ported in Table II were obtained on THF solutions while Lindner and Behrens used a methylene chloride solution of the anion. Figure 1 shows the infrared spectrum of the $Cr_2(CO)_{10}I^-$ ion taken on (a) a THF solution and (b) a CH_2Cl_2 solution. Obviously the resolution is poorer in the second case. Whether this is due to cation–anion interaction or to another solvent effect is not known. However, a similar loss in resolution has been observed in the solution infrared spectra of other metal carbonyl compounds when the solvent is changed.[23,24] The most likely impurity present in the anions prepared in this study is the mononuclear species. Therefore, the infrared spectra of mixtures of the $Cr(CO)_5I^-$ and $Cr_2(CO)_{10}I^-$ ions were obtained over the concentration range of 25–75% impurity. Only the bands at 2050 and 1918 cm^{-1} increased as the impurity was increased. A new band at 1858 cm^{-1} also appeared. Thus, the spectrum of the monoanion agrees closely with that observed by Lindner and Behrens.[20] However, the agreement between the spectra of the dinuclear species is not good even for the CH_2Cl_2 solution since the strongest reported by Lindner and Behrens is at 1940 cm^{-1}. Thus, it is not obvious whether the differences observed in the spectra are due to (a) a difference in the structure of the two anions or (b) a difference in resolution or other solvent effects.[23,24]

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DAAH01-67-C-0655.

---

(23) G. Bor, *Spectrochim. Acta*, **18**, 817 (1962).
(24) W. Beck and K. Lottes, *Z. Naturforsch.*, **19b**, 987 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND INSTITUTE FOR ATOMIC RESEARCH,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Transition Metal Complexes of Constrained Phosphite Esters. VI. Phosphorus–Metal Stretching Frequencies in Metal Carbonyl Complexes of Polycyclic Phosphites

BY A. C. VANDENBROUCKE, JR., D. G. HENDRICKER, R. E. McCARLEY, AND J. G. VERKADE[1]

Received March 4, 1968

The far-infrared spectra of complexes 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, W) where L = $P(OCH_2)_3CCH_3$, $As(OCH_2)_3CCH_3$, or $N(C_2H_4)_3CH$ (quinuclidine) have been obtained and the absorption bands assigned to ligand vibrations, ν(M–C), δ(M–C–O), and ν(M–P), and bending modes of the general form δ(X–M–Y), where X and Y = C and C, C and P, C and N, or P and P. The preparations and characterization of the new complexes in this study are also given. Improved synthetic and purification techniques now allow an unambiguous assignment of the configurations from infrared data of the *cis* and *trans* group VI complexes of the type $M(CO)_4L_2$, where M = Cr, Mo, and W and L = $P(OCH_2)_3CCH_3$ or $P(OCH)_3(CH_2)_3$. The greater increase in ν(M–P) from the mono- to the corresponding disubstituted *trans*-octahedral carbonyl complexes of $P(OCH_2)_3CR$ (R = CH_3 or $(CH_2)_2CH_3$) compared to the *cis* isomers is tentatively interpreted in terms of the number of π metal orbitals common to both phosphorus ligands and the probable relative π-bonding powers of the carbonyl and phosphorus ligands. The opposite trends in ν(C–O) and ν(M–P) in $Ni(CO)_{4-x}L_x$ (L = PF_3 or $P(OCH_2)_3CCH_3$) upon stepwise substitution of the carbonyl groups are ascribed to the contrasting π-bonding abilities of these two ligands compared to those of a CO group.

Introduction

The degree of metal to phosphorus π bonding in transition metal carbonyl complexes containing phosphorus ligands and the influence of this mode of bonding on the carbonyl stretching frequencies have been interpreted to be significant[2] and of little or no significance.[3] The present systematic far-infrared study of a series of metal carbonyl complexes of the polycyclic phosphites $P(OCH_2)_3CR$ (where R = CH_3 or $(CH_2)_2CH_3$) permitted the assignment of the metal–phosphorus vibration ν(M–P). The trends in ν(M–P) on substitution of carbonyl groups in $Ni(CO)_4$ and $M(CO)_6$ (where M = Cr, Mo, and W) appear in all cases to be dominated by the π-bonding characteristics of the ligand.

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 from the ligand on symmetry grounds. The ν(M–P) vibration(s) in the far-infrared spectra (70–800 cm^{-1}) of 15 metal carbonyl complexes of $P(OCH_2)_3CR$ (where R = CH_3 or $(CH_2)_2CH_3$) of the forms $Ni(CO)_{4-x}L_x$ (x = 1, 2, 3, 4), $Fe(CO)_{5-x}L_x$ (x = 1, 2), and $M(CO)_{6-x}L_x$ (x = 1, 2, and M = Cr, Mo, and W) were assigned by comparison of the spectra with that of *cis*-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$ in the case of the group VI complexes. The three *cis*-bis(phosphite) tetracarbonyl complexes of Cr, Mo, and W as

---

(1) Alfred P. Sloan Fellow.
(2) See for example F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964), and references therein.
(3) See for example A. Loutellier and M. Bigorgne, *Bull. Soc. Chim. France*, 3186 (1965), and references therein.

well as *cis*-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$ and the quinuclidine pentacarbonyl complexes of Cr, Mo, and W are new and their syntheses are described. Bands were also assigned as arising from ligand modes or complex modes of the types 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, or 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.

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[4] to the reduction of symmetry by the ligands led us to suspect the purity of *trans* compounds discussed earlier.[4] The *trans* isomers of these complexes where L is either $P(OCH_2)_3CR$ or $P(OCH)_3(CH_2)_3$[5] are indeed shown to exhibit only one ν(C–O) band whereas the *cis* compounds exhibit three.

Experimental Section

The infrared spectra from 70 to 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 a Beckman Model 12 grating spectrometer. The carbon and hydrogen contents of the phosphite and arsenite complexes were determined by combustion, and the carbon, hydrogen, and nitrogen analyses of the amine complexes were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.; the data are given in Table I.

Nickel tetracarbonyl and iron pentacarbonyl were purchased from A. D. MacKay, Inc., chromium and tungsten hexacarbonyls were purchased from Pressure Chemical Co., and 4-hydroxyethylpiperidine was purchased from Reilly Tar and Chemical Co. The ligands $P(OCH_2)_3CCH_3$,[6] $P(OCH)_3(CH_2)_3$,[6] and $As(OCH_2)_3CCH_3$[7] were prepared by methods described previously. Chromium norbornadiene tetracarbonyl,[8] molybdenum norbornadiene tetracarbonyl,[9] and tungsten 1,5-cyclooctadiene tetracarbonyl[10] were also prepared as described elsewhere.

Quinuclidine.—A modification of Brown's procedure[11] 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 were collected in a Dry Ice–2-propanol 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.—The method of Stanclift and Hendricker[12] was used to prepare the *cis*- and *trans*-$M(CO)_4(P(OCH_2)_3C(CH_2)_2CH_3)_2$, where M = Mo and W. Two general methods were used to prepare the remaining 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 was 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 monosubstituted 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.

TABLE I

ANALYTICAL AND SYNTHETIC DATA[a]

Compound	% carbon Calcd	% carbon Found	% hydrogen Calcd	% hydrogen Found
trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$[b]	36.54	36.33	3.94	3.90
cis-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$[c]	36.54	36.01	3.94	4.01
cis-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$[d]	30.65	30.13	3.37	3.29
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$[e]	33.35	32.82	3.60	3.58
cis-$W(CO)_4(P(OCH_2)_3CCH_3)_2$[f]	28.40	28.36	3.06	3.00
trans-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$[g]	39.60	39.30	3.70	3.80
cis-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$[h]	39.60	40.58[s]	3.70	4.24
trans-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$[i]	36.30	36.60	3.30	3.60
cis-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$[j]	36.30	36.34	3.30	3.28
trans-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$[k]	31.10	31.90[s]	2.90	2.90
cis-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$[l]	31.10	32.33[s]	2.90	3.12
$Cr(CO)_5N(C_2H_4)_3CH$[m,n]	47.52	47.28	4.32	4.41
$Mo(CO)_5N(C_2H_4)_3CH$[o,p]	41.51	41.44	3.77	3.85
$W(CO)_5N(C_2H_4)_3CH$[q,r]	33.12	33.32	3.01	3.09

[a] The amount of $M(CO)_6$ or $(M(CO)_4(diene))$ in grams, amount of ligand in grams, temperature in degrees centigrade, time in hours, and yield in per cent are given in appropriate footnotes as follows. [b] 1.00, 1.70, 55, 4, 50. [c] (0.70), 0.90, 25, 48, 95. [d] (0.70), 1.10, 25, 48, 90. [e] (0.60), 0.75, 25, 2, 95. [f] (0.10), 0.10, 80, 6, 85. [g] 0.69, 1.20, 55, 4, 45. [h] (0.37), 0.50, 25, 36, 55. [i] 0.37, 0.50, 136, 24, 85. [j] (0.30), 0.35, 25, 2, 90. [k] 0.50, 0.50, 55, 4, 30. [l] (0.30), 0.74, 80, 8, 80. [m] Nitrogen %: calcd, 4.62; found, 4.46. [n] 2.00, 0.81, 55, 12, 60. [o] Nitrogen %: calcd, 4.03; found, 3.98. [p] 2.00, 0.68, 55, 12, 55. [q] Nitrogen %: calcd, 3.22; found, 3.17. [r] 2.00, 0.51, 55, 12, 50. [s] The reason for the significant deviation of this analysis is not apparent. However the infrared spectrum remained unchanged after repeated crystallizations.

Method B, which was used to prepare all the *cis*-disubstituted complexes and *trans*-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$, consisted of stirring an ethylbenzene 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.

Footnotes to Table I list the amount of hexacarbonyl or olefin-substituted tetracarbonyl and ligand used, the reaction temperature and time, and the per cent 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 1 or 2 days, while those of $As(OCH_2)_3CCH_3$ and $N(C_2H_4)_3CH$ decompose in several minutes.

Discussion

Structures of Group VI Complexes.—Examination of the infrared spectra of the new *cis*-bis-$P(OCH_2)_3CCH_3$ complexes of tetracarbonylchromium, -molybdenum,

---

(4) J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).

(5) D. G. Hendricker, R. E. McCarley, R. W. King, and J. G. Verkade, *ibid.*, **5**, 639 (1966).

(6) J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *ibid.*, **4**, 83 (1965).

(7) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

(8) R. B. King, *Organometal. Syn.*, **1**, 122 (1965).

(9) R. B. King, *ibid.*, **1**, 124 (1965).

(10) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

(11) H. C. Brown and N. R. Eldred, *J. Am. Chem. Soc.*, **71**, 445 (1949).

(12) W. E. Stanclift and D. G. Hendricker, *Inorg. Chem.*, **7**, 1242 (1968).

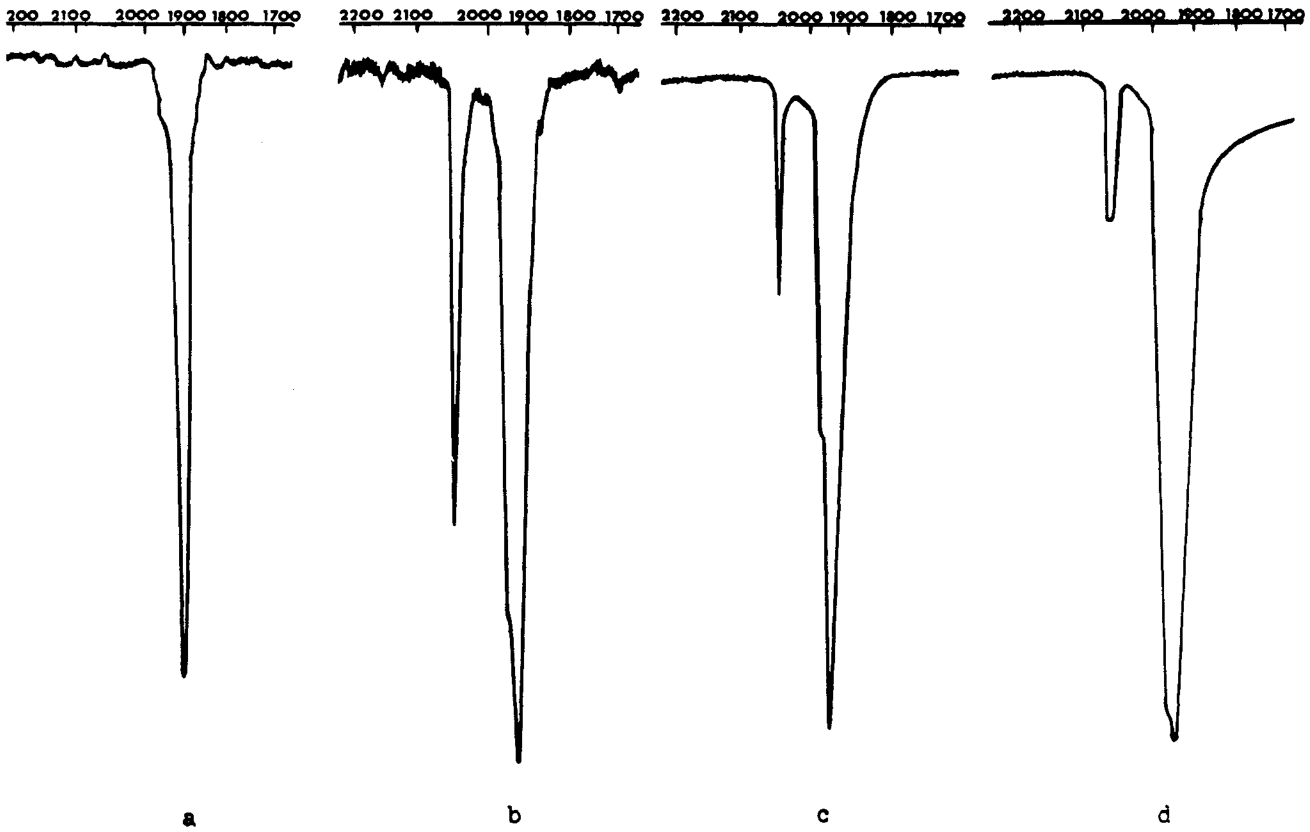

Figure 1.—The carbonyl stretching region of *trans*-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ (a), *cis*-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ (b), a mixture of these two complexes (c), and a sample of *trans*-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ (d) reported earlier.[4]

and -tungsten in the carbonyl stretching region revealed that the high-frequency band and the shoulder on the very strong main band (Table II) seemed to be the same bands which were observed with weaker intensities in the *trans* isomers reported earlier.[4] 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[13] 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 were 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), and a mixture of these two (c), and an example of a spectrum reported previously[4] 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 earlier[4] 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. Using the ligand $P(OCH_2)_3C(CH_2)_2CH_3$, Stanclift and Hendricker[12] showed that both the *cis*- and *trans*-disubstituted tetracarbonyls could easily be synthesized with molybdenum and tungsten whereas only the *trans* complex was obtained with chromium.

TABLE II

INFRARED SPECTRA OF COMPLEXES IN THE METAL CARBONYL REGION[a]

Compound	C–O str freq, 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-$W(CO)_3(P(OCH)_3(CH_2)_3)_2$		1924 vs	
cis-$W(CO)_4(P(OCH)_3(CH_2)_3)_2$	1927 vs	1950 sh	2053 m
$Cr(CO)_5N(C_2H_4)_3CH$[b]	1905 vs	1925 vs	2062 w
$Mo(CO)_5N(C_2H_4)_3CH$[b]	1901 vs	1925 vs	2067 w
$W(CO)_5N(C_2H_4)_3CH$[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.

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[5] to exhibit two similar weak bands in addition to the main peak, it became

---

[13] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

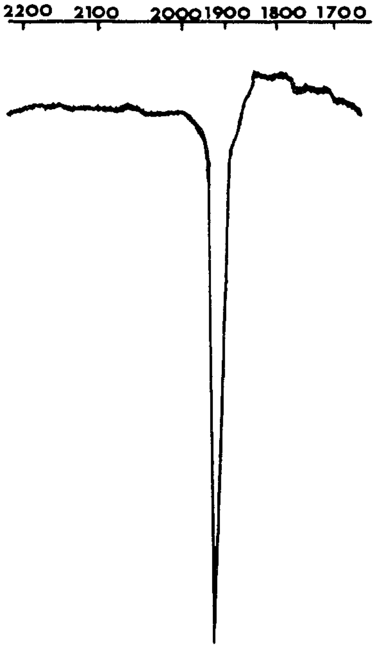

Figure 2.—The carbonyl stretching region of pure *trans*-W(CO)$_4$-(P(OCH$_2$)$_3$CCH$_3$)$_2$.

necessary to synthesize the *cis* isomer for spectral comparison. Again, it is apparent that the compounds assigned the *trans* configuration earlier[5] 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.[5] Values for ν(C–O) are given in Table II for both isomers of each of the three metal complexes with this ligand.

It is not clear why the preparations of the *trans* isomers of Mo(CO)$_4$(P(OCH$_2$)$_3$CCH$_3$)$_2$ and W(CO)$_4$-(P(OCH$_2$)$_3$CCH$_3$)$_2$ could not be repeated (except once in the case of tungsten) even though reaction 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$_2$)$_3$CCH$_3$ 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 methylcyclohexane solution at 80° and during attempted recrystallizations from CH$_3$CN. In contrast, *cis*-M(CO)$_4$(P-(OCH$_2$)$_3$CCH$_3$)$_2$ (M = Mo or W) may be the more stable isomer owing to the smaller steric requirements of the ligand. The apparent stability of both isomers of the bis-P(OCH$_2$)$_3$CCH$_3$ 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. That these small changes in steric requirements and metal size are important is borne out by the observation[12] that the *trans*-disubstituted molybdenum and tungsten complexes of P(OCH$_2$)$_3$C(CH$_2$)$_2$CH$_3$ are stable and more easily made than with the slightly less bulky P(OCH$_2$)$_3$CCH$_3$. Moreover, only the *trans*- and not the *cis*-disubstituted chromium complex of the bulkier ligand is observed[12] whereas both isomers are now shown to exist using P(OCH$_2$)$_3$CCH$_3$.

General Infrared Spectral Features.—The infrared spectra of P(OCH$_2$)$_3$CCH$_3$ and As(OCH$_2$)$_3$CCH$_3$ 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$_2$)$_3$CCH$_3$ is simplified to basically five peaks which occur in the ranges 650–680 (vs), 500–520 (s) (frequently accompanied by a weak peak or shoulder on the low-frequency side at 490–505 cm^{-1}), 400–415 (m–w), 360–385 (m–w), and 200–275 cm^{-1} (w). The spectrum of complexed As(OCH$_2$)$_3$CCH$_3$ is similar but consists of only four bands at 602 (vs), 481 (m), 381 (vs), and 298 cm^{-1} (w). Table III contains the species of the molecular vibrations and the number of infrared-active bands to be expected for each type of complex excluding the ligand vibrations.

In Ni(CO)$_4$,[14] Fe(CO)$_5$,[15] Cr(CO)$_6$, and Mo(CO)$_6$[16] the metal–carbon stretching frequencies ν(M–C) generally occur at lower wavelengths than the metal–carbon–oxygen bending modes δ(M–C–O). Other studies of these regions indicate that the range observed for δ(M–C–O) is 450–680 cm^{-1} and that of ν(M–C) is 340–475 cm^{-1}.[3,17–20] 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 molydenum to tungsten. 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 IV it can be seen that P(OCH$_2$)$_3$-CCH$_3$ fits well into Bigorgne's series[19a] of ligands wherein these frequencies decrease in the order P(C$_2$-H$_5$)$_3$ > P(OCH$_2$)$_3$CCH$_3$ > P(OCH$_3$)$_3$ > PCl$_2$(OC$_2$H$_5$) > PCl$_3$. Our assignments in the ν(M–C) and δ(M–C–O) region in the case of the nickel carbonyl derivatives of P(OCH$_2$)$_3$CCH$_3$ gain excellent support from similar assignments made by Bigorgne, *et al.*,[19b] for the anal-

---

(14) L. H. Jones, *Spectrochim. Acta*, **19**, 1899 (1963).

(15) W. F. Edgell, W. E. Wilson, and R. Summitt, *ibid.*, **19**, 863 (1963).

(16) H. Murata and K. Kawai, *J. Chem. Phys.*, **27**, 605 (1957).

(17) D. M. Adams, *J. Chem. Soc.*, 1771 (1964).

(18) M. A. Bennett and R. J. H. Clark, *ibid.*, 5560 (1964).

(19) (a) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962); (b) G. Bouquet, A. Loutellier, and M. Bigorgne, *J. Mol. Structure*, **1**, 211 (1968).

(20) A. A. Chalmers, J. Lewis, and R. Whyman, *J. Chem. Soc., A*, 1817 (1967).

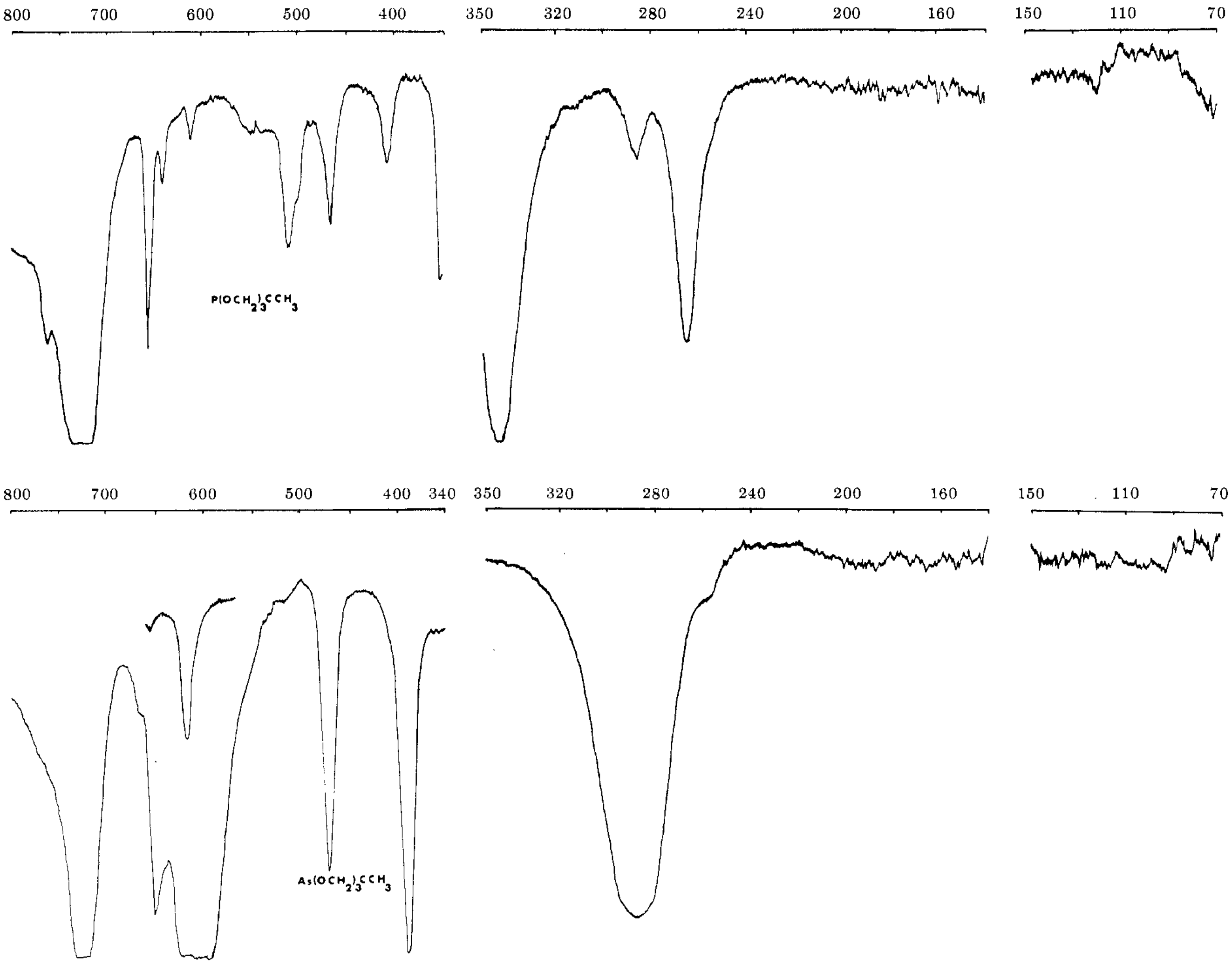

Figure 3.—The infrared spectra of $P(OCH_2)_3CCH_3$ and $As(OCH_2)_3CCH_3$ in the region 800–70 cm^{-1}.

TABLE III

METAL–LIGAND AND CO VIBRATIONS OF SUBSTITUTED METAL CARBONYLS

Molecule	Point group	$\nu(MX)^{a,b}$	$\nu(MC)$ or $\nu(CO)^b$	$\delta(M-C-O)^b$	$\delta(M-X-Y)^{b,c}$
$Ni(CO)_4$	T_d		$a_1 + t_2$ (1)	$e + t_1 + t_2$ (1)	$e + t_2$ (1)
$Ni(CO)_3L$	C_{3v}	a_1 (1)	$a_1 + e$ (2)	$a_1 + a_2 + 2e$ (3)	$a_1 + 2e$ (3)
$Ni(CO)_2L_2$	C_{2v}	$a_1 + b_2$ (2)	$a_1 + b_1$ (2)	$a_1 + a_2 + b_1 + b_2$ (3)	$2a_1 + a_2 + b_1 + b_2$ (4)
$Ni(CO)L_3$	C_{3v}	$a_1 + e$ (2)	a_1 (1)	e (1)	$a_1 + 2e$ (3)
NiL_4	T_d	$a_1 + t_2$ (1)			$e + t_2$ (1)
$Fe(CO)_5$	D_{3h}		$2a_1' + e' + a_2''$ (2)	$a_2' + 2e' + a_2'' + 2e''$ (3)	$2e' + a_2'' + e''$ (3)
$Fe(CO)_4L$	C_{3v}	a_1 (1)	$2a_1 + e$ (3)	$a_1 + a_2 + 3e$ (4)	$a_1 + 3e$ (4)
$Fe(CO)_3L_2$	D_{3h}	$a_1' + a_2''$ (1)	$a_1' + e'$ (1)	$a_2' + e' + a_2'' + e''$ (2)	$2e' + a_2'' + e''$ (3)
$M(CO)_6$	O_h		$a_{1g} + e_g + t_{1u}$ (1)	$t_{1g} + t_{2g} + t_{1u} + t_{2u}$ (1)	$t_{2g} + t_{1u} + t_{2u}$ (1)
$M(CO)_5L$	C_{4v}	a_1 (1)	$2a_1 + b_1 + e$ (3)	$a_1 + a_2 + b_1 + b_2 + 3e$ (4)	$a_1 + 2b_1 + b_2 + 3e$ (4)
trans-$M(CO)_4L_2$	D_{4h}	$a_{1g} + a_{2u}$ (1)	$a_{1g} + b_{1g} + e_u$ (1)	$a_{2g} + b_{2g} + e_g + a_{2u} + b_{2u} + e_u$ (2)	$e_g + a_{2u} + b_{2u} + e_u$ (3)
cis-$M(CO)_4L_2$	C_{2v}	$a_1 + b_2$ (2)	$2a_1 + b_1 + b_2$ (4)	$2a_1 + 2a_2 + 2b_1 + 2b_2$ (6)	$3a_1 + 2a_2 + 2b_1 + 2b_2$ (7)

[a] X = P, As, N. [b] Number of infrared-active bands is given in parentheses. [c] X, Y = C, C; C, P; C, N; P, P.

ogous $P(OCH_3)_3$ complexes. The values attributed to $\nu(M-C)$ and $\delta(M-C-O)$ in the group VI complexes are rendered very reasonable by assignments made for analogs containing different phosphorus ligands (Table IV), the observation of nearly the same bands in the quinuclidine complexes while quinuclidine itself exhibits no bands in this region, and the fact that the required number of $\nu(M-C)$ and $\delta(M-C-O)$ bands could be seen in the case of four of the complexes studied: $Fe(CO)_4L$, *trans*-$Fe(CO)_3L_2$, *cis*-$Mo(CO)_4L_2$, and *trans*-$Cr(CO)_4L_2$ (where L = $P(OCH_2)_3CCH_3$). No band attributable to a metal–nitrogen stretching mode was observed in the spectra of the quinuclidine complexes.

In transition metal carbonyls,[14–16,19] carbon–metal–carbon bending modes, $\delta(C-M-C)$, generally occur below 100 cm^{-1}. The bands listed in Table V which occur below those assigned to $\nu(M-P)$ can be attributed to any or all of the following bending modes where

TABLE IV

ABSORPTION BANDS OF SUBSTITUTED METAL CARBONYLS IN THE 300–700-CM^{-1} REGION

Compound	Total bands possible (obsd)	ν(M–C) and δ(M–C–O), cm^{-1}									
$Ni(CO)_3PF_3$[a]	5 (4)						452 m[b]	439 s	407 vs	401 m	
$Ni(CO)_2(PF_3)_2$[a]	6 (2)						464 s	452 m			
$Ni(CO)(PF_3)_3$[a]	2 (2)							451 s	434 m		
$Ni(PF_3)_4$	0 (0)										
$Ni(CO)_3(P(OCH_2)_3CCH_3)$	5 (4)					493 s	471 m	450 vs			348 m
$Ni(CO)_3(P(OCH_3)_3$[a]	5 (4)				530 m		473 m	453 s		377 m	
$Ni(CO)_2(P(OCH_2)_3CCH_3)_2$	5 (5)	656 vs				490 s		457 s[c]		377 m	
$Ni(CO)_2(P(OCH_3)_3)_2$[a]	5 (4)					489 s	462 m	455 m		365 s	
$Ni(CO)(P(OCH_2)_3CCH_3)_3$	2 (1)						461 w				
$Ni(CO)(P(OCH_3)_3)_3$[a]	2 (2)					499 s	459 m				
$Ni(P(OCH_2)_3CCH_3)_4$	0 (0)										
$Fe(CO)_4(P(C_2H_5)_3)$[d]	7 (3)		621 vs		526 m	493 w					
$Fe(CO)_4(P(OCH_2)_3CCH_3)$	7 (7)	659 s	620 vs	534 m	525 s			447 vw		390 vw	368 m
trans-$Fe(CO)_3(P(OCH_2)_3CCH_3)_2$	3 (3)		628 vs	584 vs			460 m				
$Cr(CO)_5Cl$[e]	7 (8)	670 w	653 vs	563 m	553 sh	499 w	472 w	437 s	411 m		
$Cr(CO)_5(P(OCH_2)_3CCH_3)$	7 (6)	672 m	653 vs		538 w		470 s	452 m	427 vw		
$Cr(CO)_5(P(C_6H_5)_3)$[f]	7 (5)	673 s	654 s		548 m		462 s		414 m		
$Cr(CO)_5(N(C_2H_4)_3CH)$	7 (5)	671 s	652 vs		537 m				439 s	415 m	
$Mo(CO)_5Cl$[e]	7 (7)		608 sh	602 vs		543 s	472 w	454 w	391 w		346 s
$Mo(CO)_5(P(C_2H_5)_3)$[g]	7 (5)		610 vs	580 vs				424 w	402 m		381 s
$Mo(CO)_5(P(OCH_2)_3CCH_3)$	7 (5)		606 vs	581 vs			489 w	424 s			382 s
$Mo(CO)_5(P(OCH_3)_3)$[g]	7 (5)		600 vs	576 vs				417 m	400 m		377 s
$Mo(CO)_5(P(C_6H_5)_3)$[f]	7 (5)		609 s	584 vs					402 m	387 m	374 s
$Mo(CO)_5(P(OC_2H_5)Cl_2)$[g]	7 (5)		593 vs	572 vs				401 w	390 m		370 s
$Mo(CO)_5PCl_3$[g]	7 (5)		589 vs	571 vs				400 w	382 m		366 s
$Mo(CO)_5(N(C_2H_4)_3CH)$	7 (5)		612 s	598 vs		538 s			391 w		361 vs
$W(CO)_5Cl^-$	7 (7)		594 vs	554 s		528 w	444 w	426 w	410 w		355 s
$[W(CO)_5P(CH_3)_2]_2$[d]	7 (2)		594 vs	568 vs							
$W(CO)_5(P(OCH_2)_3CCH_3)$	7 (6)		590 vs	566 vs		527 vw	492 w	422 m	414 w		
$W(CO)_5(N(C_2H_4)_3CH)$	7 (5)		590 vs	546 s				430 w	409 w		367 vs
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			552 w	493 w	459 w		372 w	
cis-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$	10 (5)	656 s	648 vs			543 w	450 w			391 m	
cis-$Mo(CO)_4(P(C_6H_5)_3)_2$[f]	10 (7)		611 s	582 vs		548 m	452 m	444 m	412 s	376 s	
cis-$Mo(CO)_4(P(C_6H_5)(C_2H_5)_2)_2$[d]	10 (3)		610	587	578						
cis-$Mo(CO)_4(P(C_2H_5)_3)_2$[g]	10 (7)		608 vs	586 vs	575 vs			428 m	413 m	404 m	392 s
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$	10 (10)	649 vs	595 vs	585 vs	566 vs	531 vw	478 m	427 s	405 m	387 s	358 m
cis-$W(CO)_4(P(C_6H_5)(C_2H_5)_2)_2$[d]	10 (3)		600	583	565						
cis-$W(CO)_4(P(OCH_2)_3CCH_3)_2$	10 (6)	661 vs	590 vs	582 vs	560 s		490 w	426 s			
trans-$Cr(CO)_4(P(C_6H_5)_3)_2$[f]	3 (3)	671 s	640 s				477 m				
trans-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$	3 (3)	648 vs	636 vs				477 m				
trans-$Mo(CO)_4(P(C_2H_5)_3)_2$[g]	3 (3)		631 vs	573 vs					405 s		
trans-$Mo(CO)_4(P(OCH_3)_3)_2$[g]	3 (3)		618 vs	570 vs					397 s		
trans-$Mo(CO)_4(P(C_6H_5)_3)_2$[f]	3 (3)		629 s	580 vs					394 s		

[a] See ref 19b. [b] vs = very strong, s = strong, m = medium, sh = shoulder, w = weak, vw = very weak. [c] The strong band at 457 cm^{-1} is assumed to be composed of the two bands at 462 (m) and 455 (m) cm^{-1} found in the analogous $P(OCH_3)_3$ complex. [d] See ref 17. [e] See ref 18. [f] See ref 20. [g] See ref 19a.

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 IV are not observed and no attempt was made to make specific assignments.

M–P Bands in Nickel 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). Similarly, the five expected M–C and M–C–O bands for $Ni(CO)_2(P(OCH_2)_3CCH_3)_2$ could be observed in the region 656–377 cm^{-1} (Table V) allowing the two observed bands at 155 and 144 cm^{-1} to be ascribed to the asymmetric and symmetric ν(M–P) vibrations (Table VI). The compounds $M(P(C_6H_5)_3)_2X_2$[21] (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 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 trend of the metal–phosphorus stretching frequencies taken from Table VI for the nickel PF_3 complexes is toward lower energies from the mono- to the tetrasubstituted complex. The values for the anal-

---

(21) G. B. Deacon and J. H. S. Green, *Chem. Commun.*, 629 (1966).

TABLE V

BANDS IN THE FAR-INFRARED SPECTRUM BELOW THOSE ASSIGNED TO ν(M–P)

Compound	Total bands possible (obsd)	δ(X–M–Y),[a] cm^{-1}
$Ni(CO)_3PF_3$	3 (2)	80, 61[b]
$Ni(CO)_2(PF_3)_2$	4 (2)	78, 59[b]
$Ni(CO)(PF_3)_3$	3 (2)	76, 52[b]
$Ni(PF_3)_4$	1 (2)	57, 50[b]
$Ni(CO)_2(P(OCH_2)_3CCH_3)_2$	4 (1)	118
trans-$Fe(CO)_3(P(OCH_2)_3CCH_3)_2$	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; P, P. [b] Raman values (see ref 3).

TABLE VI

INFRARED-ACTIVE METAL–PHOSPHORUS STRETCHING FREQUENCIES OF SOME SUBSTITUTED METAL CARBONYLS

Compound	Total bands possible (obsd)	ν(M–P), cm^{-1}
$Ni(CO)_3(PF_3)$	1 (1)	262[a]
$Ni(CO)_2(PF_3)_2$	2 (2)	254,[a] 209[a]
$Ni(CO)(PF_3)_3$	2 (2)	253,[a] 216[a]
$Ni(PF_3)_4$	2 (2)	218,[a] 195[a,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
$Ni(P(OCH_2)_3CCH_3)_4$	2 (1)	157
$Fe(CO)_4(P(OCH_2)_3CCH_3)$	1 (1)	169
trans-$Fe(CO)_3(P(OCH_2)_3CCH_3)_2$	1 (1)	192
$Cr(CO)_5(P(OCH_2)_3CCH_3)$	1 (1)	164
$Cr(CO)_5(P(C_6H_5)_3)$[c]	1 (1)	206
$Mo(CO)_5(P(OCH_2)_3CCH_3)$	1 (1)	195
$Mo(CO)_5(P(C_6H_5)_3)$[c]	1 (1)	204
$W(CO)_5(P(OCH_2)_3CCH_3)$	1 (1)	180
$W(CO)_5(P(C_6H_5)_3)$[c]	1 (1)	204
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
trans-$Mo(CO)_4(P(OCH_2)_3C(CH_2)_2CH_3)_2$	1 (1)	226
trans-$Mo(CO)_4(P(C_6H_5)_3)_2$[c]	1 (1)	194
cis-$Mo(CO)_4(P(OCH_2)_3CCH_3)_2$	2 (1)	201
cis-$Mo(CO)_4(P(C_6H_5)_3)_2$[c]	2 (2)	173, 160
trans-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	1 (1)	237
cis-$Mo(CO)_4(P(OCH)_3(CH_2)_3)_2$	2 (1)	200
trans-$W(CO)_4(P(OCH_2)_3C(CH_2)_2CH_3)_2$	1 (1)	204
trans-$W(CO)_4(P(C_6H_5)_3)_2$[c]	1 (1)	194
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

[a] Raman values (see ref 3). [b] Raman active only. [c] See ref 20.

ogous series of $P(OCH_2)_3CCH_3$ complexes are substantially lower, and contrastingly the trend rises. The larger ν(M–P) values for the PF_3 complexes can be attributed to the greater π-bonding ability and smaller mass of PF_3. The opposite trends in ν(M–P) on stepwise substitution of PF_3 and $P(OCH_2)_3CCH_3$ for CO can be accounted for by a difference in π-bonding abilities of the two phosphorus ligands. There is substantial evidence which indicates that PF_3 is nearly equal or better in π-bonding ability than CO[2,22–24] and better than a phosphite.[23] The trends in ν(M–P) in the nickel PF_3 and $P(OCH_2)_3CCH_3$ complexes might be interpreted to support this claim since 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 PF_3 as well as the remaining CO groups to release some of their π-electron density since the metal electron density liberated by the departing CO group is insufficient to satisfy the superior π-accepting character of the incoming PF_3. The metal–phosphorus π-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 π-bonding which results in increasing the ν(M–P) stretching frequency.

This interpretation is also consistent with the decrease in the CO force constant (k) as calculated with Cotton's equations[2] using data obtained in chloroform[4] for the same series of $P(OCH_2)_3CCH_3$ complexes upon replacement of all but the last CO group in $Ni(CO)_4$: 17.18,[3] 16.8, 16.4, and 15.8 mdyn/Å. The increased metal electron density upon CO substitution would thus decrease the CO bond order. For the analogous series of PF_3 complexes, an increasing trend in k is obtained using Cotton's approach: 17.18,[3] 17.27, 17.32, and 17.36 mdyn/Å. The initial increase in the force constant would follow from the arguments given above for ν(M–P) since removal of metal electron density by the better π acid PF_3 allows an increase in the CO bond order. The near 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 π bonding among the remaining CO groups also approaches a minimum. Thus additional PF_3 ligands are increasingly forced to share the π-electron density of PF_3 groups already in the complex. Although these arguments are attractive, it is well to recognize that a more refined treatment of the infrared data by Bigorgne[3] taking into account coupling of various modes indicates that the CO force constant *decreases* slightly on substitution of $Ni(CO)_4$ with PF_3 and that the NiP force constant does not change appreciably in the same process. At best it would appear from Bigorgne's study[3] that PF_3 and CO are comparable in ligand properties. Although it is difficult to say how the CO and NiP force constants in the nickel $P(OCH_2)_3CCH_3$ complexes would behave in Bigorgne's treatment, it is tentatively postulated that the more pronounced trend in the Cotton CO force constant upon substitution is

---

(22) R. J. Clark and E. O. Brimm, *Inorg. Chem.*, **4**, 651 (1965).
(23) G. R. Van Hecke and W. D. Horrocks, *ibid.*, **5**, 1960 (1966).
(24) W. A. G. Graham, *ibid.*, **7**, 315 (1968).

significant of a real decrease in the CO bond order. If the increase in ν(M–P) on substitution actually then reflects an increase in NiP bond order, the arguments presented above based on increasing π bonding best explain these trends. Assumption of basicity of the phosphite as the dominant factor would predict a decrease in NiP bond order as more electron density accumulates on the nickel from departing CO groups.

M–P Bands in Group VI Metal Complexes.—The assignments of ν(M–P) values listed in Table VI for the group VI complexes of $P(OCH_2)_3CCH_3$ are made reasonable by comparison of the spectra of *cis*-$Cr(CO)_4(P(OCH_2)_3CCH_3)_2$ and *cis*-$Cr(CO)_4(As(OCH_2)_3CCH_3)_2$. 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. The M–As stretch probably occurs at lower frequency and could fall in the C–M–C, C–M–As, and As–M–As bending region. The assignment of the single metal–phosphorus mode for *trans*-$Cr(CO)_4(P(OCH)_3(CH_2)_3)_2$ at 190 cm^{-1} (Table VI) is substantiated by the appearance of the expected three M–C and M–C–O modes (Table IV). Among the *cis* group VI complexes, the asymmetric and symmetric metal–phosphorus stretches were resolved only in *cis*-$W(CO)_4(P(OCH_2)_3CCH_3)_2$ and the separation (3 cm^{-1}, Table VI) was quite small. It is probable, then, that the two modes in the remaining *cis* complexes are very nearly superimposed.

The free $P(OCH_2)_3C(CH_2)_2CH_3$ shows two weak bands near the M–P stretching region at 160 and 175 cm^{-1} which also appear weakly in the *cis* and *trans* molybdenum and tungsten complexes at 180 and 195 cm^{-1}. Although the *trans* molybdenum and tungsten compounds definitely exhibit a new band assignable to ν(M–P) at 226 (m) and 204 cm^{-1} (w), respectively, their *cis* analogs revealed no new bands. Since ν(M–P) could be assigned with some certainty in the *cis* compounds containing $P(OCH_2)_3CCH_3$, which is free of ligand bands in this region, it is concluded that the weak asymmetric and symmetric M–P stretches in the *cis* complexes of the heavier ligand are masked by the two ligand bands. The assignments of ν(M–P) in the disubstituted group VI complexes of $P(OCH)_3(CH_2)_3$ are reasonable in that they are consistent with those already discussed and in that there are no other bands in this region of the ligand and complex spectra from 300 to 160 cm^{-1}.

As in the case of nickel complexes, ν(M–P) increased from the mono- to the analogous disubstituted octahedral complexes of $P(OCH_2)_3CR$. This increase is greater in all cases when the ligands are *trans*. Further importance to this observation is given by the increase in ν(M–P) from the *cis* to the *trans* complexes of the type $M(CO)_4(P(OCH)_3(CH_2)_3)_2$, where M = Cr, Mo, or W (Table VI). Carbonyl groups are very likely more strongly π-bonding ligands than phosphites and their depleting effect on the π-electron density available to the phosphite is expected to be greater when oriented *trans* to a phosphite. This arises from the fact that *trans* ligands share two dπ orbitals whereas *cis* ligands share only one.[13] Thus the stronger metal–phosphorus π bond and higher-frequency ν(M–P) is expected in the *trans* isomers. Because π effects of the phosphorus ligand on the CO force constants are "symmetry factored" from σ influences,[2] force constant calculations on the various CO vibrations in these compounds should complement the ν(M–P) data. Since Raman studies have not yet been carried out on these compounds and because some of the infrared-active bands overlap and are not resolved in $CHCl_3$ or CH_2Cl_2, such calculations could not be made. However, those infrared CO frequencies which can be observed for $Mo(CO)_5P(OCH_2)_3CCH_3$[4] and the disubstituted *cis* molybdenum tetracarbonyl given in Table II are within 10 cm^{-1} of those reported by Bigorgne[19a] for the analogous $P(OCH_3)_3$ complexes. The single strong infrared band at 1939 cm^{-1} reported by Stanclift and Hendricker[12] for *trans*-$Mo(CO)_4(P(OCH_2)_3C(CH_2)_2CH_3)_2$ in CH_2Cl_2 could well be an average of the two bands reported by Bigorgne[19a] at 1972 and 1921 cm^{-1} for *trans*-$Mo(CO)_4(P(OCH_3)_3)_2$ in a hydrocarbon solvent. The trends in CO force constants are therefore very probably the same in these compounds and examination of those values given by Cotton[2] for the $P(OCH_3)_3$ complexes shows as expected that k_1 and k_2 are both larger in the monosubstituted $P(OCH_3)_3$ derivative (16.38, 16.46 mdyn/Å) than in the *cis* (15.35, 15.60 mdyn/Å) and k_2 in the *cis* (15.60 mdyn/Å) is larger than k_2 in the *trans* (15.55 mdyn/Å). Because the ν(M–P) region is quite free of nearby modes with which coupling could take place and because the same trends in ν(C–O) and ν(M–P) are noted in all three derivatives of chromium, molybdenum, and tungsten, we feel that these trends are reflections of the changing M–P bond order. If this is so, our results mitigate strongly against arguments based solely on σ-donor properties of phosphorus ligands since on these grounds a decrease in ν(M–P) would have been expected from mono- to disubstitution and no significant change in ν(M–P) from the *cis* to the *trans* isomer would have been predicted.

Other reports of ν(M–P) values[21,25–28] have dealt mainly with Ni(II), Pd(II), and Pt(II) compounds of the form $M(R_3P)_2X_2$, where R = CH_3, C_2H_5, or C_6H_5 and X = Cl, Br, I, NCS, CN, C_6H_5, or SCH_3. For $P(CH_3)_3$[27] complexes, ν(M–P) values fall in the range 341–377 cm^{-1}, while the range for the $P(C_2H_5)_3$[25,26,28] complexes is 406–442 cm^{-1}. The different ranges reported by others and in this work are undoubtedly related to variations in electronic and stereochemical configurations in the complexes. The only other assignments of ν(M–P) modes in zerovalent group VI systems in addition to those of the present work is that of Chalmers, *et al.*[20] wherein a number of $P(C_6H_5)_3$ complexes were studied (Table IV). The series $Mo(CO)_5L$ (204 cm^{-1}), *cis*-$Mo(CO)_4L_2$ (173, 160 cm^{-1}), *trans*-$Mo(CO)_4L_2$ (194 cm^{-1}), and *cis*-$Mo(CO)_3L_3$ (200 cm^{-1}), where L = $P(C_6H_5)_3$, shows an increasing

---

(25) D. M. Adams and P. J. Chandler, *Chem. Commun.*, 69 (1966).
(26) D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.*, 5275 (1965).
(27) G. E. Coates and C. Parkin, *ibid.*, 421 (1963).
(28) D. Goggin and R. J. Goodfellow, *ibid.*, *A*, 1462 (1966).

trend in ν(M–P) as expected on the basis of our arguments, except for the first member. Since the appropriate k_1 and k_2 values given by Cotton[2] for the carbonyl groups are slightly smaller for these complexes than for the analogous $P(OCH_3)_3$ compounds and hence also for the $P(OCH_2)_3CCH_3$ analogs (see above), the general shift toward smaller values of ν(M–P) in the $P(C_6H_5)_3$ complexes (except the monosubstituted one) can be ascribed to the slightly lower π-bonding properties of $P(C_6H_5)_3$ compared to $P(OR)_3$ and the larger mass effect of the former ligand. The reason(s) for the peculiarly larger ν(M–P) value found for $Mo(CO)_5P(C_6H_5)_3$ (204 cm^{-1}) compared to $Mo(CO)_5P(OCH_2)_3CCH_3$ (195 cm^{-1}) is (are) not known at this time. The same obtains for the situation found with $Ni(CO)_3P(C_6H_5)_3$ (192 cm^{-1})[29] *vs.* $Ni(CO)_3P(OCH_2)_3CCH_3$ (143 cm^{-1}) (Table VI). No ν(M–P) values are available for higher substitution complexes of the $Ni–P(C_6H_5)_3$ series for comparison with the $Ni(CO)_{4-x}(P(OCH_2)_3CCH_3)_x$ series, however. If the higher ν(M–P) values in these two $P(C_6H_5)_3$ complexes are due to stronger M–P bonds, it is strange that a similar disparity is not found in the trend of the k_1 and k_2 values for the carbonyl modes in the case of the molybdenum complexes. It is tentatively proposed, therefore, that at least in the molybdenum mono $P(C_6H_5)_3$ complex, some other effect (coupling to another mode perhaps) operates to raise the frequency of the M–P mode. Because the M–P stretching region is quite free of other absorptions in the polycyclic phosphite complexes utilized in this research, further studies on other polycyclic phosphorus ligands exhibiting a variety of ligand properties as well as PF_3[30] are in progress.[31]

Acknowledgments.—The authors thank Miss E. E. Conrad for obtaining the far infrared spectra. J. G. V. thanks the National Science Foundation for a grant (GP-2328), supporting part of this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

---

(29) W. F. Edgell and M. P. Dunkle, *Inorg. Chem.*, **4**, 1629 (1965).

(30) R. Clark and J. G. Verkade, to be submitted for publication.

(31) NOTE ADDED IN PROOF.—Recently Singh, *et al.* [S. Singh, P. P. Singh, and R. Rivest, *Inorg. Chem.*, **7**, 1236 (1968)], were unable to assign any bands in the spectra of $Fe(CO)_4P(C_6H_5)_3$ and *trans*-$Fe(CO)_3(P(C_6H_5)_3)_2$ in the 700–200 cm^{-1} region and suggested that coupling with M–C modes brought the ν(M–P) absorptions below the 200 cm^{-1} limit of their instrument. Inasmuch as our work and that of Chalmers, *et al.*,[20] indicates that ν(M–P) stretches frequently appear below 200 cm^{-1} for zerovalent phosphorus complexes, we suggest that ν(M–P) in all probability occurs below 200 cm^{-1} and that it is not necessary to invoke the coupling argument at this time.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FACULTY OF ENGINEERING SCIENCE, OSAKA UNIVERSITY, TOYONAKA, OSAKA, JAPAN

Metal-Stabilized Thionitroso Compounds

BY SEI OTSUKA, TOSHIKATSU YOSHIDA, AND AKIRA NAKAMURA

Received April 19, 1968

Reaction between $(t\text{-}C_4H_9N)_2S$ and $Fe(CO)_5$ in hexane at ambient temperature produced an alkylthionitroso complex, $Fe_2(CO)_6(t\text{-}C_4H_9NS)$ (**1**), in small yield whereas $(C_6H_5N)_2S$ with $Fe(CO)_5$ or with $Fe_2(CO)_9$ yielded azobenzene as the main isolable product. The phenyl analog of **1**, $Fe_2(CO)_6(C_6H_5NS)$ (**2**), was obtained by treating C_6H_5NSO with $Fe_2(CO)_9$. On the basis of infrared, nmr, and mass spectroscopy the structures for **1** and **2** were deduced.

Studies on reactions of sulfur diimides $(RN)_2S$ with metals or metal compounds have been undertaken in expectation of formation of nitrene or metal-stabilized nitrene complexes. Generally facile cleavage of the N–S bond or abstraction of the sulfur atoms takes place under mild reaction conditions giving rise to a variety of products depending upon the substituent R or the metal. Thus, the reaction of $(t\text{-}C_4H_9N)_2S$ with $Ni(C_5H_5)_2$ or with $(C_5H_5NiCO)_2$ produced a cluster complex, $(NiC_5H_5)_3(t\text{-}C_4H_9N)$, which may be regarded as a nitrene complex,[1] whereas the reaction with $Co(C_5H_5)(CO)_2$ gave a binuclear complex, $(CoC_5H_5)_2(t\text{-}C_4H_9NCON\text{-}t\text{-}C_4H_9)$,[1,2] which was supposedly derived from a nitrene complex intermediate, $Co(C_5H_5)(CO)(t\text{-}C_4H_9N)$. Treating dodecacarbonyltriiron with C_6H_5NCO, Pauson, *et al.*,[3] prepared a similar iron carbonyl complex, $Fe_2(CO)_6(C_6H_5NCONC_6H_5)$, which was called an "ureylene" complex.[4]

We now wish to describe the reaction of $(RN)_2S$ or RNSO with iron carbonyls which affords iron carbonyl complexes of thionitrosoalkane or -benzene.

Reaction of $(t\text{-}C_4H_9N)_2S$ with $Fe(CO)_5$ was carried out in hexane, under irradiation with sunlight, to give an orange, diamagnetic, crystalline complex (**1**), mp 48–50°, in 3% yield. It is thermally stable and fairly volatile. The elemental analysis and molecular weight measurement (mass spectrometry) corresponded to the molecular formula $Fe_2(CO)_6(t\text{-}C_4H_9NS)$, indicat-

---

(1) S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.*, **7**, 261 (1968).

(2) Y. Matsu-ura, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, T. Yoshida, and S. Otsuka, *Chem. Commun.*, 1122 (1967).

(3) W. T. Flannigan, G. R. Knox, and P. L. Pauson, *Chem. Ind.* (London), 1094 (1967).

(4) J. A. J. Jarvis, B. R. Job, B. T. Kilbourn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Commun.*, 1149 (1967).