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CHEMICAL SHIFT CORRELATIONS IN THE ^{13}C, ^{17}O and ^{31}P NMR SPECTRA OF SOME $Mo(CO)_4((PPh_2O)_2Y(R)R')$ (Y(R) = P(O), Si(Me); R′ = ALKYL, HALOALKYL, ARYL) AND $[Mo(CO)_4(PPh_2O)_2]_2Si$ COMPLEXES

GARY M. GRAY and KEITH A. REDMILL

Department of Chemistry, the University of Alabama in Birmingham, University Station, Birmingham, Alabama 35294 (U.S.A.)

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Summary

The syntheses and ^{13}C, ^{17}O, ^{29}Si and ^{31}P NMR spectra of a series of $Mo(CO)_4((PPh_2O)_2Y(R)R')$ (Y(R) = P(O), Si(Me); R′ = alkyl, haloalkyl, aryl) and $[Mo(CO)_4(PPh_2O)_2]_2Si$ complexes are given. The chemical shift ranges of the *cis* and *trans* carbonyl ^{13}C and ^{17}O, phenyl C(1) ^{13}C and ^{31}P resonances are relatively large and, with the exception of the *cis* carbonyl ^{17}O chemical shifts, the correlations between the chemical shifts of the various resonances are excellent. These correlations are consistent with the model of metal carbonyl ^{13}C and ^{17}O chemical shifts proposed by Bodner and Todd. In addition they allow the model to be extended to include the diphenylphosphinite ^{31}P chemical shifts in these complexes. The excellent correlations may be due to the presence of the chelate ring which limits the rotation around the molybdenum–phosphorus bond and to the fact that all three groups directly bonded to the phosphorus remains constant.

Introduction

Although the correlations between the chemical shifts of the various NMR active nuclei of metal complexes of phosphorus-donor ligands with variation in the phosphorus-donor ligand are generally poor [1–9], good correlations can be observed when changes in the steric parameters of the phosphorus-donor ligands are minimized [7,9–11]. Since these correlations appear to extend to a wide variety of complexes and to have potential uses in relating changes in the σ-donor/π-acceptor abilities of the ligands to important molecular properties such as catalytic activity [7,11], it is important to determine what constraints should be placed upon the changes in the phosphorus-donor ligands in order to obtain good correlations. One type of phosphorus-donor ligand which appears to give good correlations is $Ph_2POC_6H_4$-*p*-R in which variation in the *para* substituent, R, influences the σ-donor/π-acceptor ability of the ligand but does not appreciably affect the cone

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TABLE 1

YIELDS, MELTING POINTS AND CARBONYL INFRARED STRETCHING ABSORPTIONS FOR THE $Mo(CO)_4((PPh_2O)_2Y(R)R')$ COMPLEXES

Y(R)	R′	Complex	Yield (%)	M.p. (°C) [a]	IR ν(CO) (cm^{-1}) [b]			
					A_1^1	A_1^2	B_1	B_2
P(O)	Me	**1**	52.1	185	2041m	1944sh	1933s	1925sh
P(O)	Et	**2**	47.1	178–181.5	2040m	1945sh	1933s	1925sh
P(O)	CH_2Ph	**3**	72.4	175–178.5	2040m	1945sh	1936s	1926sh
P(O)	Ph	**4**	45.4	180	2041m	1944sh	1935s	1925sh
P(O)	C_6H_4-*p*-OMe	**5**	65.1	215	2040m	1944sh	1935s	1925sh
P(O)	CH_2CH_2Cl	**6**	50.4	185–189	2041m	1947sh	1936s	1926sh
P(O)	CH_2Cl	**7** [c]	–	–	2042m	1948sh	1936s	1927sh
Si(Me)	Me	**8** [d]	–	–	2028m	1929sh	1914s	1899sh
Si(Me)	Et	**9**	87.9	184–190	2029m	1929sh	1916s	1899sh
Si(Me)	Ph	**10** [d]	–	–	2029m	1929sh	1915s	1899sh
Si(Me)	CH_2Cl	**11**	42.9	144–148	2031m	1937sh	1918s	1903sh
$\frac{1}{2}$Si		**12** [d]	–	–	2032m	1937sh	1920s	1906sh

[a] All compounds decompose upon melting. [b] Dichloromethane solutions in 0.20 mm NaCl cells s = strong, m = medium, sh = shoulder [c] From ref. 12. [d] From ref. 11.

angle of the ligand [11]. Unfortunately, the magnitude of the changes in the σ-donor/π-acceptor abilities of these ligands with changes in the R substituent is relatively small.

Another approach to the development of a series of phosphorus-donor ligands in which the steric properties remain relatively constant is the use of ligands of the type $(Ph_2PO)_2YRR'$ in which the three groups directly bonded to the phosphorus remain constant and in which the motion of the phenyl group is restricted by the presence of the chelate ring. Molybdenum tetracarbonyl complexes of ligands of this type ($YRR' = P(O)CH_2Cl$ (**7**), $SiMe_2$ (**8**), SiMe(Ph) (**9**)) and $[Mo(CO)_4(PPh_2O)_2]_2Si$ (**12**) have previously been reported [12,13] and preliminary multinuclear NMR studies indicated that good correlations existed between the ^{13}C and ^{17}O NMR chemical shifts of the *trans* carbonyl ligands [13]. These complexes are similar to those reported by Wong [14–16] and others [17–18] which undergo some unusual rearrangements and which can be used in the synthesis of heterobimetallic complexes.

In this study a series of $Mo(CO)_4((PPh_2O)_2YRR')$ (YR = P(O), Si(Me); R' = alkyl, haloalkyl, aryl) complexes has been synthesized and their multinuclear (^{13}C, ^{17}O, ^{29}Si, ^{31}P) NMR spectra obtained. The correlations between the ^{13}C and ^{17}O carbonyl, ^{13}C phenyl C(1) and ^{31}P chemical shifts are reported and the relationship between these correlations and the electron density changes in the complexes are discussed.

Experimental

The new complexes used in this study were synthesized by procedures similar to those reported for the syntheses of $Mo(CO)_4((PPh_2O)_2P(O)CH_2Cl)$ [12] and $Mo(CO)_4((PPh_2O)_2SiMe_2)$ [13]. The yields and uncorrected melting points of the complexes are reported in Table 1.

Infrared spectra of the carbonyl region (2050–1850 cm^{-1}) were taken of dichloromethane solutions of the complexes in a 0.2 mm NaCl liquid cell on a PE 283B infrared spectrometer. The absorbances observed are also reported in Table 1.

$^{13}C\{^1H\}$,^{17}O,$^{29}Si\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were run on either a JEOL FX 90Q multinuclear NMR spectrometer in 10 mm tubes or a Nicolet, 300 MHz, wide bore NMR spectrometer in 12 mm tubes. $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were referenced to internal tetramethylsilane while ^{17}O NMR spectra were referenced to external H_2O and $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Downfield shifts were reported as positive. The spectra were taken of 0.15 *M* chloroform-d_1 solutions of the YR = P(O) complexes and 0.20 *M* chloroform-d_1 solutions of the YR = Si(Me) complexes due to differences in the solubilities of the two types of complexes. The NMR data of these complexes are summarized in Tables 2 and 3.

Results and discussion

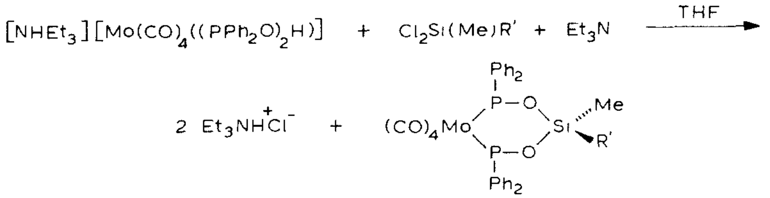
Synthesis of the $Mo(CO)_4((PPh_2O)_2Y(R)R')$ complexes. The new $Mo(CO)_4$-$((PPh_2O)_2Si(Me)R')$ complexes were synthesized by the reaction of $[Et_3NH][Mo(CO)_4(PPh_2O)_2H]$ with the appropriate dichlorosilane in the presence of triethylamine as shown in eq. 1. This synthesis is similar to that which was reported for other $Mo(CO)_4((PPh_2O)_2Si(Me)R')$ complexes [13]. The products were

TABLE 2

IMULTINUCLEAR NMR DATA FOR THE $Mo(CO)_4((PPh_2O)_2P(O)R'$ COMPLEXES (δ in ppm, J in HZ)[a]

R′	Complex	*trans*-CO			*cis*-CO		
		$\delta(^{13}C)^b$	$\lvert ^2J(PC)+{}^2J(P'C)\rvert^h$	$\delta(^{17}O)^c$	$\delta(^{13}C)^d$	$\lvert ^2J(PC)\rvert$	$\delta(^{17}O)^c$
P(O)Me	**1**	212.94	20.5	370.5	208.45	10.6	359.7
					205.30	10.3	
P(O)Et	**2**	213.03	19.8	369.3	208.29	10.6	357.7
					205.59	10.3	
$P(O)CH_2Ph$	**3**	213.10	20.5	369.7	207.44	10.3	357.7
					206.14	11.4	
P(O)Ph	**4**	213.10	20.1	370.1	207.67	10.3	358.8
					206.21	10.3	
$P(O)C_6H_4$-p-OMe	**5**	213.23	20.5	369.7	207.74	10.3	358.8
					206.24	10.6	
$P(O)CH_2CH_2Cl$	**6**	212.68	20.5	370.5	207.87	10.3	359.6
					205.79	10.6	
$P(O)CH_2Cl$	**7**	212.55	20.5	371.3	207.22	9.9	361.4
					206.05	10.6	

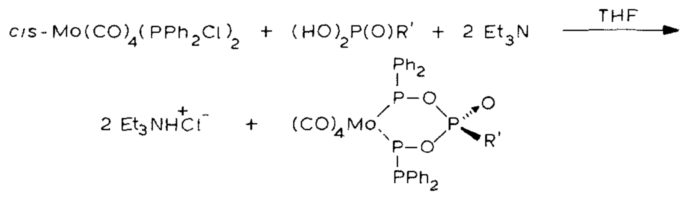
[a] 0.15 *M* chloroform-d_1 solutions. ^{13}C data ± 0.7 Hz (0.03 ppm). ^{17}O data + 5 Hz (0.4) ppm), ^{31}P data ± 1.2 Hz (0.03) ppm). [b] Apparent triplet. [c] Singlet. [d] Triplet or doublet of triplets. [e] Apparent triplet or doublet of apparent triplets. [f] Doublet. [g] Triplet. [h] For the A portion of an AXX′ system.



(1)

purified by recrystallization from dichloromethane/hexane or dichloromethane/methanol mixtures and are white crystalline solids soluble in ethers, acetone and chlorinated hydrocarbons.

As has been previously reported, the reaction of $[Et_3NH][Mo(CO)_4((PPh_2O)_2H]$ with $Cl_2P(O)R'$ does not yield the desired $Mo(CO)_4((PPh_2O)_2P(O)R')$ complexes. Instead all of these complexes have been synthesized by the reaction of *cis*-$Mo(CO)_4(PPh_2Cl)_2$ with the appropriate phosphonic acid as shown in eq. 2. This procedure was first used for the synthesis of $Mo(CO)_4((PPh_2O)_2P(O)CH_2Cl)$ [12]. The products were purified by recrystallization from dichloromethane/hexanes



(2)

mixtures and are white crystalline solids soluble in ethers, acetone and chlorinated hydrocarbons.

phenyl C(1)			^{31}P		
$\delta(^{13}C)$ [e]	$\lvert {}^1J(PC)+{}^3J(P'C) \rvert$ [h]	$\lvert {}^3J(P''C) \rvert$	$\delta(^{31}P)(Ph_2P)$ [f]	$\delta(^{31}P)(O_2P(O)R)$ [g]	$\lvert {}^2J(PP) \rvert$
140.42	39.6	2.2	151.94	19.10	8.5
139.20	38.2	4.4			
140.42	39.6	2.2	149.75	24.45	11.0
139.54	39.8	3.6			
139.86	35.8	<1	149.06	17.89	9.8
139.85	40.3	5.9			
140.24	36.4	1.4	151.01	10.08	7.3
139.59	40.4	5.9			
140.30	40.1	1.5	150.09	11.06	7.3
139.72	40.3	5.9			
139.88	38.1	1.5	152.51	16.37	8.5
139.29	39.9	5.6			
139.88	39.6	1.5	155.89	8.58	11.0
139.31	40.0	5.4			

$^{13}C\{^1H\}$ NMR spectra of the carbonyl ligands. Two equal intensity $^{13}C\{^1H\}$ NMR resonances are observed for the carbonyl ligands of $[Mo(CO)_4(PPh_2O)_2]_2Si$ and the *cis*-$Mo(CO)_4((PPh_2O)_2YRR')$ complexes, in which $R = R'$. The downfield resonance is an apparent triplet (the A portion of an AXX' spin system) [19,20] and is due to the carbonyl ligands *trans* to one of the phosphorus-donor ligands (*trans* carbonyls). The upfield resonance is a 1/2/1 triplet (the A portion of an AX_2 spin system) and is due to the carbonyl ligands *cis* to both the phosphorus donor ligands (*cis* carbonyls). The presence of two different substituents on the Y group causes the *cis* carbonyl ligands to become inequivalent, as shown in Fig. 1, and two 1/2/1 resonances are observed. The phosphorus–carbon coupling constants for the *trans*

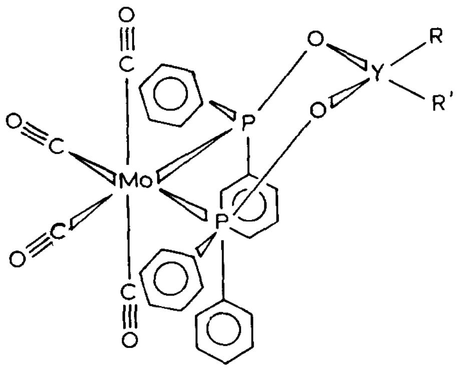


Fig. 1. Proposed structure of the $Mo(CO)_4((PPh_2O)_2YRR')$ complexes.

TABLE 3

MULTINUCLEAR NMR DATA FOR THE $Mo(CO)_4((PPh_2O)_2Si(Me)R')$ AND $[Mo(CO)_4(PPh_2O)_2]_2Si$ COMPLEXES (δ in pm, J in Hz)[a]

R′	Complex	*trans* CO			*cis* CO			phenyl C(1)		^{29}Si	^{31}P
		$\delta(^{13}C)$[b]	$\vert ^2J(PC)+^2J(P'C)\vert$[f]	$\delta(^{17}O)$[c]	$\delta(^{13}C)$[d]	$\vert ^2J(PC)\vert$	$\delta(^{17}O)$[c]	$\delta(^{13}C)$[e]	$\vert ^1J(PC)+^3J(P'C)\vert$[f]	$\delta(^{29}Si)$[c]	$\delta(^{31}P)$[c]
Me	**8**	214.94	18.3	367.4	208.57	10.6	358.0	142.42	38.0	1.08	128.39
Et	**9**	214.94	18.0	367.3	208.72	10.8	357.9	142.60	37.9	1.06	128.16
					208.41	10.9		142.42	36.5		
Ph	**10**	214.83	18.8	367.7	209.28	10.7	358.2	142.58	39.0	−14.35	130.50
					207.55	10.3		142.16	36.7		
CH_2Cl	**11**	214.43	18.6	368.0	208.43	10.9	358.4	142.86	38.4	−12.05	132.17
					208.30	10.8		142.01	38.0		
$[Mo(CO)_4(PPh_2O_2)_2]_2Si$	**12**	214.10	19.7	369.1	207.65	10.1	358.9	141.90	39.0	-	145.71

[a] 0.20 *M* chloroform-d_1 solutions. ^{13}C data ± 1.2 Hz (0.02 ppm). ^{17}O data ± 20 Hz (0.5 ppm). ^{29}Si data ± 1.2 Hz (0.02 ppm). ^{31}P data ± 1.5 Hz (0.01 ppm). [b] Apparent triplet. [c] Singlet. [d] Triplet or doublet of triplets. [e] Apparent triplet or doublet of apparent triplets. [f] For the A portion of an AXX′ system

and *cis* carbonyl ligand resonances show little variation (18.3–20.9 and 9.9–10.6 Hz, respectively) while, in contrast, the chemical shift ranges of the resonances are surprisingly large (2.41 ppm for the *trans* carbonyls and 3.47 ppm for the *cis* carbonyls). These ranges are comparable in size to those observed for a series of *cis*-$Mo(CO)_4(PPh_2XR)_2$ (X = NH, O, S; R = alkyl, aryl, $SiMe_3$ or XR = Cl) complexes [8] and are approximately one-half the total ranges of the carbonyl ^{13}C chemical shifts which have been observed for molybdenum carbonyl complexes of a wide variety of phosphorus-donor ligands [4]. The sizes of the chemical shift ranges for the carbonyl ^{13}C chemical shifts of the $Mo(CO)_4((PPh_2O)_2YRR')$ complexes are rather surprising in light of what appear to be rather small changes in the ligands. In particular the $(PPh_2O)_2P(O)R$ ligands are unusual since they are similar to the PPh_2Cl ligand in π-acceptor ability and much better π-acceptors than the $(PPh_2O)_2Si(Me)R$ ligands based upon the model of carbonyl chemical shifts proposed by Bodner and Todd [5,21].

$^{13}C\{^1H\}$ NMR spectra of the phenyl C(1) carbons. The $^{13}C\{^1H\}$ resonances of the phenyl carbons directly bonded to the phosphorus (phenyl C(1)) are apparent triplets for $[Mo(CO)_4(PPh_2O)_2]_2Si$ and for the $Mo(CO)_4((PPh_2O)_2SiRR')$ complexes in which R = R′ but become two overlapped apparent triplets for the complexes in which R = R′ since the unsymmetrical substitution at the Si causes the two phenyl groups on the phosphorus to become inequivalent as shown in Fig. 1. The $^{13}C\{^1H\}$ resonances of the phenyl C(1) carbons in the $Mo(CO)_4((PPh_2O)_2$-$P(O)R')$ complexes are even more complex due to coupling of the two inequivalent phenyl C(1) carbons to the phosphonate phosphorus. The magnitudes of these coupling constants ($|^3J(PC)|$ 1.0–2.2 Hz) and the diphenylphosphinite phosphorus phenyl C(1) coupling constants ($|^1J(PC) + {}^3J(P'C)|$ 35.8–40.4 Hz) show only small variation with change in the Y and R groups but appear to be different for the non-equivalent phenyl C(1) carbons in the $Mo(CO)_4((PPh_2O)_2YRR')$ complexes. The chemical shift range of the phenyl C(1) resonances of 4.26 ppm is large for complexes of this type and, as for the carbonyl ^{13}C chemical shifts, this is surprising in view of the relatively small changes in the $(PPh_2O)_2YRR'$ ligands.

^{17}O NMR spectra of the carbonyl ligands. The ^{17}O NMR spectra of the carbonyl ligands of the $Mo(CO)_4((PPh_2O)_2YRR')$ and $[Mo(CO)_4(PPh_2O)_2]_2Si$ complexes consist of a sharper downfield resonance ($\nu_{1/2}$ 25–40 Hz) due to the *trans* carbonyls and a broader upfield resonance ($\nu_{1/2}$ 45–60 Hz) due to the *cis* carbonyls. The *cis* carbonyl ^{17}O resonance is sufficiently broad that no inequivalence is observed for the unsymmetrically substituted ($R \neq R'$) complexes. The chemical shift ranges of the *trans* and *cis* carbonyl ^{17}O resonances, 4.4 and 3.5 ppm, are comparable to those previously reported for a series of *cis*-$Mo(CO)_4(PPh_2XR)_2$ (X = NH, O, S; R = alkyl, aryl, silyl or XR = Cl) complexes [8] and thus are consistent with the surprisingly large carbonyl ^{13}C chemical shifts which are observed.

$^{29}Si\{^1H\}$ NMR spectra. The proton decoupled ^{29}Si NMR spectra of the $Mo(CO)_4((PPh_2O)_2Si(Me)R')$ complexes consist of singlets which are observed from 1 ppm downfield to −14 ppm upfield of the internal TMS reference. The fact that the ^{29}Si resonances of the R′ = Ph and CH_2Cl complexes are found upfield of the R′ = alkyl complexes is surprising since the Ph and CH_2Cl groups are more electron withdrawing than are the alkyl groups and might be expected to cause a downfield rather than an upfield shift. The lack of two-bond, P–Si coupling in these complexes appears to be due to the combination of the P–O–Si linkage with the chelate ring

since two-bond, P–Si coupling is observed for both *cis*-$Mo(CO)_4(PPh_2OSiMe_3)_2$ and $Mo(CO)_4((PPh_2NH)_2Si(Me)R')$ (R′ = Me, Ph) [8].

$^{31}P\{^1H\}$ NMR spectra. The ^{31}P NMR spectra of the $Mo(CO)_4((PPh_2O)_2P(O)R')$ complexes consist of a downfield doublet from the diphenylphosphinite ^{31}P nuclei and an upfield triplet from the phosphonate ^{31}P nucleus in a 2/1 ratio with $|^2J(PP)|$ varying from 7.3 to 11.0 Hz. The chemical shifts of the diphenylphosphinite ^{31}P resonances are downfield of those reported for the diphenylphosphinite ^{31}P resonances of a series of *cis*-$Mo(CO)_4(PPh_2OR)_2$ (R = alkyl, aryl, silyl) complexes [8] which is consistent with carbonyl ^{13}C chemical shift data which suggests that the $(Ph_2PO)_2P(O)R'$ ligands are better π-acceptors than are PH_2PXR (X = NH,O,S; R = alkyl, aryl, silyl) ligands. The ^{31}P NMR spectra of the $Mo(CO)_4((PPh_2O)_2$-$Si(Me)R')$ and $[Mo(CO)_4(PPh_2O)_2]_2Si$ complexes consist of a singlet 128 to 145 ppm downfield of the external, 85% H_3PO_4 reference. These chemical shifts are consistent with those previously reported for similar complexes [8]. No indication of the change in the ^{31}P chemical shift upon coordination could be obtained due to the instability of the free $(PPh_2O)_2Y(R)R'$ ligands.

Chemical shift correlations. The observation of good correlations between the chemical shifts of the ^{31}P resonances and the carbonyl ^{13}C and ^{17}O resonances of metal carbonyl complexes of phosphorus-donor ligands would provide considerable insight into the electron density changes which occur in these complexes as a result of changes in the phosphorus-donor ligands. Unfortunately, previous multinuclear studies have shown that poor correlations are generally observed between these chemical shifts when both the steric and electron σ-donor/π-acceptor properties of the phosphorus substituents are varied [1–5,7–10] due to the ease of rehybridization of the phosphorus [7,22]. Only in one case, for a series of $Mo(CO)_5(PPh_2OC_6H_4\text{-}p\text{-}X)$ (X = H, alkyl, alkoxy, Cl, COMe, CN, NO_2 etc.) complexes, have good correlations between the chemical shifts of the ^{31}P resonances and the chemical shifts of other resonances in the complex been reported [11]. In this instance, however, the chemical shift ranges observed were rather small (0.89 and 0.39 ppm for the ^{13}C carbonyl resonances, 1.28 ppm for the phenyl C(1) ^{13}C resonances, 2.8 and 1.2 ppm for the carbonyl ^{17}O resonances and 5.72 ppm for the ^{31}P resonances) and limited the conclusions which could be drawn from the correlations which were observed. Also, the analysis of the correlation data was complicated by the necessity of separating resonance and polar electronic effects.

The $Mo(CO)_4((PPh_2O)_2Y(R)R')$ and $[Mo(CO)_4(PPh_2O)_2]_2Si$ complexes of this study are also useful for a study of chemical shift correlations since the three groups attached to the phosphorus remain constant and the presence of the chelate ring minimizes the changes in the steric effects of the ligands by restricting rotation about the Mo–P bonds. These complexes also offer several advantages over those mentioned above. The first is that the chemical shift ranges for the complexes in this study cover a significant portion of the total chemical shift range reported for molybdenum carbonyl complexes of a wide variety of phosphorus donor ligands. Secondly, the electronic effects observed for the substituents in these complexes should be almost entirely polar in nature since no π-system is present between the diphenylphosphinite phosphorus and the Y nucleus to transmit resonance effects.

The coefficients (r) calculated for the correlations between the chemical shifts of the *cis* and *trans* carbonyl ^{13}C and ^{17}O, phenyl C(1) ^{13}C and diphenylphosphinite ^{31}P resonances of the $Mo(CO)_4((PPh_2O)_2Y(R)R')$ and $[Mo(CO)_4(PPh_2O)_2]_2Si$ com-

TABLE 4

CORRELATION COEFFICIENTS CALCULATED BETWEEN THE CHEMICAL SHIFTS OF THE VARIOUS NUCLEI IN THE $Mo(CO)_4((PPh_2O)_2Y(R)R')$ COMPLEXES

	^{13}C(*cis*-CO)avg	^{17}O(*trans*-CO)	^{17}O(*cis*-CO)	^{13}C(phenyl C(1)avg	$^{31}P(Ph_2P)$
^{13}C(*trans*-CO)	0.985	−0.963	−0.567	0.983	−0.975
^{13}C(*cis*-CO)avg [a]		−0.951	−0.501	0.996	−0.985
^{17}O(*trans*-CO)			0.773	−0.946	0.969
^{17}O(*cis*-CO)				−0.498	0.535
^{13}C(phenyl C(1))avg [b]					−0.980

[a] Average value of the two *cis* carbonyl ^{13}C chemical shifts. [b] Average value of the two phenyl C(1) ^{13}C chemical shifts.

plexes are summarized in Table 4. Coefficients for correlations involving the *cis* carbonyl ^{13}C and phenyl C(1) ^{13}C chemical shifts of the unsymmetrical (R=R′) complexes were calculated using the average of the chemical shifts for the two nonequivalent resonances. The averages of the chemical shifts for the nonequivalent resonances were used since they should reflect equal contributions from each of the two Y substituents which should also be the case for the chemical shifts of the *trans* carbonyl ^{13}C and ^{17}O, *cis* carbonyl ^{17}O and ^{31}P resonances since these nuclei are equidistant from the two substituents. Thus, the correlations between the average chemical shifts of the *cis* carbonyl ^{13}C and phenyl C(1) ^{13}C resonances and the other chemical shifts should be better than the correlations between the chemical shifts of the upfield or downfield *cis* carbonyl ^{13}C and phenyl C(1) ^{13}C resonances with the other chemical shifts. This is exactly what is observed.

The correlations summarized in Table 4 are all excellent with the exception of the correlations involving the *ccis* carbonyl ^{17}O chemical shifts which are poor. This appears to be due to through space interaction of the Y substituents and the *cis* carbonyl oxygen since the correlations for a given Y(R) group are better than the overall correlations. The excellent positive correlations between the chemical shifts of the diphenylphosphinite ^{31}P and *trans* carbonyl ^{17}O chemical shifts and the excellent negative correlations between these chemical shifts and the *cis* and *trans* carbonyl ^{13}C chemical shifts are consistent with the model of metal carbonyl ^{13}C and ^{17}O chemical shifts proposed by Bodner and Todd [21,5]. Increased electron density at the diphenylphosphinite phosphorus should result in increased π-back donation of electron density from the metal *d* orbitals into the carbonyl $\pi^\star$ orbitals with a commensurate increase in electron density at the carbonyl oxygen and decrease in electron density at the carbonyl carbon. Since the electron density around both the diphenylphosphinite ^{31}P and carbonyl ^{17}O nuclei is increased, a positive correlation between the two chemical shifts should occur. Similarly, the decreased electron density at the carbonyl carbon should result in negative correlations between the chemical shift of the carbonyl ^{13}C resonances and the chemical shifts of the carbonyl ^{17}O and diphenylphosphinite ^{31}P resonances. Although the negative correlations between the carbonyl ^{13}C and ^{17}O chemical shifts is well established [5,8,9], this is the first study in which it has been possible to relate the changes in electron density observed in the carbonyl ligands to changes in electron density at a phosphorus-donor ligand.

It is more difficult to rationalize the negative correlation which exists between the chemical shifts of the phenyl C(1) ^{13}C and diphenylphosphinite ^{31}P resonances. It might be expected that as the electron density on the diphenylphosphonite phosphorus increases, the electron density on the adjacent phenyl C(1) should also increase, however, exactly the opposite occurs. This behavior may be due to π-interaction between the phosphorus and the ring which reduces the π-electron density at the C(1) carbon even though there is a net electron transfer to the ring. This would be similar to the behavior which has previously been reported for the ^{13}C chemical shifts of the phenoxide ion [23], the phenylmethylcarbonium ion [24] and the $Ph_{2-n}PH_n^-$ ($n = 0$–2) ions [25].

Conclusions

Complexes of the type $Mo(CO)_4((PPh_2O)_2Y(R)R')$ (Y(R) = P(O), Si(Me); R' = alkyl, chloroalkyl, aryl) and $[Mo(CO)_4(PPh_2O)_2]_2Si$ exhibit large carbonyl ^{13}C and ^{17}O, phenyl C(1) ^{13}C and diphenylphosphinite ^{31}P NMR chemical shift ranges. Since the three groups directly bonded to the diphenylphosphinite phosphorus remain constant and since the chelate ring restricts rotation about the molybdenum–phosphorus bond excellent correlations are observed between the chemical shifts mentioned above with the exception of the *cis* carbonyl ^{17}O chemical shift. The wide chemical shift ranges and the excellent correlations observed allow the theory of metal carbonyl chemical shifts proposed by Bodner and Todd to be extended to include the chemical shifts of the diphenylphosphinite phosphorus and the phenyl C(1). This is the first series of metal carbonyl complexes of phosphorus-donor ligands in which it has been possible to relate changes in electron density at phosphorus to changes in electron density at the carbonyl carbon and oxygen.

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