3$ and presumably the rest of the chalcogen derivatives of 2. Such pi effects could very well be carried over into the metal carbonyl complexes of 2.

Proton NMR Spectra

The ^{1}H-NMR spectra of some metal carbonyl complexes of 1 (184) and 2 (188) have been reported previously. In the case of 1, the spectra were used mainly for characterization but some inferences about ^2JPMP in the complexes were made. The spectra for complexes of 2 were obtained during an investigation of the aromatic solvent induced shift (ASIS) effect upon these complexes in addition to an attempt to obtain ^2JPMP values from ^{1}H-NMR spectra (188). In the present work, the ^{1}H-NMR spectra were examined to see whether small changes in metal-phosphorus bonding were detectable. The ^{1}H-NMR spectral data for metal carbonyl complexes of 1 and 2 are displayed in Table 28.

Table 28. Proton NMR spectral data for metal carbonyl derivatives of $P(NMe_2)_3$, $P(NMeCH_2)_3CMe$ and $P(NMeNMe)_3P$

Compound	δNMe[a]	$^3J_{PNCH_3}$[b,c]	δNCH_2[a]	$^3J_{PNCH_2}$[b,c]	δCMe[a]	Solvent	Reference
$Cr(CO)_5(\underline{1})$	2.26	10.1	--	--	--	C_6H_6	184, 185
$Cr(CO)_5(\underline{2})$	2.55	15.0	2.31	4.4	0.26	C_6D_6	This work
$Cr(CO)_5(\underline{2})$	2.57	15.2	2.34	4.5	0.28	C_6H_6	188
$Mo(CO)_5(\underline{1})$	2.25	10.2	--	--	--	C_6H_6	184, 185
$Mo(CO)_5(\underline{2})$	2.54	15.8	2.31	4.5	0.29	C_6D_6	This work
$Mo(CO)_5(\underline{2})$	2.57	15.8	2.37	4.3	0.37	C_6H_6	188
$W(CO)_5(\underline{1})$	2.19	11.0	--	--	--	C_6H_6	185
$W(CO)_5(\underline{1})$	2.26	10.2	--	--	--	C_6D_6	This work
$W(CO)_5(\underline{2})$	2.54	15.5	2.33	4.8	0.27	C_6D_6	This work
$Fe(CO)_4(\underline{1})$	2.34	9.6	--	--	--	C_6H_6	184, 185
$Fe(CO)_4(\underline{2})$	2.51	15.9	2.34	6.3	0.30	C_6D_6	This work
$Ni(CO)_3(\underline{2})$	2.38	16.0	2.35	5.5	0.43	C_6D_6	This work
$(OC)_5W(\underline{3})W(CO)_5$	2.68	13.0[d]	--	--	--	C_6D_6	This work
$(OC)_3Ni(\underline{3})Ni(CO)_3$	2.62	14.7[d]	--	--	--	C_6D_6	This work
trans-$Cr(CO)_4(\underline{1})_2$	2.58	9.7	--	--	--	C_6H_6	184, 185
trans-$Cr(CO)_4(\underline{2})_2$	2.95	14.2	2.60	4.4	0.40	C_6D_6	This work
trans-$Cr(CO)_4(\underline{2})_2$	2.93	14.3	2.62	4.3	0.45	C_6H_6	188
trans-$Mo(CO)_4(\underline{1})_2$	2.67	10.0	--	--	--	--[e]	184
trans-$Mo(CO)_4(\underline{2})_2$	2.92	15.2	2.59	4.7	0.43	C_6D_6	This work

trans-Mo(CO)$_4$(2)$_2$	2.88	15.1	2.62	4.4	0.48	C_6H_6	188
trans-W(CO)$_4$(1)$_2$	2.55	10.2	--	--	--	--[e]	184
trans-W(CO)$_4$(2)$_2$	2.90	15.5	2.62	4.6	0.42	C_6D_6	This work
trans-W(CO)$_4$(2)	2.89	14.9	2.63	5.0	0.44	C_6H_6	188
trans-Fe(CO)$_3$(1)$_2$	2.65	9.4	--	--	--	--[e]	184
trans-Fe(CO)$_3$(2)$_2$	2.82	15.6	2.56	6.7	0.47	C_6D_6	This work
trans-Fe(CO)$_3$(2)$_2$	2.88	15.5	2.62	6.6	0.48	C_6H_6	188
Ni(CO)$_2$(1)$_2$	2.47	9.3	--	--	--	--[e]	184
Ni(CO)$_2$(2)$_2$	2.74	15.6	2.54	4.8	0.50	C_6D_6	This work

---

[a] Values reported from this work are ±0.01 ppm.

[b] Value reported from this work are ±0.1 Hz.

[c] ^{3}JPNCH values for *trans* species are pseudotriplets due to ^{2}JPMP coupling. The value reported is the separation of the two outermost peaks.

[d] Pseudotriplet due to ^{3}JPP coupling. Value reported is actually $|^{4}$JPH + ^{3}JPH$|$.

[e] Solvent not specified but may be CS_2, $CHCl_3$ or C_6H_6.

Of note is the difference in $^3JPNCH_3$ between complexes of 1 and 2. Here again, as mentioned in the ^{13}C-NMR work (*vide ante*), the free rotation about the P-N bond in 1 leads to an "averaging" of the *cis* and *trans* ^3JPNCH couplings. If one averages $^3JPNCH_3$ and $^3JPNCH_2$ for the monosubstituted complexes of 2, it is seen that ^3JPNCH (avg.) is 9.7, 10.2, 10.2 and 11.1 Hz for the Cr, Mo, W and Fe species, respectively, as compared to 10.1, 10.2, 11 and 9.6 Hz for the analogous complexes of 1. A similar result is obtained for the *trans* disubstituted species. It is interesting that for complexes of 2 the ^3JPNCH values are large for the cisoid coupling ($^3JPNCH_3$) and small for the transoid coupling ($^3JPNCH_2$). This is similar to the findings for ^2JPNC values in P^{III} compounds (144). In the latter case the cisoid couplings are positive in sign while the transoid couplings were negative. The signs of ^3JPNCH for complexes of 2 were not determined in this work.

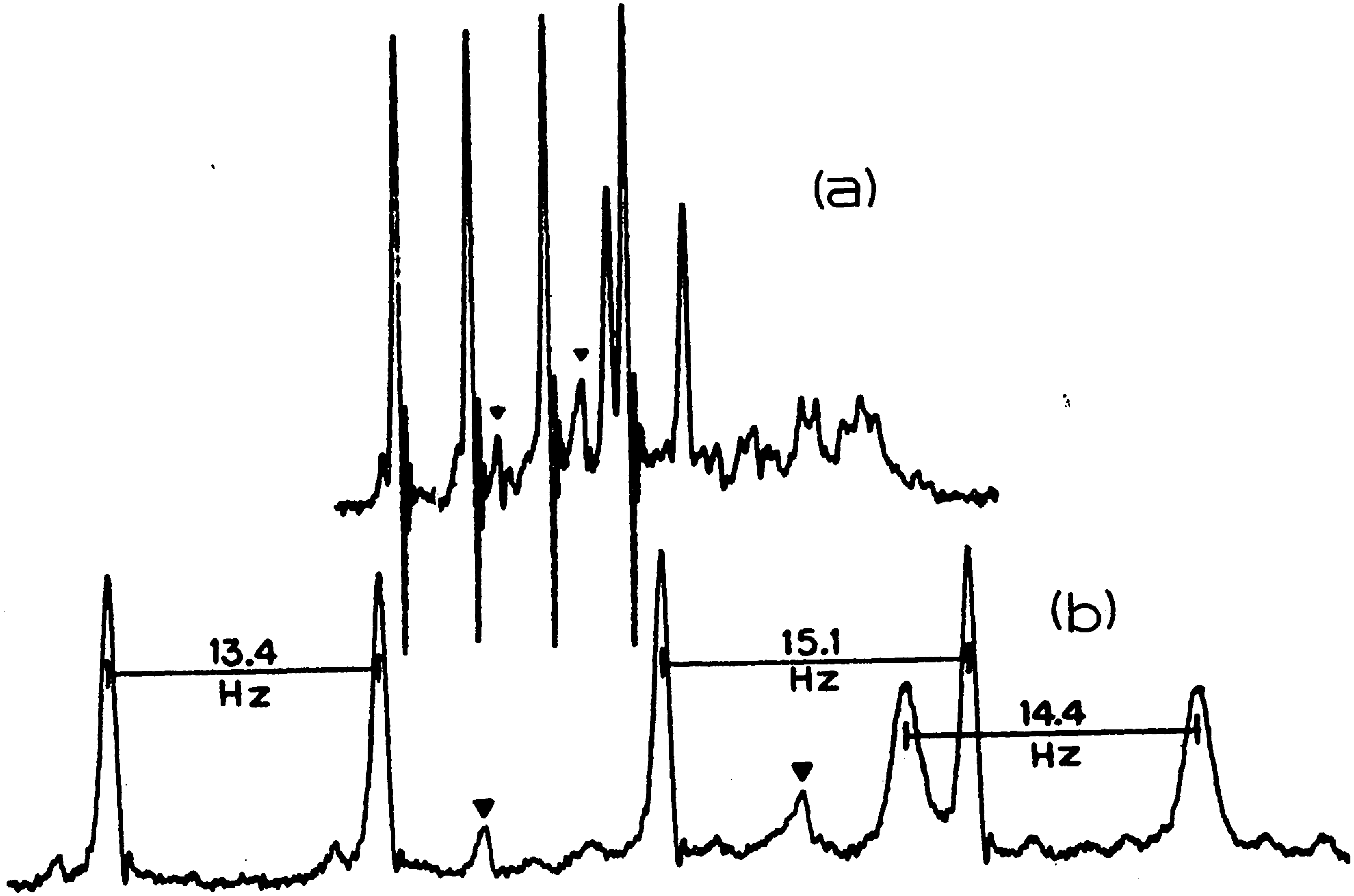
In the monosubstituted complexes of 1 and 2 the ^{1}H-NMR spectra look similar to those observed for organic derivatives of the ligands. However, in the *trans* disubstituted species the NMe and NCH_2 protons no longer appear as doublets but rather are pseudotriplets due to ^2JPMP couplings. This phenomenon has been noticed in other metal complexes of phosphorus ligands (109) and the amount of the triplet character was used by King (184) to estimate qualitatively the magnitude of ^{2}JPMP. The triplet appearance varies from none in $Ni(CO)_2L_2$, to very slight (a 3:1:3 triplet) in trans-$Cr(CO)_4L_2$, to moderate (1:1:1) in the trans Mo and W species, to substantial (2:3:2) in trans-$Fe(CO)_3L_2$.

King states that if the coupling between the phosphorus nuclei were small compared to ^{3}JPNCH then one would observe the doublet band shape as seen in the Ni complexes. But if ^{2}JPMP were very large compared to ^{3}JPNCH a 1:2:1 triplet would be observed. The order of ^{2}JPMP would then appear to be Ni << Cr < Mo $\approx$ W < Fe. As shall be seen later, this order is generally correct. It has been observed in all tetrahedral Ni complexes that ^{2}JPMP is practically zero (109) and this is also seen for complexes of 1 and 2.

Upon BH_3 adduction of one cage nitrogen on 2 the ^{1}H-NMR spectrum becomes fairly complex. This occurs because all the NMe and NCH_2 groups become non-equivalent owing to nitrogen adduction. An example is the ^{1}H-NMR spectrum of $W(CO)_5(2{\cdot}BH_3)$ shown in Figure 18. The three doublets which arise from the NMe protons stand out noticeably but the NCH_2 proton resonances are masses of multiplets. Each proton in a particular NMe group is magnetically equivalent to the other two protons in that group thus giving the three doublets observed for the NMe groups. However, because of cage constraint, all six NCH_2 protons are non-equivalent and thus should give rise to six doublets of doublets (from ^{3}JPNCH and ^{2}JHCH) which are all in a very narrow range. It was not

Figure 18a. Proton NMR spectrum of $W(CO)_5(\underline{2}\cdot BH_3)$ in the NMe and NCH_2 region.

Figure 18b. An expansion of the NMe region showing broadened Me resonances of the adducted NMe moiety. The peaks marked with ▼ arise from the NMe groups of $W(CO)_5(\underline{2})$.


(a)
(b)
13.4
Hz
15.1
Hz
14.4
Hz

possible to analyze the NCH_2 resonances, but the NMe resonances were analyzed and are listed in Table 29. It should be mentioned that while the ^1H-NMR spectra for the diadducts of the disubstituted metal complexes of 2 were recorded they were too complex to analyze. This could very well arise from the diastereoisomerism which stems from the cis and transoid relationships of the two BH_3 moieties in these complexes. Assignments of the NMe resonances for the adducts were difficult at first until it was noticed that one of the doublets is broader than the other two. Such broadening could be due to the proximity of a quadrupolar B atom and so these resonances are assigned to the adducted NMe group. The other two resonances are not as easy to assign but it will be noted in Table 29 that the chemical shifts for the NMe_c protons are very similar to the corresponding chemical shifts for the non-adducted species (cf. Table 28). Thus it would appear resonable to assign the NMe protons as shown below. Interestingly, it is seen that ^3JPNCH for the NMe_a and NMe_b protons is usually smaller than for the NMe_c protons. Although such a phenomenon might be expected for the NMe_a protons because of the rehybridization of nitrogen from sp^2

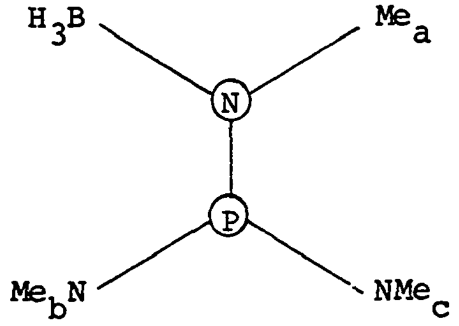


Table 29. Proton NMR resonances of the NMe groups in $(X)P(NMeCH_2)_3CMe{\cdot}BH_3$[a,b]

X	δNMe_a, ^3JPNCH	δNMe_b, ^3JPNCH	δNMe_c, ^3JPNCH
BH_3	2.72, 12.5	2.85, 12.1	2.77, 10.2
O	2.81, 10.9	2.84, 11.2	2.76, 11.4
S	2.79, 13.1	2.94, 13.4	2.87, 14.0
Se	2.74, 14.2	2.96, 14.5	2.74, 14.2
$Cr(CO)_5$	2.43, 13.9	2.77, 12.8	2.50, 14.7
$Mo(CO)_5$	2.34, 14.2	2.77, 13.6	2.46, 15.2
$W(CO)_5$	2.36, 14.4	2.76, 13.4	2.48, 15.1
$Fe(CO)_4$	2.46, 14.7	2.80, 13.8	2.54, 16.1
$Ni(CO)_3$	2.29, 14.1[c]	2.68, 14.7[c]	2.31, 14.0[c]

[a] Spectra were recorded in $CDCl_3$ solution (X = BH_3, O, S and Se) or in C_6D_6 solution (X = metal carbonyl).

[b] Coupling constants are ±0.2 Hz except as noted.

[c] ±0.5 Hz.

Table 30. ^{31}P-NMR spectral data for metal carbonyl derivatives of P(NMe$_2$)$_3$, P(NMeCH$_2$)$_3$CMe and P(NMeNMe)$_3$P[a]

Compound	$\delta\,^{31}$P[b]	$\Delta\delta\,^{31}$P[c]	$^1J_{WP}$[d]
1	-122.3	--	
Cr(CO)$_5$(1)	-159.9	-37.6	
Mo(CO)$_5$(1)	-145.6[e]	-23.3	
W(CO)$_5$(1)	-126.5	- 4.2	314.1
Fe(CO)$_4$(1)	-155.4	-33.1	
Ni(CO)$_3$(1)	-144.7[e]	-22.4	
trans-Cr(CO)$_4$(1)$_2$	-173.5[f]	-51.2	
trans-Mo(CO)$_4$(1)$_2$	-159.1[g]	-36.8	
trans-W(CO)$_4$(1)$_2$	-133.9[h]	-11.6	347.3
trans-Fe(CO)$_3$(1)$_2$	-169.8[i]	-47.5	
Ni(CO)$_2$(1)$_2$	-147.1[e]	-24.8	

---

[a] All spectra were recorded in C_6D_6 at room temperature unless noted.

[b] Values from this work are ±0.05 ppm.

[c] Coordination chemical shift; defined as $\Delta\delta = \delta_{complex} - \delta_{ligand}$.

[d] ±1.1 Hz.

[e] From reference 214, measured by CW-NMR in C_6H_6.

[f] Reference 215 reports -178.19 ppm in CS_2 (CW-NMR).

[g] Reference 215 reports -159.39 ppm in C_6D_6; reference 214 reports -159.4 ppm in C_6H_6 (CW-NMR).

[h] Reference 215 reports -134.17 ppm in C_6D_6 (CW-NMR) but no ^{1}JPW value.

[i] Reference 215 reports -170.18 ppm in C_6D_6 (CW-NMR).

Table 30. continued

Compound	$\delta^{31}P$	$\Delta\delta^{31}P$	$^1J_{WP}$
$\underline{2}$	- 83.5	--	
$\mathrm{Cr(CO)_5(\underline{2})}$	-145.0	-61.5	
$\mathrm{Mo(CO)_5(\underline{2})}$	-126.8	-43.3	
$\mathrm{W(CO)_5(\underline{2})}$	-109.7[j]	-26.2	320.7
$\mathrm{Fe(CO)_4(\underline{2})}$	-152.3	-68.8	
$\mathrm{Ni(CO)_3(\underline{2})}$	-121.1	-37.6	
<u>trans</u>-$\mathrm{Cr(CO)_4(\underline{2})_2}$	-159.4	-75.9	
<u>trans</u>-$\mathrm{Mo(CO)_4(\underline{2})_2}$	-138.8	-55.3	
<u>trans</u>-$\mathrm{W(CO)_4(\underline{2})_2}$	-116.1	-32.6	359.6
<u>trans</u>-$\mathrm{Fe(CO)_3(\underline{2})_2}$	-162.1	-78.6	
$\mathrm{Ni(CO)_2(\underline{2})_2}$	-121.7	-38.2	
$\underline{3}$	-107.4	--	
$\mathrm{(OC)_5W(\underline{3})W(CO)_5}$	-134.6	-27.2	338.2[k]
$\mathrm{(OC)_3Ni(\underline{3})Ni(CO)_3}$	-131.2	-23.8	

[j] Reference 186 reports -112.0 ppm in CH_2Cl_2 (CW-NMR) for complex where L = $P(NMeCH_2)_3CC_5H_{11}$; ^1JPW reported as 318 Hz.

[k] Calculated using ITRCAL; see text.

to sp^3 upon adduction, it should be noted that in the organophosphorus derivatives this coupling is usually smaller for NMe_a than NMe_b protons. The reason for these opposite coupling relationships in the two classes of compounds is presently obscure.

^{31}P-NMR Spectra

Much information may be gleaned from changes in the ^{31}P-NMR spectra for metal complexes of 1, 2 and 3 discussed in this work and they shall be examined shortly. First, however, the ^{31}P-NMR data for those metal carbonyl complexes mentioned in the Experimental section must be examined.

There are several trends apparent upon inspection of the data in Table 30. The first of these is the chemical shift trend for Cr, Mo and W where, for both mono- and disubstituted complexes of 1 and 2, the $\delta^{31}P$ values are W < Mo < Cr. This trend is more easily seen in the column for the coordination chemical shift, $\Delta\delta^{31}P$. A satisfactory explanation for this trend has not yet been put forward. Analyses based on both sigma-pi (216) and pi only (217) interactions have been proposed but have not proven general enough to rationalize all cases. It is generally agreed, however, that changes in $\delta^{31}P$ are dominated by the paramagnetic term of equation 25 (218) since the diamagnetic term is orders of magnitude smaller (125).

25. $$\delta^{31}P = \delta^{31}P_{\text{diamagnetic}} + \delta^{31}P_{\text{paramagnetic}}$$

Braterman et al. (219) have tried to rationalize $\delta^{13}C$ values for metal carbonyl groups using only the paramagnetic term but this method has been questioned by Evans and Norton (220).

It is seen in Table 30 that $\Delta\delta^{31}P$ is consistently larger for complexes of 2 compared to the analogous complexes of 1. Assuming the dominance of $\delta^{31}P_{\text{paramagnetic}}$ in equation 25, it may be possible to rationalize the greater $\Delta\delta^{31}P$ values for 2 on the basis of increased pi bonding of 2 to a metal center compared to 1. As indicated in equation 21, an increase in either ζ_1 or ζ_2 can lead to a more negative ^{31}P chemical shift. Since, upon adduction, the phosphorus atoms are expected to become poorer sigma donors (a decrease in ζ_1) a greater pi acidity and, consequently, greater back bonding (increase in ζ_2) might account for $\Delta\delta^{31}P$. Of course, the assumption of equal geometry changes in 1 and 2 upon coordination must be made since increasing the X-P-X angle in M-PX_3 compounds will cause $\delta^{31}P$ to shift downfield (125) for a given electronegativity of X. Such an explanation would also be consistent with the greater coordination chemical shifts of the trans disubstituted complexes of both 1 and 2 compared to their monosubstituted complexes. In the latter cases, the phosphorus is forced to compete for metal d electrons with a strongly pi bonding CO group trans to it, whereas in the former cases there are two phosphorus atoms of identical pi bonding ability competing for the same metal d electrons with the overall effect of increased M-P pi bonding and hence a greater $\Delta\delta^{31}P$. Unfortunately, the similarity of the $\Delta\delta^{31}P$ values for the mono and disubstituted nickel complexes is not consistent with this rationale and the reason for this anomaly is not obvious. If the above reasoning is correct, it would also be consistent with the previously demonstrated sigma-pi abilities of ligands 1 and 2.

The ^{1}JWP values quoted in Table 30 are comparable to previous one bond couplings involving ^{31}P in that the couplings for 2 are larger than for 1. Unlike $^{1}JPSe$, however, the present couplings are very dependent upon metal s orbital density in the W-P bond as well as both ψ^2 and α^2 terms arising from phosphorus (171). The small difference in ^{1}JWP for the two ligands is probably due to a small difference in the ψ^2 term of the phosphorus nuclei in 1 and 2 since a similar difference in coupling is seen in $^{1}JPSe$ for 29 and 30.

In a study (186) which tested a previous correlation of ^{1}JWP and $\nu(CO)$ for various $W(CO)_5L$ complexes (221), it was found that ^{1}JWP was linearly correlated with the electronegativities of the groups on phosphorus in much the same manner (and probably for the same reasons) as $^{1}JPSe$ (vide ante). It was not possible to correlate ^{1}JWP with any $\nu(CO)$

modal frequencies or the sigma and pi parameters derived by the method of Graham (222), however.

As mentioned in Table 30, the value of ^1JWP for $(OC)_5W(\underline{3})W(CO)_5$ was determined by ITRCAL utilizing a spectrum essentially the same as that shown for compound 31 in Figure 10. A value of 74.5 Hz was calculated for ^3JPP in the process of solving the spectrum. The RMS error for the calculation was 2.64 Hz and so the values of ^1JWP and ^3JPP are probably only accurate to about ±5 Hz. It is gratifying to see, however, that ^1JWP for $(OC)_5W(\underline{3})W(CO)_5$ falls in about the same range as for $W(CO)_5(\underline{2})$ but less than for trans-$W(CO)_4(\underline{2})_2$. This result concurs with the larger ^1JPSe value for 31 as compared to 30 which was ascribed (*vide ante*) to both a "hinge" and electronegativity effect in the cage of 3. The smaller difference between ^1JWP for $W(CO)_5(\underline{2})$ and $(OC)_5W(\underline{3})W(CO)_5$ than the ^1JPSe difference for 30 and 31 may be due to the greater importance of the metal s orbital density in the coupling expression or the electronegativity difference between W(2.36) and Se(2.55) (156).

Upon reaction of the derivatives of 2 with B_2H_6, changes are observed in their ^{31}P-NMR spectra. The pertinent parameters are displayed in Tables 31 and 32 for the metal carbonyl and chalconide and BH_3 derivatives of 2, respectively. Comparison with the data in Table 30 shows that all the metal complex resonances have moved downfield from 9.6 to 17.8 ppm.

Table 31. ^{31}P-NMR spectral data for metal complexes of $P(NMeCH_2)_3CMe\cdot BH_3$[a]

Compound	$\delta^{31}P$[b]	$\Delta\delta^{31}P$[c]	$^1J_{WP}$[d]
$Cr(CO)_5(\underline{2}\cdot BH_3)$	-162.8	-17.8	
$Mo(CO)_5(\underline{2}\cdot BH_3)$	-143.1	-16.3	
$W(CO)_5(\underline{2}\cdot BH_3)$	-127.5	-17.8	331.8
$Fe(CO)_4(\underline{2}\cdot BH_3)$	-169.7	-17.4	
$Ni(CO)_3(\underline{2}\cdot BH_3)$	-131.3	-10.2	
<u>trans</u>-$Cr(CO)_4(\underline{2}\cdot BH_3)_2$	-178.0	-18.6	
<u>trans</u>-$Mo(CO)_4(\underline{2}\cdot BH_3)_2$	-156.1	-17.3	
<u>trans</u>-$W(CO)_4(\underline{2}\cdot BH_3)_2$	-132.6	-16.5	376.2
<u>trans</u>-$Fe(CO)_3(\underline{2}\cdot BH_3)_2$	-176.4	-14.3	
$Ni(CO)_2(\underline{2}\cdot BH_3)_2$	-131.3	- 9.6	

[a] All spectra were recorded in C_6D_6 at room temperature.

[b] ±0.05 ppm.

[c] $\Delta\delta \equiv \delta_{adduct} - \delta_{complex}$.

[d] ±1.1 Hz.

Table 32. ^{31}P-NMR spectral data for BH_3 adducts of $(X)P(NMeCH_2)_3CMe$[a]

X	$\delta^{31}P_{adduct}$[b]	$\delta^{31}P_{substrate}$[b]	$\Delta\delta^{31}P$
O	- 19.9	-19.8	- 0.1
S	- 78.0	-73.2	- 4.8
Se	- 85.7[c]	-77.4[d]	- 8.3
BH_3	-101.6[e]	-89.1[e]	-12.5[f]

[a] All spectra were recorded in $CDCl_3$ solution.

[b] ±0.05 ppm except as noted.

[c] $^1J_{PSe}$ = 943.3 Hz.

[d] $^1J_{PSe}$ = 854.5 Hz.

[e] Peak broadening makes the $\delta^{31}P$ assignment accurate to ±0.2 ppm.

[f] ±0.4 ppm due to peak broadening.

Much smaller downfield shifts are observed for the remaining derivatives of 2 as shown in Table 32. The almost non-existent shift for the BH_3 adduct of 23 was, at first, thought to be an instrument error of the HX-90 spectrometer. However, both ^1H-NMR and IR spectroscopy showed that the adduct had been formed. As a check, the experiment was repeated twice with the same results each time. It would thus appear that $\Delta\delta^{31}P$ for the four compounds in Table 32 is inversely related to the electronegativity of the exocyclic group X, viz. if χ_X is large then $\Delta\delta^{31}P$ is small. For the metal carbonyls of 2, a similar trend is difficult to define because of the uncertainty in estimating χ for the metal carbonyl moieties. If it can be assumed that χ_{metal} should increase with an increasing number of CO groups on a metal, the trend Cr > Fe > Ni appears to agree with this hypothesis. On the other hand, the Pauling electronegativities of the metals are reversed, being 1.66, 1.83 and 1.91, respectively (156). The empirical trends, especially for the disubstituted metal complexes, tend to give credence to the carbonyl number hypothesis. When Riess and Van Wazer (223) investigated the ^{31}P-NMR behavior of the various BH_3 and $Ni(CO)_3$ derivatives of P_4O_6, they found that the empirical formula for calculating the chemical shift of a complexed phosphorus was quadratic in χ of the Lewis acid. In this work, $\Delta\delta^{31}P$ for the BH_3 and $Ni(CO)_3$ derivatives of 2 are of the same magnitude, correlating well with their Pauling electronegativities of 2.04 and 1.91, respectively.

A consideration of the NPN bond angle and individual nitrogen electronegativity changes that occur in 2 upon its reaction with a BH_3 fragment would enable one to use Letcher and Van Wazer's tables and graphs (125) to calculate the amount of sigma and pi contribution to the ^{31}P resonance. However, as the equations are very sensitive to small geometry changes, the absence of a crystal structure for a BH_3 adduct of $M(CO)_x(\underline{2})_y$ make such quantification attempts foolhardy.

The changes observed in both ^1JPSe and ^1JWP upon adduction are worth mentioning as they appear to show that, once again, $\psi^2_{3s(O)P}$ plays a dominant role in one bond phosphorus couplings. Adduction of a cage nitrogen causes rehybridization of that nitrogen from sp^2 to sp^3 along with destruction of any P-N pi bonding for the affected nitrogen. Both of these factors will tend to cause the P-N bond distance to increase. Most likely this would cause an increase in the N-P-N bond angles due to the constraint of the cage. Such an increase would tend, therefore, to increase the p character in the P=M bond and thus lead to a decrease in ^1JPM. Such a decrease is not observed and may be rationalized by asserting the dominance of the ψ^2 terms of equation 20. The greater electronegativity of the adducted nitrogen may be expected to increase the positive charge on phosphorus and lead to a greater value of ^1JPM. The much larger change in ^1JPSe for 30 to 30$\cdot BH_3$ (10.4%) compared to the change in ^2JPW for $W(CO)_5(2)$ to $W(CO)_5(2\cdot BH_3)$ (3.5%) may be a result of the greater ability of a metal to offset this effect by back-donation to the phosphorus d orbitals.

When the ratio of B_2H_6 reacted with a disubstituted metal complex of 2 is limited to 0.5:1, the desired product, $M(CO)_x(2)(2\cdot BH_3)$, is found to occur in a mixture of di- and non-adducted complexes with the mono-adduct greatly predominating. The ^{31}P-NMR spectra for the mono-adducts produced in this work are listed in Table 33. The spectra consist of two AB doublets with a coupling that corresponds to ^2JPMP. Such spectra give valuable insights on the P-P interactions which produce virtually coupled ^1H-NMR spectra of disubstituted metal complexes of 1 and 2. While it is obvious that the present compounds utilize two chemically distinct phosphorus nuclei to enable the observation of ^2JPMP, the small change in ^1JWP for $W(CO)_5(2)$ and its BH_3 adduct would indicate that the present couplings are rather close in magnitude to those wherein the nuclei are identical.

It is seen that King's qualitative ordering of ^2JPMP ($Ni \ll Cr < Mo \approx W < Fe$) appears to be valid for the first four members of the series but not for Fe. The order observed with the present system is $Ni \ll Cr < Fe < W \approx Mo$. It may be noted that the same order was determined by Bertrand *et al.*

Table 33. ^{31}P-NMR chemical shifts and ^{2}JPMP for metal complexes of the type $M(CO)_x[P(NMeCH_2)_3CMe]$-$[P(NMeCH_2)_3CMe \cdot BH_3]$[a]

Compound	$\delta^{31}P_{adduct}$[b]	$\delta^{31}P_{non\text{-}adduct}$[b]	$^{2}JPMP$[c]
trans-$Cr(CO)_4$(2) (2·BH_3)	-180.2	-158.2	20.0
trans-$Mo(CO)_4$(2) (2·BH_3)	-157.6	-137.3	116.5
trans-$W(CO)_4$(2) (2·BH_3)	-135.3[d]	-113.6[e]	113.2
trans-$Fe(CO)_3$(2) (2·BH_3)	-178.5	-159.3	82.1
$Ni(CO)_2$(2) (2·BH_3)	-135.2	-120.2	0[f]

[a] Spectra were recorded on $CD_3C_6D_5$ solutions at room temperature. The resulting AB spectra were analyzed for $\delta^{31}P$ and coupling constants using ITRCAL.

[b] ±0.05 ppm.

[c] ±1.1 Hz.

[d] $^{1}JWP = 377.4$ Hz

[e] $^{1}JWP = 357.5$ Hz.

[f] Coupling, if any, was not resolvable.

(215) for the trans-complexes of 1 by analysis of the ^{1}H-NMR spectra. The ^{2}JPMP values determined in that work were Cr, -17 ± 5 Hz; Fe, +65 ± 10 Hz; W, +81 ± 5 Hz and Mo, +101 ± 1 Hz. It is possible, however, for a small value of ^{2}JPMP to produce a proton spectrum which appears to represent a large degree of virtual coupling if ^{3}JPH is also small. However, it was previously seen that ^{3}JPH values for all the metal complexes of 1 and 2 are of a similar magnitude (ca. 15 Hz).

Platinum Metal Complexes

Platinum complexes of 1 were first reported by Jenkins and Verkade in 1967 (195) as part of a study concerned with transition metal complex stereochemistries. Since these compounds were readily synthesized in high yield from the bis(benzonitrile)platinum dichloride complex, it was felt that a comparison of the ligating abilities of 1 and 2 towards a divalent metal would be of interest. According to Pidcock's chart (Figure 16), a divalent metal and an aminophosphine ligand should be very close to the borderline where metal-phosphorus bonding loses the pi component. Both the chloride and iodide complexes of the ligands with Pt were prepared as described in the Experimental section and their properties are listed in Table 34.

For the most part, the stereochemistries were determined by the patterns in the ^{1}H-NMR spectra; a cis complex giving simple doublets for NMe or NCH_2 resonances while a trans

Table 34. Stereochemistry and ^{31}P-NMR spectral data for complexes of $P(NMe_2)_3$ and $P(NMeCH_2)_3CMe$ with Pt(II)

Complex	Isomer[a]	$\delta\,^{31}P$[b]	$\Delta\delta\,^{31}P$[c]	$^{1}J_{PtP}$[d]
$PtCl_2(\underline{1})_2$	trans	-89.1	+33.2	3220.1
$PtCl_2(\underline{1})_2$	cis[e]	-66.6	+55.7	5023.7
$PtI_2(\underline{1})_2$	trans	-87.1	+35.2	3065.1
$PtCl_2(\underline{2})_2$	trans	-76.4	+ 7.1	3482.3
$PtCl_2(\underline{2})_2$	cis[e]	-70.7	+12.8	4640.8
$PtI_2(\underline{2})_2$	cis	-70.2	+13.3	4496.6

[a] Stereochemistries of complexes were determined by ^{1}H-NMR patterns; doublets for cis and pseudotriplets for trans.

[b] Spectra recorded in C_6D_6 solution; ±0.05 ppm.

[c] $\Delta\delta\,^{31}P = \delta\,^{31}P(\text{complex}) - \delta\,^{31}P(\text{ligand})$.

[d] ±1.1 Hz.

[e] Determined from ^{31}P-NMR spectrum, see text.

complex yields pseudotriplets. In this respect, the spectra are similar to cis and trans isomers of metal carbonyl complexes of 1 and 2 (184). It is interesting to note that while both $(PhCN)_2PtCl_2$ and $(PhCN)_2PtI_2$ are cis complexes (201), the two complexes of 1 and the chloride complex of 2 obtained by metathesis exist in the trans configuration while the iodide complex of 2 is cis. It would therefore appear that the trans complexes are at least kinetically favored in much the same manner as the metal carbonyl complexes of 1 and 2.

The ^{31}P-NMR spectra of these complexes reveal some unusual behavior. Firstly, the coordination chemical shifts are positive for Pt(II) complexes in contrast to the negative shifts seen in metal carbonyl complexes. Most phosphorus ligands display negative $\Delta\delta^{31}P$ values for Pt(II) complexes but some phosphites and PF_3 give positive shifts (171). Pidcock et al. (224) observed that for a particular phosphine ligand the chemical shift increased and ^1JPtP decreased as the halide in the complex varied from Cl to Br to I. It is seen that trans-$PtCl_2(1)_2$ and trans-$PtI_2(1)_2$ as well as cis-$PtCl_2(2)_2$ and cis-$PtI_2(2)_2$ follow this trend. It was proposed that this trend could possibly reflect the successive weakening of the Pt-P sigma bond since ^1JPtP decreased. Such an explanation seems simplistic in view of the complex nature of the Pt-P coupling constant. It is also expected that the

$\delta^{31}P$ values for cis complexes should be upfield from the analogous trans isomer (224) and again the results accord with this expectation. Interestingly, however, the size of the difference for the $PtCl_2(1)_2$ isomers compared to the $PtCl_2(2)_2$ isomers is substantial (22.5 ppm vs. 5.7 ppm, respectively). It is entirely probable that this difference stems from the different sigma-pi characteristics of the two ligands. It will be recalled from earlier discussion that 2 appears to be the poorer Lewis base and presumably the better pi acceptor.

When trans-$PtCl_2(2)_2$ was first isolated its ^1H-NMR spectrum showed it to be the pure trans isomer. The same sample solution used for ^{31}P-NMR about two hours later revealed that there were two peaks observed in a ratio of 7:1 (later determined to be trans:cis). After ten hours this ratio was 2.25:1. On the other hand, a solution of trans-$PtCl_2(1)_2$ isomerized so slowly that after 57 hours the cis isomer was barely visible and after 21 days the trans:cis ratio was 3.2:1.

The interesting aspects of these isomerizations are that (1) while the PhCN starting materials are cis, the isolated 1 or 2 complexes are predominantly trans; (2) the trans isomers are expected to be the least demanding sterically because of the cone angles of 1 and 2 (vide supra) and (3) the chloride complex of 2 appears to isomerize much faster than the analogous complex of 1.

The first observation indicates that isomerization during formation from the cis starting complex and ligand (presumably by Berry pseudorotation or an associative pathway involving a distorted 5-coordinate structure (225)) is a very low energy process and is kinetically favored. This may be due to the steric demands which 1 and 2 place on the complex due to their cone angles of about 157° (129). Once formed however, the relative kinetic inertness of $PtCl_2L_2$ complexes allows their isolation. Upon standing in solution the more thermodynamically favored situation appears to be the formation of an equilibrium mixture of trans and cis isomers. Such isomerizations are believed to be catalyzed by free ligand (225) and so it is difficult to say whether the observed different isomerization rates are due to differing amounts of free ligand or some subtle electronic difference. The difference in pi acidities of 1 and 2 could be used to rationalize the data in that the more acidic 2 can better compete against a trans Cl atom for metal d orbital density rather than another molecule of 2 thereby giving a faster rate of isomerization. However, in the absence of a more detailed rate study such speculation is of questionable value.

It has been repeatedly found that $^1J_{PtP}$ values are larger for cis-PtX_2L_2 complexes than for the trans isomers (171) and again the compounds of interest are no exceptions. As pointed out by Pidcock et al. (224) the value of $^1J_{PtP}$ is more dependent upon the group trans to P than the groups cis to it and this is caused principally by variations in the metal s orbital character in the Pt-P bond. Interestingly, however, the differences in this coupling between cis and trans isomers of 1 are greater than for 2 which may reflect the better sigma donating ability of 1 compared to 2 ($\psi^2_{3S(O)P}$).

Finally, note should be taken that in all the examples of one bond couplings for 1 and 2, the latter are always larger than the former with the exception of the two cis-$PtCl_2L_2$ complexes. The reason for this reversal is not clear.

REFERENCES

1. H. Staudinger and J. Meyer, Helv. Chim. Acta, 2, 619 (1919).
2. H. Staudinger and J. Meyer, Helv. Chim. Acta, 2, 635 (1919).
3. G. Singh and H. Zimmer, Organomet. Chem. Rev., Sect. A, 2, 279 (1967).
4. L. Horner and A. Gross, Justus Liebigs Ann. Chem., 591, 117 (1955).
5. G. Wittig and K. Schwarzenbach, Justus Liebigs Ann. Chem., 650, 1 (1961).
6. W. F. Mosby and M. L. Silva, J. Chem. Soc., 1003 (1965).
7. J. E. Leffler, U. Honsberg, Y. Tsuno and I. Forsblad, J. Org. Chem., 26, 4810 (1961).
8. J. S. Thayer and R. West, Inorg. Chem., 3, 406 (1964).
9. H. Bock and M. Schnöller, Angew. Chem., Int. Ed. Eng., 7, 636 (1968).
10. H. Malz (Farbenfabricken Bayer A. G.), Ger. Offn. 1,104,958 [Chem. Abstr., 56, 10041d (1962)].
11. H. J. Vetter and H. Nöth, Chem. Ber., 96, 1308 (1963).
12. V. Gutmann, Ch. Kemenater and K. Utvary, Monatsh. Chem., 96, 836 (1965).
13. K. Utvary, V. Gutmann and Ch. Kemenater, Inorg. Nucl. Chem. Lett., 1, 75 (1965).
14. J. Lorberth, H. Krapf and H. Nöth, Chem. Ber., 100, 3511 (1967).
15. G. I. Derkach and S. K. Mikhailik, Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim., 59 (1967) [Chem. Abstr., 69, 2757a (1968)].
16. V. A. Shokol, G. A. Golik, V. T. Tsyba, Yu. P. Egerov and G. I. Derkach, Zh. Obshch. Khim., 40, 1680 (1970) [J. Gen. Chem. USSR, 40, 1668 (1970)].

17. V. A. Shokol, L. I. Molyavko, N. K. Mikhailyuchenko and G. I. Derkach, Zh. Obshch. Khim., 41, 318 (1971) [J. Gen. Chem. USSR, 41, 312 (1971)].

18. V. A. Shokol, G. A. Golik and G. I. Derkach, Zh. Obshch. Khim., 41, 545 (1971) [J. Gen. Chem. USSR, 41, 539 (1971)].

19. K. Pilgram, F. Görgen and G. Pollard, J. Heterocycl. Chem., 8, 951 (1971).

20. M. Bermann and J. R. Van Wazer, J. Chem. Soc., Dalton Trans., 813 (1973).

21. M. Bermann and J. R. Van Wazer, Inorg. Chem., 12, 2186 (1973).

22. M. Bermann and J. R. Van Wazer, Inorg. Chem., 13, 737 (1974).

23. J. Lorberth, J. Organomet. Chem., 71, 159 (1974).

24. P. Haasemann and J. Goubeau, Z. Anorg. Allg. Chem., 408, 293 (1974).

25. V. S. Petrenko, A. P. Martynyuk, L. V. Dyrenko, M. P. Kardakova, A. I. Panasyuk and V. N. Tertyshnyi, Fiziol. Akt. Veshchestva, 6, 10 (1974) [Chem. Abstr., 82, 171140t (1975)].

26. H. Goldwhite, P. Gysegem, S. Schow and C. Swyke, J. Chem. Soc., Dalton Trans., 12 (1975).

27. H. Goldwhite, P. Gysegem, S. Schow and C. Swyke, J. Chem. Soc., Dalton Trans., 16 (1975).

28. R. Goetze, H. Nöth and D. S. Payne, Chem. Ber., 105, 2637 (1972).

29. R. D. Kroshefsky and J. G. Verkade, Inorg. Chem., 14, 3090 (1975).

30. D. S. Payne, H. Nöth and G. Henniger, Chem. Commun., 327 (1965).

31. S. F. Spangenberg and H. H. Sisler, Inorg. Chem., 8, 1004 (1969).

32. E. G. Finer and R. K. Harris, Prog. N.M.R. Spectrosc., 6, 99 (1970).

33. W. Van Doorne, G. W. Hunt, R. W. Parry and A. W. Cordes, Inorg. Chem., 10, 2591 (1971).

34. J. W. Gilje and K. Seff, Inorg. Chem., 11, 1643 (1972).

35. A. W. Cordes, C. K. Fair, M. Bermann and J. R. Van Wazer, J. Cryst. Mol. Struct., 5, 279 (1975).

36. L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, NY, 1960.

37. D. S. Milbrath, J. P. Springer, J. C. Clardy and J. G. Verkade, J. Amer. Chem. Soc., 98, 5493 (1976).

38. D. M. Nimrod, D. R. Fitzwater and J. G. Verkade, J. Amer. Chem. Soc., 90, 2870 (1968).

39. H. Nöth and R. Ullmann, Chem. Ber., 109, 1089 (1976).

40. E. Heilbronner and K. A. Muszkat, J. Amer. Chem. Soc., 92, 3818 (1970).

41. M. J. S. Dewar and J. S. Wasson, J. Amer. Chem. Soc., 92, 3506 (1970).

42. R. Hoffman, Accts. Chem. Res., 4, 1 (1971).

43. A. H. Cowley, D. W. Goodman, N. A. Kuebler, M. Sanchez and J. G. Verkade, Inorg. Chem., 16, 854 (1977).

44. R. D. Bertrand, D. A. Allison and J. G. Verkade, J. Amer. Chem. Soc., 92, 71 (1970).

45. H. Nöth and R. Ullmann, Chem. Ber., 109, 1942 (1976).

46. W. McFarlane and J. A. Nash, Chem. Commun., 913 (1969).

47. R. A. Dwek, R. E. Richards, D. Taylor, G. J. Penny and G. M. Sheldrick, J. Chem. Soc. A, 935 (1969).

48. W. J. Stec, A. Okruszek, B. Uznański and J. Michalski, Phosphorus, 2, 97 (1972).

49. W. McFarlane and D. S. Rycroft, Chem. Commun., 902 (1972).

50. W. McFarlane and D. S. Rycroft, J. Chem. Soc., Dalton Trans., 2162 (1973).

51. W. W. DuMont and H. J. Kroth, J. Organomet. Chem., 113, C35 (1976).

52. R. P. Pinnell, C. A. Megerle, S. L. Manatt and P. A. Kroon, J. Amer. Chem. Soc., 95, 977 (1973).

53. I. A. Nuretdinov and E. I. Loginova, Izv. Akad. Nauk SSSR, Ser. Khim., 2360 (1971) [Bull. Acad. Sci. USSR, Div. Chem. Sci., 2252 (1971)].

54. E. I. Loginova, I. A. Nuretdinov and Yu. A. Petrov, Teor. Eksp. Khim., 10, 75 (1974) [Theor. Exp. Chem., 10, 47 (1974)].

55. H. W. Roesky and W. Kloker, Z. Naturforsh., 28b, 697 (1973).

56. G. M. Cree, The Use of ^{31}P-^{77}Se Coupling to Characterize the P=Se Bond, Perkin-Elmer NMR Quarterly, August, p. 6, 1971.

57. W. J. Stec, K. Lesiak, D. Mielczarek and B. Stec, Z. Naturforsh., 30b, 710 (1975).

58. W. J. Stec, R. Kinas and A. Okruszek, Z. Naturforsh., 31b, 393 (1976).

59. I. A. Nuretdinov, N. A. Buina, E. V. Boyandina and F. G. Sibgatulina, Izv. Akad. Nauk SSSR, Ser. Khim., 483 (1974) [Bull. Acad. Sci. USSR, Div. Chem. Sci., 455 (1974)].

60. A. Okruszek and W. J. Stec, Z. Naturforsh., 30b, 430 (1975).

61. T. J. Bartczak, A. Christensen, R. Kinas and W. J. Stec, Tetrahedron Lett., 3243 (1975).

62. W. J. Stec and A. Okruszek, J. Chem. Soc., Perkin I, 1828 (1975).

63. W. J. Stec, A. Okruszek and J. Michalski, J. Org. Chem., 41, 233 (1976).

64. I. A. Nuretdinov, L. K. Nikonorova, N. P. Grechkin and R. G. Gainullina, Zh. Obshch. Khim., 45, 533 (1975) [J. Gen. Chem. USSR, 45, 526 (1975)].

65. D. W. W. Anderson, E. A. V. Ebsworth, G. D. Meikle and D. W. H. Rankin, Mol. Phys., 25, 381 (1973).

66. W. J. Stec, Z. Naturforsh., 29b, 109 (1974).

67. B. Uznański and W. J. Stec, Synthesis, 735 (1975).

68. A. Okruszek and W. J. Stec, Z. Naturforsh., 31b, 354 (1976).

69. W. McFarlane and R. J. Wood, J. Chem. Soc., Dalton Trans., 1397 (1972).

70. J. A. Pople and D. P. Santry, Mol. Phys., 8, 1 (1964).

71. W. McFarlane, Quart. Rev., 23, 187 (1969).

72. E. R. Malinowsky, J. Amer. Chem. Soc., 83, 4479 (1961).

73. R. K. Harris, J. Chem. Phys., 66, 768 (1962).

74. W. McFarlane and R. F. M. White, Chem. Commun., 744 (1969).

75. V. F. Bystrov, A. A. Neimysheva, A. V. Stepanyants and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 156, 637 (1964).

76. C. J. Jameson and H. S. Gutowsky, J. Chem. Phys., 51 2790 (1969).

77. C. J. Jameson, J. Amer. Chem. Soc., 91, 6232 (1969).

78. L. J. Vande Griend and J. G. Verkade, Phosphorus, 3, 13 (1973).

79. L. J. Vande Griend, Ph.D. Thesis, Iowa State University, Ames, 1975.

80. L. J. Vande Griend, J. G. Verkade, J. F. M. Pennings and H. M. Buck, J. Amer. Chem. Soc., 99, 2459 (1977).

81. D. B. Siano and D. E. Metzler, J. Chem. Phys., 51, 1856 (1969).

82. A. C. Vandenbroucke, R. W. King and J. G. Verkade, Rev. Sci. Instrum., 39, 558 (1968).

83. J. A. Mosbo, private communication, Iowa State University, Ames, 1972.

84. ITRCAL, Iteration of Calculated NMR Spectra Using Least Squares Criteria, Nicolet Instruments Corp., Madison, WS, 53711, July, 1973.

85. S. Castellano and A. A. Bothner-By, J. Chem. Phys., 41, 3863 (1964).

86. T. W. Campbell and J. D. McCullough, J. Amer. Chem. Soc., 67, 1965 (1945).

87. H. J. Dauben, Jr., L. R. Honneau and K. M. Harman, J. Org. Chem., 25, 1442 (1960).

88. R. O. Lindsay and C. F. H. Allen in Organic Syntheses, Collect. Vol. 3, Edited by E. C. Horning, John Wiley and Sons, New York, 1955, p. 710.

89. B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton and J. G. Verkade, Inorg. Chem., 6, 173 (1967).

90. J. C. Clardy, R. L. Kolpa and J. G. Verkade, Phosphorus, 4, 133 (1974).

91. H. Nöth and R. Ullmann, Chem. Ber., 109, 1942 (1976).

92. T. Reetz and B. Katlafsky, J. Amer. Chem. Soc., 82, 5036 (1960).

93. F. Räuchle, W. Pohl, B. Blaich and J. Goubeau, Ber. Bunsenges. Phys. Chem., 75, 66 (1971).

94. H. Nöth and H. J. Vetter, Chem. Ber., 98, 1981 (1965).

95. K. Dimroth and A. Nürrenbach, Chem. Ber., 93, 1649 (1960).

96. D. W. White, R. D. Bertrand, G. K. McEwen and J. G. Verkade, J. Amer. Chem. Soc., 92, 7125 (1970).

97. J. G. Verkade, T. J. Hutteman, M. K. Fung and R. W. King, Inorg. Chem., 4, 83 (1965).

98. I. A. Nuretdinov and N. P. Grechkin, Izv. Akad. Nauk SSSR, Ser. Khim., 2831 (1968) [Bull. Acad. Sci. USSR, Div. Chem. Sci., 2685 (1968)].

99. J. W. Emsley, J. Feeney and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 1, Pergamon Press, Oxford, 1965, pp. 392-398.

100. J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, McGraw-Hill, New York, 1959, pp. 138-142.

101. D. W. White and J. G. Verkade, Phosphorus, 3, 9 (1973).

102. D. W. White and J. G. Verkade, Phosphorus, 3, 15 (1973).

103. H. A. Bent, Chem. Rev., 61, 275 (1961).

104. L. J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen and Co., London, 1958.

105. H. Wantanabe and K. Nagasawa, Inorg. Chem., 6, 1068 (1967).

106. C. W. Heitsch and J. G. Verkade, Inorg. Chem., 1, 863 (1962).

107. W. J. Lehmann, J. Mol. Spectrosc., 7, 261 (1961).

108. J. E. Leffler and R. D. Temple, J. Amer. Chem. Soc., 89, 5235 (1967).

109. J. G. Verkade, Coord. Chem. Rev., 9, 1 (1972).

110. J. G. Verkade, Bioinorg. Chem., 3, 165 (1974).

111. J. G. Verkade, Phosphorus and Sulfur, 2, 251 (1976).

112. R. F. Hudson and J. G. Verkade, Tetrahedron Lett., 3231 (1975).

113. W. O. Davies and E. Stanley, Acta Crystallogr., 15, 1092 (1962).

114. A. H. Cowley, M. J. S. Dewar, D. W. Goodman and J. R. Schweiger, J. Amer. Chem. Soc., 95, 6506 (1973).

115. D. Besserre and M. Troquet, Bull. Soc. Chim. Fr., 845 (1974).

116. B. L. Laube, M.S. Thesis, Iowa State University, Ames, 1965.

117. J. Fayet, C. R. Acad. Sci., 270, 9 (1970).

118. M. Schafer and C. Curran, Inorg. Chem., 4, 623 (1965).

119. J. E. DuBois and H. H. Viellard, J. Chim. Phys., 62, 699 (1965).

120. D. A. Allison and J. G. Verkade, Phosphorus, 2, 257 (1973).

121. I. F. Halverstadt and W. D. Kumler, J. Amer. Chem. Soc., 64, 2988 (1942).

122. A. S. Tarasevich and Yu. P. Egerov, Teor. Eksp. Khim., 7, 828 (1971) [Theor. Exp. Chem., 7, 676 (1971)].

123. Yu. P. Egerov and A. S. Tarasevich, Teor. Eksp. Khim., 8, 422 (1972) [Theor. Exp. Chem., 8, 353 (1972)].

124. A. S. Tarasevich and Yu. P. Egerov, Teor. Eksp. Khim., 9, 73 (1973) [Theor. Exp. Chem., 9, 54 (1973)].

125. J. H. Letcher and J. R. Van Wazer, Top. Phosphorus Chem., 5, 75 (1967).

126. D. W. White, G. K. McEwen, R. D. Bertrand and J. G. Verkade, J. Chem. Soc. B, 1454 (1971).

127. F. S. Mortimer, Spectrochim. Acta, 9, 270 (1957).

128. R. M. Silverstein, G. C. Bassler and T. C. Morrill, Spectrometric Identification of Organic Compounds, 3rd ed., John Wiley and Sons, New York, 1974, p. 248.

129. C. A. Tolman, J. Amer. Chem. Soc., 92, 2956 (1970).

130. G. K. McEwen and J. G. Verkade, Chem. Commun., 668 (1971).

131. S. M. McElvain and L. R. Morris, J. Amer. Chem. Soc., 73, 206 (1951).

132. R. L. Kolpa and J. G. Verkade, Unpublished results, work performed in Chemistry Department, Iowa State University, Ames, 1973.

133. B. J. Walker, Organophosphorus Chemistry, Penguin Books, Baltimore, MD, 1972, pp. 162-167.

134. J. J. Monagle, J. Org. Chem., 27, 3851 (1962).

135. B. Castro and J. R. Dormoy, Bull. Soc. Chim. Fr., 3359 (1973).

136. F. B. Ogilvie, J. M. Jenkins and J. G. Verkade, J. Amer. Chem. Soc., 92, 1916 (1970).

137. A. H. Cowley and M. C. Damasco, J. Amer. Chem. Soc., 93, 6815 (1971).

138. E. G. Finer and R. K. Harris, Private communication to the authors of Reference 44.

139. A. Schmidpeter and H. Brecht, Z. Naturforsh., 24b, 179 (1969).

140. K. C. Yee and W. G. Bentrude, Tetrahedron Lett., 2775 (1971).

141. W. G. Bentrude, H. W. Tan and K. C. Yee, J. Amer. Chem. Soc., 94, 3264 (1972).

142. F. S. Mandel, R. H. Cox and R. C. Taylor, J. Mag. Res., 14, 235 (1974).

143. G. A. Gray and T. A. Albright, J. Amer. Chem. Soc., 98, 3857 (1976).

144. M. P. Shimmonnin, R. M. Tegnan and F. W. Wehrli, Chem. Commun., 1204 (1972).

145. W. McFarlane, Proc. Roy. Soc., Ser. A, 306, 185 (1968).

146. R. B. Wetzel and G. L. Kenyon, J. Amer. Chem. Soc., 96, 5189 (1974).

147. W. H. Chang, J. Org. Chem., 29, 3711 (1964).

148. A. E. Arbuzov and N. A. Razumova, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk, 187 (1956) [Bull. Acad. Sci. USSR, Div. Chem. Sci., 179 (1956)].

149. R. W. King, T. J. Hutteman and J. G. Verkade, Chem. Commun., 561 (1965).

150. A. Yamasaki and E. Fluck, Z. Anorg. Allg. Chem., 396, 297 (1973).

151. D. S. Milbrath, J. G. Verkade and R. J. Clark, Inorg. Nucl. Chem. Lett., 12, 921 (1976).

152. N. F. Ramsey, Phys. Rev., 91, 303 (1953).

153. C. A. Coulsen and H. C. Longuet-Higgins, Proc. Roy. Soc., Ser. A, 191, 39 (1947).

154. J. N. Schoolery, J. Chem. Phys., 31, 1427 (1959).

155. D. M. Grant and W. M. Litchman, J. Amer. Chem. Soc., 87, 3994 (1965).

156. J. E. Huheey, Inorganic Chemistry: Principles of Structure and Reactivity, Harper and Row, New York, 1972, p. 160.

157. J. Chatt and A. A. Williams, J. Chem. Soc., 3061 (1951).

158. W. L. Gilliland and A. A. Blanchard, J. Amer. Chem. Soc., 48, 410 (1926).

159. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, NY, 1939.

160. B. J. Ransil, Rev. Mod. Phys., 32, 245 (1960).

161. E. W. Abel, M. A. Bennett and G. Wilkinson, J. Chem. Soc., 2325 (1959).

162. W. D. Horrocks, Jr. and R. C. Taylor, Inorg. Chem., 2, 723 (1963).

163. F. A. Cotton and C. S. Kraihanzel, J. Amer. Chem. Soc., 84, 4432 (1962).

164. C. S. Kraihanzel and F. A. Cotton, Inorg. Chem., 2, 533 (1963).

165. F. A. Cotton, Inorg. Chem., 3, 702 (1964).

166. M. Bigorgne, J. Inorg. Nucl. Chem., 26, 107 (1964).

167. C. Tolman, J. Amer. Chem. Soc., 92, 2953 (1970).

168. C. Tolman, Chem. Rev., 77, 313 (1977).

169. R. J. Angelici, J. Inorg. Nucl. Chem., 28, 2627 (1966).

170. R. J. Angelici and M. D. Malone, Inorg. Chem., 6, 1731 (1967).

171. J. F. Nixon and A. Pidcock, Annu. Rev. Spectrosc., 2, 345 (1969).

172. H. J. Plastas, J. M. Stewart and S. O. Grim, J. Amer. Chem. Soc., 91, 4326 (1969).

173. H. S. Preston, J. M. Stewart, H. J. Plastas and S. O. Grim, Inorg. Chem., 11, 161 (1972).

174. J. C. Green, D. I. King and J. H. D. Eland, Chem. Commun., 1121 (1970).

175. A. Pidcock in Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands, Edited by C. A. McAuliffe, John Wiley and Sons, New York, 1973.

176. O. Stelzer and R. Schmutzler, J. Chem. Soc. A, 2867 (1971).

177. A. C. Vandenbroucke, D. G. Hendricker, R. E. McCarley and J. G. Verkade, Inorg. Chem., 7, 1825 (1968).

178. R. L. Keiter and J. G. Verkade, Inorg. Chem., 9, 707 (1970).

179. K. Nakamoto, J. Amer. Chem. Soc., 92, 3332 (1970).

180. V. G. Meyers, F. Basolo and K. Nakamoto, Inorg. Chem., 8, 1204 (1969).

181. N. F. Ramsey, Phys. Rev., 86, 243 (1952).

182. C. A. Tolman, L. W. Yarbrough, II and J. G. Verkade, Inorg. Chem., 16, 479 (1977).

183. H. Nöth and H. J. Vetter, Chem. Ber., 96, 1479 (1963).

184. R. B. King, Inorg. Chem., 2, 936 (1963).

185. R. B. King and T. F. Korenowski, Inorg. Chem., 10, 1188 (1971).

186. R. L. Keiter and J. G. Verkade, Inorg. Chem., 8, 2115 (1969).

187. J. A. Mosbo, J. R. Pipal and J. G. Verkade, J. Mag. Res., 8, 243 (1972).

188. J. R. Pipal, Senior Thesis, Chemistry Department, Iowa State University, Ames, 1967.

189. J. Emsley and D. Hall, The Chemistry of Phosphorus, John Wiley and Sons, New York, 1976, Chapter 5.

190. A. A. Grinberg, The Chemistry of Complex Compounds, Pergamon Press, Oxford, 1962.

191. J. Chatt and R. G. Wilkins, J. Chem. Soc., 525 (1956).

192. R. Eisenberg and J. A. Ibers, Inorg. Chem., 4, 773 (1965).

193. G. G. Messner, E. L. Amma and J. A. Ibers, Inorg. Chem., 6, 725 (1967).

194. G. G. Messner and J. A. Ibers, Inorg. Chem., 5, 1775 (1966).

195. J. M. Jenkins and J. G. Verkade, Inorg. Chem., 6, 2250 (1967).

196. T. Glonek and J. R. Van Wazer, J. Mag. Res., 8, 243 (1972).

197. E. W. Abel, I. S. Butler and J. G. Reid, J. Chem. Soc., 2068 (1963).

198. R. B. King and F. G. A. Stone, Inorg. Syn., 7, 193 (1963).

199. R. B. King in Organometallic Syntheses, Vol. 1, Edited by R. B. King and J. J. Eisch, Academic Press, New York, 1965, pp. 122-125.

200. R. B. King and A. Fronzaglia, Inorg. Chem., 5, 1837 (1966).

201. M. J. Church and M. J. Mays, J. Inorg. Nucl. Chem., 33, 253 (1971).

202. K. Mödritzer, Inorg. Syn., 10, 131 (1967).

203. M. J. McInerney, National Science Foundation Undergraduate Research Fellow, Synthesis performed in Chemistry Department, Iowa State University, Ames, 1966.

204. A. D. Norman and W. L. Jolly, Inorg. Syn., 11, 15 (1968).

205. D. F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, 1969, pp. 265-289.

206. R. W. Parry, D. R. Schultz and P. R. Girardot, J. Amer. Chem. Soc., 80, 1 (1958).

207. R. Mathieu and R. Poilblanc, C. R. Acad. Sci., Paris, Ser. C, 69, 1053 (1967).

208. F. B. Ogilvie, J. M. Jenkins and J. G. Verkade, J. Amer. Chem. Soc., 92, 1916 (1970).

209. J. A. Connor, E. M. Jones and G. K. McEwen, J. Organomet. Chem., 43, 357 (1972).

210. H. Zimmer and G. Singh, J. Org. Chem., 29, 3412 (1964).

211. J. A. Bowden and R. Colton, Austr. J. Chem., 24, 2471 (1971).

212. J. B. Wilford and F. G. A. Stone, Inorg. Chem., 4, 389 (1965).

213. P. S. Braterman, Metal Carbonyl Spectra, Academic Press, New York, 1975, p. 71.

214. R. Mathieu, M. Lenzi and R. Poilblanc, Inorg. Chem., 9, 2030 (1970).

215. R. D. Bertrand, F. B. Ogilvie and J. G. Verkade, J. Amer. Chem. Soc., 92, 1908 (1970).

216. L. S. Meriwether and J. R. Leto, J. Amer. Chem. Soc., 83, 3192 (1961).

217. G. S. Reddy and R. Schmutzler, Inorg. Chem., 6, 823 (1967).

218. A. Saika and C. P. Slichter, J. Chem. Phys., 22, 26 (1954).

219. P. S. Braterman, D. W. Milne, E. W. Randall and E. Rosenberg, J. Chem. Soc., Dalton Trans., 1027 (1973).

220. J. Evans and J. R. Norton, Inorg. Chem., 13, 3042 (1974).

221. S. O. Grim and D. A. Wheatland, Inorg. Chem., 8, 1716 (1969).

222. W. A. G. Graham, Inorg. Chem., 7, 315 (1968).

223. J. G. Riess and J. R. Van Wazer, J. Amer. Chem. Soc., 89, 851 (1967).

224. A. Pidcock, R. E. Richards and L. M. Venanzi, J. Chem. Soc. A, 1707 (1966).

225. P. Haake and R. M. Pfeiffer, J. Amer. Chem. Soc., 92, 4996 (1970).