^{95}Mo NMR Spectroscopic Evidence for the Weak π-Acceptor Ability of PCl_3

Elmer C. Alyea* and Shuquan Song

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Received January 5, 1995®

Stepwise-displaced molybdenum carbonyl complexes $Mo(CO)_{6-n}L_n$ (n = 1–3) of chlorosubstituted phosphine ligands $PPh_{3-m}Cl_m$ (m = 0–3) were prepared and studied by ^{95}Mo, ^{31}P, and ^{13}C NMR spectroscopies. The extremely deshielding influence of the PCl_3 ligand (and related ligands) on the transition metal NMR chemical shift and the shielding trend on the ^{31}P NMR resonance position indicate that this putatively strong π-acceptor is actually a weaker π-acceptor than all other phosphorus ligands employed (except for PBr_3). This conclusion is consistent with ^{13}C NMR and IR spectroscopic results for all the complexes and is also in agreement with the known very weak bond strength of M–PCl_3 in Mo and Ni carbonyl complexes as well as a theoretical calculation. The traditionally used infrared parameters for phosphine-substituted metal carbonyls are not suitable for evaluating the σ- and π characters of *trans* phosphorus ligands because both a weaker σ-donor and a stronger π-acceptor would lead to a high carbonyl vibrational frequency. The expectation of very short Mo–PCl_3 and Mo–PBr_3 bond distances (consistent with literature X-ray crystallographic results for a few related transition metal complexes), coupled with the evidence for the low π-acceptor ability of these phosphorus ligands, leads to an unconventional conclusion: a weak σ-donor may form a short M–P bond with weak bond strength in the absence of a π-bonding contribution. It is also concluded that the ^{31}P NMR chemical shift, or coordination chemical shift $\Delta\delta(^{31}P)$, can reflect the electronic and steric variations in Mo–P bonding: both π- and σ-bonding will increase the $\Delta\delta(^{31}P)$ by inducing a deshielding effect on the ^{31}P nucleus, while steric effects decrease the $\Delta\delta(^{31}P)$ by inducing a shielding effect.

Introduction

The phosphine ligand PCl_3 has been considered a good π-acceptor on the basis of the high *trans* carbonyl stretching force constants[1] and metal–phosphorus NMR coupling constants[1a,2] observed for its metal complexes. In most inorganic chemistry text books this ligand is still treated as a good π-acid like PF_3 or the phosphites. Although its weak bonding ability was recognized via kinetic studies over 30 years ago,[3] the conclusion, derived initially from IR parameters, about the strong π-acceptor ability of PCl_3 has not been modified. Recently, Braga proposed, on theoretical grounds,[4] that the PCl_3 ligand is a weak π-acceptor. The QALE method (quantitative analysis of ligand effects)[5] suggests it is a pure σ-donor.[5e] However, no experimental evidence has been presented. Many theoretical studies have been carried out to evaluate the electronic effects of trivalent phosphorus ligands and their metal carbonyl complexes, and most researchers pay more attention to PF_3, PH_3, CO, and PMe_3.[6] Two other theoretical studies[7] of the PCl_3 ligand did not show significant difference between PCl_3 and PF_3. It appears that IR parameters and bond distances are the two most commonly used indicators for judging the π character in M–P bonding of OC–M–P complexes; i.e., it is generally thought that the higher the ν_{CO}, the more π character there is in M–P bonds; or the shorter the M–P bond distance, the more π character, and the stronger the M–P bond should be. As pointed out in other related papers,[6,8] however, ν_{co} and bond distance may not be reliable parameters in evaluating the electronic nature of M–P bonding. The remarkable deshielding behavior of the PCl_3 ligand compared with most other trivalent phosphorus ligands indicates that the transition metal NMR shielding parameter, δ_M, can unambiguously differentiate the π-acceptor abilities of ligands.[9] To verify such an important observation, a series of chlorophosphine-substituted molybdenum carbonyl complexes, $Mo(CO)_{6-n}L_n$ (n = 0–3; L = $PCl_{3-m}Ph_m$, m = 0–3) were synthesized and studied by ^{95}Mo NMR spectroscopy. The proposed nature of σ- and π-bonding in Mo complexes of PCl_3 and related ligands, which is further supported by ^{31}P and ^{13}C NMR spectroscopy, is still consistent with the earlier misinterpreted infrared data.

® Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) (a) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983. (b) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315. (c) McAuliffe, C. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Chapter 14, p 1033 references therein.

(2) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *J. Organomet. Chem.* **1980**, *195*, C17.

(3) (a) Zingales, F.; Canziani, F.; Basolo, F. *J. Organomet. Chem.* **1967**, 7, 461. (b) Meriwether, L. S.; Fiene, M. L. *J. Am. Chem. Soc.* **1959**, *81*, 4200. (c) Nolan, S. P.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *290*, 365.

(4) Braga, M. *Quim. Nova* **1988**, *11*, 71.

(5) (a) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering W. P. *Organometallics* **1985**, *4*, 1981. (b) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650. (c) Rahman M. M.; Liu H. Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1. (d) Liu, H. Y.; Eriks, K.; Giering, W. P.; Prock, A. *Inorg. Chem.* **1989**, *28*, 1759. (e) Liu, H. Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758. (f) Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 1742.

(6) Song, S.-Q.; Alyea, E. C. Submitted for publication.

(7) (a) Hillier, I. H.; Saunders, V. R. *Chem. Commun.* **1970**, 1510. (b) Hillier, I. H.; Saunders, V. R. *J. Chem. Soc., Dalton Trans.* **1972**, 21. (c) Topol, I. A.; Kondratenko, V.; Mazalov, L. N.; Doelnko, G. N.; Chesnyi, S. A. *J. Struct. Chem.* (*Engl. Transl.*) **1981**, *22*, 161.

(8) (a) Alyea, E. C.; Song, S.-Q. Submitted for publication. (b) Song, S.-Q.; Alyea, E. C. Submitted for publication. (c) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *J. Magn. Reson.* **1985**, *64*, 142.

(9) (a) Alyea, E. C.; Song, S.-Q. *Inorg. Chem.* **1992**, *31*, 4909. (b) Song, S.-Q.; Alyea, E. C. Paper presented at the 74th Canadian Chemical Conference, Hamilton, 1990; see Abstract 340.

0020-1669/95/1334-3864$09.00/0

Table 1. ^{95}Mo NMR Data for $Mo(CO)_{6-n}[PCl_{3-m}Ph_m]_n$ (n = 1–3, m = 1–3)[a]

no.	compound	$\delta(^{95}Mo)$ (ppm)	^1J(Mo–P) (Hz)	solvent	ref
I	$Mo(CO)_5PCl_3$	−1523	250	MeC_6H_{11}	
II	*cis*-$Mo(CO)_4[PCl_3]_2$	−1206	250	MeC_6H_{11}	
III	*fac*-$Mo(CO)_3[PCl_3]_3$	−910[b]	251	CH_2Cl_2	
IV	$Mo(CO)_5PCl_2Ph$	−1615	197	$ClCH_2CH_2Cl$	
V	*cis*-$Mo(CO)_4[PCl_2Ph]_2$	−1369	194	$ClCH_2CH_2Cl$	
VI	*fac*-$Mo(CO)_3[PCl_2Ph]_3$	−1124	198	$ClCH_2CH_2Cl$	
VII	$Mo(CO)_5PClPh_2$	−1702	165	$CDCl_3$	11
VIII	*cis*-$Mo(CO)_4[PClPh_2]_2$	−1522	166	$CDCl_3$	11
IX	*fac*-$Mo(CO)_3[PClPh_2]_3$	−1320[b]	154	CH_2Cl_2	
X	$Mo(CO)_5PPh_3$	−1743	137	CH_2Cl_2	
XI	*cis*-$Mo(CO)_4[PPh_3]_3$	−1556	140	CH_2Cl_2	
XII	*fac*-$Mo(CO)_3[PPh_3]_3$	−1265	120	CH_2Cl_2	
XIII	$Mo(CO)_5PBr_3$	−1396	242	MeC_6H_{11}	
XIV	*cis*-$Mo(CO)_4[PBr_3]_2$	−977	235	CH_2Cl_2	
XV	*fac*-$Mo(CO)_3[PBr_3]_3$	(−500)[c]			
XVI	$Mo(CO)_5PF_3$	−1860[d]	284	neat	12
XVII	*cis*-$Mo(CO)_4PF_3$	−1860[d]	281	neat	12
XVIII	*fac*-$Mo(CO)_3PF_3$	−1860[d]	290	neat	12
XIX	$Mo(CO)_5P(OMe)_2Ph$	−1816	183	CH_2Cl_2	
XX	*cis*-$Mo(CO)_4[P(OMe)_2Ph]_2$	−1740	184	CH_2Cl_2	
XXI	*fac*-$Mo(CO)_3[P(OMe)_2Ph]_3$	−1611	184	CH_2Cl_2	
XXII	$Mo(CO)_5Py$	−1398		CH_2Cl_2	8c
XXIII	*cis*-$Mo(CO)_4(Py)_2$	−1053		CH_2Cl_2	8c
XXIV	*fac*-$Mo(CO)_3(Py)_3$	−805		Py	8c

[a] The line width is a few hundred hertz for **XXIII** and 5–50 Hz for others. [b] ±1 ppm for two experiments. [c] Estimated value due to failure of synthesis. [d] −1860 ppm was taken from the original data, which did not differentiate between the complexes.

Experimental Section

The molybdenum carbonyl complexes $Mo(CO)_{6-n}L_n$ (n = 1–3) of PCl_3 and related ligands were prepared according to published procedures.[8a,10] $Mo(CO)_3$(cycloheptatriene), $Mo(CO)_4$(2,5-norbornadiene), and $Mo(CO)_5$(piperidine) were used as precursors to make *fac*-, *cis*-, and mono-displaced Mo derivatives, respectively, which are listed in Table 1. Complexes **I**–**III** are yellowish liquids; **IV**–**VIII** are soluble yellow solids, and **IX** is a sparingly soluble bright yellow solid. The *cis*-$Mo(CO)_4(PBr_3)_2$ and $Mo(CO)_5PBr_3$ species are very air sensitive. f3-PBr_3 could not be made at all despite several attempts. Physical measurements were carried out as described in detail in a related paper.[8a] Figure 1 presents the ^{95}Mo NMR spectrum for a mixture of *fac*-$Mo(CO)_3(PCl_3)_3$, *cis*-$Mo(CO)_4(PCl_3)_2$, and $Mo(CO)_5PCl_3$, which was obtained by refluxing an n-octane solution containing 0.25 g of $Mo(CO)_6$ and 5 ml of PCl_3 overnight. However, the m1-(mono), c2-(*cis*), and f3-(*fac*)PCl_3 derivatives have all been synthesized by separate routes and unambiguously characterized by ^{95}Mo, ^{31}P, and ^{13}C NMR and IR spectroscopies.

Results and Discussion

1. ^{95}Mo Nuclear Magnetic Shielding and M–P Bonding. The spectroscopic properties of the chlorophenylphosphine molybdenum complexes are compiled in Tables 1–4. Literature data are included for comparison. The assignments for all compounds except for the PBr_3 derivatives are made with confidence by a combination of ^{95}Mo, ^{31}P, and ^{13}C NMR and infrared spectroscopies.[8a]

The precision for ^{95}Mo chemical shifts is believed to be less than 3 ppm according to several repeated measurements for this class of complexes (see notes in Table 1 as well as other current related ^{95}Mo papers.[8]) Figure 2 shows the ^{95}Mo resonance trends as stepwise displacement of CO is effected by chlorophenylphosphines and other selected phosphorus ligands and pyridine. It can be readily seen that good π-acceptors such as PF_3 give rise to ^{95}Mo resonances at low frequency because a good π-acceptor affects all of the terms of the Ramsey expression $\delta_M \propto (\Delta E)^{-1} r_d^{-3} \langle 0|L^2|0\rangle$[6,20] toward the shielding direction. In a complex containing a good π-acceptor such as CO and PF_3 ($\delta(^{95}Mo)$ = −1857 and −1860 ppm, respectively), delocalized metal d_π electrons would enlarge the energy gap between the ground state and the excited states by lowering the energy level of the HOMO, giving a small $(\Delta E)^{-1}$. In contrast, the "closer paramagnetic circulation" [20b] (d_π electrons) in the case of a weaker π-acceptor ligand would lead to deshielding on the nucleus by affecting all the terms toward high frequency (decreased ΔE and r_d and increased $\langle 0|L^2|0\rangle$ due to the larger angular momentum of a d electron). Therefore, π-acceptors weaker than CO or PF_3 should bring, in principle, the metal resonance to high frequency. These are the major reasons for the observations illustrated in Figure 2.

It should also be kept in mind that both weak σ character and steric bulk of ligands also cause deshielding.[6,8] A weaker σ-donor narrows the energy gap by lowering the LUMO (σ_M^* or π_L^*(in MLCT complexes)) level, decreases the overall electron density around the resonant nucleus, and makes the paramagnetic circulation closer to the metal (small r_d). So, in both the cases of weak σ-bonding and large steric hindrance, all terms of the Ramsey expression are increased in their

---

(10) (a) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959. (b) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680. (c) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 2323.

(11) Gray, G. M. *Inorg. Chim. Acta* **1984**, *81*, 157.

(12) Bailey, J. T.; Clark, R. J.; Levy, G. C. *Inorg Chem.* **1982**, *21*, 2085.

(13) *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987.

(14) Stelzer, O.; Schmutzler, R. *J. Chem. Soc. A* **1971**, 2867.

(15) Andrews, G. T.; Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1982**, 2353.

(16) Bodner, G. M. *Inorg. Chem.* **1975**, *14*, 2694.

(17) Poilblanc R.; Bigorgne, M. *Z. Anorg. Allg. Chem.* **1962**, *314*, 1301.

(18) Daly, J. J. *J. Chem. Soc. A* **1964**, 3799.

(19) Dobson, G. R.; Stolz, I. W.; Sheline, R. K. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 1.

(20) (a) Grieves, R. A.; Mason, J. *Polyhedron* **1986**, *5*, 415. (b) Mason, J. *Chem. Rev.* **1987**, *87*, 1299. (c) Nakatsuji, H.; Sugimoto, M. *Inorg. Chem.* **1990**, *29*, 1221. (d) Kececi, A.; Rehder, D. *Z. Naturforsch.* **1981**, *36B*, 20. (e) Rehder, D.; Bechthold, H. C.; Kececi, A.; Schmidt, H.; Siewing, M. *Z. Naturforsch.* **1982**, *37B*, 631.

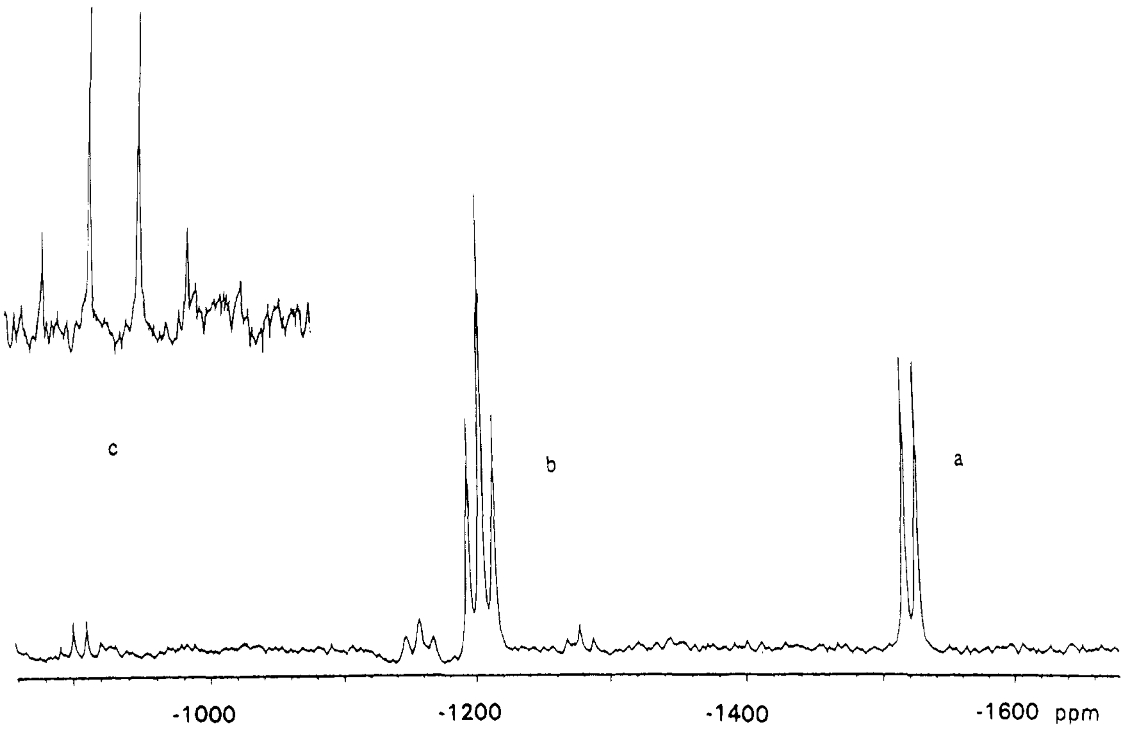

Figure 1. ^{95}Mo NMR spectrum for molybdenum complexes of PCl_3 in *n*-octane: (a) $Mo(CO)_5(PCl_3)$; (b) *cis*-$Mo(CO)_4(PCl_3)_2$; (c) *fac*-$Mo(CO)_3(PCl_3)_3$. The small triplets occurring at −1160 and −1280 ppm were not identified but may be due to hydrolysis products.

Table 2. ^{31}P NMR Data for $Mo(CO)_{6-n}[PCl_{3-m}Ph_m]_n$ ($n = 1-3$, $m = 1-3$)[a]

no.	compound	$\delta(^{31}P)^b$ ppm)	$\Delta\delta(^{31}P)^c$ ppm)	solvent	ref
I	$Mo(CO)_5PCl_3$	152.4	−64.1	MeC_6H_{11}	
II	*cis*-$Mo(CO)_4[PCl_3]_2$	154.3	−62.2	MeC_6H_{11}	
III	*fac*-$Mo(CO)_3[PCl_3]_3$	159.9	−56.4	CH_2Cl_2	
IIIm	*mer*-$Mo(CO)_3[PCl_3]_3$	164.2 (2)	−52.2 (38)	CH_2Cl_2	
		160.5 (1)	−55.9 (38)		
IV	$Mo(CO)_5PCl_2Ph$	167.6	9.2	$ClCH_2CH_2Cl$	
V	*cis*-$Mo(CO)_4[PCl_2Ph]_2$	168.9	10.4	$ClCH_2CH_2Cl$	
VI	*fac*-$Mo(CO)_3[PCl_2Ph]_3$	169.3	10.8	$ClCH_2CH_2Cl$	
VIm	*mer*-$Mo(CO)_3[PCl_2Ph]_3$	175.8 (2)	17.3 (34)	$ClCH_2CH_2Cl$	
		170.5 (1)	12.0 (34)		
VII	$Mo(CO)_5PClPh_2$	123.01	39.71	$CDCl_3$	11
VIII	*cis*-$Mo(CO)_4[PClPh_2]_2$	124.77	41.47	$CDCl_3$	11
IX	*fac*-$Mo(CO)_3[PClPh_2]_3$	121.2	42.0	CH_2Cl_2	
X	$Mo(CO)_5PPh_3$	38.0	42.9	CH_2Cl_2	
XI	*cis*-$Mo(CO)_4[PPh_3]_3$	38.3	43.3	CH_2Cl_2	
XIt	*trans*-$Mo(CO)_4[PPh_3]_3$	51.8	56.7	CH_2Cl_2	
XII	*fac*-$Mo(CO)_3[PPh_3]_3$	35.0	40.0	CH_2Cl_2	
XIII	$Mo(CO)_5PBr_3$	64.3	−159.7	MeC_6H_{11}	
XIV	*cis*-$Mo(CO)_4[PBr_3]_2$	80.4	−148.3	CH_2Cl_2	
XVI	$Mo(CO)_5PF_3$	147.0	50		13
XVII	*cis*-$Mo(CO)_4PF_3$	148.5	51.5		14
XVIII	*fac*-$Mo(CO)_3PF_3$	150.6	53.5		14
XIX	$Mo(CO)_5P(OMe)_2Ph$	176.4	17.0	CH_2Cl_2	15
XX	*cis*-$Mo(CO)_4[P(OMe)_2Ph]_2$	179.6	19.8	CH_2Cl_2	
XXI	*fac*-$Mo(CO)_3[P(OMe)_2Ph]_3$	181.0	21.6	CH_2Cl_2	

[a] The data for **IIIm** and **VIm** were obtained from the side product observation in the **III** and **VI** substitution reaction. [b] The numbers in parentheses are relative intensities. [c] Numbers in parentheses are $^2J(P-M-P)$ coupling constants.

magnitude.[8b] The bulkiness of a ligand may decrease the average energy gap by splitting the degeneracies of d orbitals under geometric distortion or make the σ-bond weaker due to an extended M−P bond.[8a] The high-frequency shift, therefore, would result from any one or a combination of the above three ligand effects, weaker σ, weaker π, and larger steric bulk. Figure 2 shows exactly such a pattern of shielding. The molybdenum resonances for PCl_3 derivatives occur at high frequency far from the positions for phosphites and PF_3 (right side) but close to those for the σ-donor pyridine[8b,21] (left side). Similar experimental data, not included in this paper, for two other series of Mo-N complexes (N = amines and nitriles) are consistent with a dominant σ-ability for nitrogen ligands.[22] The occurrence of the ^{95}Mo resonance for f3-$P(OMe)_2Ph$ at 138 ppm to higher frequency relative to that of f3-$P(OMe)_3$ can be

---

(21) (a) Cotton, F. A.; Darensbourg, D. J.; Fang, A.; Kolthammer, B. W. S.; Reed, D.; Thompson, J. L. *Inorg. Chem.* **1981**, *20*, 4090. (b) Reedijk, J. In ref 1c, Chapter 13.2, p 73.

(22) (a) Song, S.-Q.; Alyea, E. C. Unpublished results. (b) Merlic, C. A.; Adams, B. *J. Organomet. Chem.* **1992**, *431*, 313.

Table 3. ^{13}C NMR Data for Mo(CO)$_{6-n}$[PCl$_{3-m}$Ph$_m$]$_n$, (n = 1−3, m = 1−3)

no.	compound	$\delta(^{13}C)$ (ppm)	$\Delta\delta(^{13}C)$ (ppm)	^2J(C−P) (Hz)	solvent	ref
	Mo(CO)$_6$	201.1			CH$_2$Cl$_2$, MeC$_6$H$_{11}$	
I	Mo(CO)$_5$PCl$_3$	206.0(1)	5.5	66	MeC$_6$H$_{11}$	
		200.7(4)	0.7	11		
II	*cis*-Mo(CO)$_4$[PCl$_3$]$_2$	207.8	6.6	56	CH$_2$Cl$_2$	
		202.7	1.5	12	CH$_2$Cl$_2$	
III	*fac*-Mo(CO)$_3$[PCl$_3$]$_3$	208.6	7.2			
IV	Mo(CO)$_5$PCl$_2$Ph	208.3(1)	7.2	50	CH$_2$Cl$_2$	
		203.0(4)	2.0	10		
V	*cis*-Mo(CO)$_4$[PCl$_2$Ph]$_2$	210.2(2)	9.1	16	CH$_2$Cl$_2$	
		204.9(2)	3.8	11	CH$_2$Cl$_2$	
VI	*fac*-Mo(CO)$_3$[PCl$_2$Ph]$_3$	211.6	10.5			
VIm	*mer*-Mo(CO)$_3$[PCl$_2$Ph]$_3$	209.1(1)	11.1	10(q)[a]	CH$_2$Cl$_2$	
		203.7(2)	5.7	11(q)		
VII	Mo(CO)$_5$PClPh$_2$	209.4(1)	8.3	31.5	CDCl$_3$	
		202.3(4)	3.4	10		11
VIII	*cis*-Mo(CO)$_4$[PClPh$_2$]$_2$	212.3	11.4		CDCl$_3$	
		207.7	6.5			11
IX	*fac*-Mo(CO)$_3$[PClPh$_2$]$_3$	215.8	14.7		CH$_2$Cl$_2$	
X	Mo(CO)$_5$PPh$_3$	210.2(1)	9.4	23	CHCl$_3$	
		205.6(4)	4.9	9		16
XI	*cis*-Mo(CO)$_4$[PPh$_3$]$_2$	214.7	14.3		CH$_2$Cl$_2$	
		209.6	9.3			
XII	*fac*-Mo(CO)$_3$[PPh$_3$]$_3$	219.1	18.0		CH$_2$Cl$_2$	

[a] "q" in the parentheses represents quartets observed.

Table 4. ν_{CO} (cm^{-1}) Data for Mo(CO)$_{6-n}$[PCl$_{3-m}$Ph$_m$]$_n$ (n = 1−3, m = 1−3)

no.	compound	A$_1^{(2)}$	A$_1^{(1)}$	B$_1$	B$_2$	E	ref[c]
	Mo(CO)$_6$	2118[a]					17
I	Mo(CO)$_5$PCl$_3$	2095	2001	2013		1988	10a
II	*cis*-Mo(CO)$_4$[PCl$_3$]$_2$	2072	2004	1994	1986		18
III	*fac*-Mo(CO)$_3$[PCl$_3$]$_3$		2040			1983	CH$_2$Cl$_2$
IV	Mo(CO)$_5$PCl$_2$Ph	2086	1969[b]	2011		1969[b]	CH$_2$Cl$_2$
V	*cis*-Mo(CO)$_4$[PCl$_2$Ph]$_2$	2052	1980	1960	1942		CH$_2$Cl$_2$
VI	*fac*-Mo(CO)$_3$[PCl$_2$Ph]$_3$		2016			1943	19
VII	Mo(CO)$_5$PClPh$_2$	2081	1969	2020		1962	11
VIII	*cis*-Mo(CO)$_4$[PClPh$_2$]$_2$	2035	1950	1925	1907		CH$_2$Cl$_2$
IX	*fac*-Mo(CO)$_3$[PClPh$_2$]$_3$		1977[d]			1885[d]	19
X	Mo(CO)$_5$PPh$_3$	2073	1952	1984		1952	17
XI	*cis*-Mo(CO)$_4$[PPh$_3$]$_2$	2022	1929	1911	1899		18
XII	*fac*-Mo(CO)$_3$[PPh$_3$]$_3$		1948			1848	Nujol

[a] A$_{1g}$ mode. [b] The A$_1$(1) mode should be greater than 1969 cm^{-1} (estimated 1984 cm^{-1}) and the E mode smaller than 1969 cm^{-1} despite the unresolved bands. [c] The ν_{CO} data for most compounds in this table have been reported except those for IV, V, and VIII, and the values for III and XII were remeasured in this work. [d] The values recorded in this work, in Nujol, were 1971 and 1883 cm^{-1}.

attributed to the weaker π character and/or larger cone angle for the former ligand. The generally increasing size of ligands, as indicated by cone angle values, from right to left at the top of Figure 2, demonstrates that the deshielding trend is at least partially due to steric effects.[8,23] Evidently, the more deshielded resonance for f3-PPh$_3$ (ligand cone angle 145° [23]) as compared to f3-PClPh$_2$ (smaller ligand cone angle, 138°, [23] and weaker σ-donor than PPh$_3$) indicates the extra steric effect of a phenyl group relative to a Cl atom in this crowded complex. Therefore, the surprisingly high frequency position of $\delta(^{95}Mo)$ for the PCl$_3$ (cone angle 124° vs 145° for PPh$_3$) and PBr$_3$ (cone angle 131°) derivatives can only be explained by the combination of immeasurably low basicity (weaker σ character) and very low π-acceptor ability. As a matter of fact, the dramatic deshielding effect of chlorophosphines has been observed previously in several other transition metal complexes,[24] some of which clearly show no significant steric effects.[24d] The reported $\delta(^{95}Mo)$ = −1885 ppm for f3-PCl$_3$[25] was most likely due to spectral foldover due to insufficient spectral width. The observation, here, of ^{95}Mo chemical shift values for the four complete displacement series for PPh$_{3-m}$Cl$_m$ (m = 0−3) and the two PBr$_3$ derivatives, as well as the corresponding ^{31}P, ^{13}C, and ν_{CO} parameters (*vide infra*), verify the authenticity of the extreme high-frequency position of the resonances for the PCl$_3$ complexes. Therefore, we have confirmed that chlorophosphines have very weak π-acceptor ability as well as weak σ-donor ability. This is in agreement with earlier reports of the low strength[3b,26] of the Mo−PCl$_3$ bond and the facile exchange[3a] of the PCl$_3$ ligand.

---

(23) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(24) (a) Kidd, R. G.; Goodfellow, R. J. In *NMR and Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 8 and references therein. (b) McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616. (c) McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1974**, 324. (d) Hao, N.; McGlinchey, M. J.; Sayer, B. G.; Schrobilgen, G. J. *J. Magn. Reson.* **1982**, *46*, 158.

(25) Dysart, S.; Georgii, I.; Mann, B. E. *J. Organomet. Chem.* **1981**, *213*, C10.

(26) (a) Mukerjee, S. L.; Lang, R. F.; Ju, T.; Kiss, G.; Hoff, C. D. *Inorg. Chem.* **1992**, *31*, 4885. (b) Nolan, S. P.; Vega, R. L.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529. (c) Daamen, H.; Van Der Poel Stufkens, D. J.; Oskama, A. *Thermochim. Acta* **1979**, *34*, 69.

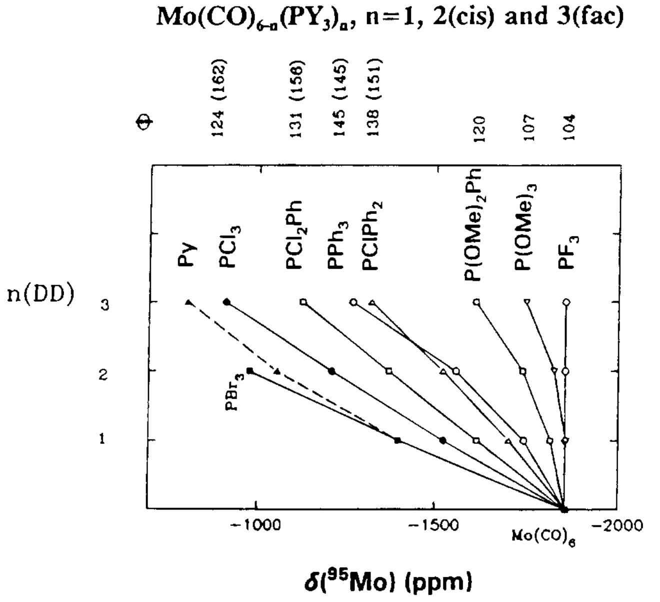

Figure 2. Deshielding trends for the ^{95}Mo nucleus with increasing degree of displacement (n) in $Mo(CO)_{6-n}L_n$ for various P(III) ligands and pyridine (Py). The values at the top of the figure refer to the Tolman cone angles, and those in parentheses are calculated from 162°, estimated in ref 3c, for PCl_3.

Nolan and Hoff attributed the low strength of the $Mo-PCl_3$ bond to a possible effective cone angle of 162° for PCl_3 by taking into account the intrinsic repulsion between adjacent lone pairs on chlorine.[3c] This explanation would seem to be consistent with the ^{95}Mo NMR observations in terms of a steric effect, whether along an individual displacement line for a specific ligand or in terms of the increased cone angles from right to left at top of Figure 2. In particular, the values in parentheses (calculated from 162° for PCl_3) just make the trend smooth and extendable in accordance with the deshielding effect of steric crowding as interpreted above. However, the crossover between the resonances for f3-$PClPh_2$ and f3-PPh_3 complexes firmly suggests that the Cl group is less sterically demanding than the phenyl group. At the same time, the deshielding effect of small nitrogen ligands such as pyridine,[8b] compared with phosphorus ligands, mainly results from an electronic effect, i.e., σ-bonding, not steric bulkiness. The reasons for the low M−P bond strengths in chlorophosphine complexes should be attributed to both the weak σ- and the weak π characters of these ligands. It is expected that the $Mo-PCl_3$ bond length should be short because of the low electron density on the phosphorus atom and low p-character in the lone pair. Therefore the ligand has to approach closely to the metal to bond, as observed for the shorter M−P bond of *cis*-$Mo(CO)_4[P(p\text{-}F\text{-}Ph)_3]_2$ relative to that of the PPh_3 analogue.[8a,27] If this is true, a more opened P−M−P angle and/or depressed Y−P−Y angles (Y represents a general substituent on P) might result directly from a shorter M−P bond distance for a complex of a weak σ- and weak π-ligand. For a weak but bulky σ-donor, it has not yet been clarified which effect, shorter σ-bonding or opened P−M−P angle, contributes more to the metal deshielding because these two effects are usually coexistent. We attempted to test this hypothesis with bulky amine ligands. Triphenylamine is just such a ligand with weak σ-ability ($pK_a = 4.2$) and bulky size. Attempted syntheses of m1-, c2-, and f3-NPh_3 molybdenum carbonyl complexes (and also of m1-, c2-, and f3-derivatives of *N,N*-dimethylaniline) were unfortunately unsuccessful.

Repeated attempts to grow a single crystal for any of the chlorophosphine−molybdenum derivatives in Table 1 have been unsuccessful. Relevant structural data reported in the literature have nevertheless confirmed the above prediction. The M−P bond distances in the $[(\eta^5\text{-}C_5H_5)(1,2\text{-}C_6H_4(PMePh)_2)Fe(PCl_3)]Cl$[28] complex are 2.06(1) and 2.205(8) Å for Fe−P(Cl) and Fe−P(aryl), respectively. The value of 2.06 Å is the shortest known M−P bond distance thus far reported. The Cl−P−Cl angle is 98.2(5)°, which is 2° smaller than 100.3° for free PCl_3.[7c,23,29] This compressed Cl−P−Cl angle is most likely related to the electronic nature of σ-bonding. An "effective cone angle" for the PCl_3 ligand in the above Fe complex can be estimated to be 129° if the M−P bond distance of 2.06 Å, instead of 2.28 Å (adopted by Tolman for Ni complexes[23]), is used in Tolman's calculation. The $Mo-PCl_3$ bond length is probably about 2.3−2.4 Å ($\geq$2.28 Å) by comparison to the bond distance of $Mo-PF_3$ (2.369 Å) in $Mo(CO)_5PF_3$.[30] Therefore, the original cone angle value of 124° for PCl_3 is still applicable; and the remarkable high-frequency resonances for $Mo-PCl_3$ complexes are primarily caused by electronic, not steric, effects. In another complex, $(\eta^4\text{-}C_5H_5\text{-}5\text{-}CCl_3)Re(NO)(PPh_3)(PCl_2Ph)$, the $Re-PCl_2Ph$ bond distance of 2.311(3) Å is much shorter than the $Re-PPh_3$ bond distance of 2.414(2) Å in the same molecule.[31a] The only known crystal structure of a group VI metal carbonyl complex of a phosphorus trihalide other than $Mo(CO)_5PF_3$ is $Cr(CO)_5PBr_3$.[31b] The Cr−P bond length of 2.263(3) Å was observed to be the shortest one of all known complexes with the $(OC)_5Cr-P$ fragment. It is even much shorter than the Cr−P distance of 2.309(1) Å for $Cr(CO)_5(P(OPh)_3)$, in which the phosphite ligand is a strong π-acceptor. Moreover, the P−Br bond length of 2.208(3) Å in the Cr complex is slightly shorter than that in the free ligand (2.220(3) Å[31c]). This cannot be explained by Orpen and Connelly's work[32] in which M−P π-bonding would lengthen the P−X bond due to the population of σ^* orbitals. If the $Cr-PBr_3$ bond strength is as weak as that of the analogous bonds in the $Mo-PCl_3$ and $Ni-PCl_3$ complexes, the shorter $Cr-PBr_3$ bond will originate from the ligand weak σ-ability, not strong π-interaction. It is, therefore, suggested that weak σ-bonding by itself can also lead to a short M−P bond distance without the supplementary assistance of π-bonding.[6] This would appear to be the case in the only other known structure of a metal−PCl_3 compound, Cl_3PAuCl, for which no π-bonding is expected.[31d]

2. ^{31}P NMR Shielding and M−P Bonding. Like other heavy atom chemical shifts, according to theoretical treatments of free phosphorus ligands,[33] ^{31}P NMR chemical shifts are thought to arise primarily from variations in the paramagnetic contribution from electrons in valence orbitals. In the paramagnetic shielding expression for σ_p, the asymmetry term, $\langle 0|L^2|0\rangle$, is divided into two parts as P and D for p orbital (σ-bonding) and d orbital (π-bonding), respectively:

---

(27) Alyea, E. C.; Ferguson, G.; Gallagher, J.; Song, S.-Q. *Acta Crystallogr.* **1994**, *C50*, 1084.

(28) Hey, E.; Wild, S. B.; Bott, S. G.; Atwood, J. L. *Z. Naturforsch.* **1989**, *44B*, 615.

(29) Guns, M. F.; Claeys, E. G.; Kelen, G. P. V. *J. Mol. Struct.* **1979**, *54*, 101.

(30) Bridges, D. M.; Holywell, G. C.; Rankin, D. W. H.; Freeman, J. M. *J. Organomet Chem.* **1971**, *32*, 87.

(31) (a) Buhro, W. E.; Arif, A. M.; Gladysy, J. A. *Inorg. Chem.* **1989**, *28*, 3837. (b) Fink, H. J.; Duesler, E. N.; Paine, R. T. *Acta Crystallogr.* **1987**, *C43*, 635. (c) Kuchitsu, K.; Shibata, T.; Yokozeki, A. *Inorg. Chem.* **1971**, *10*, 2584. (d) Jones, P. G.; Bembenek, E. *J. Crystallogr. Spectrosc. Res.* **1992**, *22*, 397.

(32) (a) Orpen, A. G.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310. (b) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206.

(33) (a) Letcher, J. H.; Van Wazer, J. R. *J. Chem. Phys.* **1966**, *44*, 815. (b) Meriwether, L. S.; Leto, J. R. *J. Am. Chem. Soc.* **1961**, *83*, 3192.

$$\sigma_{\rm p}(^{31}{\rm P}) = -\frac{2e^2\hbar^2}{3m^2c^2}\frac{1}{\Delta E}\left(\left\langle\frac{1}{r_{\rm p}^{\,3}}\right\rangle P + \left\langle\frac{1}{r_{\rm d}^{\,3}}\right\rangle D\right) \qquad (1)$$

In eq 1, the energy term ((ΔE^{-1}) and radial term (r^{-3}) are usually considered to be constant or to exhibit minor change.[33] Most of the previous work has focused on the asymmetry terms, P and D.[34] Thus, substituent electronegativity (related to σ-bonding), bond angle Y$-$P$-$Y (related to σ-bonding and steric bulkiness), and extent of π-bonding are used to account for the shifts of free phosphine ligands. In phosphine-displaced transition metal carbonyl complexes, it has been generally observed that the ^{31}P chemical shift for a strong σ-donor such as P(alkyl)$_3$ moves by a larger amount toward high frequency upon coordination, while $\delta(^{31}\mathrm{P})_c$ for a weak σ-donor such as P(OR)$_3$ (also a strong π-acceptor) moves by a small shift also toward high frequency upon coordination.[8a,35,36] This high-frequency coordination chemical shift, designated as $\Delta\delta(^{31}\mathrm{P})$ and equal to the difference between the chemical shift upon coordination ($\delta(^{31}\mathrm{P})_c$) and the chemical shift of the free phosphorus ligand ($\delta(^{31}\mathrm{P})_f$), has been attributed, with little argument, to the σ(P$\rightarrow$M) charge transfer and the opened Y$-$P$-$Y angle of PY$_3$, which approaches T_d from C_{3v} geometry on coordination.[35,36] There are many other interpretations in the literature. Some include π-bonding,[14] and some even suggest that $\Delta\delta(^{31}\mathrm{P})$ reflects only the nature of the central transition metal.[15] The π-bonding contribution (whether the effectiveness or its operating direction) toward the ^{31}P shift is still controversial even in the free-ligand cases.[37] However, the ^{31}P spectral results for chlorophosphine complexes, in this work, corroborate the above interpretation of ^{95}Mo NMR data and support the importance of both σ- and π-contributions to the ^{31}P NMR shift (see below).

Table 2 and Figure 3 present the data and the trends for ^{31}P NMR spectral parameters for the chlorophenylphosphine complexes according to their degree of displacement (DD). A relatively good σ-donor, such as PPh$_3$, gives rise to a larger positive $\Delta\delta(^{31}\mathrm{P})$, and a poor σ-donor, such as P(OMe)$_2$Ph, a small positive $\Delta\delta(^{31}\mathrm{P})$. (Other alkylphosphines having strong σ-donor ability lead to even larger positive $\Delta\delta(^{31}\mathrm{P})$.[38]) This variation in the magnitude of $\Delta\delta(^{31}\mathrm{P})$ was previously explained in such a way that in a phosphite complex the Y$-$P$-$Y angle may not quite reach 109.5° (T_d) unlike the case for an alkylphosphine complex.[33b] In other words, the $\Delta\delta(^{31}\mathrm{P})$ would be, to a certain extent, a reflection of ΔA (defined in this work as a change of the Y$-$P$-$Y angle upon coordination; the sign is consistent with that of $\Delta\delta(^{31}\mathrm{P})$). A preliminary survey of Y$-$P$-$Y angle values for some common free and coordinated phosphorus compounds studied by X-ray crystallography indicates that the above correlation is true in many phosphorus compounds; i.e., the large $\Delta\delta(^{31}\mathrm{P})$ correlates with the opened Y$-$P$-$Y angles.[39] *However, there are also some reversed cases in which the values of $\Delta\delta(^{31}P)$ are positive but the Y$-$P$-$Y angles are invariant or compressed upon coordination.*[40] For example, the C$-$P$-$C angle of PPh$_3$ changes to 101.5(4)°[41] in the *cis*-Mo(CO)$_4$L$_2$ complex from 102.9°[42e] for the free ligand; 103.0°[29] in free PEt$_3$ becomes 102.0(3)°[43] in its *cis*-Mo(CO)$_4$L$_2$ complex; and the F$-$P$-$F angle of 97.8(6)°[29,42a] becomes 95.3(9)°[44] when the HRh(PF$_3$)(PPh$_3$)$_3$ complex is formed. In all these cases the $\Delta\delta(^{31}\mathrm{P})$ values are large and positive. Some authors have attributed the small positive $\Delta\delta(^{31}\mathrm{P})$ for phosphite complexes to a compensation by π-bonding for the high-frequency shift by σ-donation,[29,33b,34,37,45] which means that the π(M$\rightarrow$P or P$\leftarrow$Y) bonding component should bring the ^{31}P resonance to *low frequency*. In contrast with this point of view, the greater positive $\Delta\delta(^{31}\mathrm{P})$ observed in *trans* isomers of pseudooctahedral geometry has been attributed to good π(M$\rightarrow$P) back-bonding.[33a,34a,37c,38b] Considering the fact that most phosphorus ligands of good π-acceptor ability are also weak σ-donors, the small positive $\Delta\delta(^{31}\mathrm{P})$ is actually also explicable in terms of only σ-bonding. According to the magnetic shielding theory and the results here, it can be concluded that both σ(M$\leftarrow$P) and π(M$\rightarrow$P) components should bring the ^{31}P

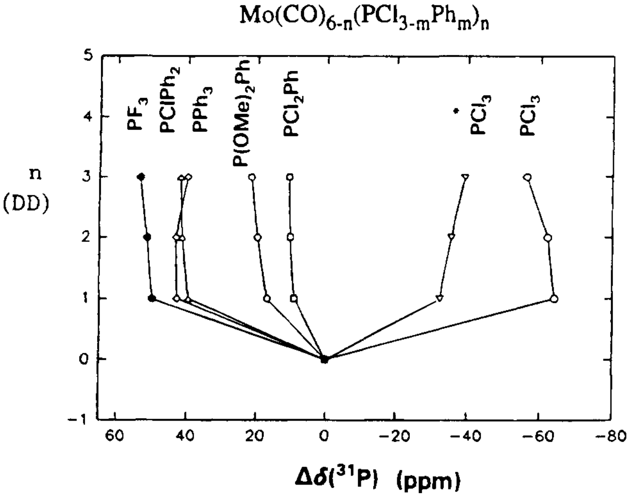

Figure 3. Variation in $\Delta\delta(^{31}\mathrm{P})$ for metal complexes of chlorophenylphosphines with degree of displacement (the plot for the PCl$_3$ labeled by an asterisk refers to the Ni(CO)$_{4-n}$(PCl$_3$)$_n$ series taken from ref 33b).

---

(34) (a) Muller, N.; Lauterbur, P. C.; Goldenson, J. *J. Am. Chem. Soc.* **1956**, *78*, 3557. (b) Packer, K. J. *J. Chem. Soc.* **1963**, 960. (c) Schenk, W. A.; Buchner, W. *Inorg. Chim. Acta* **1983**, *70*, 189.

(35) Song, S.-Q. Ph.D. Thesis, University of Guelph, Guelph, 1994.

(36) Dias, P. B.; Minas de Piedade, M. E.; Simões, J. A. M. *Coord. Chem. Rev.* **1994**, *135/136*, 737.

(37) (a) Ionin, B. I. *J. Gen. Chem. USSR* **1968**, *38*, 1618. (b) Vincent, E.; Verdonck, L.; Van Der Kelen, G. P. *J. Mol. Struct.* **1980**, *65*, 239. (c) Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133.

(38) (a) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1. (b) Mathieu, R.; Lenzi, M.; Poilblanc, R. *Inorg. Chem.* **1970**, *9*, 2030. (c) *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers, Inc.: Boca Raton, FL, 1987.

(39) (a) Cotton, F. A.; Darensbourg, D. J. *Inorg. Chem.* **1981**, *20*, 4440: W(CO)$_5$PMe$_3$, C$-$P$-$C 107.3° > 99° (for free PMe$_3$, ref 29 and 42a), ΔA = 8°. (b) Lee, K. J.; Brown, T. L. *Inorg. Chem.* **1992**, *31*, 289: Cr(CO)$_5$PMe$_3$, C$-$P$-$C 102.4° > 99° (for free ligand, ref 29 and 42a), ΔA = 3°. (c) Hengefeld, A.; Kopf, J.; Rehder, D. *Organometallics* **1983**, *2*, 114: Cr(CO)$_5$P(C≡CPh)$_3$, C$-$P$-$C 102.6° > 100.7°(for free ligand, ref 42c), ΔA = 2°. (d) Pickardt, V. J.; Rosch, L.; Schumann, H. *Z. Anorg. Allg. Chem.* **1976**, *426*, 66: W(CO)$_5$P(*t*-Bu)$_3$, C$-$P$-$C 106.7° > 105.7° (for free ligand, ref 23); Ni(CO)$_3$P(*t*-Bu)$_3$, C$-$P$-$C 107.8° > 105.7°. (e) Reference 42e: fourteen transition metal complexes of PPh$_3$, average C$-$P$-$C 103.5° > 103°(for free ligand, ref 18).

(40) (a) Cotton, F. A.; Darensbourg, D. J.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 578: Mo(CO)$_5$PPh$_3$, ΔA = $-$0.4° (decreased). (b) Plastas, H. J.; Steward, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265: Cr(CO)$_5$PPh$_3$, ΔA = $-$0.4° (decreased). (c) Affandi, S.; Nelson, J. H.; Alcock, N. W.; Howarth, O. W.; Alyea, E. C.; Sheldrick, G. M. *Organometallics* **1988**, *7*, 1724: *mer*-Cr(CO)$_3$(5-PhDBP)$_3$, ΔA = $-$2.5° (decreased). (d) Reference 21a: *cis*-Cr(CO)$_4$(pip)(P(OMe)$_3$), ΔA(O$-$P$-$O) = $-$2.6° (decreased).

(41) Cotton, F. A.; Darensbourg. D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 294.

(42) (a) Yarbrough, L. W.; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2269. (b) Kraatz, H. B.; Jacobsen, H.; Ziegler, T.; Boorman, P. M. *Organometallics* **1993**, *12*, 76. (c) Mootz, V. D.; Sassmannshausen, G. *Z. Anorg. Allg. Chem.* **1967**, *355*, 200. (d) Alyea, E. C.; Ferguson, G.; Gallagher, J. F. *Acta Crystallogr.* **1992**, *C48*, 959. (e) Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* **1968**, 2970.

(43) Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 2661.

(44) Hitchcock, P. B.; Nixon, J. F.; Sinclair, J. *Acta Crystallogr.* **1977**, *B33*, 179.

(45) Grim, S. O.; Wheatland, D. A.; McFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573.

chemical shift to high frequency, and the $\Delta\delta(^{31}P)$ may have comparable sensitivity to σ- and π-bonding.

As seen from Table 2 and Figure 3, all PCl_3 and PBr_3 complexes have large negative $\Delta\delta(^{31}P)$ values. These unusual shifts have been observed before and explained in the different ways mentioned above, i.e., $P\leftarrow X$ π-bonding,[29] weaker $\sigma(M\leftarrow P)$ or $\pi(M\rightarrow P)$ bonding, a strong $P\rightarrow X$ electron density drift, or changed X−P−X angle.[33b] For example, the highly negative value of $\Delta\delta(^{31}P)$ for Cl_3P-BCl_3 was attributed to the higher electronegativity of BCl_3.[34c] These negative $\Delta\delta(^{31}P)$ values are just consistent with the ^{95}Mo NMR results in terms of weaker σ- and weaker π-ability of PCl_3 and PBr_3 ligands and are best explained if the σ- and π-components are considered equally important factors in ^{31}P screening. Owing to the small p character, and the greatly contracted lone pair of PCl_3, the metal carbonyl moiety has to interact with an ineffective donor pair on the phosphorus atom to form a strained (unstable) bond with little π-compensation. This kind of special bond situation may decrease remarkably the dipole moment of both the P−X bonds and the PX_3 molecule and perhaps induces a drift of σ electrons from X groups to phosphorus. Consequently, there is a decrease in the paramagnetic screening term on the phosphorus center.[34a,b] So there seems to be a balance between the requirement for σ electrons on the metal moiety side and the availability of σ electrons on the phosphorus donor side in the formation of M−P σ-bond. The change in sign of $\Delta\delta(^{31}P)$ from plus to minus may imply that the "availability" could not just match the "requirement", and the M−P bond would be weak (see also Table 6 of Chapter 13 in ref 13). As to the influence of a π-bonding component on shielding, it seems that the d electrons which are brought from the metal to another heavy nucleus via a π orbital should cause a deshielding on that nucleus. This does happen in transition metal NMR[46] and ^{13}C NMR,[47] and so it should in ^{31}P NMR due to the similar expression of the paramagnetic screening term, σ_p. In other words, the M−P π-bonding, if any, should deshield the phosphorus nucleus, not shield it. The quite positive $\Delta\delta(^{31}P)$ values for PF_3 derivatives strongly support this explanation (see Figure 3). It might be expected that $\Delta\delta(^{31}P)$ for PF_3 derivatives would have become negative as for other PX_3 analogues without the compensation from the strong π-bonding.

If the $M-PCl_3$ bond is weaker and primarily σ in character, there should be some structural features of PCl_3 reflecting such a σ-bonding. First, UV-photoelectron studies have shown that the lone pair stabilization energies of 0.54 and 0.52 eV for PCl_3 and PBr_3 in $Cr(CO)_5PCl_3$ and $Cr(CO)_5PBr_3$ complexes, respectively, are much greater than that of 0.2 eV in the PF_3 analogue.[48] Second, the Cl−P−Cl bond angle is most likely to be compressed in group 6 metal complexes of pseudooctahedral geometry, as observed in other transition metal complexes (see previous section). Both features would lower the HOMO (a_1) orbital of the PCl_3 ligand and hence increase ΔE_σ and r (σ electrons)[32b,49] for the phosphorus atom, and bring the ^{31}P chemical shift toward the shielding side according to the ^{31}P shielding expression (eq 1).

Although the steric effects seemingly cause the ^{31}P chemical shifts to move to low frequency,[8a,34c,35,50] the negative $\Delta\delta(^{31}P)$ values for PCl_3 derivatives should not arise from the compression of the Cl−P−Cl angles nor from the "effective bulkiness" of PCl_3, as already pointed out above, because of the following additional observations from ^{31}P NMR spectroscopy. (i) The negative coordination shift occurs also in the mono-displaced derivative, $Mo(CO)_5PCl_3$ (even larger in magnitude than for c2 and f3 geometries), as shown in Figure 3. In this geometry, steric crowding is normally not considered important except for an extreme case, such as for the $P(t\text{-}Bu)_3$ complex[51] (there is a significant steric effect in $Mo(CO)_5L$ derivatives but it is much less than those in c2's and f3's[35]). (ii) The $\Delta\delta(^{31}P)$ values for the $PClPh_2$ and PPh_3 analogues in m1 and c2 geometries are similar and switched-over between their f3 derivatives due to the more congested structure of the f3-PPh_3 species (see Figure 3). (iii) The $\Delta\delta(^{31}P)$ values for nickel carbonyl complexes[38b] are all large and negative, also. It is usually accepted that there is no serious steric effect in $Ni(CO)_3L$ (C_{3v}) complexes, even when $L = P(t\text{-}Bu)_3$ ligand[51] (the steric situation in $Ni(CO)_3L$ derivatives is still being questioned). This firmly indicates that predominantly electronic, rather than steric, factors are active in determining $\delta(^{31}P)$ and both the magnitude and the sign of $\Delta\delta(^{31}P)$ reflect the nature of the M−P bond in terms of σ- and π electronic effects. It does not make sense to state that the parameter, $\Delta\delta(^{31}P)$, is primarily a measure of free ligand and "cannot be used to discuss any properties of the metal−phosphorus bond".[34c] Further discussion of this controversy will be published in the near future.

3. The Coupling Constant, ^1J(Mo−P). The large ^1J(Mo−P) values for PCl_3 compounds can be attributed to mainly s character in the $Mo-PCl_3$ bond. Although the magnitude for ^1J(M−P) is widely employed to estimate the σ/π synergic effect and π-bonding, the current study agrees with the significance of s character,[50,52] rather than σ-bonding (strong σ-donation is usually associated with high ratio of p/s character in the lone pair) and π-bonding,[45,53] in determining the magnitude of ^1J(M−P). The values of ^1J(Mo−P) for PCl_3 complexes are greater than those for all phosphite (good π-acceptor) ligands and much greater than those for alkylphosphine (*good σ-donor*) analogues.[46] It should be noted that both the σ- and the π-abilities of $P(OPh)_3$ are greater than those for PCl_3, but the ^1J(Mo−P)'s for PCl_3 complexes are on average greater than those for $P(OPh)_3$ analogues by 6%. (^1J(Mo−P) of c2-$P(OPh)_3$ has been remeasured to be 229 Hz, not 250 Hz.[35,54]) In the reviews by Tolman[23] and Pidcock,[50] a rough correlation of ^1J(Pt−P) with Pt−P bond length was reported. Therefore, the shorter $M-PCl_3$ bonds (*vide supra*) should be taken into account, in addition to the well-known electronegativity factor, rather than a "good" π-ability of PCl_3,[1] to explain the large ^1J(Mo−P) values for PCl_3 complexes. Such a weak π-accepting ability of PCl_3 suggests that the ligand π character may not considerably

---

(46) (a) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169. (b) *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978.

(47) (a) Buchner, W.; Schenk, W. A. *J. Magn. Reson.* **1982**, *48*, 148. (b) Buchner, W.; Schenk, W. A. *Inorg. Chem.* **1984**, *23*, 132. (c) Bodner, G. M.; Kahl, S. B.; Bork, K.; Storhoff, B. N.; Wuller, J. E. *Inorg. Chem.* **1973**, *12*, 1071. (d) Farnum, D. G. *Adv. Phys. Org. Chem.* **1975**, *11*, 123.

(48) (a) Daamen, H.; Boxhoorn, G.; Oskam, A. *Inorg. Chim. Acta* **1978**, *28*, 263. (b) Distefano, G.; Innorta, G.; Pignataro, S.; Foffani, A. *J. Organomet. Chem.* **1968**, *14*, 165.

(49) (a) Gilheany, D. G. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley & Sons: Chichester, U.K., 1990; Vol. 1, Chapter 2.

(50) Pidcock, A. In *Catalytic Aspects of Metal Phosphine Complexes*; Alyea, E. C., Meek, D. W., Eds.; Advances in Chemistry 196; American Chemical Society: Washington, D.C., 1982; p 1.

(51) Pickardt, V. J.; Rosch, L.; Schumann, H. *Z. Anorg. Allg. Chem.* **1976**, *426*, 66.

(52) (a) Pidcock, A. In *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*; McAuliffe, C. A., Ed.; Macmillan: London, 1973; Part 1. (b) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc.* **1966**, 1707.

(53) (a) Grim, S. O. *Inorg. Chem.* **1968**, *7*, 161. (b) Grim, S. O. *Inorg. Chim. Acta* **1970**, *4*, 277.

(54) Alyea, E. C.; Somogyvari, A. *Can. J. Chem.* **1988**, *66*, 397.

influence the magnitude of ^1J(Mo−P) for Mo(0) phosphorus complexes. On the other hand, most P(alkyl)$_3$ ligands are strong σ-donors and form strong Mo−P bonds,[3b,23,26,55] but the ^1J(Mo−P) values for these strong σ-donor complexes are almost the smallest.[35,46] It should be also kept in mind that the M−PCl_3 (M = Mo or Ni) bond strengths are very weak[3,26,55] despite the much higher ^1J(Mo−P) values for M−PCl_3 complexes.[46,24a,b] Thus, an important conclusion may come from these observations: when σ-bonding is dominant in a series of similar Mo-L complexes, the larger ^1J(Mo−P) values parallel weak, rather than strong, σ-donation because a highly electronegative substituent increases the s character in the lone pair of the donor ligand (Bent's rule). However, for a given P(III) ligand in different complex geometries or metal residues, ^1J(M−P) may be also related to π-bonding. In these cases, it is extremely difficult to interpret the magnitude of ^1J(M−P) in terms of σ- or π-bonding, as often argued for the *trans* effect.[56]

4. ν_{CO} and $\delta(^{13}CO)$ as Indicators of Electronic and Steric Effects. The IR parameters (k or υ_{CO}) for CO's have been used to discuss the σ- and π- bonding abilities of phosphorus and other ligands in transition metal carbonyls for the last 30 years.[1b,10a,42a,48b,57] The second spectroscopic technique used to systematically examine M−P bonding was ^{13}C NMR spectroscopy in the 1970's and early 1980's.[47b,58] The proposed strong π-ability, or low σ/π ratio, of PCl_3, like PF_3, was derived from these two methods.[6] The above two traditional techniques, however, cannot readily distinguish the "stronger π" and "weaker σ" properties of phosphorus ligands due to the fact that strong π-bonding parallels with weak σ-bonding and a good π-acceptor is also usually a weaker σ-donor for most trivalent phosphorus ligands.[6]

Relevant ^{13}C NMR and IR data are collected in Tables 3 and 4. Triphenylphosphine, compared to PCl_3, leads to a higher frequency ^{13}C carbonyl resonance as any other better σ-donor should do. This general observation has been attributed either to increased M−C bond order (dominant valence orbital imbalance term ΔQ_{AB}(B = A)[47]) or decreased ΔE_{CO} (dominant $\Delta(E)^{-1}$ term in σ_p[58b,c]). The stretching frequency, ν_{CO}, for a better σ-donor goes to lower frequency for just the same reason of increased population (from the metal d electrons) in the π^* orbitals of CO's. On the other hand, trends for these two parameters would move in the other direction for either a weaker σ-donor or a good π-acceptor. It is this similar response of $\delta(^{13}CO)$ and υ_{CO} to both the weak σ and strong π character of a ligand that makes it difficult to separate these two important electronic contributions in M−P bonding by IR and ^{13}C NMR spectroscopy.[6,35]

The linear correlations of $\delta(^{13}C)_{cis}$ with degree of displacement (the dashed lines shown in Figure 4) are analogous to quite a few correlations reported in the literature ($\delta(^{13}CO)_{cis}$ vs υ_{co} or k_{cis}[16,47b,c,58,59] for pseudo-T_d or -O_h complexes; $\delta(^{13}CO)_{cis}$ vs $\delta(^{13}CO)_{cis}$ for complexes of the same or different geometries[16,58a]). Added together, these correlations suggest a direct or "net" dependence of $\delta(^{13}CO)_{cis}$ or k_{cis} on the σ-component[1b,16] in an M−L bond, with a possible π-influence ($\Delta k_{cis} \propto \Delta\sigma + \Delta\pi$).[1b] The nonlinearity for $\delta(^{13}CO)_{trans}$ versus n(DD) in Figure 4 (just as the previously observed irregular correlations of $\delta(^{13}CO)_{trans}$ for $M(CO)_5L$ with υ_{co} or k_{trans},[47b] or versus $\delta(^{13}CO)$ for $Ni(CO)_3L$[58a]) reflects a complicated combination of σ- and π-effects on the spectroscopic properties of *trans* CO's. The invariable difference, $\Delta\delta$(t−c) (*trans-cis*) of 5.0 ppm, between $\delta(^{13}CO)_{trans}$ and $\delta(^{13}CO)_{cis}$, however, may originate from this nonlinearity of $\delta(^{13}CO)_{trans}$ vs n(DD). What is the essential reason chemically for this nonlinearity or irregularity occurring wherever a *trans* parameter of pseudo-octahedral complexes is involved? The answer is surely π character, but how? It is easy and also sounds reasonable to attribute the tendency of the solid $\delta(^{13}CO)_{trans}$ line for PCl_3 (m = 0) with increased DD to move toward high field to a "strong π-ability" of this ligand. However, on the basis of the ^{95}Mo and ^{31}P interpretations made previously, this tendency may be better ascribed to the weak σ- and π character of PCl_3. The subsequent replacement of more CO's by much weaker π-ligands increases the d electron density around the metal, and perhaps the intrinsic π-accepting orbitals of PCl_3 begin to act at a certain stage such as a saturation point when n(DD) is high enough.[8b] In comparison, this parallel tendency between the displacement correlations of $\delta(^{13}CO)_{trans}$ and $\delta(^{13}CO)_{cis}$ with DD no longer exists for pure σ-donors such as amines.[60] Furthermore, if PCl_3 were a very strong π-ligand, it would be expected that its $\Delta\delta$(t−c) should be smaller than that for a ligand with weaker π character such as PPh_3,[35] simply because the *trans* CO is more sensitive to π-ability of a ligand ($\Delta k_{trans} = \Delta\sigma + 2\Delta\pi$, $\Delta k_{cis} = \Delta\sigma + \Delta\pi$;[1b] the $\Delta\pi$ term is actually also affected by $\Delta\sigma$ because there is no d_π orbital directly bridging the *cis* CO's and L in $M(CO)_5L$ complexes, and thus the coefficient of $\Delta\pi$ in $\Delta k_{cis} = \Delta\sigma + \Delta\pi$ may be much smaller than 1; that is, the ratio of $\Delta\pi_{trans}/\Delta\pi_{cis}$ would be greater than 2[6]). Therefore, a strong

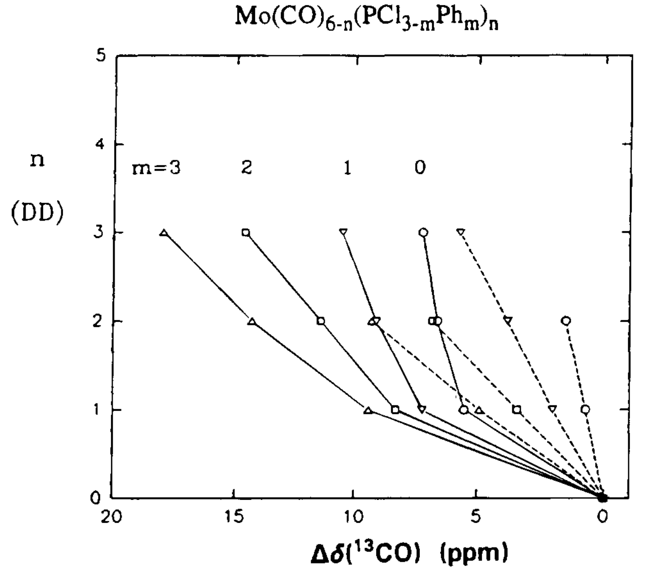

Figure 4. Magnetic shielding trends for *trans* and *cis* carbonyls in $Mo(CO)_{6-n}(PCl_{3-m}Ph_m)$ (n, m = is 0–3) with changing degree of displacement. Dashed lines represent the CO's *trans* to a CO; solid lines represent the CO's *trans* to a phosphorus. The values for $\Delta\delta(^{13}CO)$ are relative to that for $Mo(CO)_6$.

---

(55) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; Vega, R. L. *Inorg. Chem.* **1988**, *27*, 81.

(56) Emsley, J.; Hall, D. In *The Chemistry of Phosphorus*; Harper & Row: London, 1976; Chapter 5.

(57) (a) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702. (b) Daamen, H.; Oskam, A.; Stufkens, D. J. *Inorg. Chim. Acta* **1980**, *38*, 71. (c) Bursten, B. E.; Darensbourg, D. J.; Kellogg, G. E.; Lichtenberger, D. L. *Inorg. Chem.* **1984**, *23*, 4361. (d) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(58) (a) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951. (b) Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J.; King, I. J. *Inorg. Chem.* **1977**, *16*, 2497. (c) Braterman, P. S.; Milne, D. W.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1027.

(59) Chisholm, M. H.; Godleski, S. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley & Sons: New York, 1976; Vol. 20, p 299.

(60) For example, $\Delta\delta(^{13}CO)$(*trans−cis*) = 9.3 and 14.1 ppm for $Mo(CO)_5$(Pip) and *cis*-$Mo(CO)_4(Pip)_2$ complexes and $\Delta\delta(^{13}CO)$(*trans−cis*) = 8.2 and 12.2 ppm for $Mo(CO)_5$(NCPh) and *cis*-$Mo(CO)_4(NCPh)_2$ complexes were observed by these authors.

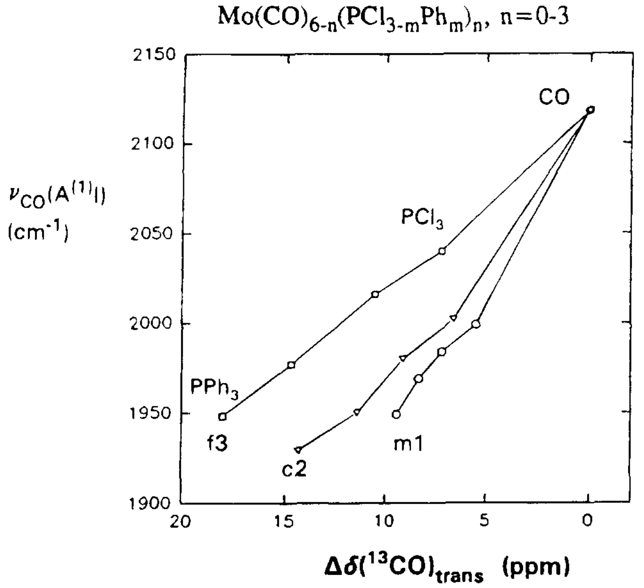

Figure 5. . Correlation between two CO *trans* parameters ($\delta(^{13}CO)$ and $\nu_{CO}(A^{(1)}_1)$ for molybdenum chlorophenylphosphine complexes.

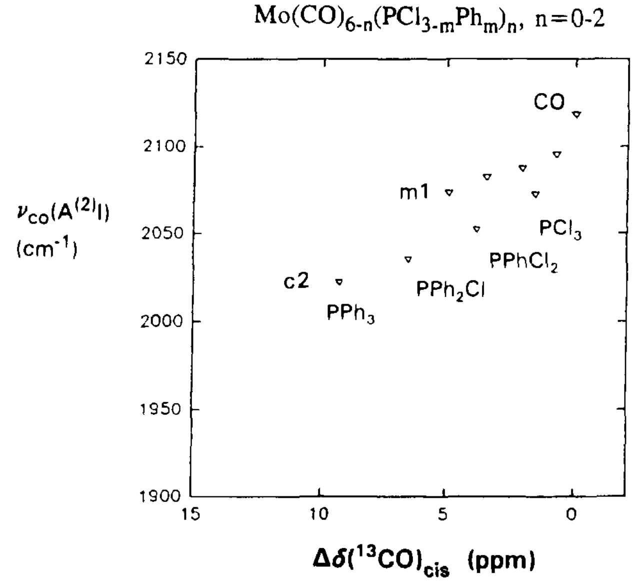

Figure 6. Correlation between two CO *cis* parameters ($\delta(^{13}CO)$ and $\nu_{CO}(A^{(2)}_1)$ for molybdenum chlorophenylphosphine complexes.

π-component would shift $\delta(^{13}CO)_{trans}$ considerably backward to lower frequency,[61] *decreasing the difference* between $\delta(^{13}CO)_{trans}$ and $\delta(^{13}CO)_{cis}$ more significantly than a weak π-component could. This has been observed in $Mo(CO)_5P(OR)_3$ derivatives for which the average $\Delta\delta(^{13}CO)(t-c)$ is only 3.9 ppm.[1b,61]

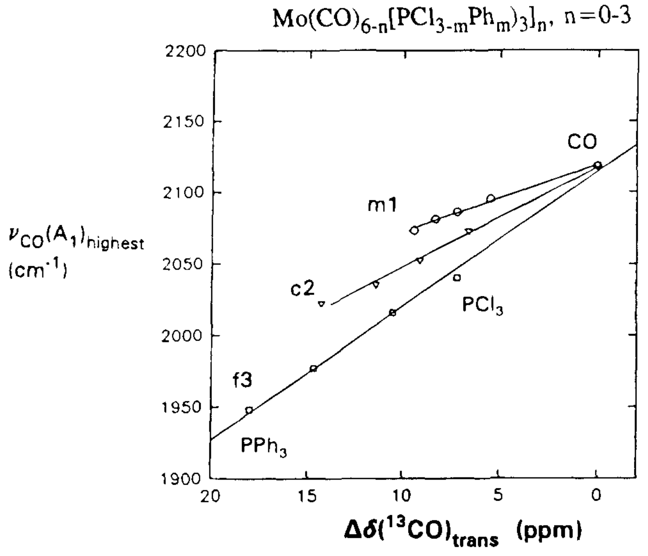

Figure 7. Correlation between $\delta(^{13}CO)_{trans}$ and $\nu_{CO}(A_1)_{cis}$ (Table 4) for molybdenum chlorophenylphosphine complexes.

Correlations for $\delta(^{13}CO)$ with the CO stretching frequencies are shown in Figures 5–7. Although a *trans* CO spectroscopic property could be an approximate indication of the π-ability of the *trans* ligand, the poor correlation plots for two *trans* parameters, as shown in Figure 5, are believed to originate from two factors: (i) the assignments for the $A_1(1)$ mode are uncertain (not the well-resolved $A_1(2)$); (ii) the chlorophosphines are weak π-acceptors. In Figure 6, the correlations between *cis* parameters appear to be better along either stepwise displacements for a given ligand or the geometry lines (m1 or c2). Therefore, the *cis* spectroscopic properties may be usable measures of some bonding property of a given ligand. It is also noted from Figure 7 that there are even some excellent correlations, along three geometry lines (ml, c2, f3), for $\Delta\delta(^{13}CO)_{trans}$ with the highest stretching frequencies which are supposed to be *cis* parameters. Therefore, both *trans* (δ and v) and *cis* (δ and v) CO's parameters contain a combined σ/π contribution from the *trans* ligands in pseudooctahedral complexes. The *trans* variables are better indicators of π character for π/σ (π-dominant) ligands, and the *cis* variables for σ character for σ/π (σ-dominant) ligands. Tolman's electronic substituent contribution, χ_i,[23] or Bodner's electronic substituent parameter, σ_i,[58a] are commonly thought of as measures of combined σ- and π-electronic effects of L; however, they may reflect more the σ-ability of ligands,[35,62] especially *since there is no real trans ligand in the T_d $Ni(CO)_3L$ geometry.*

It is worth mentioning that the steric effect in f3-PPh_3 is not reflected in Figure 7 because the deviation of v_{CO} to high frequency, caused by weakened σ-donation (decreased M–CO bond order) due to the steric effect, must correspond to a deviation of $\delta(^{13}CO)$ to low frequency for the same reason (low M–C bond order leading to shielding). As a net result, the f3-PPh_3 point has moved up along the f3 line, yielding reduced increments in $\Delta\nu_{CO}$ and $\Delta\delta(^{13}CO)$ in going from f3-$PClPh_2$ to f3-PPh_3. If π-bonding were dominant in determining $\delta(^{13}C)$ and v_{CO}, the point for f3-PPh_3 should have moved far down along the *f3 line* in Figure 7 due to the weakened π(M–P) and enhanced π(M–C) bonding (Further discussion of this point will be published in the near future.)

Conclusions

(1) The ^{95}Mo and ^{31}P NMR shielding behaviors for the phosphine ligand PCl_3 consistently indicate that this putatively strong π-acceptor is actually a weaker π-acceptor than all other phosphorus ligands employed (except for PBr_3). This conclusion is consistent with ^{13}C NMR and IR spectroscopic results. The weak π-ability of PCl_3 is also in agreement with the known very weak bond strength of M–PCl_3 in Mo and Ni carbonyl complexes as well as a theoretical calculation.

---

(61) Shen, J. K.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *Coord. Chem. Rev.* **1993**, *128*, 68.

(62) (a) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755. (b) Blomberg, M. R. A.; Brandemark, U. B.; Siegbahn, P. E. M. *J. Phys. Chem.* **1985**, *89*, 2171.

(2) The ^{95}Mo NMR shielding parameter is a good indicator of ligand π character. The carbonyl infrared parameters for phosphine-substituted metal carbonyls are not suitable for evaluating the σ and π characters of *trans* phosphorus ligands because both a weaker σ-donor and a stronger π-acceptor would lead to a high carbonyl vibrational frequency.

(3) The expectation of very short Mo−PCl_3 and Mo−PBr_3 bond distances (consistent with literature X-ray crystallographic results for a few related transition metal complexes), coupled with the evidence for the low π-acceptor ability of these phosphorus ligands, leads to an unconventional conclusion: a weak σ-donor may form a *short* M−P bond with weak bond strength in the absence of a significant π-acceptor contribution. This potentially controversial deduction is explicable in terms of increased s (decreased p) character of the PCl_3 and PBr_3 σ orbital.

(4) The ^{31}P NMR chemical shift, or coordination chemical shift $\Delta\delta(^{31}P)$, can reflect the electronic and steric variations in Mo−P bonding. Both π- and σ-bonding will increase $\Delta\delta(^{31}P)$ by inducing a deshielding effect on the ^{31}P nucleus, while steric effects decrease $\Delta\delta(^{31}P)$ by inducing a shielding effect.

(5) The higher ^{1}J(Mo−P) values for PCl_3 complexes than those for Mo phosphite and phosphine analogues agree with the s character being the primary factor in determining the one-bond metal−phosphorus coupling constant, and the magnitude of ^{1}J(M−P) thus may not be an appropriate measure of π character in an Mo−P bond.

IC941456I