A CORRELATION STUDY: ^{13}C, ^{17}O, ^{29}Si AND ^{31}P NMR CHEMICAL SHIFTS AND APPROXIMATE CO STRETCHING FORCE CONSTANTS FOR cis-DISUBSTITUTED MOLYBDENUM CARBONYL COMPLEXES

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Summary

The ^{13}C, ^{17}O, ^{29}Si and ^{31}P NMR spectral properties of cis-Mo(CO)$_4$(PPh$_2$X)$_2$, where X is Cl, OMe, 4-MeC$_6$H$_4$O, NH$_2$, NHMe, NHCH$_2$CH$_2$NH$_2$, NHCH$_2$CH$_2$NMe$_2$, 4-MeC$_6$H$_4$NH, SEt, OSiMe$_3$ or NHSiMe$_3$ and of cis-Mo(CO)$_4$(PPh$_2$YPPh$_2$), where Y is NMeCH$_2$CH$_2$NMe, NHSiMe$_2$NH, NHSiMePhNH, OSiMe$_2$O, or OSiMePhO and of cis-[Mo(CO)$_4$(PPh$_2$O)$_2$]$_2$Si have been determined. Good to excellent correlations between the ^{13}C and ^{17}O chemical shifts of carbonyl ligands *trans* to the phosphorus donor ligands are found. Only poor correlations are seen between ^{13}C and ^{17}O chemical shifts for carbonyl ligands *cis* to the two phosphine substituted carbonyl groups. Based on only seven samples, ^{29}Si and ^{13}C of *trans* carbonyl ligands also correlate well. Correlations of chemical shift data with approximate CO stretching force constants are fair to good depending upon the selection of data. In particular, much better correlations are noted in almost all instances when complexes with monodentate ligands and bidentate ligands are examined separately.

Introduction

Multinuclear magnetic resonance studies of metal carbonyl complexes of P-donor ligands have demonstrated that good correlations exist between chemical shifts of different nuclei. Chemical shifts are also known to correlate with metallocarbonyl stretching force constants. In particular, Bodner and coworkers have reported good correlations between carbonyl ^{13}C chemical shifts and Cotton–Kraihanzel stretching force constants for a wide variety of metal carbonyl complexes of P-donor ligands, and between the carbonyl ^{13}C chemical shifts for different metal carbonyl complexes of the same P-donor ligands [1–3]. Both Kowada [4] and Todd [5,6] and their respective coworkers have studied the correlation between the carbonyl ^{13}C and ^{17}O

chemical shifts. Todd has proposed a model which explains the interrelationship of these chemical shifts [6]. In an innovative study of a series of RhCl(CO)(P-donor ligand)$_2$ complexes, Derencsenyi has observed that although the carbonyl stretching force constants fail to correlate with ^{31}P chemical shifts of complexed P-donor ligands, they do correlate with ^{31}P chemical shifts of the corresponding phosphine oxide [7]. He has further noted that these shifts can also be used to predict the catalytic activity of the complexes [7].

Since the correlations discussed above appear to extend to a wide series of complexes and have a potential use in predicting important molecular properties such as catalytic activity, we have begun a study to determine the P-donor ligand properties which affect the extent and goodness of the correlations thus far reported. In this paper we report the ^{13}C, ^{17}O, ^{29}Si, and ^{31}P NMR and carbonyl infrared spectral data for a series of cis-Mo(CO)$_4$(PPh$_2$X)$_2$ complexes in which only one of the substituents on phosphorus (X) is varied, thus minimizing changes in the steric effects of the ligands and permitting a more systematic study of the change in the electronic effects of the ligand due to changes in the X group. We will also present the correlations observed between the various chemical shifts and between some of the chemical shifts and the carbonyl stretching force constants and discuss factors which have been observed to affect these correlations.

Experimental section

Complexes. Syntheses for the complexes studied in this paper have been reported previously [8,9] with the exception of trans-Mo(CO)$_4$(PPh$_2$OSiMe$_3$)$_2$, which was obtained when solutions of cis-Mo(CO)$_4$(PPh$_2$OSiMe$_3$)$_2$ in deuterochloroform were allowed to stand at room temperature for several days.

Spectra. Infrared spectra were taken of dilute, dichloromethane solutions of the complexes in 0.2 mm sodium chloride cells on a Perkin Elmer 283B infrared spectrometer.

NMR spectra were obtained on a JEOL FX90Q instrument. Saturated solutions (20°C) of complexes in deuterochloroform (1% tetramethylsilane) were filtered through silica gel into 10 mm NMR tubes under nitrogen. The instrumental parameters and standards are summarized in Table 1.

TABLE 1

NMR INSTRUMENT PARAMETERS (JEOL FX90Q Instrument)

	^{13}C	^{17}O	^{29}Si	^{31}P
Center of spectrum (MHz)	22.53330	12.15050	17.80100	36.27758
Data point resolution (Hz)	0.7	5	1.0	2.4
Spectrum width (Hz)	6000	10000	4000	10000
Pulse angle (deg)	22.5	90	45	90
Delay (sec.)	2.5	40×10^{-3}	5.0	
No. of Transients	2×10^2 -	3×10^5 -	2×10^3	1
	6×10^3	3×10^6	6×10^3	
Standard	TMS (Int.)	H$_2$O (Ext.)	TMS (Int.)	85% H$_3$PO$_4$ (Ext.)

TABLE 2

INFRARED ABSORPTIONS FOR cis-Mo(CO)$_4$(PPh$_2$X)$_2$ AND cis-Mo(CO)$_4$(PPh$_2$YPPh$_2$) COMPLEXES IN THE 2200–1850 cm^{-1} REGION [a,b]

	Complex	A$_1$(1)	A$_1$(2)	B$_1$	B$_2$	k_i	k_1	k_2
X = Cl	I	2036m	1943sh	1925s	1913sh	0.43	15.21	15.83
OMe	II	2024m	1922sh	1906s	1888sh	0.38	14.78	15.43
OC$_6$H$_4$Me-4	IV	2028m	1932sh	1912s	1896	0.40	14.92	15.57
NH$_2$	V	2022m	1921sh	1901s	1883sh	0.42	14.74	15.44
NHMe	VI	2021	1918s	1899s	1881sh	0.42	14.72	15.39
NHCH$_2$CH$_2$NH$_2$	VII	2020m	1917sh	1899s	1883sh	0.38	14.69	15.35
NHCH$_2$CH$_2$NMe$_2$	VIII	2020m	1916sh	1900s	1880sh	0.41	14.69	15.40
NHC$_6$H$_4$Me-4	X	2023m	1926m	1903s	1888sh	0.42	14.82	15.47
SEt	XI	2031m	1929sh	1918s	1888m	0.41	14.81	15.68
OSiMe$_3$	XII	2021m	1918sh	1904s	1889sh	0.36	14.77	15.37
NHSiMe$_3$	XVII	2018m	1916sh	1898s	1880sh	0.41	14.69	15.31
Y = NMeCH$_2$CH$_2$NMe	IX	2025m	1923sh	1910s	1894sh	0.39	14.87	15.52
OSiMe$_2$O	XIV	2028m	1929sh	1914s	1899sh	0.38	14.95	15.56
OSiMePhO	XV	2029m	1929sh	1915s	1899sh	0.38	14.95	15.58
NHSiMe$_2$NH	XVIII	2022m	1927m	1893s	1882sh	0.45	14.76	15.38
NHSiMePhNH	XIX	2026m	1923s	1908s	1885s	0.41	14.76	15.53
O$_4$Si [c]	XVI	2032m	1937sh	1920s	1906sh	0.38	15.05	15.65

[a] Methylene chloride solutions. Intensity designations: s = strong, m = medium, sh = shoulder Absorptions marked s or m are accurate to 1 cm^{-1} and shoulders are positioned to within 3 cm^{-1}. [b] Force constants calculated by the Cotton–Kraihanzel method. F.A. Cotton and C.S. Kraihanzel. J. Amer. Chem. Soc., 84 (1962) 4431. [c] This complex is [Mo(CO)$_4$(PPh$_2$O)$_2$]$_2$Si.

The infrared absorptions observed in the 2000 cm^{-1} region and the calculated CO stretching force constants are summarized in Table 2. The ^{13}C NMR data for the non-carbonyl carbons are summarized in Table 3 and the ^{13}C and ^{17}O NMR data for the carbonyl ligands as well as the ^{29}Si and ^{31}P NMR data are given in Table 4.

Spectral results

^{13}C {^{1}H} NMR spectra. The ^{13}C {^{1}H} resonance signals of carbonyl ligands *cis* to both phosphorus donor ligands (herein called *cis* carbonyls) in *cis*-Mo(CO)$_4$(PPh$_2$X)$_2$ complexes are 1/2/1 triplets (^2J 9–11 Hz) owing to coupling to two equivalent phosphorus nuclei. For the complexes *cis*-Mo(CO)$_4$(PPh$_2$ESiMePhEPPh$_2$) (E = O, NH), the two *cis* carbonyls are chemical shift inequivalent because of the unsymmetrical substitution at silicon and two normal triplets are observed.

TABLE 3

^{13}C NMR DATA FOR NON-CARBONYL CARBON NUCLEI IN THE COMPLEXES *cis*-Mo(CO)$_4$(PPh$_2$X)$_2$ AND *cis*-Mo(CO)$_4$(PPh$_2$YPPh$_2$) (δ in ppm, J in Hz) [a]

		Ph(C(1)) [b]		Ph(C(2,6)) [c]	
		δ	$|^1J(CP) + ^3J(CP')|$	δ	$^2J(CP) \cdot ^4J(CP')|$
cis Complexes					
X =	Cl I	139.36	25	131.04	15
	OMe II	139.07	32	131.10	14
	OC$_6$H$_4$Me-4 IV	140.43	33	130.61	14
	NH$_2$ V	141.57	37	130.16	14
	NHMe VI	136.96	37	131.43	13
	NHCH$_2$CH$_2$NH$_2$ VII	137.74	38	131.49	12
	NHCH$_2$CH$_2$NMe$_2$ VIII	137.86	36	131.52	13
	NHC$_6$H$_4$Me-4 X	136.30	38	130.81	13
	SEt XI	134.91	25	132.11	12
	OSiMe$_3$ XII	142.45	37	129.28	15
	NHSiMe$_3$ XVII	139.85	36	131.40	13
Y =	NMeCH$_2$CH$_2$NMe IX	137.28	34	131.52	13
	OSiMe$_2$O XIV	142.45	37	129.28	15
	OSiMePhO [6] XV	143.55	40	[e]	
		142.16	37		
	NHSiMe$_2$NH XVIII	141.04	39	130.19	14
	NHSiMePhNH [f] XIX	143.26	39	130.35	13
	O$_4$Si [g] XVI	141.25	39	129.44	15
trans Complexes					
X =	OMe III	141.88	36	130.74	14
	OSiMe$_3$ XIII	144.21t	35	130.42	15

[a] Deuterochloroform solvent. [b] Resonances for *cis* carbonyl ligands are apparent pentets of the general shape shown in Fig. 1 and are discussed in the text. Resonance signals for *trans* complexes are apparent triplets. [c] Signals are apparent triplets and are discussed in the text. [d] Signals are singlets unless otherwise noted. [e] Signal obscured by other aromatic resonances. [f] Two C(1) resonance signals are noted for the

The ^{13}C $\{^1H\}$ resonance signals of carbonyl ligands *trans* to the phosphorus donor ligands (herein called *trans* carbonyls) in *cis*-Mo(CO)$_4$(PPh$_2$X)$_2$ complexes are apparent triplets (due to coupling to magnetically inequivalent phosphorous nuclei) which are found 5 to 8 ppm downfield of the corresponding *cis* carbonyl signals. The AXX' spin system giving rise to the apparent triplets is a special case of the well known X$_n$AA'X'$_n$ spin system first described by Harris [10] and has been applied to bis(phosphine) transition metal complexes by other investigators [11–13]. Mathematical analysis of the *trans* carbonyl resonance of *cis*-Mo(CO)$_4$(PPh$_2$OC$_6$H$_4$Me-4)$_2$, shown in Fig. 1, yields values of 29 Hz for $|^2J(PP')|$ and of 30 Hz and 10 Hz for $|^2J(CP)|$ and $|^2J(CP')|$, respectively. The actual signs of $|^2J(PC)|$ and $|^2J(P'C)|$ are opposite but undetermined by the calculation. These calculated values are in good agreement with the coupling constants of a series of Group VI metal carbonyl

Ph(C(3,5))[c]		Ph(C(4))	Other[d]	
δ	$|^3J(CP)+{}^5J(CP')|$	δ	δ	J
128.24	9	130.71	–	-
128.01	8	129.96	53.39(CH$_3$)	4($|^2J(CP)+{}^4J(CP')|$)
128.01	10	3	20.58 (CH$_3$)	–
128.17	9	129.41	–	.
127.98	9	129.35	29.85(CH$_3$)	9($|^2J(CP)+{}^4J(CP')|$)
128.05	9	129.41	46.46(NHCH$_2$)	8($|^2J(CP)+{}^4J(CP')|$)
			42.79(NH$_2$CH$_2$)	
127.92	9	129.21	40.97(NHCH$_2$)	9($|^2J(CP)+{}^4J(CP')|$)
			45.13(NCH$_3$)	
			59.57(NCH$_2$)	
128.47	9	^{e}	20.32(CH$_3$)	
128.18	10	129.61	27.08(CH$_2$)	
			14.53(CH$_3$)	
128.18	9	129.74	1.50(CH$_3$)	
128.01	10	129.54	1.72(CH$_3$)	
127.92	9	129.31	53.36(NCH$_2$)	20($|^2J(CP)+{}^4J(CP')|$)
			39.21(NCH$_3$)	8($|^2J(CP)+{}^4J(CP')|$)
128.18	9	129.93	1.24(CH$_3$)	
^{e}		^{e}	0.03(CH$_3$)	
128.11	8	129.35	3.12(CH$_3$)	5($|^3J(CP)+{}^5J(CP')|$)
128.18	10	129.44	1.95(CH$_3$)	5($|^3J(CP)+{}^5J(CP')|$)
128.31	10	130.32	–	
128.08	9	129.80	52.94(CH$_3$)^h	
127.85	9	129.48	1.43(CH$_3$)	

nonequivalent P-phenyl rings. The other resonance signals are experimentally coincident. Signals for Si-phenyl rings are observable but assignments are difficult. ^{g} This complex is [Mo(CO)$_4$(PPh$_2$O)$_2]_2$Si. ^{h} Phosphorus carbon coupling not observed.
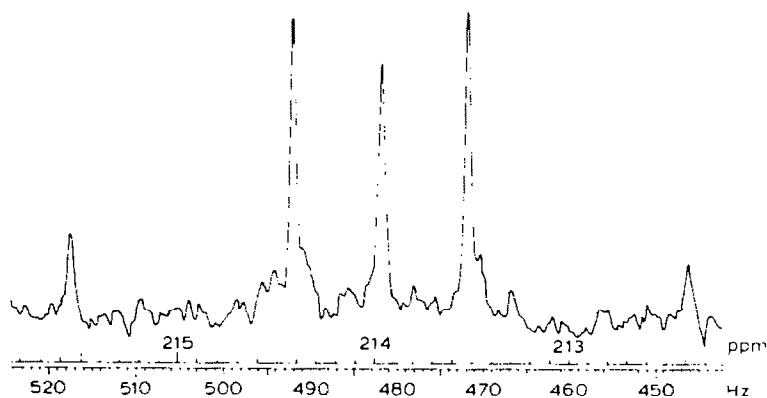
Fig. 1. ^{13}C NMR spectrum of *trans* CO in *cis*-Mo(CO)$_4$(PPh$_2$OC$_6$H$_4$Me-4)$_2$.

complexes of unsymmetrical biphosphorus ligands which were directly determined employing multiple resonance techniques [14]. For the other complexes studied, the level of data accumulation was not sufficient for all lines to be observed and only $|^2J(CP) + ^2J(CP')|$ values are reported.

The resonance signals for the phosphorus-phenyl carbons are similar for all the complexes studied. The ^{13}C resonance of C(1) is found farthest downfield and is either an apparent triplet or an apparent pentet. The signals for C(2,6) (*ortho*) and C(3,5) (*meta*) are also apparent triplets and are assigned to the 129 132 and 128 128.5 ppm ranges, respectively. These assignments are based on previous literature values cited for XPPh$_3$ (X = O. S. Se) [15]. A singlet is noted for C(4) (*para*) for all of the complexes studied. The magnitude of $|^2J(CP) + ^2J(CP')|$ is seen to decrease steadily with increasing n.

^{17}O NMR spectra. For each of the *cis*-Mo(CO)$_4$L$_2$ complexes studied in this work, two ^{17}O NMR resonances are observed although in some cases the broader, highfield signal appears as a shoulder on the lowfield peak. The sharp lowfield and broad highfield resonances are assigned to the *trans* and *cis* carbonyls, respectively, consistent with previous assignments reported for the ^{17}O NMR resonances of the carbonyl ligands in *cis*-Mo(CO)$_4$(EPh$_3$)$_2$ (E = P. As. Sb) [16], W(CO)$_4$(diphos) [6] and *cis*-Mo(CO)$_4$(PPh$_2$OH)(PPh$_2$OR) (R = Et. CH$_2$CH$_2$NMe$_2$) [17]. Additional supporting evidence for the assignment made for the ^{17}O resonances of the complexes in the study comes from:

(i) a comparison of the ^{17}O NMR spectra of the carbonyl ligands in *cis* and *trans*-Mo(CO)$_4$(PPh$_2$X)$_2$ (X = OMe and OSiMe$_3$) in which the chemical shift of the single ^{17}O NMR resonance of the carbonyls of the *trans* complexes is close to the chemical shift of the upfield resonance for the corresponding *cis* isomer and

(ii) the observation that the ^{17}O chemical shifts of the downfield resonances, assigned to the *trans* carbonyls, are more sensitive to changes in the X group on phosphorus than are the upfield resonances.

^{29}Si NMR spectra. The inherent negative Overhauser effect (NOE) of the ^{29}Si nucleus often results in decreased signal to noise ratios in the ^{29}Si NMR spectra of the complexes studied in this paper. A gated decoupling pulse sequence was employed to eliminate the NOE for those complexes whose ^{29}Si NMR spectra could

not be observed using normal ^{1}H decoupling. Although the chemical shifts of ^{29}Si nuclei are affected primarily by the electronegativities of substituents attached to silicon, this dependence on substituent electronegativity has been shown to be nonlinear [18]. Nonlinearity is noted in this work as well. For example, whereas the ^{29}Si chemical shift for cis-Mo(CO)$_4$(PPh$_2$OSiMe$_3$)$_2$ is 9.44 ppm upfield of the value of the analogous NH complex, the ^{29}Si shifts for cis-Mo(CO)$_4$(PPh$_2$OSi(Me)$_2$OPPh$_2$) and cis-Mo(CO)$_4$(PPh$_2$OSi(Me)(Ph)OPPh$_2$) are 0.47 upfield and 5.11 ppm downfield of their respective NH analogs.

The phosphorus–silicon coupling observed in these silicon containing complexes is also unusual. No coupling is observable for the complexes cis-Mo(CO)$_4$-(PPh$_2$OSi(Me)(R)OPPh$_2$) (R = Me or Ph) but is seen for all other silicon containing complexes. In all cases the coupling constants in the complexes containing a P–O–Si linkage (^2J(PSi) 5–7 Hz) are smaller than in those containing a P N–Si linkage (^2J(PSi) 7–10 Hz).

^{31}P NMR spectra. The ^{31}P NMR chemical shift data for the complexes examined here have been summarized in Table 4. As expected, only a single sharp signal is seen for each complex and this fact provides an excellent test of sample purity. An examination of the ^{31}P chemical shift data shows that the complexes of aminophosphines have chemical shifts in the range of δ 66–91 ppm. For the complexes of the phosphinite esters the chemical shifts are significantly downfield in the δ 130–156 range as a result of the greater electronegativity of oxygen relative to nitrogen.

Discussion

Although there is not complete uniformity of thought regarding the nature of bonding in metal carbonyl complexes, the fact that changing a Lewis base substituent changes the infrared frequency of the carbonyl group *trans* to the ligand to a greater extent than a *cis* carbonyl group seems indisputable. It seems only natural then to determine if substituent changes are reflected in NMR properties as well, and if the effects on *cis* and *trans* carbonyl groups are different. As will now be shown, such correlations do exist, but the level of correlation is not always very high. One very important fact which will become apparent as the results of this work are discussed is the improved correlations noted when *cis*-disubstituted complexes and complexes with chelating ligands are treated separately.

Correlations between chemical shifts and stretching force constants for carbonyl ligands

Plots of the ^{13}C chemical shifts versus C–K infrared stretching force constants for the *trans* and *cis* carbonyl ligands of cis-Mo(CO)$_4$(PPh$_2$X)$_2$ and Mo(CO)$_4$-(PPh$_2$YPPh$_2$) are shown in Fig. 2. For the *trans* carbonyl ligands the correlation of the ^{13}C chemical shifts with k_1, the approximate force constant for CO *trans* to a phosphorus donor ligand, is poor (r = linear correlation coefficient = −0.771) if one includes data for all of the *cis* complexes. The correlation in which data for only the complexes of monodentate ligands is used is very good ($r = -0.954$) whereas the data for the complexes of bidentate ligands forming six-membered rings give a fair correlation ($r = -0.843$). In contrast, only fair correlations are observed between the ^{13}C chemical shifts and the stretching force constants (k_2) for the *cis* carbonyl ligand of all *cis* complexes ($r = -0.862$), for *cis* complexes of monodentate ligands

TABLE 4

^{13}C AND ^{17}O NMR DATA FOR THE CARBONYL LIGANDS AND ^{29}SI AND ^{31}P NMR DATA FOR THE PHOSPHORUS DONOR LIGANDS IN THE COMPLEXES cis-Mo(CO)$_4$(PPh$_2$X)$_2$ AND cis-Mo(CO)$_4$(PPh$_2$YPPh$_2$) (δ in ppm. J in Hz)[a]

		Complex	^{13}C(trans CO[b])[c]		^{13}C (cis CO[b])[d]	
			δ	$^{2}J(CP) - ^{3}(CP')$	δ	$^{2}J(CP)$
X	cis-Cl	I	212.29	28	207.71	10
	cis-OMe	II	214.60	18	208.57	11
	trans-OMe	III			209.92	11
	cis-OC$_6$H$_4$Me-4	IV	213.98	20	208.39	10
	cis-NH$_2$	V	214.76	17	209.60	10
	cis-NHMe	VI	215.25	22	209.53	10
	cis-NHCH$_2$CH$_2$NH$_2$	VII	215.15	17	209.62	10
	cis-NHCH$_2$CH$_2$NMe$_2$	VIII	215.35	17	209.60	10
	cis-NHC$_6$H$_4$Me-4	X	214.21	18	209.10	9
	cis-SEt	XI	214.37	18	208.59	10
	cis-OSiMe$_3$	XII	215.12	18	210.08	11
	trans-OSiMe$_3$	XIII			210.47	10
	cis-NHSiMe$_3$	XVII	215.77	17	210.02	10
Y =	NMeCH$_2$CH$_2$NMe	IX	215.71	20	209.01	9
	OSiMe$_2$O	XIV	214.96	18	208.62	11
	OSiMe(Ph)O	XV	214.78	19	209.27	11
					207.55	11
	NHSiMe$_2$NH	XVIII	215.28	16	209.08	10
NHSiMe(Ph)NH		XIX	215.02	10	209.60	10
					207.45	10
	O$_4$Si[h]	XVI	214.02	21	207.58	11

[a] Deuterochloroform as solvent. Multiplicities: s-singlet, t = triplet, p = pentet, sh = unresolved shoulder. [b] trans CO refers to CO trans to one of the phosphorus donor ligands; cis CO refers to CO cis to both phosphorus donor ligands. [c] Relative to ^{13}C resonance of internal TMS at 0.00 ppm. All resonances are apparent triplets. See Discussion in text for compound IV. [d] Relative to ^{13}C resonance of internal TMS at

only ($r = -0.888$) and for complexes of bidentate ligands forming six-membered rings ($r = -0.898$).

Plots of the ^{17}O chemical shifts versus the infrared stretching force constants for the trans and cis carbonyls are shown in Fig. 3. For the trans carbonyl ligands the correlation of the ^{17}O chemical shifts with the stretching force constants (k_1) calculated using data for all the cis complexes is fair ($r = 0.861$) but the correlations calculated using separate data for complexes of monodentate ligands ($r = 0.962$) and the complexes of bidentate ligands forming six-membered rings ($r = 0.991$) are very good. Correlations between the ^{17}O chemical shifts with the stretching force constants (k_2) for the cis carbonyl groups are extremely poor ($r < 0.7$) regardless of the data set used.

Correlations of both ^{13}C and ^{17}O chemical shifts with the stretching force constant for the trans carbonyls of cis-Mo(CO)$_4$(PPh$_2$X)$_2$ complexes are superior to the corresponding correlations for the cis complexes although the correlation of ^{13}C chemical shift with the stretching force constant for the cis carbonyls is better than that for the trans carbonls when the data for all the complexes are considered. This

^{17}O (*trans* CO[h])[c]	^{17}O (*cis* CO[h])[c]	^{29}Si[f]		^{31}P[g]
δ	δ	δ	$|^2J(PSi)|$	δ
366.9	360.5	–	–	124.77
362.1	359.3	–	–	145.97
	359.7	–	-	156.81
362.9	360.9 sh	.	–	145.84
359.3	358.5 sh	–	–	67.17
359.3	356.0 sh	–	–	78.67
359.3	358.9 sh	.	..	77.39
358.4	358.0	.	–	76.32
360.5	358.5	–	–	69.72
361.3	356.4 sh	–	–	60.24
360.9	357.6	17.50t	5	131.44
–	357.2	16.60t	7	139.78
359.3	356.0	8.06t	7	73.49
359.3	354.4	–	–	91.12
366.9	356.8	1.18s		128.00
367.3	359.2	– 14.37s		129.96
360.9	356.0	0.71st	10	65.82
361.2	356.4	–9.16t	10	66.43
368.9	357.7	–99.24p	6	145.29

0.00 ppm. All resonances are triplets. [c] Relative to ^{17}O resonance of internal H_2O at 0.00 ppm. [f] Relative to ^{29}Si resonance of internal TMS at 0.00 ppm. [x] Relative to ^{31}P resonance of external 85% phosphoric acid at 0.00 ppm. [h] This complex is $[Mo(CO)_4(PPh_2O)_2]_2Si$.

behaviour can be compared to that reported by Bodner [2] for the correlation between the ^{13}C NMR carbonyl resonances and stretching force constants for a series of $LM(CO)_5$ complexes (M = Cr, Mo, W) in which superior correlations were reported for the *cis* carbonyls. However recalculation of these correlations using only Bodner's data for complexes of phosphorus donor ligands yields equally good correlations ($r \geqslant -0.95$) for both the *cis* and *trans* carbonyls. Thus, it would appear that the correlation between the chemical shifts and stretching force constants is affected by a complex mixture of steric and electronic factors.

Correlations between the ^{13}C and ^{17}O chemical shifts

Graphs showing relationships between the ^{13}C and ^{17}O chemical shifts for *cis* and *trans* carbonyl ligands are shown in Fig. 4. For the *trans* carbonyl groups a good correlation ($r = -0.915$) is obtained when data for complexes of monodentate ligands are used. An even better correlation is found using only the data for monodentate phosphinamide ligands. Excellent correlations are obtained using the data for complexes of ligands containing P–N–Si bonds ($r = -0.980$) and for
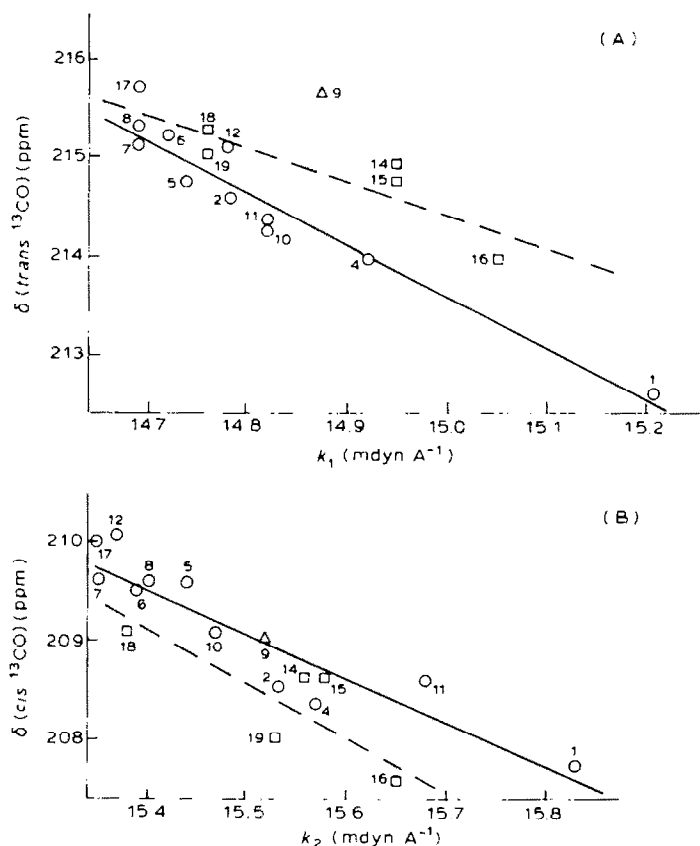
Fig. 2. Plots of ^{13}C NMR chemical shifts (ppm) vs. Cotton–Kraihanzel stretching force constants (mdyn A^{-1}) for the *trans* (A) and *cis* (B) carbonyl of *cis*-Mo(CO)$_4$L$_2$. L = PPh$_2$X($\bigcirc$); L$_2$ = Ph$_2$PESiR$_2$EPPh$_2$($\square$); L$_2$ = Ph$_2$PNMeCH$_2$CH$_2$NMePPh$_2$ ($\triangle$). Least squares lines are drawn for complexes with non-chelating ligands (———) and complexes with six-atom chelate rings ( ).

complexes of chelating ligands with P–O–Si bonds ($r \simeq -0.999$) although in each case the data for only three complexes are used. That several correlations are necessary to fit all the data for the structurally homogeneous series of complexes studied in this work may explain why earlier investigators, examining series of complexes whose ligands varied more widely in cone angle and electronic properties, reported poor correlations between the ^{13}C and ^{17}O chemical shifts of the carbonyl ligands [4,5].

Other chemical shift correlations

No correlation is observed between the ^{31}P chemical shifts and either of the carbonyl stretching force constants or ^{13}C or ^{17}O chemical shifts. This lack of correlation may be a reflection of the well recognized fact that ^{31}P chemical shifts of P-donor ligands are very sensitive to changes in the hybridization of the phosphorus and thus changes in the steric bulk of the groups attached to the phosphorus will have a much greater effect on the chemical shift of the phosphorus than on the
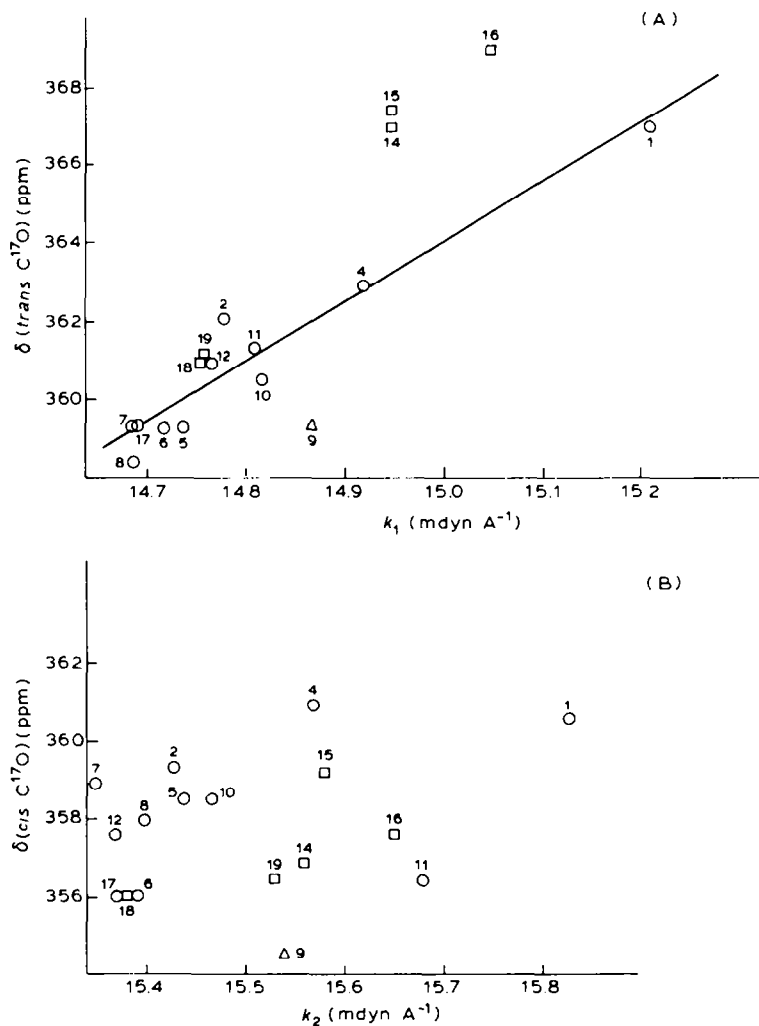
Fig. 3. Plots of ^{17}O NMR chemical shifts (ppm) vs. Cotton–Kraihanzel stretching force constants (mdyn A^{-1}) for *trans* (A) and *cis* (B) carbonyls of *cis*-$Mo(CO)_4L_2$. $L = PPh_2X(O)$; $L_2 = Ph_2PESiR_2EPPh_2$ (□); $L_2 = Ph_2PNMeCH_2CH_2NMePPh_2$ (△). A least squares line is drawn for complexes with non-chelating ligands (*trans* only).

carbonyl ^{13}C or ^{17}O chemical shifts. Tolman has used similar arguments to explain the lack of correlation between the ^{31}P chemical shifts and carbonyl stretching force constants for a series of $Ni(CO)_3$(phosphine) complexes [19].

Furthermore, we note no correlation between the chemical shifts for the aromatic carbons of the phosphorus donor ligands and other chemical shifts or carbonyl stretching force constants. The chemical shifts of the phenyl carbons, expecially those of the carbon bonded to phosphorus, change drastically as the substituents on the phosphorus are changed but in a manner different from the changes observed for any of the other chemical shifts or for the carbonyl stretching force constants.
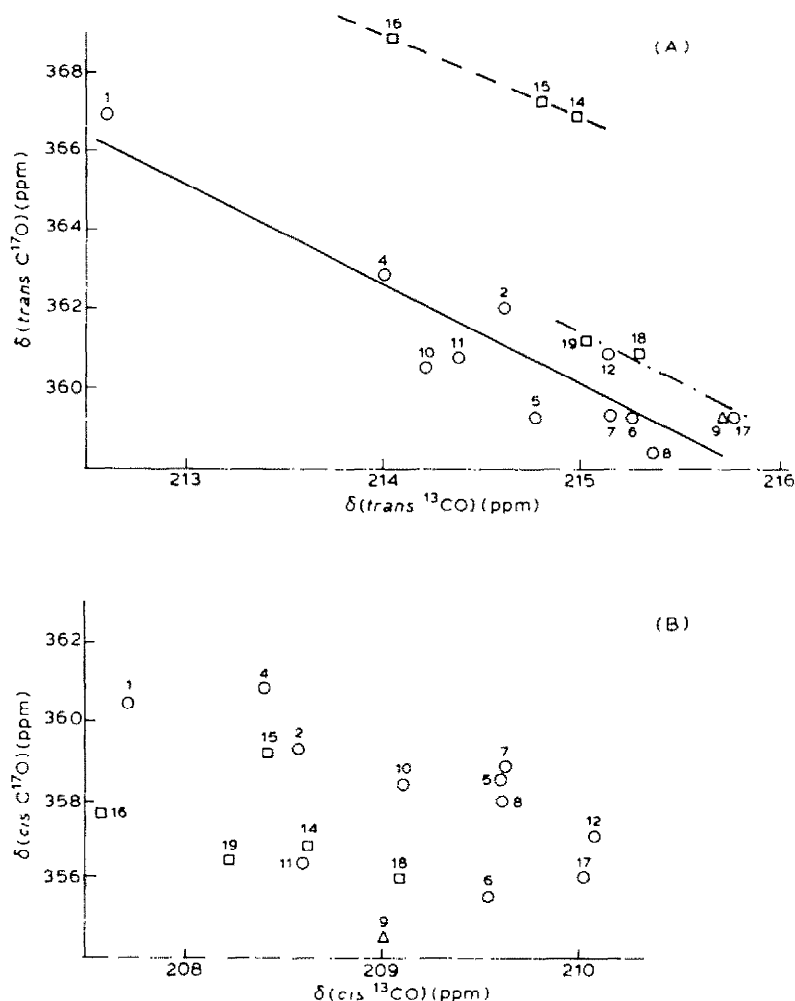
Fig. 4. Plots of ^{17}O vs. ^{13}C NMR chemical shifts (ppm) for *trans* (A) and *cis* (B) carbonyls of *cis*-Mo(CO)$_4$L$_2$. L = PPh$_2$X(O); L$_2$ = Ph$_2$PESiR$_2$EPPh$_2$ (□); L$_2$ = Ph$_2$PNMeCH$_2$CH$_2$NMePPh$_2$ (△). Least squares lines drawn for non-chelating ligands (————); complexes with six-atom chelate rings containing P O–Si bonds (– – –); and ligands containing P–N Si bonds (· · · ·) (*trans* carbonyls only).

Based on a limited number of new complexes, we have observed good correlations between the ^{29}Si chemical shifts of the silicon containing phosphorus donor ligands and the ^{13}C chemical shifts of the *trans* carbonyl ligands and fair correlations between the ^{29}Si chemical shifts and the ^{17}O chemical shifts of the *trans* carbonyl ligands as shown in Fig. 5. The complexes XVII, XVIII, and XIX which contain a P–N· Si linkage show a good correlation between the ^{13}C and ^{29}Si chemical shifts ($r = 0.966$) and a fair correlation between the ^{17}O and ^{29}Si chemical shifts ($r = -0.897$). Complexes XII, XIV, XV, and XVI show an excellent correlation between the ^{13}C and ^{29}Si chemical shifts ($r = 0.999$) and a poor correlation between the ^{17}O
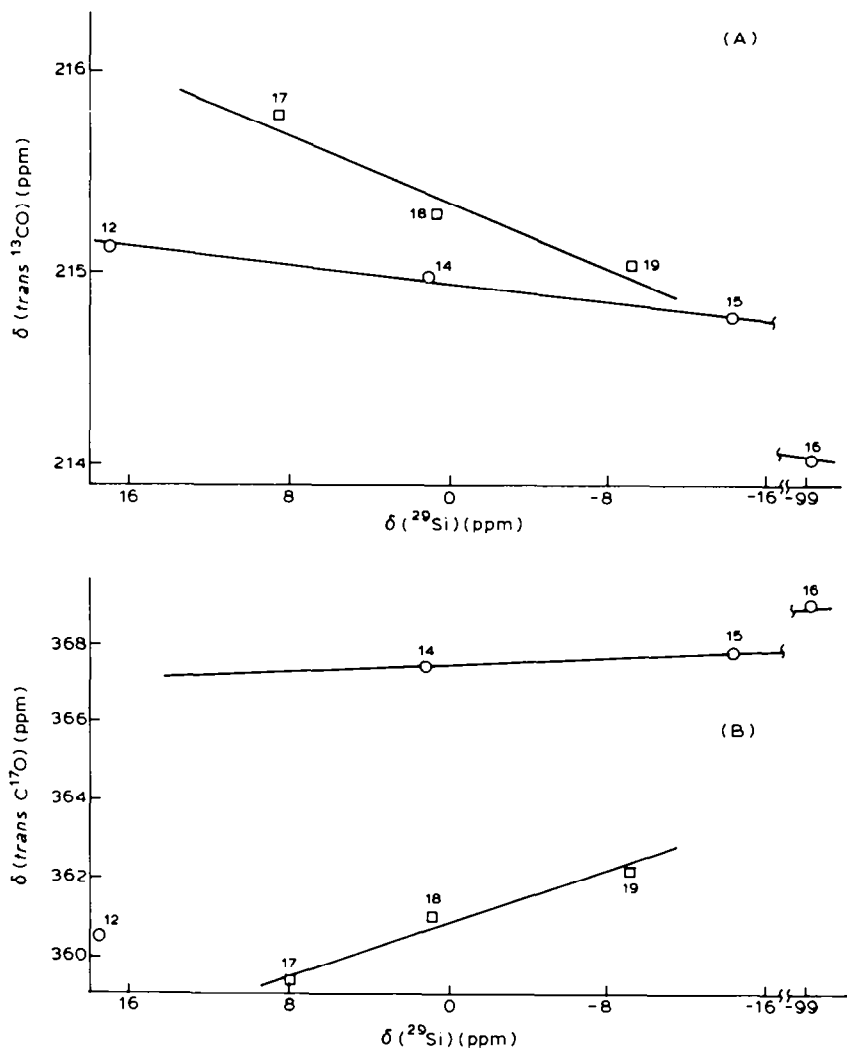
Fig. 5. Plots of ^{13}C NMR chemical shifts (ppm) (A) and ^{17}O NMR chemical shifts (ppm) (B) for *trans* carbonyl ligands vs. ^{29}Si chemical shifts for phosphorus donor ligands of *cis*-Mo(CO)$_4$(Ph$_2$PESiMe$_3$)$_2$, Mo(CO)$_4$(Ph$_2$PESiMeREPPh$_2$) and [Mo(CO)$_4$(Ph$_2$PO)$_2$]$_2$Si. E = O (◯); E = NH (☐). Least squares lines are drawn for complexes containing P-O-Si bonds and complexes containing P N-Si bonds.

and ^{29}Si chemical shifts ($r = -0.721$) unless the data for complex XII are dropped at which point the correlation becomes excellent ($r = -0.999$). There is some justification in dropping the data for complex XII as it is the only one of the complexes in this study which was observed to undergo a *cis* to *trans* rearrangement in solution at ambient temperature implying significant steric interaction between the trimethylsilyl groups and other portions of the complex. The reason for the good correlations observed between the ^{29}Si chemical shifts and ^{13}C and ^{17}O carbonyl chemical shifts is not readily apparent. Additional complexes containing P-O-Si and P-N-Si linkages should be synthesized to test the extent of these correlations.

214

Conclusion

The trends of the ^{13}C and ^{17}O chemical shifts for the *trans* carbonyl ligands fit the model proposed by Todd and coworkers [6]. In their model, back-donation by the metal into the orbitals of the carbonyl ligands will disrupt one of the π bonds concurrently lowering the electron density on the carbon and raising the electron density on the oxygen. The effect of the X-group of the phosphorus donor ligands on this back-donation is as follows: $NHSiMe_3 \gg OSiMe_3 \approx NHalkyl > NH_2 > OMe > SEt > NHC_6H_4Me-4 > OC_6H_4Me-4 \gg Cl$ which is similar to that reported by Bodner for the PX_3 ligands in $(PX_3)Ni(CO)_3$ complexes [3].

Of special importance is the observation that a poor correlation is found whenever complexes with unidentate and chelating ligands are included in the same data set. Further studies with ligands of less steric bulk and less problematical diamagnetic anisotropic factors, for example Me_2PX and Me_2PYPMe_2, are suggested to determine if better correlations will be seen in the absence of these complicating factors.

Acknowledgements

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