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Synthesis and Multinuclear NMR and Mass Spectroscopic Study of some $Mo(CO)_5(PPh_2XR)$ (X = O, S, NH; R = alkyl, aryl, Me_3Si) Complexes. Chemical Shift Correlations with *cis*-$Mo(CO)_4(PPh_2XR)_2$ Chemical Shifts

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The syntheses of a series of $Mo(CO)_5(PPh_2XR)$ complexes are reported. The complexes have been characterized by multinuclear NMR-, infrared-, and mass spectroscopy. Chemical shift correlations between the carbonyl ^{13}C and ^{17}O, P–C ^{13}C, ^{31}P and ^{95}Mo chemical shifts are demonstrated to depend upon the similarity in size of the XR groups. Fair to excellent correlations between these chemical shifts and similar chemical shifts of some cis-*$Mo(CO)_4(PPh_2XR)_2$ complexes are reported and indicate that the steric effect of the PPh_2XR ligands are similar in the two sets of complexes.*

Introduction

If multinuclear NMR spectroscopy is to be used as a probe for electron density changes in metal complex catalysts it is necessary to understand the relationship between changes in the steric and electronic properties of the ligands and the observed multinuclear chemical shifts of the complexes. Toward this goal, it has recently been demonstrated that the multinuclear NMR chemical shifts of molybdenum carbonyl complexes of P-donor ligands can be related to changes in the electron donor/acceptor properties of the P-donor ligands only when the cone-angles of the P-donor ligands remain constant [1–4]. These results are consistent with previous reports of poor correlations between the various chemical shifts of metal carbonyl complexes of P-donor ligands in which both the electron donor/acceptor properties and cone angles of the P-donor ligands are simultaneously varied [5–8].

Although the effect of changes in the cone angles of P-donor ligands on the chemical shifts of their metal carbonyl complexes has been demonstrated for a series of (P-donor ligand)pentacarbonylmolybdenum(0) complexes [3], the effect of multiple P-donor ligands on the steric contribution to the chemical shifts of their metal carbonyl complexes has not been studied in detail. Masters *et al.* [9] have reported that a good correlation exists between the ^{95}Mo chemical shifts of some phosphine and phosphinite mono- and *cis*-disubstituted molybdenum carbonyl complexes which would indicate that the ligands have similar steric effects in the two complexes even though the *cis* complex should be more severely crowded.

In order to determine if the correlation reported by Masters *et al.* can be observed for other nuclei in the mono- and *cis*-di-substituted P-donor ligand molybdenum carbonyl complexes, a series of $Mo(CO)_5(PPh_2XR)$ (X = O, S, NH; R = alkyl, aryl, silyl) complexes has been synthesized and their ^{13}C, ^{17}O, ^{31}P, and ^{95}Mo NMR spectra obtained. The correlations observed between the various chemical shifts of the mono-substituted complexes and between similar chemical shifts in these complexes and in a series of *cis*-$Mo(CO)_4(PPh_2XR)_2$ complexes, whose ^{13}C, ^{17}O, ^{31}P and ^{95}Mo NMR spectra have been reported previously [1, 2], are discussed in terms of the changes in the cone angles of the PPh_2XR ligands.

Experimental

The molybdenum pentacarbonyl complexes were prepared in dry THF under an atmosphere of dry nitrogen using literature methods [3, 4, 10] with the exception of the complexes discussed below.

(Alkyl Diphenylthiophosphinite)pentacarbonylmolybdenum(0), $Mo(CO)_5(PPh_2SR)$ (R = n-Pr, i-Pr), (5) and (6)

A solution of 1.37 g (3.00 mmol) of $Mo(CO)_5(PPh_2Cl)$ (1), 3.00 mmol of n-propyl or i-propylmercaptan, and 0.42 ml (3.00 mmol) of triethylamine in 20 ml of THF was stirred at ambient temperature for two hours before being filtered to remove the precipitated triethylammonium chloride. The filtrate

TABLE I. Infrared- and Mass Spectroscopic Data for $Mo(CO)_5(PPh_2XR)$ Complexes.

XR	IR Carbonyl Stretching Absorptions (cm^{-1})[a,b]				Mass Spectra – Major Ions for ^{98}Mo
	$A_1^{(1)}$	B_1	$A_1^{(2)}$	E	M/e
Cl(1)	2081m	2020w	1969sh	1962s	458, 402, 346, 318, 284, 240
NH_2(2)	2074m	1990w	1958s	1951s	439, 411, 355, 299, 221
O–n-Pr(3)	2074m	1992w	1962s	1953s	482, 454, 398, 342, 297, 284, 222
O–i-Pr(4)	2074m	1992w	1961s	1952s	482, 454, 398, 342, 297, 284, 222
S–n-Pr(5)	2076m	1994w	1958s	1954sh	498, 470, 414, 386, 356, 313, 284, 238
S–i-Pr(6)	2076m	1994w	1958s	1954sh	498, 470, 414, 386, 356, 313, 284, 238
NH–n-Pr(7)	2073m	1990w	1957s	1948s	481, 453, 397, 341, 284, 259, 206
NH–i-Pr(8)	2073m	1990w	1956s	1949s	481, 453, 397, 341, 284, 206
OPh(9)	2077m	1998w	1965s	1955s	516, 488, 432, 376, 346, 296
OC_6H_4-*p*-Me(10)	2076m	1997w	1963s	1954s	530, 502, 446, 390, 310, 283
SC_6H_4-*p*-Me(11)	2076m	1994w	1959sh	1957s	546, 518, 462, 406, 326, 313, 284, 205
NHPh(12)	2074m	1992w	1960s	1950s	515, 487, 431, 375, 297
NHC_6H_4-*p*-Me(13)	2074m	1992w	1959s	1950s	529, 501, 445, 389, 311, 283
$OSiMe_3$(14)	2075m	1997w	1961s	1946s	512, 484, 428, 372
$NHSiMe_3$(15)	2072m	1994w	1956s	1946s	511, 483, 427, 371

[a] Hexanes solution in 0.2 mm NaCl cells; ±1 cm^{-1} except for shoulders which are ±3 cm^{-1}. [b] Abbreviations: w = weak; m = medium; s = strong; sh = shoulder.

TABLE II. NMR Instrument Parameters and Standards.[a]

Parameter Nucleus:	^{13}C	^{17}O	^{31}P	^{95}Mo[b]
Center of Spectrum (MHz)	22.53330	12.15050	36.27400	5.8300
Data Point Resolution (Hz)	0.7	5	1.2	1.2
Spectrum Width (Hz)	6.000	10.000	10.000	5.000
Pulse Angle (°/μs)	30/7	90/23	90/23	90/91
Pulse Delay	2.5 sec	40 msec	–	0.35 sec
Accumulations	2×10^3	3×10^5	1	1×10^4
Standard	int TMS	ext H_2O	ext 85% H_3PO_4	ext 2 *M* Na_2MoO_4

[a] JEOL FX90Q multinuclear NMR spectrometer. [b] Low band probe.

was evaporated to dryness and the residue taken up in 30 ml of hexanes. This solution, followed by 20 ml of hexanes, was filtered through a 3.5 X 1 cm column of neutral alumina and the filtrate evaporated to dryness to yield the desired product ((5), 1.01 g, 68%; (6) 0.99 g, 66%).

(p-Tolyl Diphenylthiophosphinite)pentacarbonylmolybdenum(0), $Mo(CO)_5(PPh_2SC_6H_4$-p-Me), (11)

A solution of 1.37 g (3.00 mmol) of $Mo(CO)_5(PPh_2Cl)$ (1), 0.37 g (3.00 mmol) of *p*-thiocresol and 0.42 ml (3.00 mmol) of triethylamine in 20 ml of THF was stirred at ambient temperature for 1 hr before being filtered to remove the precipitated triethylammonium chloride. The filtrate was evaporated to dryness and the residue recrystallized from methanol to yield 1.17 g (72%) of product.

(Aryl Diphenylphosphinamide)pentacarbonylmolybdenum(0), $Mo(CO)_5(PPh_2NHR)$ (R = Ph, C_6H_4-p-Me), (12) and (13)

A solution of 1.37 g (3.00 mmol) of $Mo(CO)_5(PPh_2Cl)$ (1) and 12.0 mmol of aniline or *p*-toluidine in 20 ml of THF was stirred at ambient temperature for 20 hr before being evaporated to dryness. The residue was washed with 30 ml of methanol and the insoluble product collected by nitrogen pressure filtration ((12), 0.82 g, 53%; (13), 0.72 g, 46%).

TABLE II. Multinuclear NMR Data for the Mo(CO)$_5$(PPh$_2$XR) Complexes.[a]

XR	Trans Carbonyl			Cis Carbonyl			Phenyl C-1		P	Mo	
	$\delta\,^{13}$C(ppm)[b]	$^2J_{PC}$(Hz)	$\delta\,^{17}$O(ppm)[c]	$\delta\,^{13}$C(ppm)[b]	$^2J_{PC}$(Hz)	$\delta\,^{17}$O(ppm)[c]	$\delta\,^{13}$C(ppm)[b]	$^1J_{PC}$(Hz)	$\delta\,^{31}$P(ppm)[d]	$\delta\,^{95}$Mo(ppm)[e]	$^1J_{MoP}$ (Hz)
Cl(1)	209.37	32	371.1	202.34	10	362.1	138.87	35	123.01	−1701.6	165
NH_2(2)	210.02	24	365.3	205.48	10	360.9	140.65	40	66.50	−1767.4	148
O–n-Pr(3)[f]	209.95	26	367.3	205.48	10	362.1	139.08	34	141.86	−1787.9	156
O–i-Pr(4)[f]	209.98	26	366.9	205.53	10	362.5	140.66	37	140.45	−1782.7	159
S–n-Pr(5)	210.36	26	366.1sh	204.98	9	361.3	134.35	28	58.64	−1726.2	142
S–i-Pr(6)	210.46	26	365.7sh	204.94	9	361.3	134.91	28	59.75	−1722.9	145
NH–n-Pr(7)[f]	210.47	23	364.9sh	205.68	10	360.9	136.99	40	75.90	−1763.4	146
NH–i-Pr(8)[f]	210.50	23	365.3	205.61	10	360.9	138.20	40	74.18	−1759.6	146
OPh(9)[g]	209.19	28	366.5sh	204.73	10	362.5	140.47	38	149.51	−1775.4	161
OC_6H_4–*p*-Me(10)[g]	209.29	29	366.9sh	204.80	9	362.9	140.56	38	149.11	−1775.9	162
SC_6H_4–*p*-Me(11)	210.38	26	366.1sh	204.82	9	361.7	135.00	28	71.16	−1727.7	150
NHPh(12)	209.89	25	366.5	205.22	10	361.7	135.78	39	72.91	−1736.1	150
NHC_6H_4–*p*-Me(13)	210.03	24	366.1sh	205.30	9	361.3	136.03	39	72.30	−1736.5	153
$OSiMe_3$(14)	210.33	27	367.7	205.66	10	360.9	141.78	34	129.68	−1765.1	161
$NHSiMe_3$(15)	210.73	23	366.5	205.77	10	360.1	138.82	39	71.46	−1725.3	149

[a] 0.50 *M* $CDCl_3$ solutions of the complexes; sh = shoulder. [b] Doublet; ±0.7 Hz. [c] Singlet; ±5 Hz. [d] Singlet; ±1.2 Hz. [e] Doublet; ±1.2 Hz. [f] Data from Reference 3. [g] Data from Reference 4.

(Trimethylsilyl Diphenylphosphinamide)pentacarbonylmolybdenum(0), Mo(CO)$_5$(PPh$_2$NHSiMe$_3$), (15)

A solution of 1.00 g (2.29 mmol) of Mo(CO)$_5$(PPh$_2$NH$_2$) in 20 ml of THF was stirred at ambient temperature under N_2 as 1.43 ml (2.29 mmol) of 1.6 *M* n-butyllithium in hexanes was slowly added from a syringe. When the addition was completed, 0.29 ml (2.29 mmol) of chlorotrimethylsilane was added and the mixture was stirred for 30 min before being filtered. The filtrate was evaporated to dryness to yield the crude product. This material was dissolved in 30 ml of hexanes and the solution filtered through a 2.5 X 1.0 cm column of neutral alumina. The filtrate was evaporated to dryness to yield 0.74 g (63%) of the desired product.

All of the Mo(CO)$_5$(PPh$_2$XR) complexes in this study were characterized by their mass spectra which were run on a Hewlett Packard 5993/95 GC/MS system using the solids inlet probe. The major ions observed are tabulated in Table I.

Infrared spectra of dilute hexanes solutions of the Mo(CO)$_5$(PPh$_2$XR) complexes in 0.2 mm NaCl liquid cells were run using a Perkin Elmer 283B infrared spectrometer. Spectra were recorded in the 2100–1900 cm^{-1} region and the results are given in Table I.

Multinuclear (^{13}C, ^{17}O, ^{31}P and ^{95}Mo) NMR spectra of 0.50 *M* d$_1$-chloroform solutions of the Mo(CO)$_5$(PPh$_2$XR) complexes in 10 mm NMR tubes were taken using a JEOL FX90Q NMR spectrometer equipped with either a broad band or low frequency probe insert. The instrumental parameters for data acquisition and work up and the standards used are summarized in Table II. The multinuclear NMR data are summarized in Table III.

Results and Discussion

Syntheses

The syntheses of the aryl diphenylphosphinamide (12) and (13) and the alkyl- and aryl diphenylthiophosphinite (5), (6) and (11) complexes are similar to those reported for *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ complexes of the same ligands [12] and involve a nucleophilic displacement of the chloride from Mo(CO)$_5$(PPh$_2$Cl) as shown in eqn. 1.

$$\mathrm{Mo(CO)_5(PPh_2Cl) + HXR + B \xrightarrow{THF} Mo(CO)_5(PPh_2XR) + B{\cdot}HCl\,(ppt)} \qquad (1)$$

The synthesis of Mo(CO)$_5$(PPh$_2$NHSiMe$_3$) also has a literature precedent [12] and is shown in eqn. 2. The intermediate in this reaction is assumed to be

$$Mo(CO)_5(PPh_2NH_2) + n\text{-}BuLi \xrightarrow{THF} \xrightarrow{ClSiMe_3} Mo(CO)_5(PPh_2NHSiMe_3) \quad (2)$$

$Mo(CO)_5(PPh_2NHLi)$ although this complex has not been isolated. All of the complexes in this study are white air stable solids which yellow when exposed to strong light.

Mass Spectra

All of the complexes in this study were characterized by mass spectroscopy and the major fragments observed are summarized in Table I. Parent ions were observed for all of the complexes. The major fragmentation appears to be the loss of one, three and five carbonyl ligands with the $Mo(PPh_2XR)^+$ ion being the most abundant. The $Mo(PPh_2X)^+$, $Mo(PPh_2)^+$, $Mo(PPhX)^+$ and $Mo(PPh)^+$ ions resulting from P-donor ligand fragmentation were also commonly observed. The distinctive molybdenum isotope distribution allowed facile assignment of molybdenum containing fragments.

^{13}C NMR Spectra

The ^{13}C NMR data for the *cis* and *trans* carbonyl carbons and the phenyl carbon adjacent to the phosphorus (P–C) of the $Mo(CO)_5(PPh_2XR)$ complexes are reported in Table III. The P–C ^{13}C resonance is a doublet having a $^1J_{PC}$ of 28 to 40 Hz. The magnitude of the coupling constant appears to be a function of the X group with S < O, Cl < NH. This may reflect small changes in the hybridization of the phosphorus due to changes in the X group.

The ^{13}C NMR spectra of the carbonyl ligands consists of two doublets with the smaller doublet of the *trans* carbonyl approximately 4.5 ppm downfield from the *cis* carbonyl doublet. The magnitude of $^2J_{PC}$ of the *cis* carbonyl is approximately constant (9 to 10 Hz) while the magnitude of $^2J_{PC}$ of the *trans* carbonyl varies from 23 to 32 Hz. The magnitude of $^2J_{PC}$ of the *trans* carbonyls appears to increase as the ^{13}C chemical shift of the carbonyl ligand decreases. The reason for this relationship is unclear but may reflect changes in the hybridization of the molybdenum-phosphorus bond due to changes in the XR group.

^{17}O NMR Spectra

The ^{17}O NMR data for the *cis* and *trans* carbonyl ligands are summarized in Table III. The smaller *trans* carbonyl resonance is found downfield of the *cis* carbonyl resonance and is in some cases found as a shoulder on the larger resonance. The chemical shifts of both the *cis* and *trans* carbonyl resonances are relatively insensitive to the nature of the XR groups, perhaps due to the distance between the XR group and the carbonyl oxygens. This suggests that there is no significant through space interaction between the carbonyl oxygens and the XR groups. The shifts observed for the carbonyl ^{17}O resonances are in the opposite direction of those observed for the carbonyl ^{13}C resonances and thus in agreement with the model of carbonyl ligand chemical shifts proposed by Todd and coworkers [7].

^{31}P NMR Spectra

The ^{31}P NMR spectra of the $Mo(CO)_5(PPh_2XR)$ complexes, summarized in Table III, consist of a single resonance. The chemical shift of this resonance is extremely sensitive to the nature of the X group with the downfield shift roughly paralleling the electronegativity of the X group, *i.e.*, O, Cl > N > S. The nature of the R group also has a measurable effect upon the chemical shift of the ^{31}P resonance with electron withdrawing groups causing a downfield shift in the resonance, *i.e.* aryl > alkyl > silyl. The effects are consistent with previous reports of the sensitivity of the chemical shift of the ^{31}P resonance to polar effects [8].

^{95}Mo NMR Spectra

The ^{95}Mo NMR spectra of the $Mo(CO)_5(PPh_2XR)$ complexes, summarized in Table III, consist of a doublet with a $|^1J_{MoP}|$ of 142 to 165 Hz. The magnitude of $^1J_{MoP}$ appears to be related to the nature of the X group with the magnitude decreasing in the order Cl ⩾ O > N ⩾ S which may reflect the effect of the electronegativity of the X group on the electron density in the molybdenum–phosphorus bonds. The chemical shift of the ^{95}Mo resonance is also sensitive to the nature of the X group with the resonance moving downfield in the order O > N > S > Cl. This behavior is similar to that reported for the ^{95}Mo chemical shifts of a series of *cis*-$Mo(CO)_4(PPh_2XR)_2$ complexes and has been attributed to changes in the ability of the X group to donate electron density into the empty phosphorus d-orbitals [2].

Chemical Shift Correlations

Poor correlations are generally observed between the chemical shifts of the various nuclei of metal carbonyl complexes of P-donor ligands as the P-donor ligand is varied [1, 2, 6–8]. The poor correlations have been attributed to the simultaneous changes in both the cone angles and electron donor/acceptor properties of the P-donor ligands used in these studies [3, 4]. Even for a series of *cis*-$Mo(CO)_4(PPh_2XR)_2$ (X = O, S, NH; R = alkyl, aryl, silyl) complexes in which only one of the three phosphorus substituents was varied, poor correlations were observed between the chemical shifts of all of the nuclei studied except between those of the *trans* carbonyl ^{13}C and ^{17}O nuclei [1, 2].

TABLE IV. Correlation Coefficients Calculated Between Various Chemical Shifts of the Mo(CO)$_5$(PPh$_2$XR) Complexes.[a]

	δ ^{13}C (*trans* CO)	δ ^{95}Mo	δ ^{31}P
δ ^{95}Mo	−0.237/−0.209/−0.973		
δ ^{31}P	−0.701/−0.941/−0.938	−0.583/−0.892/−0.991	
δ ^{13}C (P–C)	−0.416/−0.687/−0.966	−0.683/−0.937/−0.999	0.738/0.878/0.972

[a] Correlation coefficients calculated using all data/data for complexes (3) through (8)/data for complexes (9) through (13).

Since the *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ complexes appeared to be quite sterically crowded due to the two bulky *cis* P-donor ligands, it was of interest to study the correlations between the chemical shifts of similar nuclei in a less crowded system containing similar P-donor ligands and a series of Mo(CO)$_5$(PPh$_2$XR) complexes was chosen. The correlation coefficients calculated for the correlations between the chemical shifts of the *trans* carbonyl ^{13}C, P–C ^{13}C, ^{31}P and ^{95}Mo nuclei using the data for all of the complexes, for complexes (3) through (8) and for complexes (9) through (13) are summarized in Table IV. The chemical shift data for the *cis* carbonyl ^{13}C and *cis* and *trans* carbonyl ^{17}O nuclei has not been used for the correlations as these chemical shifts are relatively insensitive to the nature of the XR group. As is the case for the *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ complexes, the chemical shift correlations are uniformly poor if the data for all the complexes is employed in the calculations. Only when data for the complexes whose cone angles are approximately the same, (3) through (8) or (9) through (13), are used can good correlations be observed. As might be expected the correlations for the XC$_6$H$_4$-*p*-R complexes, (9) through (13), are better than for the X-n-Pr and X-i-Pr complexes, (3) through (8), since the variation in cone angle for the first series of complexes is significantly less.

TABLE V. Correlation Between the Chemical Shifts of Similar Nuclei in the Mo(CO)$_5$(PPh$_2$XR) and *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ (X = O, S, NH; R = n-alkyl, C$_6$H$_4$-*p*-Me, SiMe$_3$) Complexes.

Nucleus	Correlation Coefficient
^{95}Mo	0.969
^{31}P	0.998
^{13}C (P–C)	0.988
^{13}C (*trans* CO)	0.814
^{13}C (*cis* CO)	0.829
^{17}O (*trans* CO)	0.869
^{17}O (*cis* CO)	0.850

The poor chemical shift correlations observed for both the *mono*- and *cis*-di-substituted complexes

TABLE VI. NMR Chemical Shift Data for the *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ Complexes.[a]

	trans CO		*cis* CO		phenyl C-1	P	Mo
	δ ^{13}C(ppm)[b]	δ ^{17}O(ppm)[c]	δ ^{13}C(ppm)[d]	δ ^{17}O(ppm)[c]	δ ^{13}C(ppm)[b]	δ ^{31}P(ppm)[e]	δ ^{95}Mo(ppm)[f]
Cl(16)	212.29	366.9	207.71	360.5	139.36	124.77	−1522
NH$_2$(17)	214.76	359.3	209.60	358.5sh	141.57	67.17	−1652
OMe(18)	214.60	362.1	208.57	359.3	139.07	145.97	−1707
SEt(19)	214.37	361.3	209.59	356.4sh	134.91	60.24	−1540
NHMe(20)	215.25	359.3	209.53	356.0sh	136.96	78.67	−1622
OC$_6$H$_4$-*p*-Me(21)	213.98	362.9	208.39	360.9sh	140.43	145.84	−1654
SC$_6$H$_4$-*p*-Me(22)	214.47	362.5	208.45	358.1	135.04	71.47	−1537
NHC$_6$H$_4$-*p*-Me(23)	214.21	360.5	209.10	358.5	136.30	69.72	−1571
OSiMe$_3$(24)	215.12	360.9	210.08	357.6	142.45	131.44	−1623
NHSiMe$_3$(25)	215.77	359.3	210.02	356.0	139.85	73.49	−1563

[a] Saturated CDCl$_3$ solutions of the complexes; sh = shoulder. Data from references [1, 2]. [b] Apparent triplet ±0.7 Hz. [c] Singlet ±5Hz. [d] Triplet ±0.7 Hz. [e] Singlet ±2.4 Hz. [f] Triplet ±10 Hz.

give no indication as to similarity of the steric effects of the P-donor ligands in the two sets of complexes. In order to determine whether the P-donor ligands in the two sets of complexes have similar steric effects, the correlations between the chemical shifts of similar nuclei in the *mono-* and *cis*-di-substituted complexes have been determined and are summarized in Table V. The chemical shift data for the *cis*-$Mo(CO)_4(PPh_2XR)_2$ complexes used for the correlation calculations are summarized in Table VI [1, 2]. The chemical shift data for the mono substituted X-i-Pr and XPh complexes were not used in the calculations as the data for the corresponding *cis*-disubstituted complexes was not available while the PPh_2X-n-alkyl (n-alkyl = Me, Et, n-Pr) ligands were considered to be the same, regardless of the n-alkyl group present, for the correlation calculations.

The correlations for the ^{95}Mo, ^{31}P and P–C ^{13}C nuclei are excellent and indicate that the PPh_2XR ligands have nearly identical effects on the chemical shifts of these nuclei. The ^{95}Mo chemical shift correlation is better than that previously reported for the ^{95}Mo chemical shifts of a series of mono- and *cis*-di-substituted phosphine and phosphite molybdenum carbonyl complexes [9] and this may reflect the smaller changes in the cone angles of the ligands used in this study. The fair correlations for the carbonyl ^{13}C and ^{17}O chemical shifts may be a reflection of the relative insensitivity of these nuclei to changes in the XR groups or may reflect differences in the interaction of the carbonyl ligands with the P-donor ligands in the two series of complexes. This latter explanation is consistent with the results of Bodner *et al.* who demonstrated that the degree of correlation between the ^{13}C carbonyl chemical shifts of different metal carbonyl complexes varies with the position of the carbonyl ligand in the complexes [5, 13].

Conclusions

In this study it has been demonstrated that the degree of correlation between the chemical shifts of the *trans* carbonyl ^{13}C, P–C ^{13}C, ^{31}P and ^{95}Mo resonances of $Mo(CO)_5(PPh_2XR)$ complexes depends on the similarity in the cone angles of the PPh_2XR ligands used. It has also been shown that excellent correlations can be observed for the chemical shifts of the ^{95}Mo, ^{31}P and P–C ^{13}C resonances of mono- and *cis*-di-substituted molybdenum carbonyl complexes which indicates that the PPh_2XR ligands have similar effects in the two series of complexes. The presence of a second PPh_2XR ligand in the complexes does not appear to greatly affect the correlations observed.

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References

1 G. M. Gray and C. S. Kraihanzel, *J. Organomet. Chem., 241,* 201 (1983).
2 G. M. Gray and C. S. Kraihanzel, *Inorganic Chem., 22,* 2959 (1983).
3 G. M. Gray and R. J. Gray, *Organometallics, 2,* 1026 (1983).
4 G. M. Gray and R. J. Gray, submitted to *J. Magn. Reson.*
5 G. M. Bodner, M. P. May and L. E. McKinney, *Inorg. Chem., 19,* 1951 (1980).
6 D. Cozak, I. S. Butler, J. P. Hickey and L. J. Todd, *J. Magn. Reson., 33,* 149 (1979).
7 J. P. Hickey, J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem., 179,* 159 (1979).
8 T. T. Derencsenyi, *Inorg. Chem., 20,* 665 (1981).
9 A. F. Masters, G. E. Bossard, T. A. George, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, *Inorg. Chem., 22,* 908 (1983).
10 C. S. Kraihanzel and C. M. Bartish, *J. Organomet. Chem., 43,* 343 (1972).
11 C. S. Kraihanzel and C. M. Bartish, *J. Am. Chem. Soc., 94,* 3572 (1972).
12 G. M. Gray and C. S. Kraihanzel, *J. Organomet. Chem., 146,* 23 (1978).
13 G. M. Bodner, *Inorg. Chem., 14,* 2694 (1975).