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SYNTHESIS, CHARACTERIZATION AND METAL CARBONYL COMPLEX FORMATION OF POLYCYCLIC PHOSPHORUS LIGANDS.

Iowa State University, Ph.D., 1967
Chemistry, inorganic

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SYNTHESIS, CHARACTERIZATION AND METAL CARBONYL COMPLEX FORMATION OF POLYCYCLIC PHOSPHORUS LIGANDS

by

Arthur Cyril Vandenbroucke, Jr.

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

Major Subject: Inorganic Chemistry

Approved:

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In Charge of Major Work

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Ames, Iowa

1967

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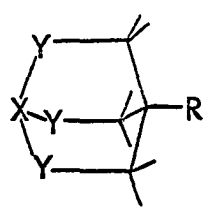
INTRODUCTION

This thesis is divided into five main parts for purposes of organization and clarity. The first four sections each deal with a different polycyclic phosphorus ligand, while the last section considers the dipole moments of these and other polycycles that have been prepared by Verkade and co-workers. The polycyclic compounds studied in this thesis are of two general types. One set has the bicyclo [2.2.2] octane structure, while the other the adamantane structure. Three

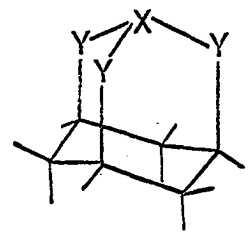


X = P, Y = O

X = P, Y = S

X = N, Y = CH_2

X = As, Y = S



X = P, Y = O

X = P, Y = CH_2

sections of this thesis are concerned mainly with the synthesis and characterization of various new polycycles. Time did not permit an investigation of their complexing properties.

A STUDY OF THE SYNTHESIS OF 1-PHOSPHAADAMANTANE

In 1952, Stetter and Steinacker (1) reported the preparation of 1-phospha-2,8,9-trioxa-adamantane, $P(OCH)_3(CH_2)_3$, and eight years later, Verkade and Reynolds (2) reported the synthesis of 4-methyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane, $P(OCH_2)_3CCH_3$. Verkade and Piper later reported a study of the use of $P(OCH_2)_3CCH_3$ as a ligand toward metal ions (3,4), and the properties of $P(OCH)_3(CH_2)_3$ and $P(OCH_2)_3CCH_3$ as Lewis bases toward Group III acids were reported by Heitsch and Verkade (5,6,7,8). The transition metal complexes of $P(OCH)_3(CH_2)_3$ were reported by Huttemann in a doctoral dissertation (9) and the complexes of $P(OCH)_3(CH_2)_3$ and $P(OCH_2)_3CCH_3$ with cobalt(III), cobalt(I), nickel(II) and nickel(0) appeared in 1965 (10,11). In a doctoral dissertation (12) Hendricker described the metal carbonyl complexes which were subsequently reported in the literature (13,14). The general results of the above investigations are that crystalline metal complexes can be isolated, many of which exhibit maximum coordination numbers for the metal with only polycyclic phosphite ligands in the coordination sphere.

From the ultraviolet spectra of complexes of the form $[CoL_6](ClO_4)_3$ (where L = $P(OCH)_3(CH_2)_3$ and $P(OCH_2)_3CCH_3$) Dq values of 3320 cm^{-1} and 3350 cm^{-1} were calculated for $P(OCH_2)_3CCH_3$ (4) and $P(OCH)_3(CH_2)_3$ (10), respectively, which

compares well with 3350 cm^{-1} obtained for $Co(CN)_6^{-3}$, indicating the presence of a strong octahedral field. The probability of d-pi-d-pi bonding was invoked to explain the unusually large ligand field strength $P(OCH)_3(CH_2)_3$ and $P(OCH_2)_3CCH_3$. Furthermore in the metal carbonyl work (13,14), the possibility of dative pi-bonding from the metal d orbitals to the phosphorus d orbitals was mentioned. Such pi-bonding could explain the high CO stretching frequencies in these compounds. A method of determining the possible presence or extent of pi-bonding in these compounds might entail a study of similar coordination compounds using a phosphine analogous in structure $P(OCH)_3(CH_2)_3$ or $P(OCH_2)_3CCH_3$. Such a ligand would be 1-phosphaadamantane, $P(CH_2CH)_3(CH_2)_3$. Because of the difference in electronegativity of oxygen and carbon, $P(CH_2CH)_3(CH_2)_3$ should be a better Lewis base than $P(OCH)_3(CH_2)_3$. However, when considering pi-bonding or back donation of electrons from a transition metal to the d orbitals on phosphorus, $P(OCH)_3(CH_2)_3$ should pi-bond more strongly than $P(CH_2CH)_3(CH_2)_3$ because of the superior electron withdrawing power of oxygen. Of particular interest would be the synthesis of metal carbonyl complexes and a study of their CO, MC, and MP stretching frequencies in the infrared region. Attempts at isolating the phosphine analogous to $P(OCH_2)_3CCH_3$, 1-phosphabicyclo [2.2.2] octane, have been the subject of three theses (15,16,17). Lukes and Galik (18) synthesized 1-aza-adamantane by the reaction of 1,3,5-tris(bromomethyl)cyclohexane

with ammonia and their procedures were used to prepare the intermediates used in the attempted preparations of $P(CH_2CH)_3(CH_2)_3$ described in this thesis.

Experimental

Hexahydromesicerol, $1,3,5\text{-}(HOCH_2)_3C_6H_9$ - This compound was prepared from triethylhexahydrotrimesate by a method previously described. (18)

1,3,5-Tris(bromomethyl)cyclohexane, $1,3,5\text{-}(BrCH_2)_3C_6H_9$ - This compound was prepared from $1,3,5\text{-}(HOCH_2)_3C_6H_9$ by a method previously described. (18)

1,3,5-Tris(iodomethyl)cyclohexane, $1,3,5\text{-}(ICH_2)_3C_6H_9$ - 20 g of $1,3,5\text{-}(BrCH_2)_3C_6H_9$ and 37 g of NaI were refluxed in 200 ml of 2-butanone for 48 hr. The solvent was removed under reduced pressure and water was added to dissolve the solid which formed. After the aqueous phase was extracted with benzene, the benzene extract was washed with $Na_2S_2O_3$, $NaHCO_3$ and water, and dried with $MgSO_4$. The benzene was removed under reduced pressure and the oily residue was taken up in methanol. The crystals which formed on cooling yielded 24 g (87%) of product (mp 87-88°).

Trilithium phosphide, Li_3P - This compound was prepared from n-butyl lithium and phosphine by a method previously described. (19)

Sodium phosphide, $NaPH_2$ - This material was prepared by a method previously described. (15)

Tribenzyl phosphine, $(C_6H_5CH_2)_3P$ - The preparation of this compound has been outlined by Hinton and Mann. (20)

Phosphine Grignard, $HP(MgBr)_2$ - This compound was prepared by a method previously described. (21)

Attempted preparations of 1-phosphaadamatane

Nine different methods were used in attempting to prepare this compound. First, following a procedure by Hinton and Mann (20), an equivalent of tribenzyl phosphine dissolved in ether was added to an ether solution of an equivalent each of $1,3,5\text{-}(BrCH_2)_3C_6H_9$ and lithium aluminum hydride, and the resulting solution refluxed for several hours. Water was added to decompose the mixture and the ether phase was separated, dried with $MgSO_4$ and evaporated to give an intractable oil.

In the second attempt, the above tribromide was combined with excess magnesium in dry ether. A drop of methyl iodide and a strip of magnesium were combined in ether, and when reaction commenced, the mixture was added to the above solution as an initiator. After 24 hours of refluxing, the tribromide and the magnesium were recovered. The use of a higher boiling solvent such as butyl ether, or the substitution of lithium for magnesium gave similar results.

Third, equimolar quantities of Li_3P and $1,3,5\text{-}(BrCH_2)_3C_6H_9$ were mixed in ether at 0°. The mixture was allowed to warm up to room temperature and then was refluxed for 24 hours. After removing the ether no volatile material was obtained from

the residue.

The fourth attempt consisted of the reaction of $HP(MgBr)_2$ with 1,3,5-tris(bromomethyl)cyclohexane in ether. Again nothing resembling the desired product was obtained.

Fifth, a solution of sodium phosphide in liquid ammonia was added to an ether solution of the tribromide and stirred for 1 hr. After removing the solvent, half of the benzene extract of the residue was refluxed over sodium for 7 days, whereas the benzene was removed under vacuum from the other half. Both portions yielded only starting material.

Following the procedure of Angstadt (22) in the sixth attempt, 1,3,5-tris(bromomethyl)cyclohexane, aluminum chloride and white phosphorus in various ratios were mixed at -10° in CS_2. After stirring 1 hr each mixture was allowed to come to room temperature and refluxed for 2 hr. Evaporation of the solvent yielded an intractable oil.

Seventh, hexahydromesicerol, red phosphorus and an excess of iodine were placed in a sealed tube and heated to 150° with explosive results.

In the eighth attempt 1,3,5-tris(iodomethyl)cyclohexane and a large excess of red phosphorus were placed in a sealed tube and heated slowly to 200°. Only a small amount of PH_4I was obtained.

In the ninth experiment, another attempt at making the lithium salt of 1,3,5-tris(iodomethyl)cyclohexane consisted of

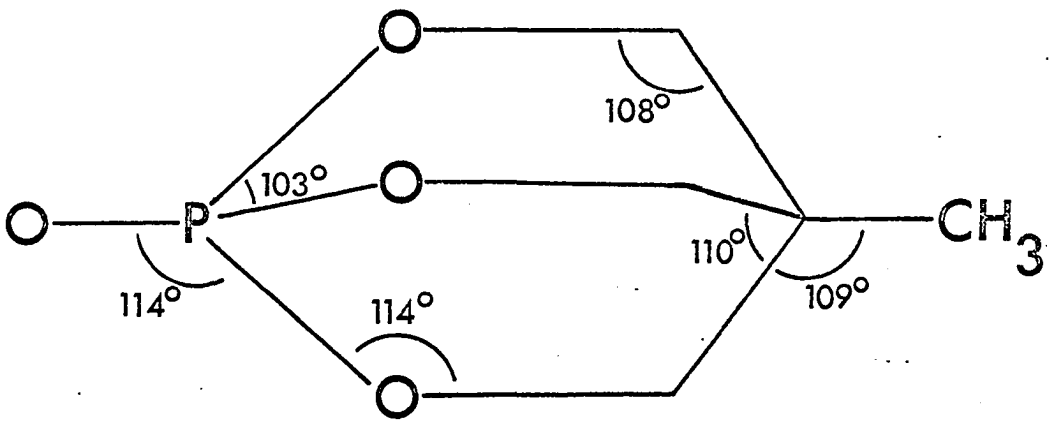
stirring n-butyl lithium, sodium and the triiodide in hexane for 48 hr. Only starting material was recovered.

Discussion

The inertness of the $1,3,5\text{-}(BrCH_2)_3C_6H_9$, and $1,3,5\text{-}(ICH_2)_3C_6H_9$ to reagents such as magnesium, lithium, sodium phosphide and n-butyl lithium in the presence of sodium may lie partially in the fact that none of these reactions is homogeneous. The reaction of the triol, $1,3,5\text{-}(HOCH_2)C_6H_9$, and the triiodide, $1,3,5\text{-}(ICH_2)_3C_6H_9$, with red phosphorus in a sealed tube were possibly thwarted by the fact that trialkyl phosphines are apparently unstable at elevated temperatures (23). Only tars were obtained even though a part of the sealed tube was cooled in order to condense any volatile materials.

The failure of cyclization to occur with reagents such as tribenzyl phosphine, trilithium phosphide, and aluminum chloride and white phosphorus can perhaps be explained on two grounds. First, compounds $1,3,5\text{-}(HOCH_2)_3C_6H_9$, $1,3,5\text{-}(BrCH_2)_3C_6H_9$ and $1,3,5\text{-}(ICH_2)_3C_6H_9$ most likely exist with their three functional groups lying in the equatorial plane of the cyclohexane ring. In order for cyclization to occur the ring must flip so that the three functional groups will be in the axial position. It is possible that the rate of flipping is slow relative to the rate of intermolecular reaction. Secondly, the C-P-C bond angles in trialkyl phosphines are closer to 90° than 109°.

Thus in forming a polycyclic phosphine of this type the P-C-C bond angles will be strained by forming angles larger than 109°. In polycyclic phosphites the oxygen atoms act as a buffer between the small O-P-O angles, thus the strain is reduced. This is substantiated by the observation that the P-O-C angles can be 114° (24). This argument may also account for the inability of



various workers (15,16,17) to prepare the analogous 1-phosphabicyclo [2.2.2] octane.

Suggestions for Future Work

From what has just been said and in the light of the other investigations directed toward the preparation of bicyclic mono-phosphines further work in this field might seem unjustified. It recently has come to our attention that J. K. Stille at the University of Iowa has prepared $(CH_2CH_2)PH$ from sodium phosphide and 1,2-dichloroethane in liquid ammonia. It might prove fruitful to investigate this reaction, especially

as a method of preparing 1-phosphabicyclo [2.2.2]octane from $(BrCH_2CH_2)_3CCH_3$.

FAR INFRARED STUDIES ON METAL CARBONYL COMPLEXES OF 4-METHYL-2,6,7-TRIOXA-1-PHOSPHABICYCLO [2.2.2] OCTANE

In recent years, double-beam grating spectrometers and interferometers have been developed which are capable of extending the usual low-frequency cut off in most infrared spectrometers from 400 cm^{-1} down to 200 cm^{-1} and in some cases down to 50 cm^{-1}. This extension has opened new fields of investigation to chemists, namely the study of metal-oxygen, metal-nitrogen, metal-sulfur, metal-phosphorus and metal-halogen stretching frequencies as well as low frequency bending modes such as δ(M-C-O), δ(M-C-N) and δ(C-M-C) vibrations in metal carbonyls, metal cyanides and their derivatives. Thus a tremendous amount of information is becoming available which can be related to the strength of metal-ligand bonds in inorganic complexes.

Although the infrared modes associated with a ligand of the type $P(OR)_3$ in a complex will be more numerous and complicated than those of PF_3, for example, complexes containing a constrained ligand such as $P(OCH_2)_3CCH_3$ are more amenable to an infrared study since fewer bands are expected on symmetry grounds. Because the nature of the phosphorus-metal bond is of particular interest in the study of phosphorus complexes, efforts were made to assign the ν(M-P) vibration in the far infrared spectra (70-800 cm^{-1}) of thirteen metal carbonyl complexes of $P(OCH_2)_3CCH_3$ of the forms $Ni(CO)_{4-x}L_x$ ($x = 1,2,3,4$),

$Fe(CO)_{5-x}L_x$ (x = 1,2), and cis and trans $M(CO)_{6-x}L_x$ (x = 1,2 and M = Cr, Mo and W). The three cis- bis(phosphite) tetracarbonyl complexes of Cr, Mo, and W as well as cis-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$ and the quinuclidine pentacarbonyl Cr, Mo, and W complexes (used for spectral comparison with the phosphite complexes) are new and their syntheses are described. Bands were also assigned as arising from ligand modes or complex modes of the type ν(M-C), δ(M-C-O), or δ(X-M-Y) where X and Y = C and C, C and P, C and N, and P and P. Except in the case of ν(M-P), the assignment of the coordination complex modes could not be rigorous because of the observance of less than the total number of expected bands in many cases and the overlap of the ν(M-C) and δ(M-C-O) regions.

The location of the ν(M-P) mode in the complexes of $P(OCH_2)_3CCH_3$ made it possible to compare its values with the relatively few such assignments in complexes of PF_3 and PR_3 (where R = CH_3, C_2H_5, and C_6H_5). Moreover, the opposite trends in frequency for ν(M-P) as carbonyl is substituted in $Ni(CO)_4$ by PF_3 and $P(OCH_2)_3CCH_3$ could be compared and correlated with the similarly opposite trends in ν(C-O) frequencies.

Finally, the discovery that two of the peaks in the CO stretching region of cis- $M(CO)_4(P(OCH_2)_3CCH_3)_2$ reported here were at the same frequency as the two "extra" peaks in the spectra of the analogous trans compounds attributed previously (13) to the reduction of symmetry by the ligands

led us to suspect the purity of trans compounds discussed earlier (13). The trans isomers of these complexes where L is either $P(OCH_2)_3CCH_3$ or $P(OCH)_3(CH_2)_3$ (14) are shown to indeed exhibit only one ν(C-O) band whereas the cis compounds exhibit three.

Experimental

The infrared spectra from 70-800 cm^{-1} were obtained on a Beckman Model 11 grating spectrometer. In all cases Nujol mulls between polyethylene plates were used with the exception of the ligands which were dispersed in fused polyethylene. The near infrared spectra were obtained on Beckman Models 8 and 12 grating spectrometers. The carbon hydrogen contents of the phosphite and arsenite complexes determined by combustion and the carbon, hydrogen and nitrogen analysis of the amine complexes carried out by Galbraith Laboratories, Inc, Knoxville, Tennessee, are given in Table 1.

Materials Nickel tetracarbonyl and iron pentacarbonyl were purchased from A. D. MacKay, Inc, chromium and tungsten hexacarbonyl were purchased from Pressure Chemical Co, and 4-hydroxyethylpiperidine was purchased from Reilly Tar and Chemical Co. The ligands $P(OCH_2)_3CCH_3$ (25), $P(OCH)_3(CH_2)_3$ (25) and $As(OCH_2)_3CCH_3$ (2) were prepared by methods described previously. Chromium norbornadiene tetracarbonyl (26), molybdenum norbornadiene tetracarbonyl (27), and tungsten 1,5-cycloocta-

diene tetracarbonyl (28) were also prepared as described elsewhere.

Quinuclidine A modification of Brown's procedure (29) was used to convert 4-hydroxyethylpiperidine to quinuclidine hydrochloride. A mixture of 12.5 g of quinuclidine hydrochloride and 25 g of KOH pellets was fused under vacuum and the volatile products collected in a Dry Ice-isopropanol trap. The quinuclidine was sublimed three times in the presence of sodium. A yield of 7.8 g (84%) of product melting at 161° was realized.

Transition metal carbonyl complexes Two general methods were used to prepare the complexes. Method A, which was used to prepare trans- $Cr(CO)_4(P(OCH_2)_3CCH_3)_2$, trans- $Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$, trans- $W(CO)_4(P(OCH)_3(CH_2)_3)_2$ and the quinuclidine complexes, consisted of irradiating with ultraviolet light (Hanovia Lamp 654-A10) a methylcyclohexane solution of the appropriate ligand and hexacarbonyl in a quartz tube, under a nitrogen atmosphere. The mixture was then filtered and the solvent removed under vacuum. The solid yellow quinuclidine complexes were recrystallized from pentane to give yellow needles. The products obtained from the reaction of the polycyclic phosphites with metal carbonyls generally consisted of a mixture of the cis and trans isomers. Small amounts of the pure trans isomer could be obtained by fractional crystallization from CH_3CN. Better yields of the

trans isomer were realized by employing chromatography to separate the mixture. The compounds were separated on a silica gel column with benzene. The mono-substituted compound, which was often present in small quantities and which moved with the solvent front, was followed closely by the trans isomer. Because the cis isomer moved rather slowly it was best removed from the column by eluting with CH_2Cl_2.

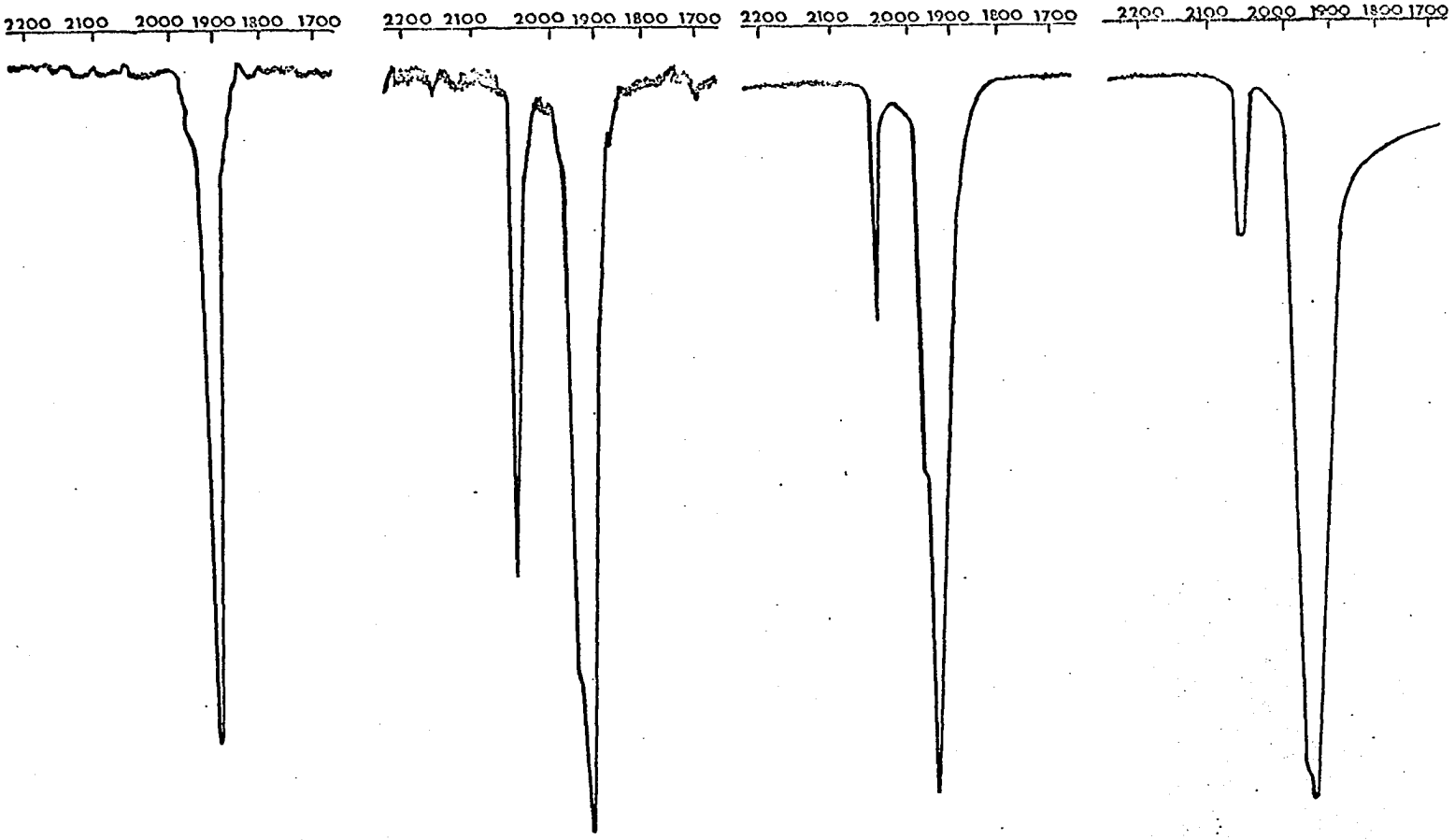
Method B was used to prepare all the cis disubstituted complexes and trans- $Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$ and consisted of stirring a methylcyclohexane solution of the appropriate ligand with chromium norbornadiene tetracarbonyl, molybdenum norbornadiene tetracarbonyl, or tungsten 1,5-cyclooctadiene tetracarbonyl for the cis complexes and with molybdenum hexacarbonyl for the trans molybdenum complex. In each case the solid was filtered off, washed with pentane and recrystallized from CH_3CN.

Table 2 lists the amount of hexacarbonyl or olefin-substituted tetracarbonyl and ligand used, the reaction temperature and time, and the percent yield for the preparation of these complexes. Complexes of the polycyclic ligands were quite stable as solids but were slowly attacked by the atmosphere and sunlight. Solutions of these complexes, however, are stable only for a day or two, while those of $As(OCH_2)_3CCH_3$ and $N(C_2H_4)_3CH$ decompose in several minutes.

Discussion

Examination of the infrared spectra of the new cis-bis($P(OCH_2)_3CCH_3$) tetracarbonyl chromium, molybdenum and tungsten compounds in the carbonyl stretching region revealed that the high frequency band and the shoulder on the very strong main band (Table 2) seemed to be the same bands which were observed with weaker intensities in the trans isomers reported earlier (13). Although these "extra" bands in the trans isomers could be attributed to a lowering of the D_{4h} symmetry of the complex to C_1 by the C_{3v} symmetry of the ligands as had been done by Cotton and Kraihanzel (30) in the case of trans- $Cr(CO)_4(P(C_6H_5)_3)_2$, the reaction of chromium hexacarbonyl with $P(OCH_2)_3CCH_3$ was reinvestigated and the products subjected to careful chromatography and recrystallization of the fractions as described in the experimental section. In Figure 1 are shown the infrared spectra of trans- $Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ (a), cis- $Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ (b), a mixture of these two (c), and an example of a spectrum reported previously (13) as trans- $Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ (d). These absorptions show that the trans compounds reported previously contained some cis isomer. Subsequent attempts to repeat the preparation of the trans isomers of the Mo and W complexes have been unsuccessful for the most part. The spectra of the reaction products are indicative of mostly cis isomer whereas spectra reported

Figure 1. The infrared spectra in the carbonyl region for (a) trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$, (b) cis-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$, (c) a reaction mixture containing cis- and trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ and (d) the spectrum of the compound previously reported as trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$. (a), (b) and (c) were obtained in CH_2Cl_2 solution, while (d) was obtained as a KBr pellet (cm^{-1})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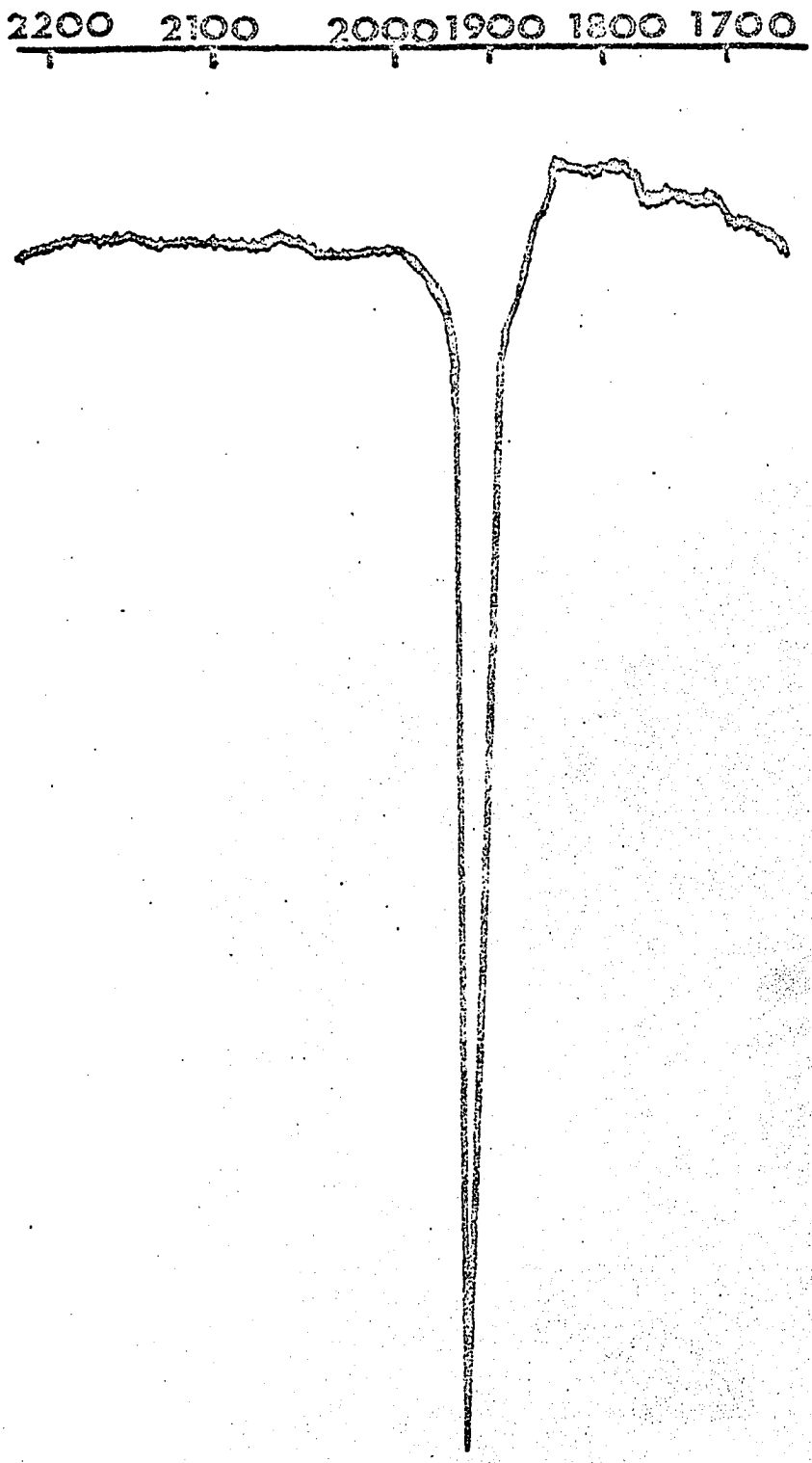
earlier (13) were indicative of mostly trans product. Only on one occasion was a very small quantity of pure trans-$W(CO)_4(P(OCH_2)_3CCH_3)_2$ isolated, but this result could not be repeated. The spectrum is shown in Figure 2.

Because the infrared spectra of the analogous series of trans complexes of the adamantane phosphite $P(OCH)_3(CH_2)_3$ with chromium, molybdenum, and tungsten were also previously reported (14) to exhibit two similar weak bands in addition to the main peak, it became necessary to synthesize the cis isomer for spectral comparison. Again it is apparent that the compounds assigned the trans configuration earlier (14) were contaminated with cis product. It should be pointed out that with $P(OCH)_3(CH_2)_3$ it was possible to prepare pure trans isomers for all three metals by the methods described earlier (14). Values for $\nu(C-O)$ are given in Table 3 for all six compounds.

It is not clear why the preparations of the trans isomers of bis$(P(OCH_2)_3CCH_3)$ tetracarbonyl molybdenum and tungsten could not be repeated (except once in the case of tungsten) even though reactions times and temperatures were varied extensively whereas with $P(OCH)_3(CH_2)_3$ no difficulties were encountered. It is possible that the trans $P(OCH)_3(CH_2)_3$ isomers of chromium, molybdenum and tungsten are more stable than the analogous $P(OCH_2)_3CCH_3$ compounds because of the more bulky geometry and increased steric requirements of $P(OCH)_3(CH_2)_3$. It was noted, for instance, that cis-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$ readily converted to the trans isomer on heating in

Figure 2. The infrared spectrum in the carbonyl region of trans-$W(CO)_4(P(OCH_2)_3CCH_3)_2$ (cm^{-1})


2200 2100 2000 1900 1800 1700

methylcyclohexane solution at 80°, and during attempted recrystallizations from CH_3CN. In contrast, cis- $M(CO)_4(P(OCH_2)_3CCH_3)_2$ (M = Mo and W) may be the more stable isomer due to the smaller steric requirements of the ligand. The apparent stability of both isomers of the bis-$(P(OCH_2)_3CCH_3)$ complex of chromium may be the result of the smaller size of the metal compared to molybdenum and tungsten which would tend to increase the stability of the trans isomer.

The infrared spectra of $P(OCH_2)_3CCH_3$ and $As(OCH_2)_3CCH_3$ are reproduced in Figure 3. Quinuclidine has no absorptions below 750 cm^{-1} with the exception of what might be a very weak peak at about 340 cm^{-1}. The more complex spectra obtained for $P(OCH)_3(CH_2)_3$ and its complexes made the study of these spectra above 300 cm^{-1} undesirable. Upon complexation the spectrum of $P(OCH_2)_3CCH_3$ is simplified to basically five peaks which occur in the ranges: 650-680 cm^{-1} (vs), 500-520 cm^{-1}(s) (frequently accompanied by a weak peak or shoulder on the low frequency side at 490-505 cm^{-1}), 400-415 cm^{-1} (m-w), 360-385 cm^{-1} (m-w) 200-275 cm^{-1} (w). The spectrum of complexed $As(OCH_2)_3CCH_3$ is similar but consists of only four bands at 602 (vs), 481 (m), 381 (vs), and 298 cm^{-1} (w). Table 4 contains the species of the molecular vibrations and the number of infrared active bands to be expected for each type of complex.

In $Ni(CO)_4$, (31) $Fe(CO)_5$, (32) $Cr(CO)_6$ and $Mo(CO)_6$ (33) the metal-carbon stretching frequencies ν(M-C) generally occur

Figure 3. The far infrared spectra of $P(OCH_2)_3CCH_3$ and $As(OCH_2)_3CCH_3$ (cm^{-1})

As(OCH2)3CCH3
70
90
110
140
180
220
260
300
340
400
500
600
700
800
Pl(OCH2)3CCH3
70
90
110
140
180
220
260
300
340
400
500
600
700
800

20b

at lower wavelengths than the metal-carbon-oxygen bending modes δ(M-C-O). Other studies of these regions indicate the range observed for δ(M-C-O) is 450-680 cm^{-1} and that of ν(M-C) is 340-475 cm^{-1} (34,35,36,37). Because of the overlap of the ranges for these modes, the observation that in most cases the required number of δ(M-C-O) and ν(M-C) bands are not observed, and the fact that significant coupling of these modes may occur, no attempt has been made to assign absorptions in this region to either of these vibrations. Some general features of this region are worthy of comment, however. In the majority of cases, most of the total number of required bands are observed. Generally, the bands shift to lower frequency for mono or disubstituted complexes progressing from chromium to molybdenum to tungsten. This trend is also noted in the hexacarbonyls of these metals (33). The positions of the bands for the monosubstituted molybdenum carbonyls containing a phosphorus ligand seem to progress toward lower frequencies with increasing electronegativity of the substituents on phosphorus. Thus from Table 5 it can be seen that $P(OCH_2)_3CCH_3$ fits well into Bigorgne's series (36) of ligands wherein these frequencies decrease in the order $P(C_2H_5)_3$ > $P(OCH_2)_3CCH_3$ > $P(OCH_3)_3$ > $PCl_2(OC_2H_5)$ > PCl_3. The bands in this region for the quinuclidine complexes are included in Table 5 to lend credence to the values assigned to the ν(M-C) and δ(M-C-O) bands of the $P(OCH_2)_3CCH_3$ and $As(OCH_2)_3CCH_3$ complexes

since quinuclidine exhibits no bands in this region in contrast to the bicyclic phosphite and arsenite. No band attributable to a metal-nitrogen stretching mode was observed in the spectra of the quinuclidine complexes.

The assignments of the values for ν(M-P) (143-157 cm^{-1}) for the $P(OCH_2)_3CCH_3$ complexes of nickel were based on the fact that the far infrared spectrum of $Ni(P(OCH_2)_3CCH_3)_4$ consists of only six bands, five of which are assignable to vibrational modes of the ligand, while the sixth at 157 cm^{-1} could be assigned as ν(M-P). The compounds $M(P(C_6H_5)_3)_2X_2$(39) (where M = Zn, Cd, Hg and X = Cl, Br, I), which are isoelectronic and undoubtedly isostructural with $Ni(CO)_2(P(OCH_2)_3CCH_3)_2$, have metal-phosphorus stretches in the ranges 153-166 cm^{-1} for M = Zn; 133-136 cm^{-1} for M = Cd and 133-137 cm^{-1} and 98-108 cm^{-1} for M = Hg. The similarity of the values for the Zn compounds to those of $Ni(CO)_2(P(OCH_2)_3CCH_3)_2$ is taken as supporting evidence for our assignments of ν(M-P).

The average of the metal-phosphorus stretching frequencies taken from Table 6 for the nickel PF_3 complexes form the decreasing series 262, 232, 235, 207 cm^{-1} from the mono to the tetra substituted complex. The values for the analogous group of $P(OCH_2)_3CCH_3$ complexes are substantially lower and contrastingly the average rises in the series 143, 150, 154, 157 cm^{-1}. The larger ν(M-P) values for the PF_3 complexes can be attributed to the greater pi-bonding ability and smaller mass of PF_3. The opposite trends in ν(M-P) on step-wise

substitution of PF_3 and $P(OCH_2)_3CCH_3$ for CO can be accounted for by the difference in the pi-bonding abilities of the two phosphorus ligands. It is generally agreed that PF_3 is at least as good a pi-bonding ligand as CO (40) and a better pi-bonding ligand than a phosphite because of the higher electronegativity of fluorine compared to oxygen. Therefore, in competing for metal electrons with CO, PF_3 is expected to be more proficient than $P(OCH_2)_3CCH_3$. On substitution of the second CO by PF_3, the second PF_3 in effect forces the first to release some of its pi-electron density since the metal electron density liberated by the departing CO group is insufficient to satisfy the superior pi-accepting character of the incoming PF_3. The average metal-phosphorus pi-bonding therefore decreases on continued substitution. On the other hand as CO groups are replaced by $P(OCH_2)_3CCH_3$, the available electron density on nickel is increased and thus the phosphorus ligands are donated increasing electron density for pi-bonding which results in increasing average ν(M-P) values. This interpretation is also consistent with the decrease in the average value of ν(C-O) observed in the same series of $P(OCH_2)_3CCH_3$ complexes upon replacement of all but the last CO group in $Ni(CO)_4$: 2057, 2055, 2021, and 1997 cm^{-1}. (41,13) The increased metal electron density upon CO substitution decreases the CO bond order. It is also significant that there is observed an initial increase in the average value of ν(C-O) from $Ni(CO)_4$ (2057 cm^{-1}) (41) to $Ni(CO)_3PF_3$ (2076 cm^{-1}) (37)

after which this value is almost constant. The force constants calculated by Bigorgne (37) also show an initial increase of 17.18 to 17.27 mdyn/Å on replacing the first CO with PF_3 after which these values are also constant. The initial increase in ν(C-O) follows from the arguments given above for ν(M-P) since removal of metal electron density by the better pi-acid PF_3 allows an increase in the CO bond order. The constancy of ν(C-O) on further substitution may be ascribed to the possibility that the first PF_3 group has already reduced the metal electron density to such a minimum that pi-bonding among the remaining CO groups is also at a minimum. Thus additional PF_3 ligands are forced to share the pi electron density of PF_3 groups in the complex.

For iron and the group VIb metals, the number of compounds for which ν(M-P) values have been measured are too few to see any significant trends. The assignments of ν(M-P) values listed in Table 6 for such complexes of $P(OCH_2)_3CCH_3$ are made reasonable by comparison of the spectra of <u>cis</u>- $Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ and <u>cis</u> -$(Cr(CO)_4(As(OCH_2)_3CCH_3)_2$. In the spectrum of the latter complex the band at 181 cm^{-1}, which was assigned to ν(M-P) in the phosphite complex, is conspicuously absent. As in the case of the nickel complexes, ν(M-P) increases from mono to disubstituted octahedral complexes. This increase seems to be greater when the ligands are <u>trans</u> as is seen in the case of chromium. Further importance to this observation is given by the increase in ν(M-P) from the <u>cis</u> to

the trans complexes of the type $M(CO)_4(P(OCH)_3(CH_2)_3)_2$ where M = Cr, Mo, and W (Table 6). The assignments of ν(M-P) in the latter complexes are reasonable in that they are consistent with the previously discussed assignments of ν(M-P) and the absence of other bands in this region of the spectrum from 300 to 160 cm^{-1}. The increase in ν(M-P) from cis to trans oriented phosphite ligands can be ascribed to two influences acting in the same direction: (1) Because trans ligands share two d-pi orbitals whereas cis ligands share only one, (30) stronger metal-phosphorus pi-bonding might be expected to increase ν(M-P) in the trans isomers. (2) Since CO groups are very likely stronger pi-bonding ligands than phosphites, their depleting effect on the pi-electron density available to the phosphite is expected to be greater when oriented trans to a phosphite.

Other reports of ν(M-P) (39,42,43,44) values have dealt mainly with Ni(II), Pd(II) and Pt(II) compounds of the form $(R_3P)_2MX_2$ where R= CH_3, C_2H_5, and C_6H_5 and X = Cl, Br, I, NCS, CN, C_6H_5, and SCH_3. For $P(CH_3)_3$(43) complexes, ν(M-P) values fall in the range 341-377 cm^{-1}, while the range for the $P(C_2H_5)_3$(44) complexes is 409-441 cm^{-1}. The different ranges reported by others and in this work is undoubtedly related to variations in electronic and stereo-chemical configurations in the complexes.

In transition metal carbonyls, (31,32,33,45) carbon-metal-carbon bending modes δ(C-M-C) generally occur below

140 cm^{-1}. The bands listed in Table 7 which occur below those assigned to ν(M-P) can be attributed to any or all of the following bending modes where appropriate: δ(C-M-C), δ(C-M-P), δ(C-M-N) and δ(P-M-P). In most cases the expected number of these bands listed in Table 4 are not observed and no attempt was made to make specific assignments.

Suggestions for Future Work

Because there are so few metal-phosphorus stretching frequencies for metal carbonyl complexes known, it should prove very beneficial to study the far infrared spectra of a series of carbonyl complexes where ligands of different electronegativity can be used while not altering the steric requirements of these ligands significantly. Such a set of ligands do exist and it has been shown that they do form characterizable carbonyl complexes. In addition to the ligands mentioned in the previous section there are $P(OCH_2)_3P$, $P(SCH_2)_3CCH_3$ and $P(N(CH_3)CH_2)_3CCH_3$ whose carbonyl complexes should be investigated with the aim of finding a correlation between metal-phosphorus stretching frequencies and the electronegativity of the groups bonded to the phosphorus.

Table 1. Analytical data

Compound	Carbon % Calcd.	Carbon % Found	Hydrogen % Calcd.	Hydrogen % Found
trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	36.54	36.33	3.94	3.90
cis-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	36.54	36.01	3.94	4.01
cis-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$	30.65	30.13	3.37	3.29
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$	33.35	32.82	3.60	3.58
cis-$W(CO)_4(P(OCH_2)_3CCH_3)_2$	28.40	28.36	3.06	3.00
trans-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$	39.60	39.30	3.70	3.80
cis-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$	39.60		3.70	
trans-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	36.30	36.60	3.30	3.60
cis-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	36.30		3.30	
trans-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$	31.10	31.90	2.90	2.90
cis-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$	31.10		2.90	
$Cr(CO)_5N(C_2H_4)_3CH$[a]	47.52	47.28	4.32	4.41
$Mo(CO)_5N(C_2H_4)_3CH$[b]	41.51	41.44	3.77	3.85
$W(CO)_5N(C_2H_4)_3CH$[c]	33.12	33.32	3.01	3.09

[a]Nitrogen % calcd.: 4.62 Found: 4.46

[b]Nitrogen % calcd.: 4.03 Found: 3.98

[c]Nitrogen % calcd.: 3.22 Found: 3.17

Table 2. Preparation of metal carbonyl complexes

Compound	Amount $M(CO)_6$ or $(M(CO)_4(diene))$, g	Amount of Ligand, g	Reaction Conditions Temp, °C (time, hr.)	Yield, %
trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	1.00	1.70	55 (4)	50
cis-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	(0.70)	0.90	25 (48)	95
cis-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$	(0.70)	1.10	25 (48)	90
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$	(0.60)	0.75	25 (2)	95
cis-$W(CO)_4(P(OCH_2)_3CCH_3)_2$	(0.10)	0.10	80 (6)	85
trans-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$	0.69	1.20	55 (4)	45
cis-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$	(0.37)	0.50	25 (36)	55
trans-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	0.37	0.50	136 (24)	85
cis-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	(0.30)	0.35	25 (2)	90
trans-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$	0.50	0.50	55 (4)	30
cis-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$	(0.30)	0.74	80 (8)	80
$Cr(CO)_5(N(C_2H_4)_3CH)$	2.00	0.81	55 (12)	60
$Mo(CO)_5(N(C_2H_4)_3CH)$	2.00	0.68	55 (12)	55
$W(CO)_5(N(C_2H_4)_3CH)$	2.00	0.51	55 (12)	50

Table 3. Infrared spectra of complexes in the metal carbonyl region[a]

Compound	C-O Stretching Frequency, cm^{-1}		
trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$		1915 vs[c]	
cis-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	1925 vs	1950 sh	2043 m
cis-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$	1955 vs	1962 sh	2065 m
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$	1923 vs	1945 sh	2038 m
cis-$W(CO)_4(P(OCH_2)_3CCH_3)_2$	1924 vs	1950 sh	2045 m
trans-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$		1926 vs	
cis-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$	1929 vs	1950 sh	2043 m
trans-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$		1932 vs	
cis-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	1934 vs	1957 sh	2050 m
trans-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$		1924 vs	
cis-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$	1927 vs	1950 sh	2053 m
$Cr(CO)_5(N(C_2H_4)_3CH)$[b]	1905 vs	1925 vs	2062 w
$Mo(CO)_5(N(C_2H_4)_3CH)$[b]	1901 vs	1925 vs	2067 w
$W(CO)_5(N(C_2H_4)_3CH)$[b]	1900 vs	1912 vs	2062 w

[a]All spectra were obtained in CH_2Cl_2 solution except where indicated otherwise.

[b]Cyclohexane solution

[c]vs = very strong, sh = shoulder, m = medium, w = weak

Table 4. Infrared-active vibration of substituted metal carbonyls

Molecule	Point Group	ν(MX)[a]	ν(MC) or ν(CO)	δ(M-C-O)	δ(X-M
$Ni(CO)_4$	T_d		$a_1 + t_2$	$e + t_1 + t_2$	$e + t$
$Ni(CO)_3L$	C_{3v}	a_1	$a_1 + e$	$a_1 + a_2 + 2e$	$a_1 +$
$Ni(CO)_2L_2$	C_{2v}	$a_1 + b_2$	$a_1 + b_1$	$a_1 + a_2 + b_1 + b_2$	$2a_1 +$ +
$Ni(CO)L_3$	C_{3v}	$a_1 + e$	a_1	e	$a_1 +$
NiL_4	T_d	$a_1 + t_2$			$e + t$
$Fe(CO)_5$	D_{3h}		$2a_1' + e' + a_2''$	$a_2' + 2e' + a_2'' + 2e''$	$2e' +$
$Fe(CO)_4L$	C_{3v}	a_1	$2a_1 + e$	$a_1 + a_2 + 3e$	$a_1 +$
$Fe(CO)_3L_2$	D_{3h}	$a_1' + a_2''$	$a_1' + e'$	$a_2' + e' + a_2'' + e''$	$2e' +$
$M(CO)_6$	O_h		$a_{1g} + e_g + t_{1u}$	$t_{1g} + t_{2g} + t_{1u} + t_{2u}$	$t_{2g} +$

[a] X = P, As, N

[b] X, Y = C, C; C, P; C, N; P, P

[c] IR active

ıted metal carbonyls

δ(M-C-O)	δ(X-M-Y)[b]	No. of ν(MX)[c]	No. of ν(MC) or ν(CO)[c]	No. of δ(M-C-O)[c]	No. of δ(X-M-Y)[b,c]
$e + t_1 + t_2$	$e + t_2$	-	1	1	1
$a_1 + a_2 + 2e$	$a_1 + 2e$	1	2	3	3
$a_1 + a_2 + b_1 + b_2$	$2a_1 + a_2 + b_1 + b_2$	2	2	3	4
e	$a_1 + 2e$	2	1	1	3
	$e + t_2$	1	-	-	1
$a_2' + 2e' + a_2'' + 2e''$	$2e' + a_2'' + e''$	-	2	3	3
$a_1 + a_2 + 3e$	$a_1 + 3e$	1	3	4	4
$a_2' + e' + a_2'' + e''$	$2e' + a_2'' + e''$	1	1	2	3
$t_{1g} + t_{2g} + t_{1u} + t_{2u}$	$t_{2g} + t_{1u} + t_{2u}$	-	1	1	1

Table 4 continued

Molecule	Point Group	$\nu(MX)$[a]	$\nu(MC)$ or $\nu(CO)$	$\delta(M-C-O)$	δ
$M(CO)_5L$	C_{4v}	a_1	$2a_1 + b_1 + e$	$a_1 + a_2 + b_1 + b_2 + 3e$	a
<u>trans</u>-$M(CO)_4L_2$	D_{4h}	$a_{1g} + a_{2u}$	$a_{1g} + b_{1g} + e_u$	$a_{2g} + b_{2g} + e_g + a_{2u} + b_{2u} + e_u$	e
<u>cis</u>-$M(CO)_4L_2$	C_{2v}	$a_1 + b_2$	$2a_1 + b_1 + b_2$	$2a_1 + 2a_2 + 2b_1 + 2b_2$	3a

-O)	δ(X-M-Y)[b]	No. of ν(MX)[c]	No. of ν(MC) or ν(CO)[c]	No. of δ(M-C-O)[c]	No. of δ(X-M-Y)[b,c]
$_{2}$ + b_1 $)_2$ + 3e	a_1 + $2b_1$ + b_2 + 3e	1	3	4	4
b_{2g} + e_g a_{2u} + b_{2u} e_u	e_g + a_{2u} + b_{2u} + e_u	1	1	2	3
$2a_2$ + $2b_1$ $2b_2$	$3a_1$ + $2a_2$ + $2b_1$ + $2b_2$	2	4	6	7

Table 5. Absorption bands of substituted metal carbonyls in the 300-70C

Compound	Total Bands Possible and (Observed)			ν(M-C
$Ni(CO)_3PF_3$[a,b]	5 (2)			
$Ni(CO)_2(PF_3)_2$[a,b]	6 (2)			
$Ni(CO)(PF_3)_3$[a,b]	2 (1)			
$Ni(PF_3)_4$[a,b]	0 (0)			
$Ni(CO)_3(P(OCH_2)_3CCH_3)$	5 (4)			
$Ni(CO)_2(P(OCH_2)_3CCH_3)_2$	5 (5)	656 vs		
$Ni(CO)(P(OCH_2)_3CCH_3)_3$	2 (1)			
$Ni(P(OCH_2)_3CCH_3)_4$	0 (0)			
$Fe(CO)_4P(C_2H_5)_3$[d]	7 (3)		621 vs	526 m

[a] Raman values.

[b] Source (37).

[c] vs = very strong, s = strong, m = medium, sh = shoulder, w = weak,

[d] Source (38).

carbonyls in the 300-700 cm^{-1} region

ν(M-C) and δ(M-C-O), cm^{-1}						
		462 s[c]		407 vs		
		467 m	456 w	429 s		
			449 w			
	493 s	471 m	450 vs		348 m	
	490 s		457 s	377 m	355 w	
			461 w			
621 vs	526 m	493 w				

h = shoulder, w = weak, vw = very weak.

Table 5 continued

Compound	Total Bands Possible and (Observed)					ν(
$Fe(CO)_4(P(OCH_2)_3CCH_3)$	7 (7)	659 s	620 vs	534 m		525
trans-$Fe(CO)_3(P(OCH_2)_3CCH_3)_2$	3 (3)		628 vs	584 vs		
$Cr(CO)_5Cl^-$ [e]	7 (8)	670 w	653 vs			563
$Cr(CO)_5(P(OCH_2)_3CCH_3)$	7 (6)	672 m	653 vs			
$Cr(CO)_5(N(C_2H_4)_3CH)$	7 (5)	671 s	652 vs			
$Mo(CO)_5Cl^-$ [e]	7 (7)		608 sh	602 vs		
$Mo(CO)_5P(C_2H_5)_3$ [f]	7 (5)		610 vs	580 vs		
$Mo(CO)_5(P(OCH_2)_3CCH_3)$	7 (5)		606 vs	581 vs		
$Mo(CO)_5P(OCH_3)_3$	7 (5)		600 vs	576 vs		
$Mo(CO)_5P(OC_2H_5)Cl_2$ [f]	7 (5)		593 vs	572 vs		
$Mo(CO)_5P(OCH_3)_3$ [f]	7 (5)		589 vs	571 vs		

[e] Source (34).

[f] Source (36).

ν(M-C) and δ(M-C-O), cm^{-1}

620 vs	534 m	525 s		447 vw			390 vw	368 m
628 vs	584 vs			460 m				
653 vs		563 m	553 sh	499 w	472 w	437 s	411 m	
653 vs			538 w		470 s	452 m	427 vw	
652 vs			537 m			439 s	415 m	
608 sh	602 vs		543 s	472 w	454 w	391 w		346 s
610 vs	580 vs				424 w	402 m		381 s
606 vs	581 vs			489 w	424 s			382 s
600 vs	576 vs				417 m	400 m		377 s
593 vs	572 vs				401 w	390 m		370 s
589 vs	571 vs				400 w	382 m		366 s

Table 5 continued

Compound	Total Bands Possible and (Observed)				
$Mo(CO)_5(N(C_2H_4)_3CH)$	7 (5)		612 s	598 vs	
$W(CO)_5Cl^-$ [e]	7 (7)		594 vs	554 s	
$[W(CO)_5P(CH_3)_2]_2$ [f]	7 (2)		594 vs	568 vs	
$W(CO)_5(P(OCH_2)_3CCH_3)$	7 (6)		590 vs	566 vs	
$W(CO)_5(N(C_2H_4)_3CH)$	7 (5)		590 vs	546 s	
cis-$Cr(CO)_4(P(C_6H_5)(C_2H_5)_2)_2$ [d]	10 (2)	677	642		
cis-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	10 (6)	673 s	648 vs		
cis-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$	10 (5)	656 s	648 vs		
cis-$Mo(CO)_4(P(C_6H_5)(C_2H_5)_2)_2$ [d]	10 (3)		610	587	5
cis-$Mo(CO)_4(P(C_2H_5)_3)_2$ [f]	10 (7)		608 vs	586 vs	5
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$	10 (10)	649 vs	595 vs	585 vs	5
cis-$W(CO)_4(P(C_6H_5)(C_2H_5)_2)_2$ [d]	10 (3)		600	583	5
cis-$W(CO)_4(P(OCH_2)_3CCH_3)_2$	10 (6)	661 vs	590 vs	582 vs	5
trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	3 (3)	648 vs	636 vs		
trans-$Mo(CO)_4(P(C_2H_5)_3)_2$ [f]	3 (3)		631 vs	573 vs	
trans-$Mo(CO)_4(P(OCH_3)_3)_2$ [f]	3 (3)		618 vs	570 vs	

	ν(M-C) and δ(M-C-O), cm^{-1}											
s	598	vs		538	s			391	w		361	vs
vs	554	s		528	w	444	w	426	w	410	w	355	s
vs	568	vs										
vs	566	vs		527	vw	492	w	422	m	414	w		
vs	546	s						430	w	409	w	367	vs
vs				552	w	493	w	459	w		372	w	
vs				543	w	450	w				391	m	
	587		578										
vs	586	vs	575	vs				428	m	413	m	404	m	392	s
vs	585	vs	566	vs	531	vw	478	m	427	s	405	m	387	s	358	m
	583		565												
vs	582	vs	560	s			490	w	426	s					
vs							477	m							
vs	573	vs								405	s				
vs	570	vs								397	s				

Table 6. Metal-phosphorus stretching frequencies of some substituted metal carbonyls

Compound	Total Bands Possible and (Observed)	ν(M-P) cm^{-1}
$Ni(CO)_3(PF_3)$[a]	1 (1)	262[b]
$Ni(CO)_2(PF_3)_2$[a]	2 (2)	254, 209[b]
$Ni(CO)(PF_3)_3$[a]	2 (2)	253, 216[b]
$Ni(PF_3)_4$[a]	2 (2)	218, 195[b]
$Ni(CO)_3(P(OCH_2)_3CCH_3)$	1 (1)	143
$Ni(CO)_2(P(OCH_2)_3CCH_3)_2$	2 (2)	155, 144
$Ni(CO)(P(OCH_2)_3CCH_3)_3$	2 (2)	157, 151
$Ni(P(OCH_2)_3CCH_3)_4$	1 (1)	157
$Fe(CO)_5(P(OCH_2)_3CCH_3)$	1 (1)	169
trans-$Fe(CO)_4(P(OCH_2)_3CCH_3)_2$	1 (1)	192
$Cr(CO)_5(P(OCH_2)_3CCH_3)$	1 (1)	164
$Mo(CO)_5(P(OCH_2)_3CCH_3)$	1 (1)	195
$W(CO)_5(P(OCH_2)_3CCH_3)$	1 (1)	180
trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	1 (1)	190
cis-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	2 (1)	181
trans-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$	1 (1)	198
cis-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$	2 (1)	182
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$	2 (1)	201
trans-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	1 (1)	237

[a]Source (37)

[b]Raman values

Table 6. (Continued)

Compound	Total Bands Possible and (Observed)	ν(M-P) cm^{-1}
cis-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	2 (1)	200
cis-$W(CO)_4(P(OCH_2)_3CCH_3)_2$	2 (1)	185
trans-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$	1 (1)	202
cis-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$	2 (2)	181, 178

Table 7. Bands in the far infrared below those assigned to ν(M-P)

Compound	Total Bands Possible and (Observed)	δ(X-M-Y),[a] cm^{-1}
$Ni(CO)_3PF_3$	3 (2)	80, 61[b]
$Ni(CO)_2(PF_3)_2$	5 (2)	78, 59[b]
$Ni(CO)(PF_3)_3$	3 (2)	76, 52[b]
$Ni(PF_3)_4$	2 (2)	57, 50[b]
$Ni(CO)_2(P(OCH_2)_3CCH_3)_2$	4 (1)	118
$Fe(CO)_4(P(OCH_2)_3CCH_3)$	3 (2)	120, 80
$Mo(CO)_5(P(OCH_2)_3CCH_3)$	4 (2)	149, 84
$W(CO)_5(P(OCH_2)_3CCH_3)$	4 (2)	150, 87
$Cr(CO)_5(N(C_2H_4)_3CH)$	4 (3)	185, 120, 106
$Mo(CO)_5(N(C_2H_4)_3CH)$	4 (3)	170, 107, 89
$W(CO)_5(N(C_2H_4)_3CH)$	4 (3)	168, 101, 88
cis-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	7 (2)	152, 130
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$	7 (4)	166, 138, 121, 89
cis-$W(CO)_4(P(OCH_2)_3CCH_3)_2$	7 (6)	166, 158, 144, 138, 93, 74

[a] X,Y = C,C; C,N; C,P; or P,P

[b] Raman values

A STUDY OF THE TRANSITION METAL CARBONYL COMPLEXES OF 2,6,7-TRIOXA-1,4-DIPHOSPHABICYCLO [2.2.2] OCTANE

In a continuation of the study of transition metal carbonyl complexes of polycyclic phosphorus ligands 2,6,7-trioxa-1,4-disphosphabicyclo [2.2.2] octane, $P(OCH_2)_3P$ (46) was reacted with the Group VIb metal carbonyls. Preliminary indications are that $P(OCH_2)_3P$ forms linkage isomers with these transition metal carbonyls and that they can be separated by chromatography. It is not known if $P(OCH_2)_3P$ forms linkage isomers with transition metal ions. Several attempts to prepare complexes of Co(II), Ni(II), Cu(II) and Ag(I) yielded compounds which could not be purified because of their very low solubilities in common solvents (47).

The linkage isomers of $P(OCH_2)_3P$ with metal carbonyls are not readily identified by their infrared spectra because the carbonyl stretching frequencies of the phosphine coordinated isomer and the phosphite coordinated isomer are very close together. Fortunately, the chemical shifts of the methylene protons of the ligand and the coupling constants, J_{POCH} and J_{PCH}, are different for the two isomers so that identification can be made from their nmr spectra.

Experimental

The infrared spectra were obtained on a Beckman Model 8 grating spectrometer. NMR spectra were obtained on a Varian A-60 spectrometer using tetramethysilane as an internal

standard. Chromium and tungsten hexacarbonyls were purchased from Pressure Chemical Co. $P(OCH_2)_3P$ (46), chromium norbornadiene tetracarbonyl (26), molybdenum norbornadiene tetracarbonyl (27), and tungsten 1,5-cyclooctadiene tetracarbonyl (28) were prepared as described elsewhere.

$Cr(CO)_5(P(OCH_2)_3P)$ - In a quartz tube were placed 1.0 g (4.5 mmoles) of $Cr(CO)_6$ and 0.50 g (3.3 mmoles) of $P(OCH_2)_3P$ dissolved in 70 ml of methylcyclohexane. While stirring, the mixture was irradiated with ultraviolet light (Hanovia Lamp 654-A10) for 2 hr. The reaction mixture was filtered and the solvent removed under reduced pressure giving a white solid recrystallizable from n-heptane. The nmr spectrum of this compound in CH_3CN (Figure 4) indicated that this was the pure phosphite linkage isomer.

$Mo(CO)_5(P(OCH_2)_3P)$ and $Mo(CO)_5(P(CH_2O)_3P)$ - A mixture of 1.0 g (3.8 mmoles) of $Mo(CO)_6$ and 0.50 g (3.3 mmoles) of $P(OCH_2)_3P$ in 30 ml of methylcyclohexane was stirred under a nitrogen atmosphere and refluxed for 7 hr. The solvent was removed under reduced pressure and the white solid was filtered and washed with pentane. The compound was recrystallized from n-heptane. The nmr spectrum of the reaction product in CH_3CN (Figure 5) indicated that it was a mixture of the phosphite and phosphine linkage isomers. A careful chromatography using a silica gel column made up with n-heptane and eluted with a mixture of 50% n-heptane and 50% benzene afforded separation of the two isomers. The phosphine linkage isomer came off

the column first followed closely by the phosphite isomer. Figure 6 shows the nmr spectra of the pure isomers.

$W(CO)_6 + P(OCH_2)_3P$ - A mixture of 2.0 g (5.7 mmoles) of $W(CO)_6$ and 0.60 g (4.0 mmoles) of $P(OCH_2)_3P$ was placed in 30 ml of ethylbenzene. While stirring under a nitrogen atmosphere, the mixture was refluxed for 24 hr. This reaction yielded only an insoluble black solid.

Cis- $Cr(CO)_4(P_2O_3C_3H_6)_2$ - A mixture of 0.20 g (0.78 mmoles) of chromium norbornadiene tetracarbonyl and 0.40 g (2.6 mmoles) of $P(OCH_2)_3P$ in 30 ml of n-heptane was stirred at 70° for 4 hr. The white solid was filtered off and washed with pentane. Its very complex nmr spectrum in CH_3CN indicated that it was a mixture of linkage isomers.

Trans- $Cr(CO)_4(P_2O_3C_3H_6)_2$ - A mixture of 0.50 g (2.3 mmoles) of $Cr(CO)_6$ and 1.0 g (6.6 mmoles) of $P(OCH_2)_3P$ was added to 30 ml of ethylbenzene and while stirring under a nitrogen atmosphere the mixture was refluxed for 30 hr. The solvent was removed under reduced pressure and the white solid was washed with pentane and filtered. An infrared spectrum of this product showed it to be a mixture of cis and trans isomers. Chromatography using a silica gel column and CH_2Cl_2 afforded separation of the cis and trans isomers with the cis isomer remaining on the column. However, an nmr spectrum of the trans isomer in CH_3CN again indicated that it was a mixture of linkage isomers.

Figure 4. The proton NMR spectrum of $Cr(CO)_5P(OCH_2)_3P$, with $J_{POCH} = 5.2$ Hz and $J_{PCH} = 8.5$ Hz

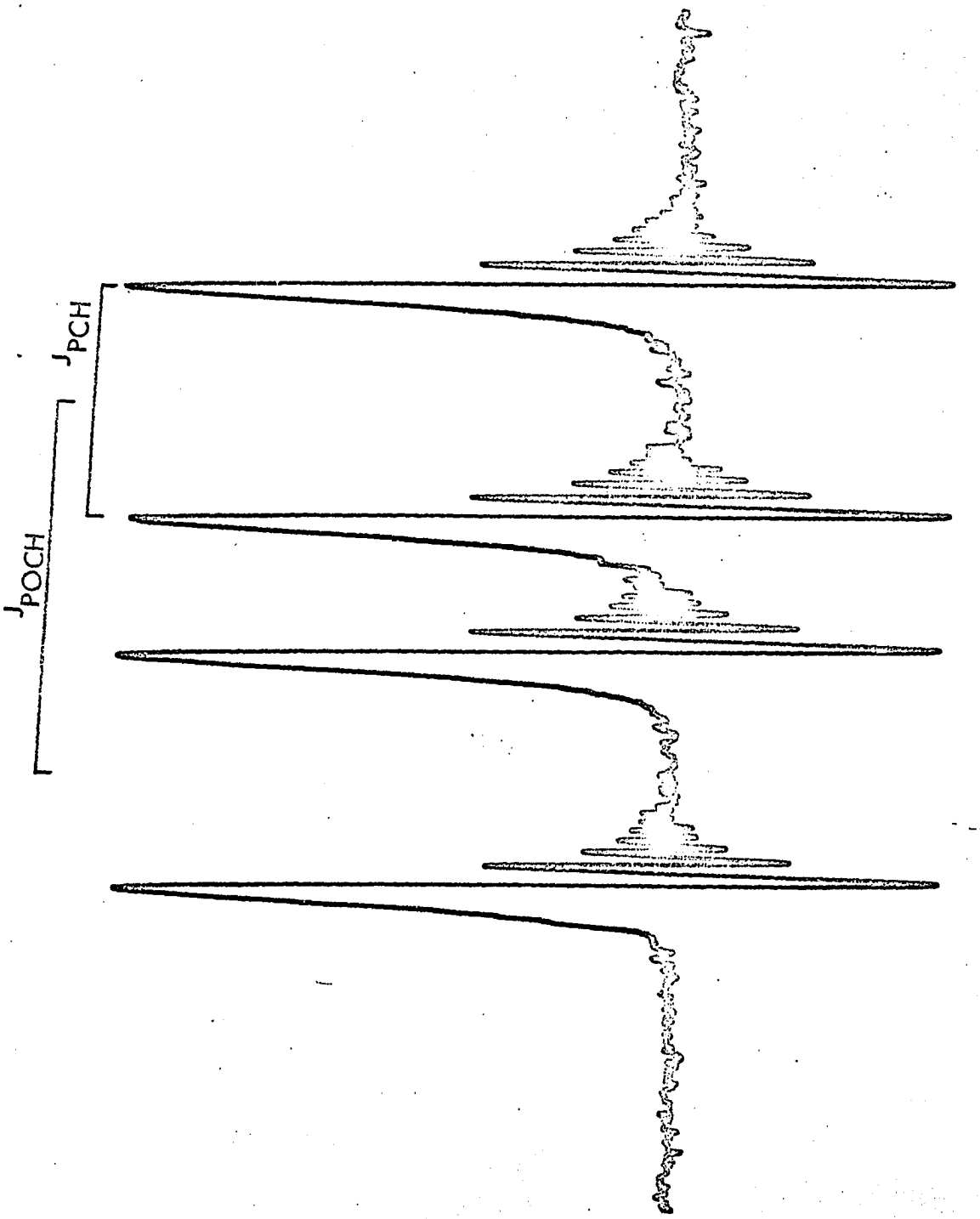

J_{PCH}
J_{POCH}

Figure 5. The proton NMR spectrum of the product from the reaction $Mo(CO)_6 + P(OCH_2)_3P$

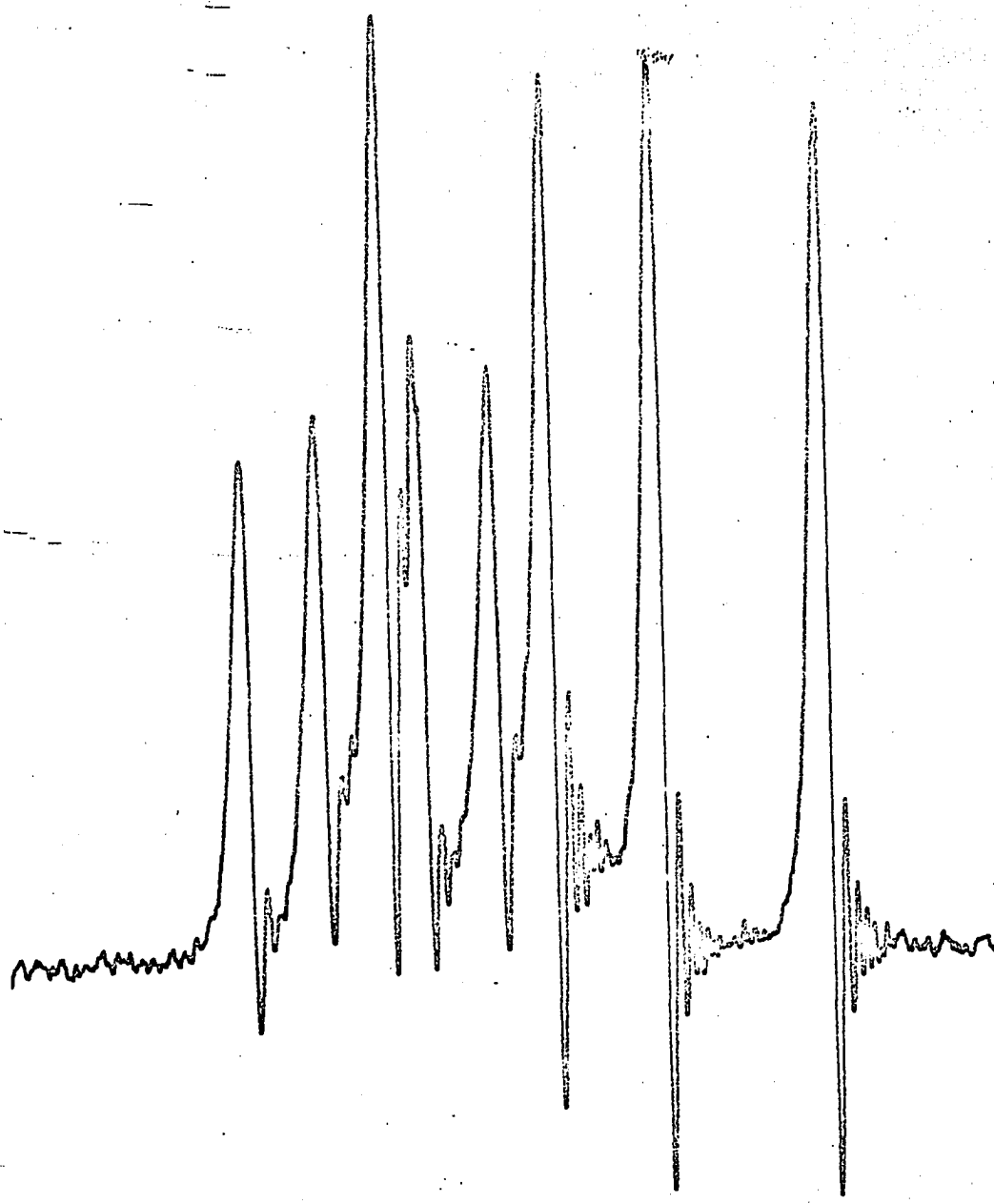
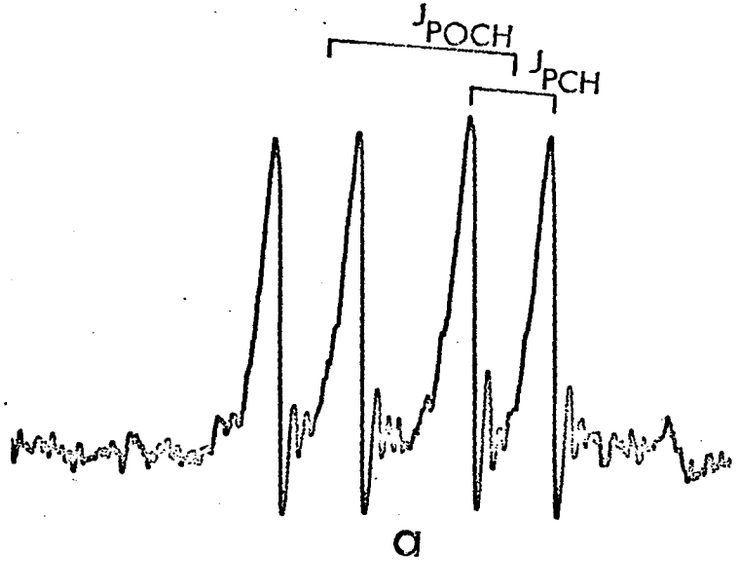


Figure 6. The proton NMR spectra of (a) $Mo(CO)_5P(CH_2O)_3P$ with $J_{POCH} = 5.4$ Hz and $J_{PCH} = 2.3$ Hz and (b) $Mo(CO)_5P(OCH_2)_3P$ with $J_{POCH} = 5.2$ Hz and $J_{PCH} = 8.4$ Hz


J_{POCH}
J_{PCH}
a

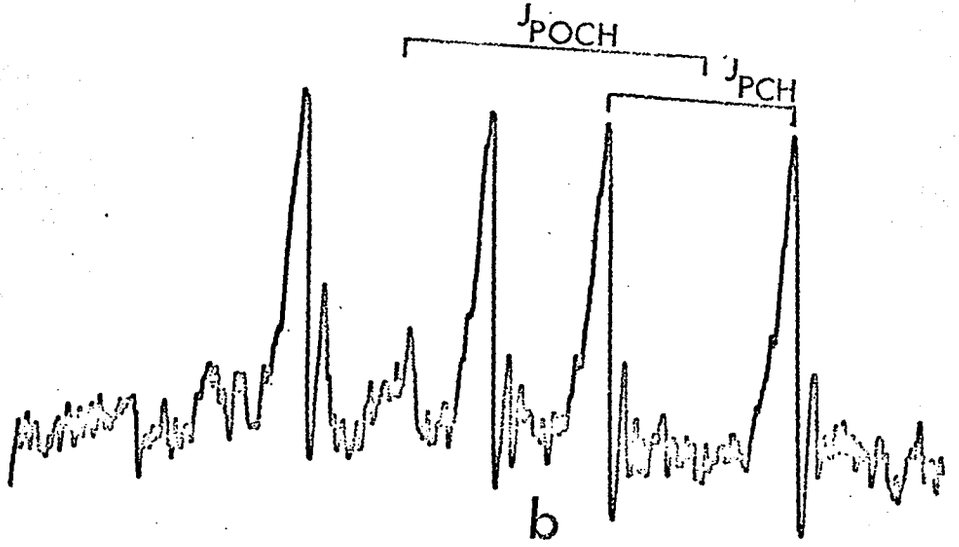
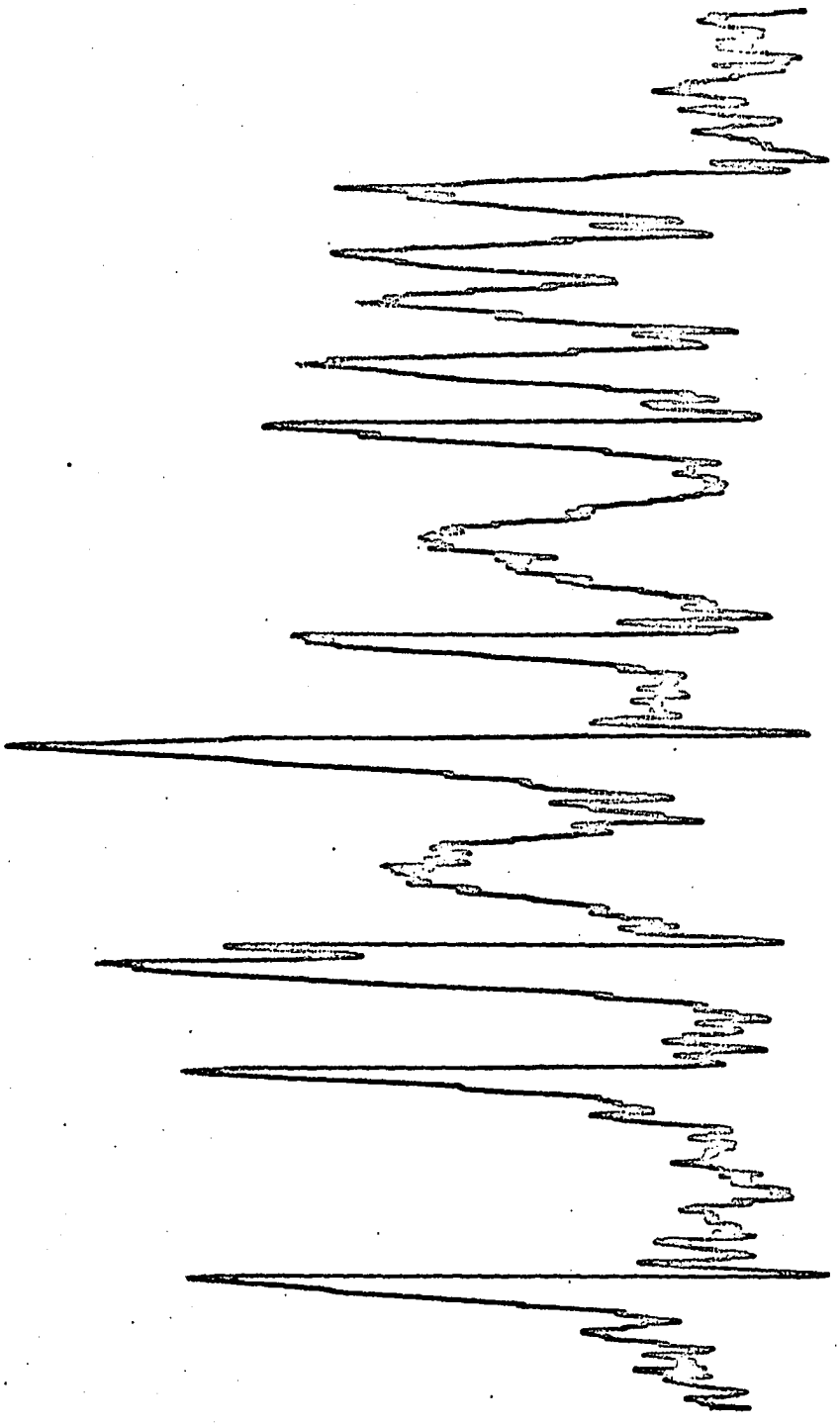

J_{POCH}
J_{PCH}
b

Figure 7. The proton NMR spectrum of the product from the reaction $W(CO)_4C_8H_{12}$ + 2 $(P(OCH_2)_3P)$



Cis- $Mo(CO)_4(P_2O_3C_3H_6)_2$ - A mixture of 0.30 g (1.1 mmoles) of molybdenum norbornadiene tetracarbonyl and 0.50 g (3.3 mmoles) of $P(OCH_2)_3P$ was added to 30 ml of n-heptane and stirred at room temperature for 3 hr. The white solid was filtered off and washed with pentane. Again a complex nmr spectrum in CH_3CN indicated that this product was a mixture of linkage isomers.

Cis-$W(CO)_4(P_2O_3C_3H_6)_2$ - A mixture of 0.40 g (1.0 mmole) of tungsten 1,5-cyclooctadiene tetracarbonyl and 0.50 g (3.3 mmoles) of $P(OCH_2)_3P$ was added to 30 ml of n-heptane and stirred for 24 hr at 70°. The solid was filtered off and washed with pentane. A complex nmr spectrum in acetone (Figure 7) again indicated a mixture of linkage isomers.

Discussion

The infrared spectra of the complexes listed in Table 8 depict one interesting feature, namely the small difference in the carbonyl stretching frequencies between the phosphine and the phosphite linkage isomers. This small difference makes it extremely difficult to tell from the spectrum whether a reaction product is a mixture of linkage isomers or not. Even the disubtituted complexes, which may be mixtures of three linkage isomers, exhibit infrared spectra which look very much like those obtained from pure compounds. This small difference in the carbonyl stretching frequencies of the linkage isomers is attributed to the fact that no matter which phosphorus group of the ligand is coordinated the electronegativity of the ligand will be about the same.

The proton nmr data for the complexes, $P(OCH_2)_3P$ and $SP(OCH_2)_3P$ (46) are given in Table 9. The similarity between the nmr spectra of $Cr(CO)_5(P(OCH_2)_3P)$ and $Mo(CO)_5(P(OCH_2)_3P)$ should be noted as an indication that in these two compounds the ligand, $P(OCH_2)_3P$, is coordinated through the same type of phosphorus. It has previously been shown that the values of J_{POCH} for transition metal carbonyl complexes of $P(OCH_2)_3CCH_3$ (13) and $P(OCH)_3(CH_2)_3$ (14) lie between the values of J_{POCH} obtained for the free ligand and its oxide and sulfide (48). The values of J_{POCH} and J_{PCH} for $Cr(CO)_5(P(OCH_2)_3P)$ and $Mo(CO)_5(P(OCH_2)_3P)$ are intermediate between the values of J_{POCH} and J_{PCH} for $P(OCH_2)_3P$ and $SP(OCH_2)_3P$. This is evidence for the contention that $P(OCH_2)3P$ is coordinated through the phosphite phosphorus in these two complexes.

Boros (17) found that in the complexes $Fe(CO)_4(P(CH_2O)_3CCH_3)$, <u>trans</u>- $Fe(CO)_3(P(CH_2O)_3CCH_3)_2$ and $Ni(CO)_2(P(CH_2O)_3CCH_3)_2$ the values of J_{PCH} were 0, 0 and 1.8 Hz respectively. The fact that the value of J_{PCH} for $Mo(CO)_5(P(CH_2O)_3P)$ is 2.3 Hz lends credence to the proposal that in this complex $P(OCH_2)_3P$ is coordinated through the phosphine phosphorus. It is not clear, however, why the values of J_{POCH} for the phosphine and the phosphite linkage isomers should be so similar.

Unfortunately because of lack of time this research could not be carried to a more definitive conclusion.

Suggestions for Future Work

First, this research should be continued by attempting to isolate all the possible linkage isomers that might be formed and investigating the feasibility of their interconversion.

An nmr study of these complexes should include an investigation of their proton spectra especially from the point of view of determining the amount of phosphorus-phosphorus coupling in the disubstituted complexes. This would be especially important if complexes with mixed, phosphine-phosphite, coordination could be obtained. P^{31} nmr spectra of such mixed coordination complexes would also be of help in studying phosphorus-phosphorus interactions within the same ligand and between ligands in the same complex. Decoupling experiments could be used to confirm assignments of phosphine or phosphite coordination.

The far infrared spectra of these complexes would be important in furthering the study of metal-phosphorus stretching frequencies. Also the possibility of isolating a complex where $P(OCH_2)_3P$ formed a bridge between two metal atoms might make a worthwhile investigation.

Table 8. Infrared spectra of transition metal complexes of $P(OCH_2)_3P$ in the carbonyl stretching region[a]

Compound	ν(CO) (cm^{-1})		
$Cr(CO)_5(P(OCH_2)_3P)$		1940 vs[b]	2075 w
$Mo(CO)_5(P(OCH_2)_3P)$		1952 vs	2078 w
$Mo(CO)_5(P(CH_2O)_3P)$		1955 vs	2079 w
cis-$Cr(CO)_4(P_2O_3C_3H_6)_2$	1920 vs	1948 sh	2040 m
trans-$Cr(CO)_4(P_2O_3C_3H_6)_2$	1918 vs		
cis-$Mo(CO)_4(P_2O_3C_3H_6)_2$	1926 vs	1950 sh	2042 m
cis-$W(CO)_4(P_2O_3C_3H_6)_2$	1930 vs	1950 sh	2042 m

[a]All spectra obtained in CH_2Cl_2 solution

[b]vs = very strong, sh = shoulder, m = medium and w = weak

Table 9. Proton chemical shifts (ppm downfield from $Si(CH_3)_4$) and coupling constants J (Hz)[a]

Compound	Methylene	J_{POCH}	J_{PCH}
$P(OCH_2)_3P$[b]	4.45	2.7	9.3
$SP(OCH_2)_3P$[c]	5.20	7.8	7.8
$Cr(CO)_5(P(OCH_2)_3P)$	4.88	5.2	8.5
$Mo(CO)_5(P(OCH_2)_3P)$	4.85	5.2	8.4
$Mo(CO)_5(P(CH_2O)_3P)$	4.98	5.4	2.3
cis-$Cr(CO)_4(P_2O_3C_3H_6)_2$	4.80[d]		
trans-$Cr(CO)_4(P_2O_3C_3H_6)_2$	4.75[d]		
cis-$Mo(CO)_4(P_2O_3C_3H_6)_2$	4.54[d]		
cis-$W(CO)_4(P_2O_3C_3H_6)_2$[e]	4.90[d]		

[a]All spectra obtained in CH_3CN solution unless otherwise indicated.

[b]CCl_4 solution

[c]DMSO solution

[d]Center of a multiplet 30 Hz wide

[e]Acetone solution

2,6,7-TRITHIA-4-METHYL-1-PHOSPHABICYCLO [2.2.2] OCTANE AND DERIVATIVES

The bicyclic phosphorus compounds $P(SCH_2)_3CCH_3$, $OP(SCH_2)_3CCH_3$ and $SP(SCH_2)_3CCH_3$ and the arsenic analogue of $P(SCH_2)_3CCH_3$, namely $As(SCH_2)_3CCH_3$, are described for the first time and their infrared and proton nmr spectral properties reported. In other reports, bicyclic analogues of these four compounds were characterized in which the bridging substituents on the group V atom are OCH_2 (2), $N(CH_3)CH_2$ (49) and CH_2O (50). $P(SCH_2)_3CCH_3$ and $As(SCH_2)_3CCH_3$ were synthesized in a continuation of our studies of the variation in ligand properties of the phosphorus atom as the electronegativity of the substituents on phosphorus is altered in these molecules of relatively constant steric requirements.

Experimental

The trimercaptan $CH_3C(CH_2SH)_3$ (51) and $P(N(CH_3)_2)_3$ (52) were prepared as described elsewhere. Tris-dimethylaminoarsine $As(N(CH_3)_2)_3$ was synthesized in 45% yield in a manner completely analogous to that used to prepare $P(N(CH_3)_2)_3$. NMR spectra were obtained on a Varian A-60 spectrometer, using tetramethylsilane as an internal standard. Molecular weights were determined by observing the peak position of the ion of highest mass on an Atlas CH4 single focusing mass spectrometer at an energy of 70 ev. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer. Dipole moments were measured by the heterodyne-beat method described elsewhere in

this thesis.

$P(SCH_2)_3CCH_3$ - In preparing the mercaptan $CH_3C(CH_2SH)_3$, difficulty was encountered in attempting to reduce the polysulfide (formed by the reaction of $CH_3C(CH_2Br)_3$ and Na_2S_4) with sodium in liquid ammonia. Often only partial reduction was achieved which may have been due to inadequate stirring of the very viscous reaction mixture. Possibly the partially reduced material is $CH_3C(CH_2SH)(CH_2S_x)_2$ wherein only the open chain is reduced while the ring remains intact. This structure was inferred from the proton nmr spectrum of benzene solution of this compound which in addition to the singlet at 49 Hz for the methyl group, the doublet for the methylene protons appearing at 144 Hz, and the triplet centered at 64 Hz for the SH group, contained an AB pattern centered at 163 Hz with a coupling constant of 11.5 Hz. It was not possible to completely separate this material from the trimercaptan by distillation.

To 3.00 g (17.9 mmoles) of the trimercaptan $CH_3C(CH_2SH)_3$, kept at 70° under an atmosphere of nitrogen while stirring, was added dropwise over a period of 15 min 3.00 g (18.4 mmoles) of $P(N(CH_3)2)_3$. After the evolution of dimethylamine subsided, the temperature was raised to 160° and held there for 30 min. The mixture which solidified on cooling was treated with 5 ml of benzene and filtered. The white solid was sublimed at 110° to give the product as white needles in 60% yield. Attempts to synthesize $P(SCH_2)_3CCH_3$ by routes analogous to that used earlier to synthesize $P(OCH_2)_3CCH_3$ (1) were only partially successful.

Thus addition of PCl_3 to a 3:1 mole ratio of pyridine to trimercaptan afforded only a small amount of product. Transesterification of $P(OCH_3)_3$ with the trimercaptan afforded no detectable product with the properties of $P(SCH_2)_3CCH_3$.

$O = P(SCH_2)_3CCH_3$ - Following the method of Poshkus and co-workers (53), to 0.5 g (2.6 mmoles) of $P(SCH_2)_3CCH_3$ in 25 ml of stirred benzene (which had been dried over sodium) in an atmosphere of nitrogen was added 7.2 g (5.3 mmoles) of SO_2Cl_2. A precipitate formed immediately and after stirring for five minutes the reaction mixture was filtered and washed with pentane. The solid, which fumed in moist air, was treated with 8 ml of water and filtered. The resulting yellow solid was shaken with 5 ml of carbon disulfide for 5 minutes. After the mixture was filtered, the remaining white solid was washed with pentane and sublimed under vacuum at 130° to give a 20% yield of $OP(SCH_2)_3CCH_3$.

Several attempts at oxidizing $P(SCH_2)_3CCH_3$ to $OP(SCH_2)_3CCH_3$ proved unsuccessful before the sulfuryl chloride method was tried. The procedure given by Lippert and Reid (54) for the oxidation of $P(SCH_3)_3$ using 3% H_2O_2 in glacial acetic acid yielded only a small amount of starting material. Similar results were obtained using 30% H_2O_2 in glacial acetic acid which was used by Doering and Levy (51) to oxidize $CH_3C(CH_2S)_3CH$ to $CH_3C(CH_2SO_2)_3CH$. Bubbling N_2O_4, O_2 and O_3 through a solution of $P(SCH_2)_3CCH_3$ in $CHCl_3$, C_2H_5OH and CH_2Cl_2, respectively, produced no characterizable solid. Similarly negative results were observed for reactions of the trimercaptan with $OP(N(CH_3)_2)_3$ or

$OPCl_3$ in the presence of a 3:1 mole ratio of N,N-dimethylaniline. The trimercaptan was reacted with sodium in liquid ammonia to form the trisodium salt of the mercaptan. After the ammonia had evaporated a THF solution of $OPCl_3$ was added and the mixture refluxed for 12 hr. This afforded only a small amount of water-insoluble material.

$S = P(SCH_2)_3CCH_3$ - In a sealed tube was placed a mixture of 2.00 g (1.02 mmoles) of $P(SCH_2)_3CCH_3$ and 0.033 g (1.02 mmoles) of sulfur. After heating the tube at 120° for 2 hr. and cooling, the pale yellow solid was finely ground and shaken with 20 ml of carbon disulfide for 2 hr. to remove any unreacted sulfur. After filering and washing with pentane, the white solid was sublimed at 180° under vacuum to give $SP(SCH_2)_3CCH_3$ in 90% yield.

$As(SCH_2)_3CCH_3$ - The reaction of 5.0 g (29 mmoles) of the trimercaptan $CH_3C(CH_2SH)_3$ with 6.0 g (29 mmoles) of $As(N(CH_3)_2)_3$ was carried out in a manner similar to that described for $P(SCH_2)_3CCH_3$. After the evlolution of dimethylamine subsided the temperature was raised to 100° for 30 min. A white solid formed on cooling which was sublimed at 110° from a yellow oil which also formed in the reaction mixture. Following two additional subliminations to remove all traces of the contaminating oil, a yield of 60% of sublimed $As(SCH_2)_3CCH_3$ was realized.

Discussion

There are two pecularities worthy of note in the synthesis of $P(SCH_2)_3CCH_3$ and $OP(SCH_2)_3CCH_3$. It is not clear why the trans-

amination reaction of the trimercaptan with $P(N(CH_3)_2)_3$ worked so well while the transesterification of $P(OCH_3)_3$ and the metathesis of PCl_3 in pyridine with the trimercaptan was unsuccessful. All three of these procedures, however, have been used to prepare $P(OCH_2)_3CCH_3$ in good yield from the trialcohol $CH_3C(CH_2OH)_3$ (2,25,55). The reason for the resistance of $P(SCH_2)_3CCH_3$ to oxidation by methods already mentioned is also not obvious. In the reaction of $P(SCH_2)_3CCH_3$ with sulfuryl chloride it is possible that the fuming solid formed is an adduct. Bell (56) claimed the isolation of an addition product between triethyl phosphite and thionyl chloride, however, other investigations (53,57,58,59,60) have not been able to substantiate this claim.

The infrared spectra of these compounds are consistent with the assigned structures. The P= S stretching frequency occurs as an intense band at 672 cm^{-1} (KBr pellet) which compares favorably with 685 cm^{-1} for $S=P(SCH_3)_3$ (61). The band attributed to the P= O stretching frequency consists of a very strong band at 1202 cm^{-1} with a shoulder at 1214 cm^{-1} (KBr pellet), which is in good agreement with the assignment of the phosphoryl stretching mode for $O=P(SC_2H_5)_3$ at 1200 cm^{-1} (62).

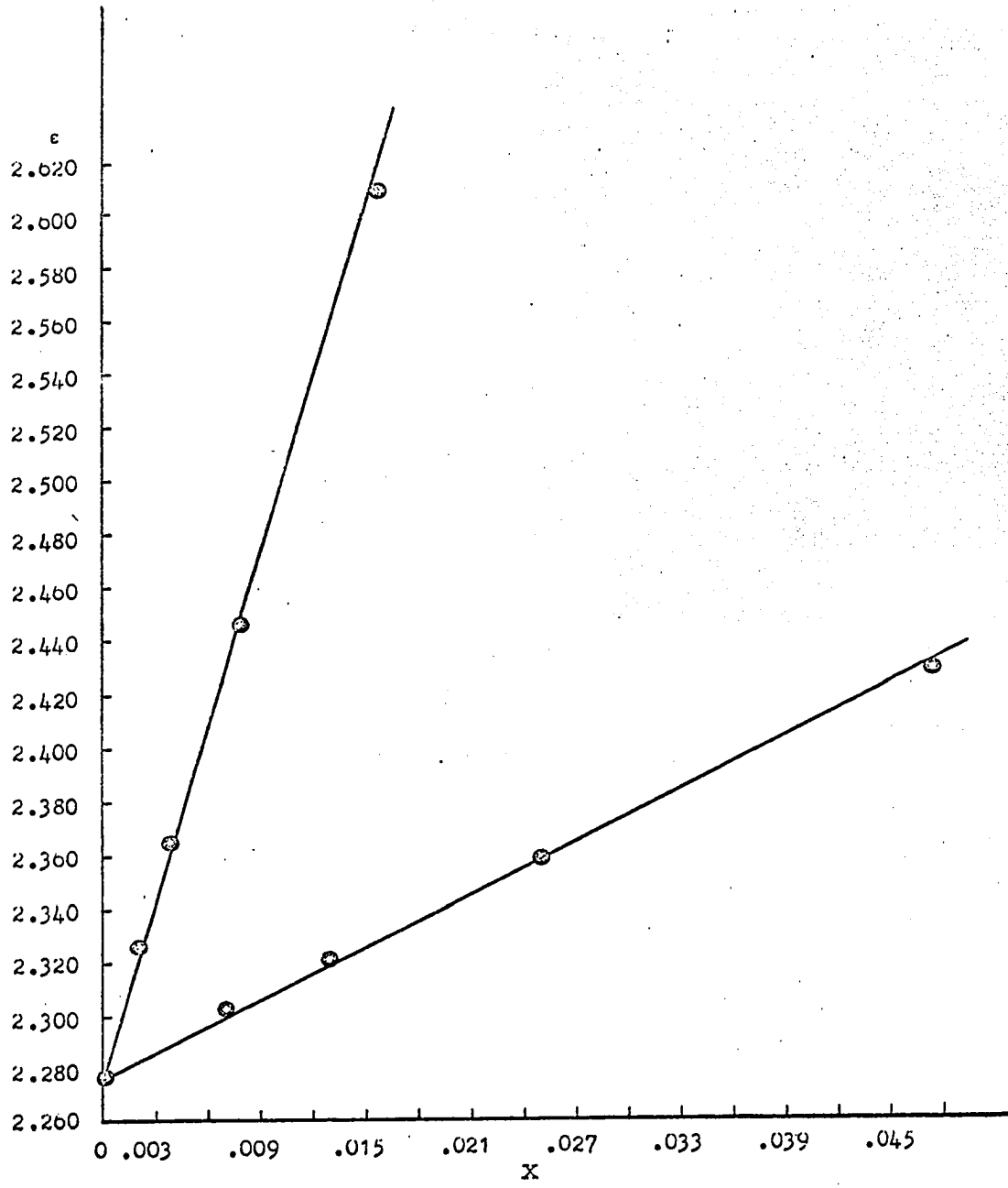
In Table 11 it can be seen that J_{PSCH} increases in the series $P(SCH_2)_3CCH_3 < SP(SCH_2)_3CCH_3 < OP(SCH_2)_3CCH_3$. Although this is not the trend observed for the 2,6,7-trioxa analogues of these compounds, in which J_{POCH} is larger for the sulfide than the oxide, it is the trend predicted by the increasing electro-

negativity of the Lewis acid bonded to phosphorus. As the electronegativity of this Lewis acid increases, there is an increase in the s character of the P-S bond and a corresponding increase in the coupling.

A plot of dielectric constant versus mole fractions of solute used in calculating the dipole moments of $P(SCH_2)_3CCH_3$ and $P(SCH_3)_3$ is given in Figure 8. On comparing the dipole moments in Table 12 for these compounds, it is seen that constraint of the thioalkyl moieties augments the overall moment. This was noted previously in the case of $P(OCH_3)_3$ and $P(OCH_2)_3CCH_3$ and was attributed to the orientation of the chalcogen lone-pair electrons in the polycycle. The lower moments of the thiophosphites relative to the phosphites (ca 0.3 D) reflects the lower C-S bond moment which arises from the smaller difference in the electronegativities between carbon and sulfur than between carbon and oxygen.

In a continuation of the study of transition metal carbonyl complexes $P(SCH_2)_3CCH_3$ was reacted with chromium hexacarbonyl. The resulting green solid proved to be a mixture of $Cr(CO)_5(P(SCH_2)_3CCH_3)$ and cis-$Cr(CO)_4(P(SCH_2)_3CCH_3)_2$ even after recrystallizing from CH_3CN. Chromatography with benzene and a silica gel column afforded separation of the two compounds. The colorless mono-substituted compound on recrystallizing from CH_3CN yielded a mixture of white plates and pale green needles. This seems to indicate that on heating the mono-substituted compound decomposes to form the green cis-disubstituted product.

Figure 8. The plot of dielectric constant (ϵ) versus solute mole fraction (X) for $P(SCH_2)_3CCH_3$ (⊙) and $P(SCH_3)_3$ (o) in benzene at 25.00±0.05°


ε
2.620
2.600
2.580
2.560
2.540
2.520
2.500
2.480
2.460
2.440
2.420
2.400
2.380
2.360
2.340
2.320
2.300
2.280
2.260
0
.003
.009
.015
.021
.027
.033
.039
.045
x

In CH_2Cl_2 solution the carbonyl stretching frequencies for $Cr(CO)_5(P(SCH_2)_3CCH_3)$ are 1950 and 2073 cm^{-1} and for cis-$Cr(CO)_4(P(SCH_2)_3CCH_3)_2$ they appeared at 1925, 1948 and 2027 cm^{-1}. Table 2 lists the nmr data for these compounds. It is interesting that there is very little change in the chemical shifts of the protons of the ligand, $P(SCH_2)_3CCH_3$, upon coordination. The differences in the spectra of the mono-substituted carbonyl compound and the free ligand are so small that an infrared spectrum was obtained on the same solution used to obtain the nmr spectrum to prove the presence of $Cr(CO)_5(P(SCH_2)_3CCH_3)$. The differences in the nmr spectra of the cis-disubstituted complex and the free ligand are greater but they are not as large as those of the analogous 2,6,7-trioxa compound and its complexes (13).

Unfortunately, this work is still in a very preliminary stage because of a lack of time necessary to complete it.

Suggestions for Future Work

A continuation of the study of the carbonyl complexes and the investigation of complexes with metal ions might prove very fruitful, especially in comparing the properties of these complexes with those of $P(OCH_2)_3CCH_3$.

Because $As(SCH_2)_3CCH_3$ seems to be more stable than $As(OCH_2)_3CCH_3$, its carbonyl complexes might also be more stable. If this is true, a study of the far infrared spectra of the carbonyl complexes of $As(SCH_2)_3CCH_3$ and $P(SCH_2)_3CCH_3$ should prove valuable in determining metal-phosphorus stretching

frequencies and possibly metal-arsenic stretching frequencies. Also, a study of the proton nmr spectra of the carbonyl complexes of $P(SCH_2)_3CCH_3$ would be interesting from the point of view of determining the amount of phosphorus-phosphorus coupling in the disubstituted complexes.

To complete the work on the polycyclic thiophosphites the synthesis of $P(SCH)_3(CH_2)_3$ and its derivatives and complexes should be attempted.

Table 10. Analytical data, molecular weights, and melting points

Compound	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Phosphorus, % Calcd	Phosphorus, % Found	Sulfur, % Calcd	Sulfur, % Found	Mol wt Calcd	Mol wt Found	Melting point °C
$P(SCH_2)_3CCH_3$	30.60	30.58	4.62	4.59	15.78	15.71	49.00	49.06	196	196	187-189
$OP(SCH_2)_3CCH_3$	28.29	28.41	4.27	4.34	14.59	14.46	45.31	45.15	212	212	236-239
$SP(SCH_2)_3CCH_3$	26.30	26.33	3.97	4.05	13.55	13.52	56.20	56.47	228	228	286-290
$As(SCH_2)_3CCH_3$	25.00	24.86	3.78	3.73	31.19[a]	31.36[a]	40.04	39.79	240	240	118-120

[a]Arsenic %

Table 11. Proton chemical shifts (ppm downfield from $Si(CH_3)_4$) and coupling constant J(Hz)[a]

Compound	Methylene	Methyl	J_{PSCH}
$P(SCH_2)_3CCH_3$	2.87	1.11	2.1
$OP(SCH_2)_3CCH_3$[b]	3.38[c]	1.05	11.6
$SP(SCH_2)_3CCH_3$[b]	3.32[c]	1.04	10.0
$As(SCH_2)_3CCH_3$	2.94	1.09	——
$Cr(CO)_5(P(SCH_2)_3CCH_3)$	2.89[c]	1.12	2.2
cis-$Cr(CO)_4(P(SCH_2)_3CCH_3)_2$	3.15[c]	1.19	3.5

[a]All spectra were obtained in CH_2Cl_2 solution except where indicated otherwise.

[b]Pyridine solution

[c]Doublet

Table 12. Dipole moments

Compound	(D)
$P(OCH_2)_3CCH_3$[a]	4.12[c,d]
$P(SCH_2)_3CCH_3$	3.90[e]
$P(OCH_3)_3$[b]	1.83[f]
$P(SCH_3)_3$	1.51[e]

[a]Source (63)

[b]Source (64)

[c]Dioxane at 25.0°

[d]4.14 in benzene at 25.00°

[e]Benzene at 25.00±0.05°

[f]Carbon tetrachloride at 20.0°

A RELIABLE HETERODYNE-BEAT DIPOLE MOMENT APPARATUS

A transistorized heterodyne-beat dipole moment apparatus has been developed which offers several advantages over commercially available instruments and research models built by other workers.

1. The instrument employs solid state circuitry which favors stability. The drift of a capacitance reading after attaining thermal equilibrium does not exceed 0.1 percent.
2. Dipole moments over a period of one year are reproducible to within 0.02 Debye and within 0.01 Debye over a period of one month.
3. No oscilloscope is necessary and the substitution of a small inexpensive milliammeter incorporated into the circuit also eliminates the appearance of more than one null reading in the measurement of capacitances.
4. The all-nickel cell which remains submerged in the constant temperature bath needs no maintenance and is virtually corrosion free. Since the cell is stationary, capacitance changes in the leads from the instrument to the cell due to movement is eliminated. Solution manipulation under inert atmosphere conditions is facile.
5. The space requirements of the instrument box is only 17 in by 11 in.

6. The sensitivity of the circuitry to temperature changes of the room is made negligible by the use of a Thermotrimmer.
7. The cost of materials and construction is about $450.

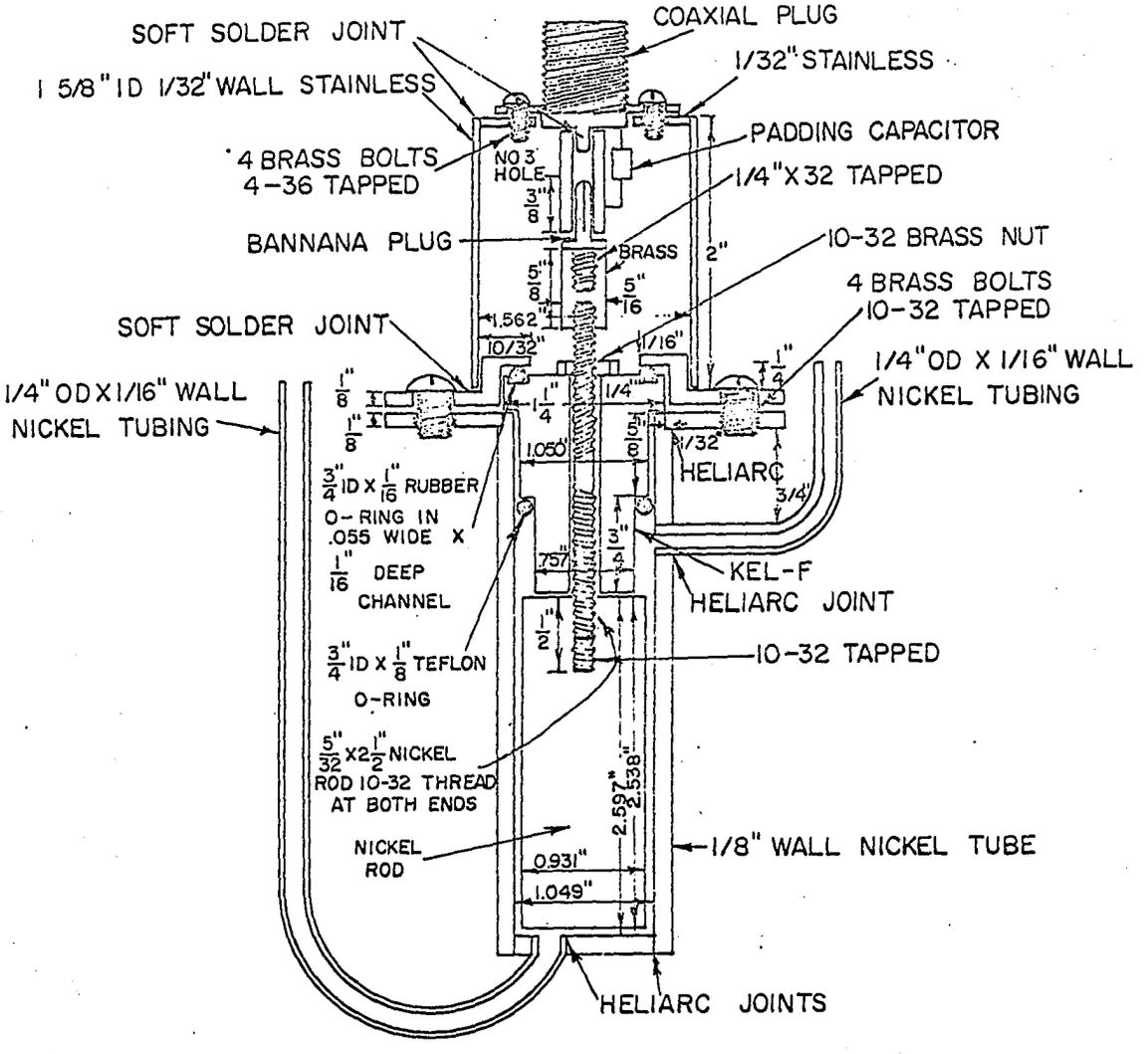
Experimental

Cells - Two cells were constructed (Figure 9) to contain the solutions to be measured. One permits dielectric measurements up to $\epsilon = 3$. This permits the use of many common non-polar solvents such as benzene, cyclohexane, carbon tetrachloride and dioxane. The second cell, which has a smaller volume capacity than the first, is used for solutions of dielectric constants up to $\epsilon = 7$. This allows the use of more polar solvents such as chloroform, when compounds of low solubility in non-polar solvents are studied. This cell can be used with non-polar solvents but the larger cell is about 2.5 times more sensitive to changes in dielectric constant.

The materials used in the construction of the cells consisted of Nickel 200 supplied by Steel Sales, Chicago, Illinois; Kel-F plastic purchased from Auburn Plastics Engineering, Chicago, Ill; Teflon O-rings obtained from Crane Packing, Morton Grove, Illinois; and brass and stainless steel from our shop.

Circuit module - Capacitance changes were measured using a 105 pF section of a General Radio 1422 ME Precision Variable Capacitor. For a more detailed discussion of the electronics of

Figure 9. Nickel cell used in dipole moment measurements; in the smaller cell the outer dimensions of the chamber are 2.644 in. by 0.500 in. with a space of 0.059 in.


SOFT SOLDER JOINT
1 5/8" ID 1/32" WALL STAINLESS
4 BRASS BOLTS
4-36 TAPPED
NO 3 HOLE
3/8
BANNANA PLUG
BRASS
2"
5/8
5/16
1.562"
10/32"
SOFT SOLDER JOINT
1/4" OD X 1/16" WALL
NICKEL TUBING
1/8
1/8
3/4 ID X 1/16 RUBBER
O-RING IN
.055 WIDE X
1/16 DEEP
CHANNEL
3/4 ID X 1/8 TEFLON
O-RING
5/32 X 2 1/2 NICKEL
ROD 10-32 THREAD
AT BOTH ENDS
NICKEL
ROD
0.931"
1.049"
COAXIAL PLUG
1/32" STAINLESS
PADDING CAPACITOR
1/4" X 32 TAPPED
10-32 BRASS NUT
4 BRASS BOLTS
10-32 TAPPED
1/16"
1/4
1/4" OD X 1/16" WALL
NICKEL TUBING
1/4
1.060
5/8
1/32
HELIARC
3/4
3/4
.757
1/4
KEL-F
HELIARC JOINT
1/2
10-32 TAPPED
2.597"
2.538"
1/8" WALL NICKEL TUBE
HELIARC JOINTS

this instrument see Appendix.

Measurements - The solutions used in these studies in general had concentrations in the range of 10^{-2} to 10^{-3} mole fraction (X) of solute. For compounds with low moments (0 - 1.5 D) the upper limit of this range might reach $8 \times 10^{-2}X$. If the compound had a large moment, the lower limit of the concentration range might be as low as $10^{-4}X$. The solutions are introduced into and removed from the cell by means of suction from a water aspirator. All the air or inert gas that enters the cell first passes through a drying tube containing indicating Drierite. Generally four or five solutions of varying concentration are used in obtaining the plot of X versus dielectric constant (ϵ) for a given compound. Because of the high stability of this instrument each sample was allowed to thermally equilibrate in the cell for five minutes before a reading was made. The drift during this period has never exceeded 0.1%. In order to maintain a uniform temperature throughout a measurement the portion of the cell containing the solution cavity is immersed in a constant temperature bath.

The actual capacitance readings, Δ, obtained from this instrument are differences of the readings with the solution in the cell minus that of dry air in the cell. This reading to four significant figures, is converted to the appropriate dielectric constant by means of a calibration equation. This expression is the equation for the straight line obtained by plotting Δ

for three or four pure solvents versus their known dielectric constants (65). A least squares analysis is then performed on the plot of dielectric constant versus mole fraction to obtain the slope, $\delta\epsilon/\delta X$, of the straight line which best fits the data points. The Cohen-Mniques Equation (66):

$$P_o = \frac{3\,M}{d(\epsilon_o + 2)^2}\,[\delta\epsilon/\delta X + 2n_\infty\,\delta n_\infty/\delta X]$$

where P_o = orientation polarization, M = molecular weight of the pure solvent, d = density of the pure solvent, ϵ_o = observed dielectric constant of the pure solvent, n_∞ = observed index of refraction of the solution extrapolated to infinite wave length, X = solute mole fraction of each solution, $\delta\epsilon/\delta X$ = slope of line of ϵ versus X, and $\delta n_\infty/\delta X$ = slope of line of n versus X is used to calculate P_o. $\delta n_\infty/\delta X$ could be assumed to be zero for the compounds discussed here because at the concentrations involved the slope is very small. (See example in Table 13). This simplifies the above equation by eliminating that part of the expression dealing with refractive index. In all calculations the atomic polarization of the solvent was assumed to be zero. The dipole moment was calculated with the Debye equation (66):

$$\mu = \sqrt{\frac{9k\,TP_o}{4\pi N}} = \sqrt{(4.9850 \times 10^{-38})P_o}$$

where M = dipole moment in e.s.u. cm., k = the Boltzmann con-

stant, 1.38047×10^{-16}, $\pi = 3.1416$, N = Avogadro's Number, and T = absolute temperature, 298.2°K at 25.0°C.

Purification of Materials - Bromobenzene was purified by refluxing over P_4O_{10} for 12 hr and fractionally distilling saving only the middle fraction. Nitrobenzene was also fractionally distilled from P_4O_{10} after refluxing for 12 hr. The middle fraction was fractionally crystallized four times and finally vacuum distilled shortly before the measurements were made. Benzene and dioxane were purified by refluxing over sodium for 24 hr and fractionally distilling with only the middle fraction being used. Cyclohexane was passed through an alumina column 3 cm in diameter and 60 cm long and fractionally distilled from P_4O_{10} through a 45 cm column packed with glass helices saving only the middle fraction. The chloroform was shaken three times with concentrated sulfuric acid, neutralized with $NaHCO_3$ and washed with water. After drying over $MgSO_4$ it was fractionally distilled under a nitrogen atmosphere saving only the middle fraction. Carbon tetrachloride was refluxed over P_4O_{10} for 12 hr and fractionally distilled retaining only the middle fraction. All these liquids were stored over Linde 4A Molecular seives, under nitrogen and in the dark. The data obtained for the bromobenzene and nitrobenzene is given in Table 14. The plots of dielectric constant versus mole fraction are shown in Figures 10 and 11.

Figure 10. The plot of dielectric constant (ϵ) versus solute mole fraction (X) for $C_6H_5NO_2$ (o) and C_6H_5Br (o) in benzene at 25.00±0.05°

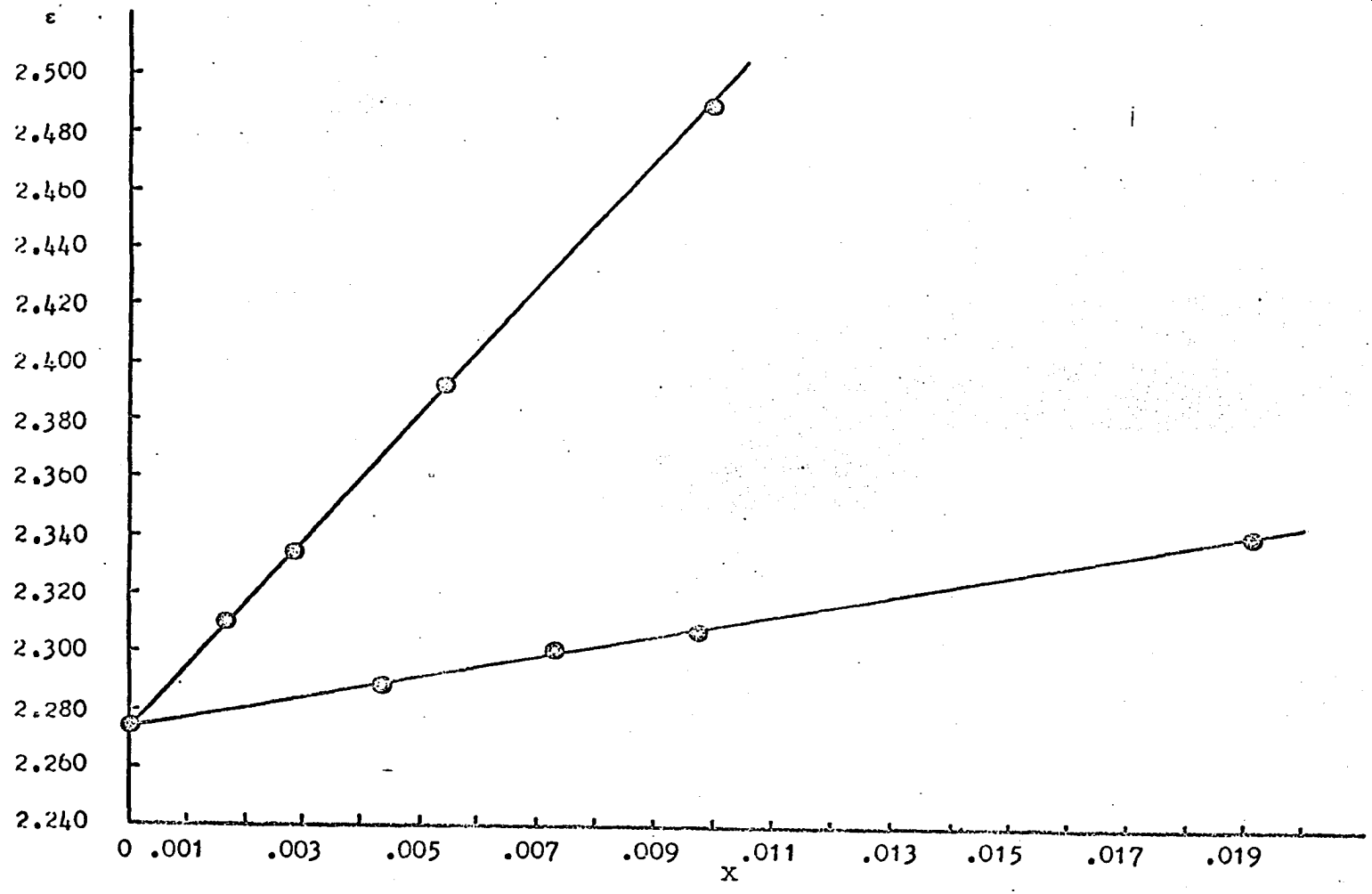
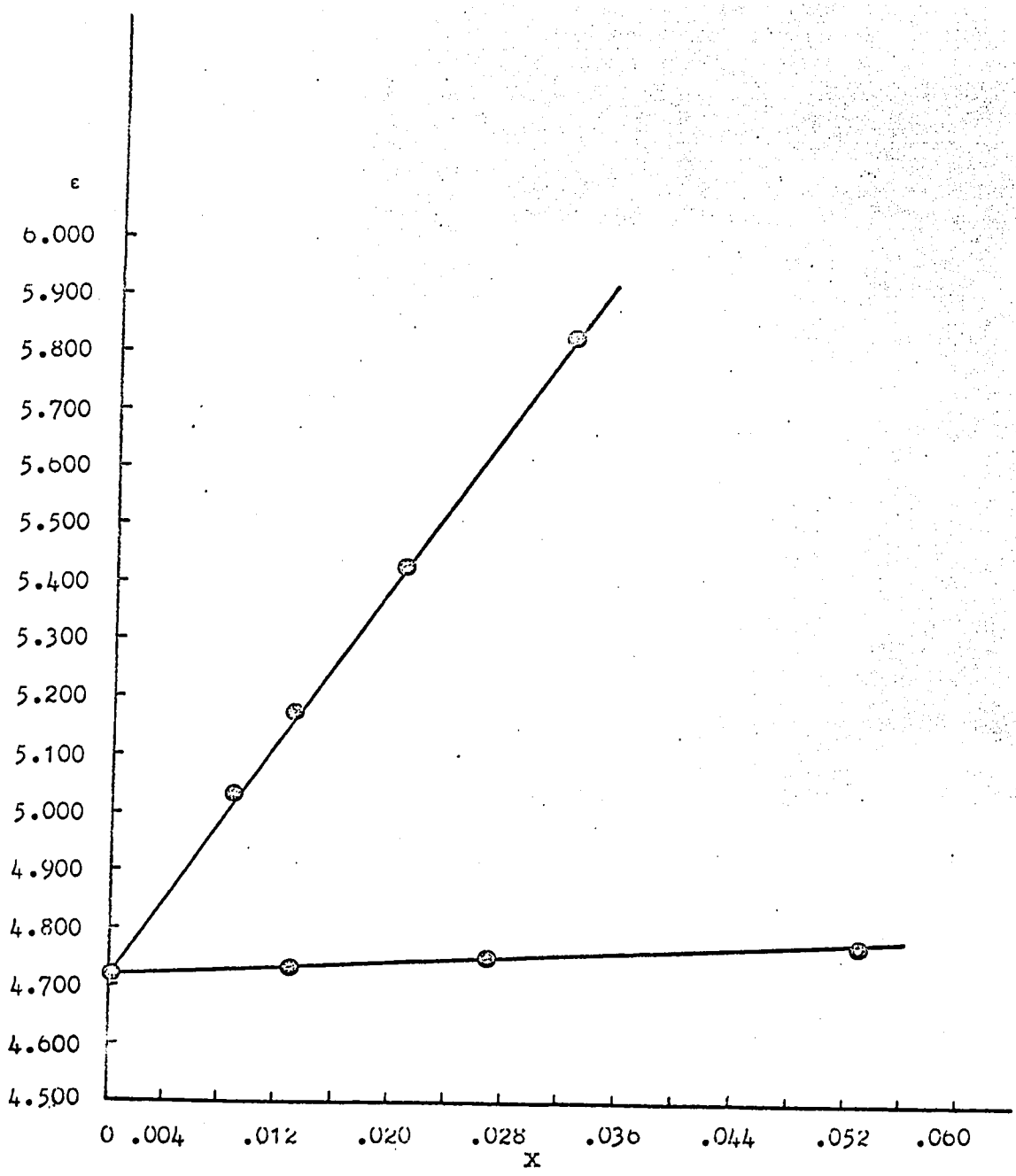

ε
2.500
2.480
2.460
2.440
2.420
2.400
2.380
2.360
2.340
2.320
2.300
2.280
2.260
2.240
0
.001
.003
.005
.007
.009
.011
.013
.015
.017
.019
x

Figure 11. The plot of dielectric constant (ϵ) versus solute mole fraction (X) for $C_6H_5NO_2$ (•) and C_6H_5Br (o) in chloroform at 25.00±0.05°


ε
6.000
5.900
5.800
5.700
5.600
5.500
5.400
5.300
5.200
5.100
5.000
4.900
4.800
4.700
4.600
4.500
0
.004
.012
.020
.028
.036
.044
.052
.060
x

Discussion

The data given in Table 15 shows that the moments of bromo and nitrobenzene obtained in benzene are in excellent agreement with the literature. The dipole moments of nitrobenzene obtained in benzene at 25° listed in the literature range from 3.85 - 4.08 D (67). By considering the large amount of data for this compound, McClellan has obtained what he calls a recommended value of 3.93 D. There was not sufficient data available for McClellan to do the same for bromobenzene. However, the values in the literature for bromobenzene in benzene at 25° fortunately cover a much smaller range 1.5 - 1.57 D (67). It should be noted that the data for both these compounds include values obtained since 1950.

In the case of the values obtained in chloroform at 25° there are very little data available for comparison. There are no data for bromobenzene, and only two values obtained at 25° for nitrobenzene. These values are 3.08 and 3.20 D (67) and were determined thirty or more years ago. Unfortunately, this is the one of the few readily available compounds for which there is more than one value reported.

The values for the other compounds listed in Table 15 have been included as further evidence for the precision and reliability of this instrument. The data used to calculate these moments is given in Table 16. The larger moment for quin-

uclidine $N(C_2H_4)_3CH$, in carbon tetrachloride than in benzene is apparently due to a weak interaction between the amine nitrogen with the chlorines of the carbon tetrachloride (68).

A consistent set of bond moments could not be found that gave calculated dipole moments comparing favorably with the measured moments given in Table 15. This is possibly due to the effect of the lone pair electrons on phosphorus and oxygen. From building models, the lone pairs on oxygen seem to be directed out over the bridge head atom and, therefore, might contribute significantly to the total moment of the molecule. The lone pair of electrons on the phosphorus bridge head atom are probably markedly influenced by the electronegativity of the groups bonded to phosphorus and the bond angles involved in these bonds. These two factors, therefore, might account for poor correlation between measured moments of rigid systems and the values calculated using bond moments obtained from non-rigid systems.

In Table 17 are listed the dipole moments of some carbonyl complexes. In comparing the moments of the quinuclidine complexes with those of triethylenediamine, it is interesting to note that the difference between the moments of complexes containing the same metal is close to the difference between the moments of the two ligands which is 1.22 D. (The moment of triethylenediamine is zero). The main reason for this agreement probably lies in the fact that the steric requirements of these two ligands are very similar. This is born out by a comparison

of the moments of the molybdenum pentacarbonyl complexes of $P(N(CH_3)2)_3$ and $P(N(CH_3)CH_2)_3CCH_3$. The moments of these ligands are 1.21 and 1.62, respectively. The fact that the difference between the moments of these complexes is about one-half the difference of the moments of the ligands is an indication that on complexation $P(N(CH_3)_2)_3$ is forced into a geometry which is more like that of the constrained $P(N(CH_3)CH_2)_3CCH_3$ than the non-rigid system. Because of this factor, it is difficult to obtain meaningful comparisons between the moments of such complexes.

Suggestions for Future Work

First of all, to make a complete study of the dipole moments of the various polycycles mentioned, a set of bond moments and lone pair moments that give a good correlation between calculated and measured moments must be obtained. Also, continued work with complexes may lead to the postulation of metal-ligand moments which could permit the calculation of the extent of pi-bonding in various metal-ligand bonds.

Table 13. Index of refraction (n) at 25.0° in Benzene

Compound	Mole Fraction	Index of Refraction	$\delta n_\infty / \delta X$
$N(C_2H_4)_3CH$	0.10943	1.5000	-0.01485
	0.06538	1.5005	
	0.006162	1.5016	
	0.0	1.5015	

Table 14. Measurements at 25.00 ± 0.05° for molar polarization (P_o) Calculations of $C_6H_5NO_2$ and C_6H_5Br

Compound	Δ	Mole Fraction	Dielectric Constant	$\delta\epsilon/\delta X$	P_o
$C_6H_5NO_2$[a]	50.63	0.009992	2.490	21.52	314.0
	47.22	0.005498	2.393		
	45.18	0.002843	2.335		
	44.33	0.001686	2.311		
	43.08	0.0	2.275		
$C_6H_5NO_2$[b]	65.47	0.03252	5.835	34.25	181.5
	60.06	0.02066	5.434		
	56.56	0.01302	5.175		
	54.68	0.009047	5.036		
	50.42	0.0	4.720		
C_6H_5Br[a]	45.41	0.01913	2.341	3.454	50.39
	44.27	0.009725	2.309		
	44.02	0.007361	2.303		
	43.62	0.004346	2.290		
	43.08	0.0	2.275		

[a]Benzene solution

[b]Chloroform solutions

Table 14. (Continued)

Compound	Δ	Mole Fraction	Dielectric Constant	$\delta\epsilon/\delta X$	P_o
C_6H_5Br[b,c]	51.23	0.05317	4.780	1.059	5.611
	50.86	0.02700	4.753		
	50.66	0.01312	4.738		
	50.47	0.0	4.724		

[c]Five solutions were prepared, but the fourth one was contaminated while adding solvent.

Table 15. Dipole moments of bromo- and nitrobenzene and various polycycles at 25.00±0.05°

Compound	Solvent	μ(D)
C_6H_5Br	C_6H_6	1.58[a,b], 1.57[a,b], 1.5-1.57[c]
	$CHCl_3$	0.52[a]
$C_6H_5NO_2$	C_6H_6	3.92[a], 3.93[c]
	$CHCl_3$	2.98[a]
$P(OCH_2)_3CCH_3$	C_6H_6	4.13[a]
	CCl_4	4.12[a]
	C_6H_{12}	3.82[a], 3.91[d]
	$O(CH_2CH_2)_2O$	4.15[d]
$P(OCH)_3(CH_2)_3$	C_6H_6	4.42[a]
	CCl_4	4.48[a]
	$O(CH_2CH_2)_2O$	4.7[d]
$As(OCH_2)_3CCH_3$	C_6H_6	2.68[a]
	CCl_4	2.64[a]
	$O(CH_2CH_2)_2O$	2.36[d]
$As(OCH)_3(CH_2)_3$	C_6H_6	2.89[a]
	CCl_4	2.98[a]
$HC(OCH_2)_3CCH_3$	C_6H_6	3.19[a]
	CCl_4	3.21[a]

[a]This work

[b]These values obtained 12 months apart

[c]Source (67)

[d]Source (63)

Table 15. (Continued)

Compound	Solvent	μ (D)
$HC(OCH)_3(CH_2)_3$	C_6H_6	3.34[a]
$CH_3C(OCH_2)_3CCH_3$	C_6H_6	2.72[a]
	CCl_4	2.76[a]
$CH_3C(OCH)_3(CH_2)_3$	C_6H_6	2.95[a]
$CH_3C(OCH_2)_3P$	C_6H_6	1.54[a]
	CCl_4	1.53[a]
$N(C_2H_4)_3CH$	C_6H_6	1.21[a,b], 1.23[a,b]
	CCl_4	1.57[a,e], 1.58[a,e]
	C_6H_{12}	1.17[a]
$P(N(CH_3)CH_2)_3CCH_3$	C_6H_6	1.62[f]

[e]These values obtained 1 month apart

[f]Source (69)

Table 16. Measurements at 25.00±0.05° for molar polarization (P_o)

Compound	Δ	Dielectric Constant	Mole Fraction	$\delta\epsilon/\delta X$	P_o
$P(OCH_2)_3CCH_3$[a]	49.33	2.454	0.01045	21.34	347.4
	45.85	2.355	0.005664		
	43.35	2.283	0.002395		
	42.39	2.256	0.001078		
	41.53	2.231	0.0		
$P(OCH_2)_3CCH_3$[b]	41.57	2.237	0.01138	19.07	298.1
	38.30	2.140	0.006200		
	36.54	2.088	0.003542		
	35.70	2.063	0.002246		
	34.20	2.019	0.0		
$P(OCH)_3(CH_2)_3$[c]	52.13	2.535	0.009455	27.38	399.4
	48.07	2.418	0.005225		
	46.10	2.362	0.003181		
	44.42	2.314	0.001352		
	43.06	2.275	0.0		

[a]Carbon tetrachloride solutions

[b]Cyclohexane solutions

[c]Benzene solutions

Table 16. (Continued)

Compound	Δ	Dielectric Constant	Mole Fraction	δε/δX	P_o
$P(OCH)_3(CH_2)_3$[a]	49.78	2.467	0.009390	25.17	409.8
	46.41	2.371	0.005638		
	45.04	2.332	0.004018		
	42.76	2.266	0.001418		
	41.50	2.230	0.0		
$As(OCH_2)_3CCH_3$[c]	46.97	2.387	0.01109	10.04	146.5
	44.70	2.322	0.005056		
	43.82	2.297	0.002273		
	43.54	2.288	0.001354		
	43.07	2.275	0.0		
$As(OCH_2)_3CCH_3$[a]	44.48	2.316	0.009583	8.721	142.0
	43.60	2.290	0.006912		
	42.46	2.258	0.002844		
	41.90	2.241	0.001187		
	41.52	2.231	0.0		
$As(OCH)_3(CH_2)_3$[c]	47.40	2.399	0.01058	11.73	171.2
	45.97	2.358	0.007144		
	44.74	2.323	0.004016		
	43.55	2.289	0.001207		
	43.05	2.275	0.0		

Table 16. (Continued)

Compound	Δ	Dielectric Constant	Mole Fraction	$\delta\epsilon/\delta X$	P_o
$As(OCH)_3(CH_2)_3$[a]	45.57	2.347	0.01049	11.14	181.4
	44.26	2.309	0.007064		
	43.31	2.282	0.004664		
	42.37	2.255	0.002194		
	41.48	2.230	0.0		
$HC(OCH_2)_3CCH_3$[c]	46.15	2.374	0.006868	14.27	208.2
	45.81	2.354	0.005273		
	43.99	2.302	0.001571		
	43.74	2.294	0.001142		
	43.05	2.275	0.0		
$HC(OCH_2)_3CCH_3$[a]	49.02	2.446	0.01650	12.93	210.6
	44.80	2.325	0.007004		
	43.16	2.278	0.003404		
	42.12	2.248	0.001077		
	41.50	2.230	0.0		
$HC(OCH)_3(CH_2)_3$[c]	47.46	2.401	0.008023	15.65	228.3
	45.77	2.352	0.004895		
	45.16	2.335	0.003721		
	43.69	2.293	0.0001065		
	43.06	2.275	0.0		

Table 16. (Continued)

Compound	Δ	Dielectric Constant	Mole Fraction	$\delta\epsilon/\delta X$	P_o
$CH_3C(OCH_2)_3CCH_3$[c]	48.63	2.434	0.01541	10.33	150.7
	45.84	2.354	0.007347		
	44.85	2.326	0.004738		
	43.71	2.294	0.001707		
	43.07	2.275	0.0		
$CH_3C(OCH_2)_3CCH_3$[a]	46.30	2.368	0.01426	9.586	156.0
	43.77	2.295	0.006726		
	43.53	2.288	0.006021		
	42.40	2.256	0.002540		
	41.51	2.231	0.0		
$CH_3C(OCH)_3(CH_2)_3$[c]	46.83	2.383	0.008763	12.18	177.7
	45.72	2.351	0.006197		
	44.30	2.310	0.002864		
	43.66	2.292	0.001298		
	43.09	2.276	0.0		
$CH_3C(OCH_2)_3P$[c]	44.61	2.319	0.01313	3.344	48.79
	43.85	2.298	0.006568		
	43.64	2.292	0.004806		
	43.30	2.282	0.001824		
	43.07	2.275	0.0		

Table 16. (Continued)

Compound	Δ	Dielectric Constant	Mole Fraction	δε/δX	P_o
$CH_3C(OCH_2)_3P$[a]	42.87	2.270	0.01314	2.948	48.00
	41.87	2.241	0.003425		
	41.59	2.233	0.0006555		
	41.51	2.231	0.0		
$N(C_2H_4)_3CH$[c,d]	50.80	2.509	0.1094	2.101	30.65
	47.67	2.416	0.06538		
	43.38	2.290	0.006162		
	42.84	2.274	0.0		
$N(C_2H_4)_3CH$[c,d]	47.98	2.416	0.06793	2.060	30.05
	45.86	2.355	0.03820		
	44.18	2.307	0.01461		
	43.54	2.289	0.006148		
	43.08	2.276	0.0		
$N(C_2H_4)_3CH$[b]	39.39	2.172	0.08599	1.801	28.15
	37.25	2.109	0.04686		
	35.52	2.058	0.02210		
	34.67	2.033	0.007711		
	34.19	2.019	0.0		

[d]These two measurements were made 12 months apart

Table 16. (Continued)

Compound	Δ	Dielectric Constant	Mole Fraction	δε/δX	P_o
$N(C_2H_4)_3CH$[a,e]	51.11	2.505	0.08844	3.104	50.52
	46.57	2.375	0.04607		
	43.85	2.298	0.02116		
	42.40	2.256	0.007651		
	41.49	2.230	0.0		
$N(C_2H_4)_3CH$[a,e]	44.55	2.318	0.02728	3.156	51.38
	42.92	2.271	0.01230		
	42.31	2.254	0.006915		
	41.54	2.232	0.0		
$Cr(CO)_5N(C_2H_4)_3CH$[c]	45.92	2.357	0.001584	51.53	751.9
	44.63	2.320	0.0008870		
	43.96	2.301	0.0005052		
	43.48	2.287	0.0002490		
	43.08	2.276	0.0		
$Cr(CO)_5N(C_2H_4)_3N$[c]	43.96	2.300	0.0007621	31.93	465.9
	43.54	2.288	0.0003684		
	43.39	2.284	0.0002340		
	43.29	2.281	0.0001812		
	43.11	2.276	0.0		

[e]These two measurements were made 1 month apart

Table 16. (Continued)

Compound	Δ	Dielectric Constant	Mole Fraction	δε/δX	P_o
$Mo(CO)_5N(C_2H_4)_3CH^c$	50.57	2.490	0.003862	55.64	811.8
	48.11	2.420	0.002587		
	45.68	2.350	0.001332		
	44.40	2.313	0.0006752		
	43.05	2.275	0.0		
$Mo(CO)_5N(C_2H_4)_3N^c$	44.77	2.323	0.001345	35.34	515.6
	44.01	2.302	0.0007339		
	43.50	2.287	0.0003454		
	43.33	2.282	0.0001668		
	43.09	2.275	0.0		
$W(CO)_5N(C_2H_4)_3CH^c$	47.61	2.405	0.002061	63.19	922.0
	45.47	2.344	0.001090		
	44.84	2.326	0.0007938		
	44.09	2.304	0.0004705		
	43.06	2.275	0.0		

Table 17. Dipole moments of various carbonyl complexes in benzene at 25.00±0.05°

Compound	μ(D)
$Cr(CO)_5N(C_2H_4)_3CH$	6.06[a]
$Mo(CO)_5N(C_2H_4)_3CH$	6.30[a]
$W(CO)_5N(C_2H_4)_3CH$	6.72[a]
$Cr(CO)_5N(C_2H_4)_3N$	4.77[a]
$Mo(CO)_5N(C_2H_4)_3N$	5.02[a]
$Mo(CO)_5P(N(CH_3)_2)_3$	5.54[b]
$W(CO)_5P(N(CH_3)_2)_3$	5.75[b]
$Mo(CO)_5P(N(CH_3)CH_2)_3CCH_3$	5.78[b]
$Mo(CO)_5P(OCH_2)_3CC_2H_5$	6.91[b]
$W(CO)_5P(OCH_2)_3CC_2H_5$	7.01[b]
$Fe(CO)_4As(OCH_2)_3CCH_3$	4.86[c]
cis-$Mo(CO)_4(P(N(CH_3)_2)_3)_2$	6.67 or 6.40[d]
cis-$Mo(CO)_4(P(N(CH_3)_2)_3)(P(OCH_2)_3CC_2H_5)$	8.38[b]
$C_5H_5Mn(CO)_2P(OCH_2)_3CCH_3$	5.39[e]

[a]This work

[b]M. J. McInerney, Ames, Iowa, Private Communications, 1966

[c]R. D. Compton, Ames, Iowa, Private Communications, 1966

[d]R. J. Pipal, Ames, Iowa, Private Communications, 1966

[e]Source (70)

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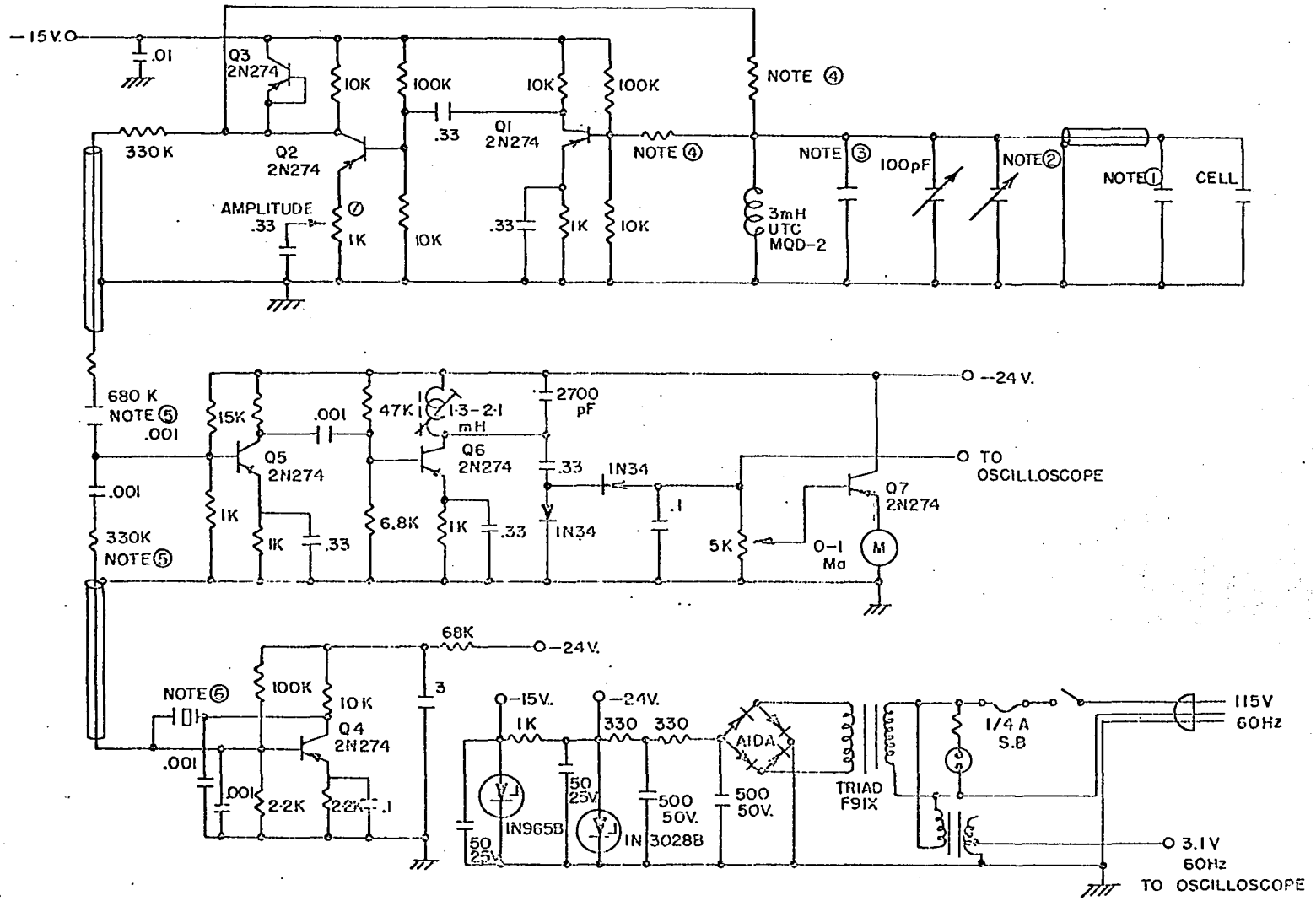
APPENDIX

The sample cell forms part of the capacitance of a parallel resonant circuit incorporating a 3 millihenry inductor, the remainder being made up of the precision variable capacitor, an air-dielectric variable capacitor for preliminary setting, fixed silver-mica capacitors in the cell cap to bring the total cell capacitance up to approximately 600 pF, a Thermotrimmer, and circuit strays. This circuit is excited into resonance at 100 KHz in a modified Franklin oscillator circuit using a transistorized amplifier and coupling resistors of approximately 1 megohm which ensure good isolation of the frequency determining circuit from the amplifier. The amplifier has low phase shift at 100 KHz; its chief contribution to frequency instability being variation of the collector-base capacitance of Q2 with collector voltage. This is compensated by an opposite change in the collector-base capacitance of Q3.

The indicated change in capacitance between a cell empty and filled with benzene was unaltered for air temperatures between 13 and 30°, showing that the temperature coefficient of the standard capacitor would have a negligible effect. Variations in other components of the oscillator were compensated by a capacitor with a variable temperature coefficient (Thermotrimmer, British Radio Electronics Corp.).

The amplifier is enclosed in a plastic foam insulated box to avoid rapid temperature change. A potentiometer in the

Figure 12. The circuit diagram for the dipole moment apparatus, with the following notes: (1) selected to bring the total cell capacitance to approximately 600pF, (2) precision variable capacitor, General Radio type 1422 ME, (3) thermotrimmer, (4) selected for reliable oscillation; nominal value 1 M., (5) selected for equal mixer output from each input. Nominal values shown and (6) Peterson Radio Z-6A, 100 KHz


-15V.
.01
Q3 2N274
10K
100K
10K
100K
NOTE ④
330K
Q2 2N274
.33
Q1 2N274
NOTE ④
NOTE ⑤
100pF
NOTE ②
NOTE ①
CELL
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.33
Ø
1K
10K
.33
1K
10K
3mH UTC MQD-2
680 K NOTE ⑤ .001
.001
330K NOTE ⑤
15K
.001
47K
1·3-2·1 mH
2700 pF
-24 V.
TO OSCILLOSCOPE
Q5 2N274
Q6 2N274
.33
IN34
Q7 2N274
1K
1K
.33
6.8K
1K
.33
IN34
.1
5K
0-1 Ma
M
68K
-24V.
NOTE ⑤
100K
10K
Q4 2N274
3
.001
.001
2·2K
2·2K
.1
-15V.
-24V.
1K
330
330
AIDA
1/4 A S.B
115V 60Hz
50 25V
IN9658
50 25V
IN 3028B
500 50V.
500 50V.
TRIAD F91X
3.1V 60Hz
TO OSCILLOSCOPE

emitter circuit of Q2 permits adjustment of the oscillation amplitude for solvents of varying dielectric loss and the mixer circuit is fed via a high resistor for isolation.

The 100 KHz crystal oscillator is of straightforward design with the crystal thermally insulated in a plastic foam block. The inputs to the mixer are carefully shielded from each other and the high input resistors and low input impedance of Q5 provide isolation of the crystal and variable oscillators sufficient for a true zero-beat to be obtained. There is no evidence of "pulling" of the variable oscillator frequency. After amplification, the combined frequencies are detected and the low-frequency difference voltage is applied to a low cost 0-1 milliampere meter via the emitter follower Q7. Zero frequency difference between the oscillators corresponds to a steady meter reading. The alternative method of comparison of the difference frequency to the 60 Hz line frequency by a Lissajous pattern on an oscilloscope can also be used, but has the disadvantage of giving two nulls.

The power supply provides singly-regulated -24 volt and doubly regulated -15 volt supplies and a 60 Hz oscilloscope reference voltage. Total power consumption is about 10 watts. enabling the instrument to be left on continually.

VITA

The author was born on June 11, 1941, in Oak Park, Illinois to Mr. and Mrs. A. C. Vandenbroucke and is the older of two sons. After completing his elementary education, he attended Immaculate Conception High School in Elmhurst, Illinois where his family had moved when he was eleven. After graduating from high school in 1959 he entered Northwestern University. The following year he entered St. Joseph's College, Rensselaer, Indiana, from which he graduated in 1963 with a B.S. in chemistry.

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The author assumed the responsibilities of an Instructor of Chemistry at Wartburg College, Waverly, Iowa in the fall, 1967.

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