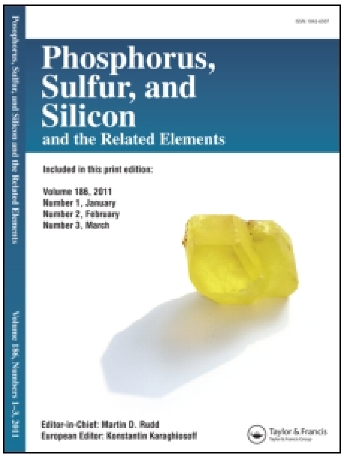

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COORDINATION PROPERTIES OF CONSTRAINED AMINOPHOSPHINES

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COORDINATION PROPERTIES OF CONSTRAINED AMINOPHOSPHINES

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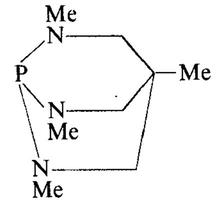
The syntheses of mono and disubstituted mononuclear carbonyls of Cr, Mo, W, Fe and Ni with the cage ligand $P(NMeCH_2)_3CMe$ (2) are reported. The $(OC)_5CrL$ and $(OC)_4FeL$ complexes are also described where L = $As(NMeCH_2)_3CMe$ (5). Borane adducts of the complexes of (2) are reported as well as adducts of $XP(NMeCH_2)_3CMe$ where X = Se and PhN. In the complexes and the selenide the BH_3 group is shown from ^1H nmr spectroscopy to bind to a nitrogen in a bridging group of the ligand whereas in the phenylimide it binds to the phenylimido nitrogen. Some *cis* and *trans* $Pt(2)_2X_2$ complexes are also described.

The CO stretching frequencies and force constant parameters of the complexes are shown to rise in the ligand order $P(NMe_2)_3 < (2) < (2)\cdot BH_3$ and this trend is discussed in terms of constraint and inductive effects. The ^{31}P spectra of the compounds are rationalized and $^2J^{31}P^{31}P$ couplings are obtained directly from the ^{31}P spectra of the (2) $(OC)_xM[(2)\cdot BH_3]$ complexes since the ^{31}P nuclei are chemically nonequivalent.

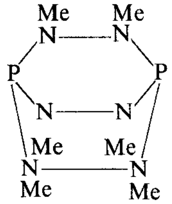
Significant effort has gone into the elucidation of the changes in ligand behavior which occur when phosphite esters of the type $P(OR)_3$ are constrained into rigid configurations such as $P(OCH_2)_3CR$[1-8] and $P(OCH_2)_2COR$.[9] Although complexes of acyclic aminophosphines such as (1) are well known,[10] spectroscopic studies of bicyclic aminophosphines have been limited to aromatic solvent induced shift effects,[11] the determination of $^2J^{31}P^{31}P$ and $^1J^{31}P^{183}W$ for some carbonyl complexes of (2)[1] and the extraction of $^3J^{31}P^{31}P$ from the ^{31}P nmr spectrum of $(OC)_5W(3)W(CO)_5$.[12] In this paper we describe the synthesis of ten mononuclear metal carbonyl complexes of (2), two of its Pt(II) complexes and two mononuclear carbonyl complexes of (5).

$P(NMe_2)_3$

(1)



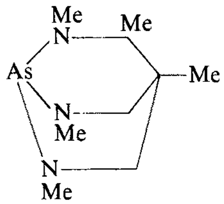
(2)



(3)

$As(NMe_2)_3$

(4)



(5)

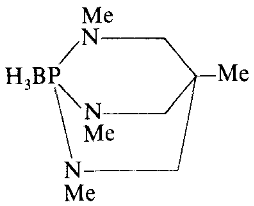
Also described is the formation of borane adducts of the carbonyl complexes of (2) wherein the BH_3 groups are shown to be bound to the nitrogen of the cage ligand. Borane binding of (2) was shown earlier to give rise to (6) or (7), while (8) and (9) give (11) and (12), respectively.[13] Similarly (10) gives (13), as we show here, but (14) gives (15) in which the exocyclic nitrogen is bound to BH_3.

Infrared studies in the CO region of the carbonyl complexes described here allow an assessment of the relative ligating properties of (1), (2) and $(2)\cdot BH_3$. Adducts of the type $(2)M(CO)_4[(2)\cdot BH_3]$ are interesting in that their proton decoupled ^{31}P nmr spectra are AB quartets from which $^2J^{31}P^{31}P$ can be determined directly.

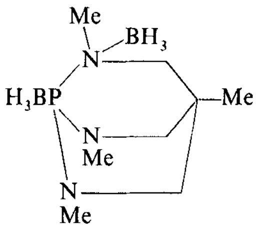
EXPERIMENTAL

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

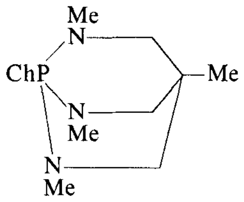
Far infrared spectra were recorded on Nujol mulls of the compounds using a Digilab FTS-18 Fourier transform infrared spectrophotometer located in the Chemistry department of the University of Wisconsin, Madison and the help of Professors E. M. Larsen and P. Bender is gratefully acknowledged.



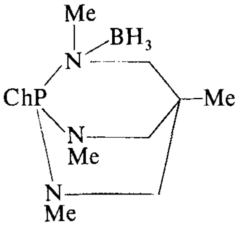
(**6**)



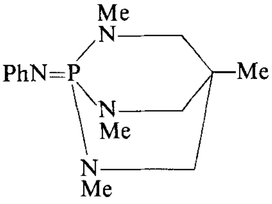
(**7**)



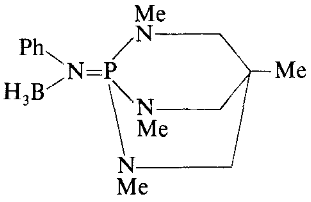
(**8**) Ch = O
(**9**) Ch = S
(**10**) Ch = Se



(**11**) Ch = O
(**12**) Ch = S
(**13**) Ch = Se



(**14**)



(**15**)

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

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

^{31}P nmr spectra were obtained on a Bruker HX-90 spectrometer operating at 36.434 MHz in the FT-mode. Solutions were run in either C_6D_6 or d_8-toluene using the ^{2}H resonance of the solvent as a frequency lock. The reference used was external 0.2 *M* $P(OH)_4^+$ ClO_4^-.[14] Chemical shifts are reported relative to 85% H_3PO_4 as positive in the downfield direction.

Preparations

All of the metal complexes described below were characterized by their ^{1}H and ^{31}P nmr spectra as well as ν(CO) spectra. The carbonyl complexes $Cr(CO)_5$(**2**), $Mo(CO)_5$(**2**), *trans*-$M(CO)_4$(**2**)$_2$ (where M = Cr, Mo, W) and *trans*-$Fe(CO)_3$(**2**)$_2$ have previously been synthesized in low yields by uv irradiation of methylcyclohexane solutions of the appropriate metal carbonyl and (**2**) at room temperature.[15] All the carbonyl complexes of (**1**) and (**4**) were synthesized according to literature methods[16–18] as were *trans*-PtX_2(**1**)$_2$ (X = Cl, I),[19] $(OC)_5W$(**3**)$W(CO)_5$[12] and $(OC)_3Ni$(**3**)$Ni(CO)_3$[12] and the starting materials $Et_4N[M(CO)_5I]$,[20] $M(CO)_4$ (norbornadiene),[21,22] *cis*-$Pt(PhCN)_2X_2$,[23] $(MeCN)M(CO)_5$,[24](**4**),[25](**5**)[13] and B_2H_6.[26] All preparations were carried out in a dry N_2 atmosphere with solvents purged with N_2.

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

Mo(CO)$_5$(2) This compound was prepared in the following manner based upon an earlier preparation by McInerney.[27] A solution of 1.32 g (5.00 mMol) of $Mo(CO)_6$, 0.90 ml (5.0 mMol) of (**2**) and 25 ml of methylcyclohexane was refluxed for 4 hours. It was then cooled to room temperature and the solvent was removed under vacuum. The tan residue was extracted in a Soxhlet apparatus with 40 ml of pentane for 3 hours. Cooling the pentane solution to −78° precipitated an off-white solid which was sublimed at 90°C (0.01 torr) to give 0.91 g (43%) of white product.

W(CO)$_5$(2) A mixture of 1.82 g (5.01 mMol) of $(MeCN)W(CO)_5$, 0.90 ml (5.0 mMol) of (**2**) and 35 ml of methylcyclohexane was heated to 85° for 10 hours during which time the color went from clear yellow to colorless. The hot solution was filtered and cooled slowly to −78° causing precipitation of an off-white solid which was sublimed at 95° (0.01 torr) to give 1.35 g (69%) of the white product.

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

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

*Cr(CO)$_5$(**5**)* A mixture of 1.35 g (3.00 mMol) of Et$_4$N[Cr(CO)$_5$I] and 0.48 ml (3.0 mMol) of (**5**) in 30 ml of CH$_2$Cl$_2$ was treated with 1.10 g (4.50 mMol) of AgNO$_3$ at room temperature for 30 minutes after which time the solvent was removed under vacuum. The residue was then extracted with 40 ml of a 1 : 1 toluene–hexane solution. After filtration, removal of solvents from the filtrate and drying, the resultant residue was extracted twice with 30 ml portions of pentane. The extracts were stripped of solvent and the yellow residue was sublimed at 85° (0.01 torr) to give 0.25 g (20%) of the pale yellow product.

*Fe(CO)$_4$(**5**)* A mixture of 1.82 g (5.00 mMol) of Fe$_2$(CO)$_9$ and 1.60 ml (10.0 mMol) of (**5**) in 50 ml of pentane was stirred at room temperature for 36 hours. The mixture was filtered and the filtrate was concentrated to 25 ml under vacuum. Cooling to −78° produced a solid which was filtered, washed twice with cold pentane and dried *in vacuo*. Sublimation at 80° (0.01 torr) produced 1.37 g (34%) of the pale yellow compound.

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

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

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

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

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

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

BH$_3$ Adducts The general procedure consisted of placing about 40 ml of 85% H$_3$PO$_4$ in a 250 ml round bottom flask and about 3 g of KBH$_4$ in an addition arm attached to the flask by a standard taper joint. This assembly was then attached to a vacuum line and evacuated for about 15 minutes. A trap was then cooled to −78° and two additional traps were cooled to −196°. The addition arm was rotated slightly and tapped so that small amounts of KBH$_4$ fell onto the surface of the magnetically stirred acid. All water vapor from the acid was trapped out in the first trap while most of the B$_2$H$_6$ was isolated in the second.

Addition of KBH$_4$ was accomplished over a two-hour period after which the first trap was isolated from the system. The condensate in the second trap was purified by warming it to −126° using a methylcyclohexane slush bath and condensing the B$_2$H$_6$ in the third trap at −196°.[28]

The purified B$_2$H$_6$ was measured out for reaction in a standard manner and condensed onto the frozen degassed solution of substrate (−196°) in a reaction tube. The solution was made by distilling dry solvent into the apparatus containing the substrate.

TABLE I

Reaction conditions and results for tensimetric titrations of (X)P(NMeCH$_2$)$_3$CMe with B$_2$H$_6$

X	Solvent	Equilibration temperature	Break point[a]
lone pair (**2**)	Et$_2$O	−78°	1.03[b]
O (**8**)	CH$_2$Cl$_2$	−78°	0.50[b]
S (**9**)	CH$_2$Cl$_2$	−78°	0.49[b]
Se (**10**)	CHCl$_3$	−45°	0.55
PhN (**14**)	CHCl$_3$	−45°	0.51
(OC)$_5$Cr	toluene	−78°	0.54
(OC)$_5$W	toluene	−78°	0.50
(OC)$_4$Fe	toluene	−78°	0.53
(OC)$_3$Ni	toluene	−78°	0.70[c]
trans-(**2**)(OC)$_4$W	toluene	−78°	0.96
trans-(**2**)(OC)$_3$Fe	toluene	−78°	1.01
(**2**)(OC)$_2$Ni	toluene	−78°	0.99

[a] Molar ratio of B$_2$H$_6$ to substrate at line intersection (see Figure 1).

[b] Ref. 13.

[c] See text.

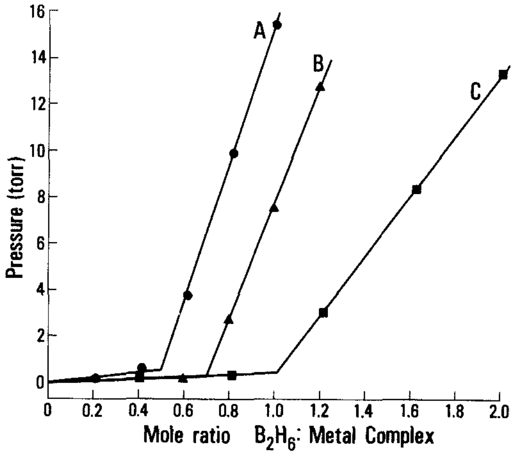


FIGURE 1 Tensimetric diborane titrations of some metal carbonyl derivatives of (2). Curve A, (●), $W(CO)_5(2)$; curve B, (▲), $Ni(CO)_3(2)$ and curve C, (■), $Fe(CO)_3(2)_2$ are illustrative of the general results obtained.

The frozen solution was then warmed to either −78° or −45° with agitation from a magnetically activated jump-stirring rod and allowed to equilibrate with the B_2H_6 for 20 minutes after which the pressure in the isolated tensimeter was measured. The isolation-equilibration process was then repeated to obtain the data presented in Table I and illustrated in Figure 1 for $W(CO)_5(2)$, $Ni(CO)_3(2)$ and *trans*-$Fe(CO)_3(2)_2$.

After the titration was finished, the cold solution was filtered under vacuum in an apparatus similar to one devised earlier[29] in order to remove any mercury that had condensed into the frozen solution at −196°. The volatiles were removed from the filtrate under vacuum to leave residues which were collected in a dry bag. The bis(borane) adducts of *trans*-$M(CO)_4(2)_2$ (M = Cr, Mo, W) were insoluble in toluene and were isolated from the filtering frit.

DISCUSSION

Syntheses

While Group VI carbonyl complexes of (**2**) have been synthesized before from the hexacarbonyls,[15,27,30] the yields were usually very low for both thermal and photolytic reactions. The one exception to this is the thermal preparation of $Mo(CO)_5(2)$ which proceeds in 43% yield. Yields of products were increased through the use of precursors such as $(MeCN)Cr(CO)_5$ and $Et_4N[Cr(CO)_5I]$. The former is made from the latter[24] as illustrated in reaction 1. The advantages of this reaction are that it produces high yields and leads only to monosubstituted products. The MeCN group is easily displaced by (**2**) at moderate temperatures to give the desired $Cr(CO)_5(2)$. It was not possible to react (**2**) and the metal carbonyl salt directly because (**2**) and its complexes will react with halogenated solvents.

$$Et_4N[Cr(CO)_5I] + MeCN + Et_3OBF_4 \xrightarrow[RT]{CH_2Cl_2} (MeCN)Cr(CO)_5 + Et_4NBF_4 + EtI + Et_2O \qquad (1)$$

Reaction of (**2**) with the $M(CO)_4(NBD)$ complexes gave good yields of *trans*-$M(CO)_4(2)_2$ even though the *cis* isomers are probably initially formed as was shown for M = Mo.[15] The greater stability of the *trans* isomers of (**2**) can also be rationalized on steric grounds as the cone angles of (**1**) and (**2**) should be quite similar.[31]

The syntheses of Fe and Ni carbonyl complexes of (**2**) are very similar to analogous preparations involving (**1**).[15,18] Of particular interest here is the unusual nature of $Ni(CO)_3(2)$. This compound is a clear, colorless liquid at room temperature which appears to be unstable towards heat and light. In contrast, $Ni(CO)_3(1)$ is a rose colored solid having a melting range from 103–113°.[18] It was observed that $Ni(CO)_3(1)$ is thermally unstable, decomposing to a dark brown oil upon standing at room temperature for a few days. Why these two compounds are so different remains obscure as the rigid cage of (**2**) might be anticipated to allow easy crystallization. The purity of $Ni(CO)_3(2)$ was verified by both infrared and ^{31}P nmr spectroscopy.

The two metal carbonyl complexes of (**3**) were synthesized to assess its ligating properties relative to (**1**) and (**2**) and, in the case of the tungsten complex, to allow calculation of $^3J^{31}P^{31}P$.

Although the tensimetric titrations of the complexes of (**2**) with B_2H_6 were not performed for each complex, at least one from each group was titrated to obtain stoichiometry. The other complexes in the group were simply reacted with an excess of B_2H_6 and their resulting compositions verified by comparison of their infrared and nmr spectra with those of a titrated compound. Except for $Ni(CO)_3(2)$, all of the complexes titrated absorbed 0.50 mole of B_2H_6 for every mole of ligated (**2**). The results of B_2H_6 adduction with $Ni(CO)_3(2)$ are quite similar to those seen earlier with $OP(NMe_2)_3$[13] which also gives a break at a ratio of 0.70 mole of B_2H_6 per mole of substrate. A difficulty with the nickel complex is its proclivity to decompose, which prevented isolation of the pure compound. To test the possibility that the reaction of (**2**) with $Ni(CO)_4$ was incomplete, thereby allowing the ligand to add two BH_3 groups to form (**7**), the complex was synthesized from (**2**) in the presence of a 20 mole % excess of $Ni(CO)_4$ in dry toluene. The solution was then degassed on the vacuum line and titrated with B_2H_6. Both ^1H and ^{31}P nmr spectra of the reaction solution before and after B_2H_6 titration showed no detectable chemical shifts for (**2**), (**6**), or (**7**). It is possible that association of a BH_3 group with a carbonyl oxygen is the cause of the extra 0.2 mole of B_2H_6 per mole of (**2**).

In addition to the adducts containing one mole of BH_3 per mole of ligated (**2**), it was possible to limit the amount of B_2H_6 in the titration to obtain the complexes in which only one of the two ligands are bound, i.e., *trans*-(**2**)M$(CO)_4$[(**2**)$\cdot BH_3$], *trans*-(**2**)Fe$(CO)_3$[(**2**)$\cdot BH_3$] and (**2**)Ni$(CO)_2$[(**2**)$\cdot BH_3$]. Although statistically, the product should be a mixture of the starting complex, the mono- and the bis-adducts, ^{31}P nmr spectroscopy shows the mono-adducts clearly dominate the other two possible species.

The solution stability of the adducts can best be described as fair. Even in dry solvents the adducts decomposed with loss of gas and production of a flocculent precipitate. Solutions in aromatic solvents were stable for several hours although peaks arising from the parent compounds could be observed to form in the nmr spectra.

*ν*CO

The CO frequencies of the metal carbonyl complexes of (**1**)–(**5**) and (**2**)$\cdot BH_3$ synthesized in this work are listed in Tables II–VII. A comparison of the data for a particular metal carbonyl moiety shows that *ν*CO increases in the order (**1**) < (**2**) < (**2**)$\cdot BH_3$. The order (**1**) < (**2**) parallels that of $P(OMe)_3$ < $P(OCH_2)_3CMe$ in such complexes,[1] and this trend can be ascribed to the decreasing sigma basicity upon molecular constraint of the ligand and/or an accompanying increase in pi acidity of phosphorus.[7] The position of the ligand (**2**)$\cdot BH_3$ is also consistent with these ideas since the BH_3 group

TABLE II

Carbonyl stretching frequencies of monosubstituted group VI metal carbonyl complexes

Compound	*ν*CO Mode[a,b]					Solvent	Reference
	A_1^2	B_1^c	A_1^1	E	$E(^{13}C)$		
$Cr(CO)_5$ (**1**)	2060.6m	1975.4	1946.7sh	1938.0vs[d]	1912.8vw	C_6H_{12}	This work
	2064w	—[e]	1943s	1934vs	—[e]	C_6H_{12}	17
$Cr(CO)_5$ (**2**)	2067.0m	1983.0	1951.0sh	1944.7vs	1915.0vw	C_6H_{12}	This work
	2066w	—[e]	1980w	1942vs	—[e]	$CHCl_3$	1, 15
$Cr(CO)_5$[(**2**)$\cdot BH_3$]	2073.2m	1995.3w[f]	1962.1s	1949.4vs[g]	1914.5vw	C_6H_{12}	This work
$Mo(CO)_5$ (**1**)	2070.6w	1985.1	1947.9sh	1945.6vs[h]	1910.2vw	C_6H_{12}	This work
	2073w	—[e]	1949s	1942s	—[e]	C_6H_{12}	17
$Mo(CO)_5$ (**2**)	2075.4w	1992.9	1954.6sh	1951.1vs	1920.8vs	C_6H_{12}	This work
$Mo(CO)_5$[(**2**)$\cdot BH_3$]	2081.6m	1999.8w[f]	1966.0s	1954.2vs[i]	1915.5vw	C_6H_{12}	This work
$W(CO)_5$ (**1**)	2074.9w	1980.5	1943.4sh	1937.4vs[j]	1903.3vw	C_6H_{12}	This work
	2070.0	1971.0	—[e]	1936.0[k]	1902.6	C_6H_{12}	30
	2074w	—[e]	1940s	1932s	—[e]	C_6H_{12}	17
$W(CO)_5$ (**2**)	2074.9w	1984.1	1949.7sh	1944.4vs	1914.4	C_6H_{12}	This work
	2071.5	—[e]	1949.0	1943.0	1914.0	C_6H_{12}	30[l]
$W(CO)_5$[(**2**)$\cdot BH_3$]	2080.0w	1990.6w	1961.4s	1947.8vs[m]	—[e]	C_6H_{12}	This work
$(CO)_5W$(**3**)$W(CO)_5$	2076.7w	2019.4	1963.4m	1954.6vs	1920.6vw	C_6H_{12}	This work
$Cr(CO)_5$ (**4**)	2074w	—[e]	1956s	1945s	—[e]	C_6H_{12}	17
$Cr(CO)_5$ (**5**)	2072.2w	—[e]	1957.8sh	1954.4vs	—[e]	C_6H_{12}	This work

[a] Frequencies quoted in this work are precise to $\pm 0.5\ cm^{-1}$.

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

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

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

[e] Either not observed or not reported.

[f] Band observed in infrared spectrum.

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

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

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

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

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

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

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

TABLE III

Carbonyl stretching frequencies of disubstituted group VI metal carbonyl complexes

Compound	νCO Mode[a,b]			Solvent	Reference
	A_{1g}[c]	B_{1g}[c]	E_u		
trans-Cr(CO)$_4$(1)$_2$	2004.5	1928.5	1883.7vs	C_6H_{12}	This work
	—[d]	—[d]	1880vs	C_6H_{12}	17
trans-Cr(CO)$_4$(2)$_2$	2019.0	1942.5	1899.8vs	C_6H_{12}	This work
	—[d]	1938w	1887vs	$CHCl_3$	1, 15
	—[d]	1931w	1876vs	Nujol	15
trans-Cr(CO)$_4$[(2)·BH$_3$]$_2$	2032.5w[e]	1946.6w[e]	1919.0vs, 1909.2vs	C_6H_{12}	This work
trans-Mo(CO)$_4$(1)$_2$	2019.5	1939.5	1892.7vs	C_6H_{12}	This work
	—[d]	—[d]	1891vs	C_6H_{12}	17
trans-Mo(CO)$_4$(2)$_2$	2032.0	1955.0	1909.2vs	C_6H_{12}	This work
	—[d]	1949w	1905vs	$CHCl_3$	1, 15
trans-Mo(CO)$_4$[(2)·BH$_3$]$_2$	2044.6w[e]	1951.6w[e]	1926.6vs, 1920.7vs	C_6H_{12}	This work
trans-W(CO)$_4$(1)$_2$	2018.0	1935.0	1884.9vs	C_6H_{12}	This work
	—[d]	—[d]	1884vs	C_6H_{12}	17
trans-W(CO)$_4$(2)$_2$	2029.5	1949.5	1902.1vs	C_6H_{12}	This work
	—[d]	1938w	1894vs	$CHCl_3$	1,15
trans-W(CO)$_4$[(2)·BH$_3$]$_2$	2042.0w[e]	—[d]	1917.9vs, 1914.5vs	C_6H_{12}	This work

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

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

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

[d] Either not observed or not reported.

[e] Band observed in infrared spectrum.

TABLE IV

Carbonyl stretching frequencies of monosubstituted iron carbonyl complexes

Compound	νCO Mode[a,b]			Solvent	Reference
	$A_1{}^2$	$A_1{}^1$	E		
Fe(CO)$_4$(1)	2047.8s	1973.3s	1936.2vs	C_6H_{12}	This work
	2053m	1975m	1937s	C_6H_{12}	17
Fe(CO)$_4$(2)	2058.0s	1985.3s	1951.4vs	C_6H_{12}	This work
	2053m	1976m	1942vs	$CHCl_3$	1, 15
Fe(CO)$_4$[(2)·BH$_3$]	2065.3s	1996.9s	1967.1vs	C_6H_{12}	This work
Fe(CO)$_4$(4)	2060m	1979m	1949s	C_6H_{12}	17
Fe(CO)$_4$(5)	2061.2s	1988.6s	1960.0vs	C_6H_{12}	This work

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

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

TABLE V

Carbonyl stretching frequencies of disubstituted iron carbonyl complexes

Compound	νCO Mode[a,b]		Solvent	Reference
	A'_1[c]	E'		
trans-Fe(CO)$_3$(1)$_2$	1962.4	1878.1vs	C_6H_{12}	This work
	—[d]	1871vs	halocarbon	16
trans-Fe(CO)$_3$(2)$_2$	1993.0	1905.2vs	C_6H_{12}	This work
	—[d]	1890vs[e]	$CHCl_3$	1, 15
trans-Fe(CO)$_3$[(2)·BH$_3$)]$_2$	—[d]	1922.5vs	C_6H_{12}	This work

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

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

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

[d] Either not observed or not reported.

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

TABLE VI
Carbonyl stretching frequencies of monosubstituted nickel carbonyl complexes

Compound	νCO Mode[a,b]		Solvent	Reference
	A_1	E		
$Ni(CO)_3$(**1**)	2064.6m	1991.5vs	C_6H_{12}	This work
	2066	1984	Nujol	18
$Ni(CO)_3$(**2**)	2075.7m	2003.4vs	C_6H_{12}	This work
	2079m	2004vs	$CHCl_3$	15
$Ni(CO)_3$[(**2**)·BH_3]	2085.8s	2023.5vs, 2005.0vs	C_6H_{12}	This work
$(OC)_3Ni$(**3**)$Ni(CO)_3$	2078.7m	2013.0s	C_6H_{12}	This work

[a] Frequencies quoted in this work are precise to ±0.5 cm^{-1}.
[b] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

TABLE VII
Carbonyl stretching frequencies of disubstituted nickel carbonyl complexes

Compound	νCO Mode[a,b]		Solvent	Reference
	A_1	B_1		
$Ni(CO)_2$(**1**)$_2$	1997.0m	1938.1s	C_6H_{12}	This work
	1996	1938	Nujol	18
	1992vs	1929vs	halocarbon	16
$Ni(CO)_2$(**2**)$_2$	2016.2m	1960.1s	C_6H_{12}	This work

[a] Frequencies quoted in this work are precise to ±0.5 cm^{-1}.
[b] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

is expected to withdraw electron density from the phosphorus *via* the sigma bond in the affected P–N link upon adduct formation with the nitrogen.

It is reasonable to expect that (**2**) and (**3**) should possess about the same cone angle as estimated for (**1**)[31] because the rigid natures of (**2**) and (**3**) force the methyl groups to point towards the phosphorus end of the molecule, and free P–N rotation in (**1**) allows similar orientations. Thus steric interactions between any of these three ligands and neighboring CO groups should be about the same and CO frequency differences in analogous complexes of (**1**), (**2**) or (**3**) should be mainly electronic in origin. That symmetry effects influence CO ir patterns is demonstrated by the *E* mode splitting of the $M(CO)_5L$ species when L is (**1**) or (**2**)·BH_3 but not when L is the highly symmetrical (**2**) or (**3**). This phenomenon has also been observed for $M(CO)_5L$ complexes of P(*o*-$MeC_6H_4)_3$[33] and was attributed to a distortion of the symmetry of the complex by the steric interaction of the bulky ligand.[34] An estimated cone angle of 194°[31] for the tris-tolyl phosphine tends to support the hypothesis. While this behavior was first observed in our laboratories for $W(CO)_5$(**1**) in C_6H_{12} solution,[30] others [17] have assigned these bands as the $A_1{}^1$ and *E* modes (see Table II) for all the $M(CO)_5L$ complexes of (**1**). These workers also assigned the CO spectrum of $Cr(CO)_5$(**4**) in an analogous manner.

The phenomenon of split E modes arises again in *trans*-$M(CO)_4L_2$ and $Ni(CO)_3L$ complexes of (**2**)·BH_3 but not for (**1**), in contrast to the $M(CO)_5L$ complexes of both of these ligands. However, no E mode splitting is observed in the $Fe(CO)_4L$ or *trans*-$Fe(CO)_3L_2$ complexes of either ligand.

TABLE VIII
Parameters for some $Mo(CO)_5L$ species calculated by the Cotton–Kraihanzel method

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

[a] Force constants are in units of millidynes/Angstrom.
[b] In cm^{-1}.
[c] Values measured by Raman spectroscopy are precise to ±1.0 cm^{-1}.
[d] Observed in the infrared spectrum.

While the direct comparison of CO frequencies can be used to interpret ligand bonding abilities, a better comparison comes from the force constants derived from νCO spectra. Using the Cotton–Kraihanzel method (CKM) to calculate the force constant parameters for $M(CO)_5L$ species,[35] the data displayed in Table VIII were obtained. The CKM can be used when only the A_1^1, A_1^2 and E modes are observed, by placing the constraints upon the system that $k_{cis} > k_{trans}$ and that all CO *cis* interactions are about equal. A check on the validity of the CKM can be made by using the various force constants to calculate the B_1 mode frequency. Good agreement can usually be found, as is the case for all the complexes in this work where B_1 was determined by Raman spectroscopy. While k_{cis} and k_{trans} both increase in the ligand order (**1**) < (**2**) < (**2**)·BH_3 for a given $M(CO)_5L$ complex, it is readily seen that k_{trans} is greatly increased by replacement of (**2**) with (**2**)·BH_3 in the complexes while the increase in k_{cis} is comparatively small.

Because the MP pi bond order might be expected to increase upon increasing the electronegativity of phosphorus by adduct formation of ligated (**2**), it was of interest to see if νPO in (**8**) would rise on formation of (**11**) since the pi donor properties of oxygen in this type of linkage are well accepted. Indeed PO of (**8**) in CCl_4 is 1285 cm^{-1} while that of (**11**) is at 1303 cm^{-1}. To what extent this effect is operative in the metal complexes is presently unclear.

^{1}H nmr Spectra

That the caged aminophosphine selenide (**10**) adds a BH_3 group to a nitrogen in (**13**) can be seen from its ^{1}H nmr spectrum which progresses from a simple set of resonances for the former (δ 0.89, 1CCH_3; δ 2.62, 3NCH_3, $^3J^{31}P^1H = 16.0$; δ 3.06, 3CH_2, $^3J^{31}P^1H = 7.0$ in CD_3CN) to a more complicated one for the latter (see later discussion in this section) which resembles those reported earlier for the analogous chalcogen derivatives (**11**) and (**12**).[13] By contrast the spectrum of (**15**) has the same appearance as that of (**14**) indicating that the BH_3 group is attached to the phenyl nitrogen. While this appears to be a general reaction of phosphinimines with Lewis acids,[36] it is noteworthy that additional B_2H_6 does not react with a ring nitrogen.

In none of the above or the following cases were the BH_3 protons observed in the spectra. However, proton signal broadenings due to $^3J^{11}B^1H$ couplings were useful in making nmr spectral assignments (see later).

The ^{1}H nmr spectra of some metal carbonyl complexes of (**1**)[16] and (**2**)[15] have been reported previously. In the case of (**1**), the spectra were used mainly for characterization but some inferences about $^2J^{31}P^{31}P$ in the complexes were made. In the present work, the ^{1}H nmr spectral data summarized in Table IX for complexes (**1**), (**2**) and (**3**) were examined to see whether changes in metal–phosphorus bonding could be discerned.

Of note is the difference in $^3J^{31}P^1H_3$ between complexes of (**1**) and (**2**). The free rotation about the P–N bond in (**1**) leads to an averaging of the *cis* and *trans* $^3J^{31}P^1H$ couplings. Averaging $^3J^{31}P^1H_3$ and $^3J^{31}P^1H_2$ for the monosubstituted complexes of (**2**), leads to average $^3J^{31}P^1H$ values of 9.7, 10.2, 10.2 and 11.1 Hz for the Cr, Mo, W and Fe species, respectively, as compared to 10.1, 10.2, 11 and 9.6 Hz for the analogous complexes of (**1**). A similar result is obtained for the *trans* disubstituted species. It is interesting that for complexes of (**2**) the $^3J^{31}P^1H$ values are large for the cisoid coupling ($^3J^{31}P^1H_3$) and small for the transoid coupling ($^3J^{31}P^1H_2$). This is similar to the findings for $^2J^{31}P^{13}C$ values in P(III) compounds.[37] In the latter case the cisoid couplings are positive in sign while the transoid couplings are negative. The signs of $^3J^{31}P^1H$ for complexes of (**2**) were not determined in this work.

While the spectra of the monosubstituted complexes of (**1**) and (**2**) are straightforward, the NCH_3 and CH_2 protons in the *trans* disubstituted complexes no longer appear as doublets but rather are pseudotriplets due to $^2J^{31}P^{31}P$ virtual coupling. This phenomenon has been noticed in other metal complexes of phosphorus ligands[1] and the amount of the triplet character has been used[16] to estimate qualitatively the magnitude of $^2J^{31}P^{31}P$. The triplet appearance varies from none in $Ni(CO)_2L_2$, to very slight (a 3 : 1 : 3 triplet) in *trans*-$Cr(CO)_4L_2$, to moderate (1 : 1 : 1) in the *trans* Mo and W species, to substantial (2 : 3 : 2) in *trans*-$Fe(CO)_3L_2$. We return to this point in the next section.

Upon BH_3 adduct formation of one cage nitrogen of (**2**) the ^{1}H nmr spectrum becomes complex owing to the non-equivalence of N-methyl groups and all of the protons of the NCH_2 bridges. An example is the ^{1}H nmr spectrum of $W(CO)_5[(\mathbf{2})\cdot BH_3]$ shown in Figure 2. The three doublets which arise from the NMe protons stand out noticeably but the NCH_2 proton resonances are masses of multiplets. Although it was not possible to analyze the NCH_2 resonances, the NMe resonances were assigned and are listed in Table X. Assuming that the broadening of one of the NMe proton doublets is due to the proximity of a quadrupolar B atom, these reson-

TABLE IX
Proton nmr spectral data for metal carbonyl derivatives of $P(NMe_2)_3$(**1**), $P(NMeCH_2)_3CMe$(**2**) and $P(NMeNMe)_3P$(**3**)

Compound	δNMe^a	$^3J^{31}P^1H_3{}^{b,c}$	$\delta NCH_2{}^a$	$^3J^{31}P^1H_2{}^{b,c}$	δCMe^a	Solvent	Reference
$Cr(CO)_5$(**1**)	2.26	10.1	—	—	—	C_6H_6	16, 17
$Cr(CO)_5$(**2**)	2.55	15.0	2.31	4.4	0.26	C_6D_6	This work
$Cr(CO)_5$(**2**)	2.57	15.2	2.34	4.5	0.28	C_6H_6	15
$Mo(CO)_5$(**1**)	2.25	10.2	—	—	—	C_6H_6	16, 17
$Mo(CO)_5$(**2**)	2.54	15.8	2.31	4.5	0.29	C_6D_6	This work
$Mo(CO)_5$(**2**)	2.57	15.8	2.37	4.3	0.37	C_6H_6	15
$W(CO)_5$(**1**)	2.19	11.0	—	—	—	C_6H_6	17
$W(CO)_5$(**1**)	2.26	10.2	—	—	—	C_6D_6	This work
$W(CO)_5$(**2**)	2.54	15.5	2.33	4.8	0.27	C_6D_6	This work
$Fe(CO)_4$(**1**)	2.34	9.6	—	—	—	C_6H_6	16, 17
$Fe(CO)_4$(**2**)	2.51	15.9	2.34	6.3	0.30	C_6D_6	This work
$Ni(CO)_3$(**2**)	2.38	16.0	2.35	5.5	0.43	C_6D_6	This work
$(OC)_5W$(**3**)$W(CO)_5$	2.68	13.0^d	—	—	—	C_6D_6	This work
$(OC)_3Ni$(**3**)$Ni(CO)_3$	2.62	14.7^d	—	—	—	C_6D_6	This work
trans-$Cr(CO)_4$(**1**)$_2$	2.58	9.7	—	—	—	C_6H_6	16, 17
trans-$Cr(CO)_4$(**2**)$_2$	2.95	14.2	2.60	4.4	0.40	C_6D_6	This work
trans-$Cr(CO)_4$(**2**)$_2$	2.93	14.3	2.62	4.3	0.45	C_6H_6	15
trans-$Mo(CO)_4$(**1**)$_2$	2.67	10.0	—	—	—	—^{e}	17
trans-$Mo(CO)_4$(**2**)$_2$	2.92	15.2	2.59	4.7	0.43	C_6D_6	This work
trans-$Mo(CO)_4$(**2**)$_2$	2.88	15.1	2.62	4.4	0.48	C_6H_6	15
trans-$W(CO)_4$(**1**)$_2$	2.55	10.2	—	—	—	—^{e}	17
trans-$W(CO)_4$(**2**)$_2$	2.90	15.5	2.62	4.6	0.42	C_6D_6	This work
trans-$W(CO)_4$(**2**)$_2$	2.89	14.9	2.63	5.0	0.44	C_6H_6	15
trans-$Fe(CO)_3$(**1**)$_2$	2.65	9.4	—	—	—	—^{e}	17
trans-$Fe(CO)_3$(**2**)$_2$	2.82	15.6	2.56	6.7	0.47	C_6D_6	This work
trans-$Fe(CO)_3$(**2**)$_2$	2.88	15.5	2.62	6.6	0.48	C_6H_6	15
$Ni(CO)_2$(**1**)$_2$	2.47	9.3	—	—	—	—^{e}	17
$Ni(CO)_2$(**2**)$_2$	2.74	15.6	2.54	4.8	0.50	C_6D_6	This work

[a] Values reported in this work are precise to ±0.01 ppm.

[b] Values reported in this work are precise to ±0.1 Hz.

[c] $^3J^{31}P^1H$ values for *trans* species are pseudotriplets due to $^2J^{31}P^{31}P$ coupling. The value reported is the separation of the two outermost peaks.

[d] Pseudotriplet due to $^3J^{31}P^{31}P$ coupling. Value reported is actually $|^4JPH + {}^3JPH|$.

[e] Solvent not specified.

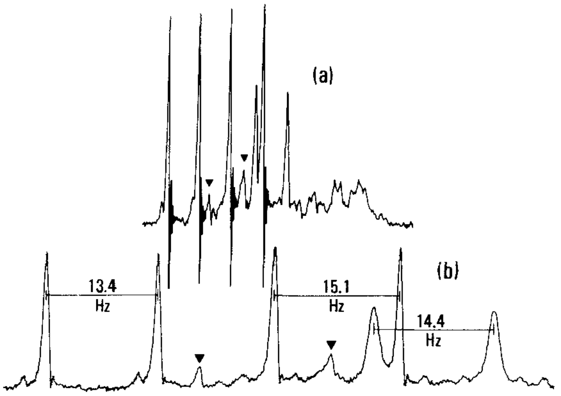


FIGURE 2 Proton nmr spectrum of $W(CO)_5[$(**2**)$\cdot BH_3]$ in the NMe and NCH_2 region (a). An expansion of the NMe region showing broadened Me proton resonances of the adducted NMe moiety (b). The peaks marked with ▼ arise from the NMe groups of $W(CO)_5$(**2**).

ances are assigned to the adducted NMe group. It will be noted in Table X that the chemical shifts for the NMe_c protons are very similar to those of the NMe protons in the non-adduct species (cf. Table IX). It seems reasonable, therefore, to assign the NMe protons as shown in Figure 3.

The spectra of the disubstituted complexes of (**2**)$\cdot BH_3$ were very complex, perhaps owing to the possibility of diastereomeric mixtures arising from the chiral nature of the ligand.

^{31}P *nmr Spectra*

The trend in $\delta^{31}P$ for the chalconide and borane derivatives of the non-adducts as well as the adducts in Table XI is interesting in that it parallels the expected increase in the dipolar nature of the X ← P link.[12] A similar trend exists for $XP(OCH_2)_3CMe$ where X = O, S, Se and H_3B ($\delta = -7.97$,[38] 57.4,[38] 60.1[39] and 97,[40] respectively). Also interesting is the

TABLE X
Proton nmr resonances of the NMe groups in $(X)P(NMeCH_2)_3CMe \cdot BH_3$[a,b]

X	δNMe_a	$^3J^{31}P^1H$	δNMe_b	$^3J^{31}P^1H$	δNMe_c	$^3J^{31}P^1H$
BH_3	2.72	12.5	2.85	12.1	2.77	10.2
O	2.81	10.9	2.84	11.2	2.76	11.4
S	2.79	13.1	2.94	13.4	2.87	14.0
Se	2.74	14.2	2.96	14.5	2.74	14.2
$Cr(CO)_5$	2.43	13.9	2.77	12.8	2.50	14.7
$Mo(CO)_5$	2.34	14.2	2.77	13.6	2.46	15.2
$W(CO)_5$	2.36	14.4	2.76	13.4	2.48	15.1
$Fe(CO)_4$	2.46	14.7	2.80	13.8	2.54	16.1
$Ni(CO)_3$	2.29	14.1[c]	2.68	14.7[c]	2.31	14.0[c]

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

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

[c] Precise to ±0.5 Hz.

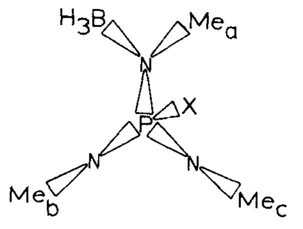


FIGURE 3 Assignment of the protons corresponding to the ^1H chemical shifts in Table X.

increase in the ^{31}P downfield shift upon adduct formation in the same order in Table X. The high field position of $\delta^{31}P$ in the phenylimido derivative (**14**) suggests that a smaller shift might have been expected upon adduct formation (i.e., more similar to the change from (**8**) to (**11**). This result coupled with the simple ^1H nmr spectrum observed for (**15**) indicates the probable presence of a $PhNBH_3$ group.

TABLE XI
^{31}P data for $XP(NMeCH_2)_3CMe$ and its BH_3 adduct in $CDCl_3$

X	$\delta^{31}P$[a]	
	Non-adduct	Adduct
O	19.8 (**8**)	19.9 (**11**)
S	73.2 (**9**)	78.0 (**12**)
Se	77.7[b] (**10**)	85.7[c] (**13**)
H_3B	89.1 (**6**)[d]	101.6 (**7**)[d]
PhN	11.4 (**14**)	30.0 (**15**)

[a] Precise to ±0.05 ppm except where noted.

[b] $^1J^{31}P^{77}Se$ = 854 Hz.

[c] $^1J^{31}P^{77}Se$ = 943 Hz.

[d] The separations between the two central peaks of the partially collapsed quartets were 77 and 74 Hz in (**6**) and (**7**), respectively. The breadth of the peaks yield $\delta^{31}P$ value precise to ±0.2 ppm.

The footnotes in Table XI record the fact that adduct formation of selenide (**10**) gives rise to a substantial increase in $^1J^{31}P^{77}Se$. This can be ascribed to the increase in phosphorus electronegativity which can increase phosphorus s character as well as its positive charge; both effects augmenting the Fermi contact contribution to this coupling.[41]

Although evidence of $^{31}P-^{11}B$ coupling could be seen in the spectra of (**6**) and (**7**), the expected quartets in each case were broad and partially collapsed owing to partial quadrupolar relaxation by ^{11}B.

The consistent upfield ^{31}P chemical shift from Cr to Mo to W analogues in Table XII for all the ligands is undoubtedly associated with the increase in the diamagnetic contribution of the metal atom.[43] Adduct formation of a ligand produces a substantial downfield shift of ligated (**2**) as was found to be the case for the more polar borane and chalconide derivatives (**6**), (**9**) and (**10**) (Table XI). Furthermore the changes in $\delta^{31}P$ (and in $^1J^{31}P^{183}W$ in the tungsten complexes) facilitated the assignments of the adduct and non-adduct forms of (**2**) in data listed in Table XIII. The rise in $^1J^{31}P^{183}W$ upon BH_3 adduct formation of ligated (**2**) footnoted in Table XII is consistent with the change in $^1J^{31}P^{77}Se$ discussed earlier for the same reaction of (**10**). The increase in $^1J^{31}P^{183}W$ on substituting two ligands in *trans* positions originates in a complex process[1] since decreases are often noted upon *cis* substitution.[44]

The relatively small change in $^1J^{31}P^{183}W$ upon adduct formation of ligated (**2**) (<5%) might be expected to affect $^2J^{31}P^{31}P$ in a similar manner. The values of the latter coupling given in Table XIII are

TABLE XII

$\delta^{31}P$ values for metal carbonyl complexes of $P(NMe_2)_3(\mathbf{1})$, $P(NMeCH_2)_3CMe(\mathbf{2})$, $(\mathbf{2})\cdot BH_3$ and $P(NMeNMe)_3P(\mathbf{3})$[a]

Compound	$\delta^{31}P$	Compound	$\delta^{31}P$
$Cr(CO)_5(\mathbf{1})$	159.9	*trans*-$Mo(CO)_4(\mathbf{2})_2$	138.8
$Mo(CO)_5(\mathbf{1})$	145.6[b]	*trans*-$W(CO)_4(\mathbf{2})_2$	116.1[c]
$W(CO)_5(\mathbf{1})$	126.5[d]	*trans*-$Fe(CO)_3(\mathbf{2})_2$	162.1
$Fe(CO)_4(\mathbf{1})$	155.4	$Ni(CO)_2(\mathbf{2})_2$	121.7
$Ni(CO)_3(\mathbf{3})$	144.7[b]	$(OC)_5W(\mathbf{3})W(CO)_5$	134.6[e]
trans-$Cr(CO)_4(\mathbf{1})_2$	173.5[f]	$(OC)_3Ni(\mathbf{3})Ni(CO)_3$	131.2
trans-$Mo(CO)_4(\mathbf{1})_2$	159.1[g]	$Cr(CO)_5[(\mathbf{2})\cdot BH_3]$	162.8
trans-$W(CO)_4(\mathbf{1})_2$	133.9[h,i]	$Mo(CO)_5[(\mathbf{2})\cdot BH_3]$	143.1
trans-$Fe(CO)_3(\mathbf{1})_2$	169.8[j]	$W(CO)_5[(\mathbf{2})\cdot BH_3]$	127.5[k]
$Ni(CO)_2(\mathbf{1})_2$	147.1[b]	$Fe(CO)_4[(\mathbf{2})\cdot BH_3]$	169.7
$Cr(CO)_5(\mathbf{2})$	145.0	$Ni(CO)_3[(\mathbf{2})\cdot BH_3]$	131.3
$Mo(CO)_5(\mathbf{2})$	126.8	*trans*-$Cr(CO)_4[(\mathbf{2})\cdot BH_3]_2$	178.0
$W(CO)_5(\mathbf{2})$	109.7[l,m]	*trans*-$Mo(CO)_4[(\mathbf{2})\cdot BH_3]_2$	156.1
$Fe(CO)_4(\mathbf{2})$	152.3	*trans*-$W(CO)_4[(\mathbf{2})\cdot BH_3]_2$	132.6[n]
$Ni(CO)_3(\mathbf{2})$	121.1	*trans*-$Fe(CO)_3[(\mathbf{2})\cdot BH_3]_2$	176.4
trans-$Cr(CO)_4(\mathbf{2})_2$	159.4	$Ni(CO)_2[(\mathbf{2})\cdot BH_3]_2$	131.3

[a] All spectra are precise to ±0.05 ppm and are recorded in C_6D_6 except as noted.

[b] From Ref. 42, measured by CW nmr in C_6H_6.

[c] $^1J^{31}P^{183}W = 360$ Hz.

[d] $^1J^{31}P^{183}W = 314$ Hz.

[e] $^1J^{31}P^{183}W = 338$ Hz was calculated using ITRCAL (see Ref. 12).

[f] Ref. 43 reports 178.19 ppm in CS_2 (CW nmr).

[g] Ref. 43 reports 159.39 ppm in C_6D_6; Ref. 42 reports 159.4 ppm in C_6H_6 (CW nmr).

[h] Ref. 43 reports 134.17 ppm in C_6D_6 (CW nmr) but no ^{1}JPW value.

[i] $^1J^{31}P^{183}W = 347$ Hz.

[j] Ref. 43 reports 170.18 ppm in C_6D_6 (CW nmr).

[k] $^1J^{31}P^{183}W = 332$ Hz.

[l] Ref. 30 reports 112.0 ppm in CH_2Cl_2 (CW nmr) for the complex where L = $P(NMeCH_2)_3CC_5H_{11}$; ^{1}JPW was reported as 318 Hz.

[m] $^1J^{31}P^{183}W = 321$ Hz.

[n] $^1J^{31}P^{183}W = 376$ Hz.

TABLE XIII

^{31}P nmr chemical shifts and $^2J^{31}P^{31}P$ for metal complexes of the type $M(CO)_x[(PNMeCH_2)_3CMe][P(NMeCH_2)_3CMe\cdot BH_3]$[a]

Compound	$\delta^{31}P_{adduct}$[b]	$\delta^{31}P_{non\text{-}adduct}$[b]	$^2J^{31}P^{31}P$
trans-$Cr(CO)_4(\mathbf{2})[(\mathbf{2})\cdot BH_3]$	180.2	158.2	(−) 20
trans-$Mo(CO)_4(\mathbf{2})[(\mathbf{2})\cdot BH_3]$	157.6	137.3	(+) 116
trans-$W(CO)_4(\mathbf{2})[(\mathbf{2})\cdot BH_3]$	135.3[c]	113.6[d]	(+) 113
trans-$Fe(CO)_3(\mathbf{2})[(\mathbf{2})\cdot BH_3]$	178.5	159.3	(+) 82
$Ni(CO)_2(\mathbf{2})[(\mathbf{2})\cdot BH_3]$	135.2	120.2	0[e]

[a] Spectra were recorded on $CD_3C_6D_5$ solutions at room temperature. The resulting AB spectra were analyzed for $\delta^{31}P$ and coupling constants using ITRCAL (see Ref. 12).

[b] Precise to ±0.05 ppm.

[c] ^{1}JWP = 377 Hz.

[2] ^{1}JWP = 358 Hz.

[e] No coupling was detected.

consonant with this idea. The order Ni < Cr < Fe < W ≈ Mo for $^2J^{31}P^{31}P$ is the same as that determined earlier in our laboratories by other methods for $M(CO)_x(\mathbf{1})_2$ where M = Cr, Fe, W and Mo.[44] Based on the sign determinations carried out in the latter work,[44] all the finite $^{31}P^{31}P$ couplings in Table XIII are probably positive expect that for the chromium complex which is very likely negative.

TABLE XIV

^{31}P nmr spectral data for platinum(II) complexes of $P(NMe_2)_3$(**1**) and $P(NMeCH_2)_3CMe$(**2**)[a]

Complex	Isomer	$\delta^{31}P$	^1JPtP
$PtCl_2(\mathbf{1})_2$	*trans*	89.1	3220
$PtCl_2(\mathbf{1})_2$	*cis*	66.6	5024
$PtI_2(\mathbf{1})_2$	*trans*	87.1	3065
$PtCl_2(\mathbf{2})_2$	*trans*	76.4	3482
$PtCl_2(\mathbf{2})_2$	*cis*	70.7	4641
$PtI_2(\mathbf{2})_2$	*cis*	70.2	4497

[a] Spectra recorded in C_6D_6 solution and chemical shifts are precise to ±0.05 ppm.

Far ir Spectra

Because the comparison of the far ir spectra of $P(OCH_2)_3CMe$, $As(OCH_2)_3CMe$ and their carbonyl complexes led to the assignment of sharp bands in the 200 cm^{-1} region of the phosphite complexes to νMP modes,[1] it was of interest to attempt similar experiments using (**2**) and (**5**). The large number of bands in the ligand spectra and the similarity of these absorption patterns to those of the complexes rendered our efforts fruitless however. Formation of BH_3 adducts of the complexes appeared only to further complicate the spectra.

Platinum(II) Complexes

In order to explore the ligand properties of constrained aminophosphines, with metals in oxidation states greater than zero, some preliminary studies were carried out in which the PtX_2L_2 complexes reported earlier from our laboratories where L = (**1**)[10] were compared with those where L = (**2**). The stereochemistries of the complexes in Table XIV were assigned on the basis of the patterns of the ^1H nmr absorptions in the NMe and NCH_2 regions (doublets for *cis* and pseudotriplets for *trans*). The expectation that $\delta^{31}P$ for *cis* complexes is upfield of the *trans* isomers[45,46] is seen to be realized in Table XIV as is the larger value of $^1J^{31}P^{195}Pt$[47] for the former isomer.

When the complexes are isolated, all but $PtI_2(\mathbf{2})_2$ are pure *trans* according to the ^{31}P nmr spectrum. Upon standing in the same solvent (C_6D_6), *trans*-$PtCl_2(\mathbf{2})_2$ isomerizes to a 2.25 : 1 trans/cis ratio in ten hours at room temperature while after twenty-one days the analogous complex of (**1**) possesses a trans/cis ratio of 3.2 : 1.

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