Synthesis and a multinuclear NMR spectroscopic study of some Mo(CO)5(PPh2XR) (X = O, NH; R = 1-4 carbon alkyls) complexes. Steric effects on phosphorus-31 and molybdenum-95 chemical shifts

Gary M. Gray, and Rita June Gray

Organometallics, **1983**, 2 (8), 1026-1031• DOI: 10.1021/om50002a015 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Data Acquisition. Compound **16b** yielded yellow platelike crystals with approximate dimensions of 0.6 × 0.4 × 0.3 mm which were readily indexed by using 12 independent reflections and an automatic indexing procedure.[50] The data were collected at ambient temperature with graphite-monochromated Mo Kα (λ = 0.70979 Å) radiation on an automated four-circle diffractometer designed and built at the Ames Laboratory: ω scan; 4151 reflections measured in almost four octants; $2\theta \leq 45°$; decomposition corrections applied; 2502 reflections with $I \geq 3\sigma_I$ after averaging; agreement between equivalent reflections is 4.2%. Accurate cell parameters and their standard deviations were obtained from a least-squares fit to $\pm 2\theta$ values of 12 high-angle reflections.

The position of the Fe atom was located by analysis of a sharpened three-dimensional Patterson function. All the remaining non-hydrogen and H1 atoms were found by successive structure factor and electron density map calculations; a combination of block and full-matrix least-squares refinement[51] of all non-hydrogen atoms was carried out. As expected for the PF_6^-, packing disorder resulted in high conventional and weighted residuals of R = 0.082 and R_w = 0.109, respectively. The scattering factors[52] were modified for anomalous dispersion effects.[53] Bond angles, bond distances, and final atom positional parameters are summarized in Tables IV and V.

Acknowledgment. We sincerely thank Professor R. A. Jacobson and James Richardson for their assistance with the X-ray diffraction studies.

Registry No. 1, 6932-11-2; **2**, 76136-44-2; **3**, 85629-24-9; **4**, 85629-25-0; **5**, 76136-46-4; **6**, 85629-26-1; **7**, 85629-27-2; **8**, 85629-29-4; **9**, 85629-31-8; **10**, 69621-11-0; **11**, 85629-33-0; **12a**, 85629-35-2; **12b**, 85629-59-0; **13**, 85629-37-4; **14**, 85629-39-6; **15**, 85629-41-0; **16a**, 85629-43-2; **16b**, 85629-61-4; **17**, 85629-45-4; **18**, 85629-47-6; **19**, 85629-49-8; **20**, 85629-51-2; **21**, 85629-53-4; **22**, 85629-55-6; **23**, 85629-56-7; **24**, 76136-47-5; **25**, 12108-33-7.

Supplementary Material Available: Tables of calculated hydrogen atom positions, interatomic distances, bond angles, thermal parameters, and observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

---

(50) Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115.

(51) Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program", U.S. DOE Report; Iowa State University and Ames Laboratory: Ames, IA, 1979.

(52) Gromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 71–97.

(53) Templeton, D. H. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England; 1962, Vol. III, Table 3.3.2c, pp 215-6.

Synthesis and a Multinuclear NMR Spectroscopic Study of Some $Mo(CO)_5(PPh_2XR)$ (X = O, NH; R = 1–4 Carbon Alkyls) Complexes. Steric Effects on ^{31}P and ^{95}Mo Chemical Shifts

Gary M. Gray* and Rita June Gray

J. T. Baker Chemical Company, Phillipsburg, New Jersey 08865

Received December 14, 1982

The syntheses and multinuclear NMR spectroscopic data for a series of $Mo(CO)_5(PPh_2XR)$ (X = O, NH; R = 1–4 carbon alkyls) complexes is presented. The steric effect of substitution at the α carbon of the R groups is shown to have an effect on the chemical shifts of the aromatic C(1) ^{13}C, ^{31}P, and ^{95}Mo resonances but not upon the chemical shifts of the carbonyl ^{13}C and ^{17}O resonances. In addition, the good correlation observed between the chemical shifts of the ^{95}Mo and aromatic C(1) ^{13}C resonances indicates that in the $Mo(CO)_5(PPh_2XR)$ complexes, the ^{95}Mo and aromatic C(1) ^{13}C resonances are similarly affected by changes in the R group.

Introduction

There has been considerable interest in the relationship between the chemical shifts observed for NMR active nuclei of transition-metal complexes and the steric and electronic parameters of the ligands in these complexes. In order to better understand this relationship, we have begun a study of the multinuclear NMR spectra of molybdenum carbonyl complexes containing phosphorus-donor ligands. The first complexes studied were a series of *cis*-$Mo(CO)_4(PPh_2XR)_2$ complexes (X = NH, O, S; R = alkyl, aryl, silyl). Good correlations were observed between the ^{13}C and ^{17}O chemical shifts of the trans carbonyl ligands but not between those of the cis carbonyl ligands or between the ^{31}P or ^{95}Mo chemical shifts and any other chemical shifts.[1,2] These results were only in partial agreement with previous results,[3-5] and the differences were attributed, in part, to variations in the steric and electronic properties of the P-donor ligands used in these studies.[1]

The reasons for the lack of correlation between many of the chemical shifts are not well understood. This is especially true for the ^{95}Mo chemical shift. Preliminary studies of the ^{95}Mo NMR spectra of some molybdenum carbonyl complexes demonstrated that the ^{95}Mo chemical shift was extremely sensitive to the number and type of non-carbonyl ligands[6-11] while two more systematic studies

---

(1) Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1983**, *241*, 201.

(2) Gray, G. M.; Kraihanzel, C. S. *Inorg. Chem.*, in press.

(3) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

(4) Kowada, Y.; Sugawara, T.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1979**, 291.

(5) Hickey, J. P.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1979**, *179*, 159.

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

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

(8) LeGall, J. Y.; Kubicki, M. M.; Petillon, F. Y. *J. Organomet. Chem.* **1981**, *221*, 287.

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

(10) Jaitner, P.; Wohlgenannt, W. *Monatsh. Chem.* **1982**, *11*, 699.

0276-7333/83/2302-1026$01.50/0 © 1983 American Chemical Society

Table I. Syntheses and Infrared and Mass Spectroscopic Results for the Mo(CO)$_5$(PPh$_2$Cl) Complexes

XR	synthetic method	yield, g (%)	MS parent ion ^{98}Mo, *m/e*	carbonyl stretching, cm^{-1}			
				$\nu(A_1{}^1)$	$\nu(B_1)$	$\nu(A_1{}^2)$	$\nu(E)$
OMe (1)	A	0.81 (54)	454	2075	1993	1964	1954
OEt (2)	A	0.80 (52)	468	2074	1993	1963	1953
O-*n*-Pr (3)	A	0.70 (44)	482	2074	1992	1961	1953
O-*i*-Pr (4)	B	1.15 (72)	482	2073	1993	1961	1951
O-*n*-Bu (5)	A	0.88 (53)	496	2074	1992	1962	1952
O-*s*-Bu (6)	B	0.69 (42)	496	2074	1992	1961	1952
O-*i*-Bu (7)	B	0.93 (56)	496	2074	1992	1963	1952
NHMe (8)	C	0.74 (49)	453	2072	1991	1957	1947
NHEt (9)	C	1.22 (78)	467	2072	1991	1957	1947
NH-*n*-Pr (10)	D	1.26 (79)	481	2072	1990	1957	1947
NH-*i*-Pr (11)	D	0.73 (46)	481	2072	1990	1956	1947
NH-*n*-Bu (12)	D	1.15 (70)	495	2073	1989	1957	1947
NH-*s*-Bu (13)	D	1.01 (62)	495	2073	1990	1956	1947
NH-*i*-Bu (14)	D	1.05 (64)	495	2073	1991	1957	1948

Table II. NMR Instrument Parameters and Standards[a]

nucleus	center of Sp, MHz	data point resolutn, Hz	Sp width, Hz	pulse delay	pulse angle, o/μs	no. of pulses	ref
^{1}H	89.604 25	0.1	1000		90/31	1	int Me$_4$Si
^{13}C	22.533 30	0.7	6000	2.5 s	30/7	2×10^3	int Me$_4$Si
^{17}O	12.150 50	5	10000	40 ms	90/23	3×10^6	ext H$_2$O
^{31}P	36.274 00	1.2	10000		90/23	1	ext 85% H$_3$PO$_4$
^{95}Mo	5.830 00	2.4	5000	350 μs	90/91	2400	ext 2 M Na$_2$MoO$_4$

[a] Key to abbreviations: Sp = spectrum; no. = number; int = internal; ext = external.

of (π-arene)Mo(CO)$_3$[12] and (η^5-cyclopentadienyl)(CO)$_3$Mo(CH$_2$C$_6$H$_4$R)[13] have shown relationships between the ^{95}Mo chemical shift and the molybdenum–arene bond strength and the Hammett σ of the R groups.

Since it appears that the ^{95}Mo chemical shifts can be correlated with other molecular parameters, it was of interest to determine if a series of complexes could be designed in which the ^{95}Mo chemical shift could be correlated with other chemical shifts. With this goal in mind we have synthesized a series of Mo(CO)$_5$(PPh$_2$XR) complexes (X = NH, O; R = alkyl) which are less sterically crowded than the *cis*-Mo(CO)$_4$(PPh$_2$XR)$_2$ complexes previously studied and in which the nature of the X group should determine the electronic effects of the XR group while the nature of the R group should determine the steric effect. The multinuclear NMR spectra of these complexes are presented and the relationship between the various chemical shifts observed is discussed in terms of changes in the steric and electronic changes in the PPh$_2$XR ligands.

Experimental Section

Reagents and Solvents. (Chlorodiphenylphosphine)pentacarbonylmolybdenum(0) was prepared by literature methods.[14] Tetrahydrofuran (THF) and triethylamine were distilled from calcium hydride under N$_2$ prior to use. Alcohols were dried over molecular sieves while other reagents were used as received from the suppliers.

Syntheses. Compounds were synthesized by one of the four methods described below. The products were characterized by multinuclear NMR, infrared, and mass spectroscopy. A summary of the syntheses and infrared and mass spectroscopic characterizations is given in Table I.

Method A. A mixture of 1.52 g (3.33 mmol) of Mo(CO)$_5$(PPh$_2$Cl) in 10 mL of the appropriate alcohol was refluxed gently for 1.5 h under N$_2$ before being poured into 50 mL of cold, deionized water. This mixture was extracted with two 20-mL portions of hexanes which were combined, dried over anhydrous magnesium sulfate, and then filtered through a 3.5 cm by 1 cm column of chromatography grade 40–140 mesh silica gel. The filtrate was evaporated to dryness to yield the product.

Method B. A mixture of 0.085 g (3.70 mmol) of freshly cut sodium in 10 mL of the appropriate alcohol was stirred under N$_2$ until the sodium had dissolved at which point 1.52 g (3.33 mmol) of Mo(CO)$_5$(PPh$_2$Cl) was added to the reaction mixture. After 1 h this solution was poured into 50 mL of deionized water, and the resulting mixture was extracted with two 20-mL portions of hexanes. The extracts were combined, dried with anhydrous magnesium sulfate, and then filtered through a 3.5 cm by 1.0 cm column of neutral alumina. The filtrate was evaporated to dryness to yield the product.

Method C. A solution of 1.52 g (3.33 mmol) of Mo(CO)$_5$(PPh$_2$Cl) in 20 mL of THF was stirred under N$_2$ as a stream of the gaseous amine was bubbled into the solution for 1 h. The solution was then evaporated to dryness and the residue washed with two 20-mL portions of hexanes. The washes were combined and filtered through a 3.5 cm by 1.0 cm column of neutral alumina. The filtrate was evaporated to dryness to yield the product.

Method D. A solution of 1.52 g (3.33 mmol) of Mo(CO)$_5$(PPh$_2$Cl) in 20 mL of THF was added dropwise to a solution of 7.00 mmol of the amine in 20 mL of THF under N$_2$ over a 20-min period. The mixture was stirred at ambient temperature overnight and then evaporated to dryness. The residue was washed with two 20-mL portions of hexanes, and the washes were combined and filtered through a 3.5 cm by 1.0 cm column of neutral alumina. The filtrate was evaporated to dryness to yield the product.

Spectroscopy. Mass spectra were obtained on a Hewlett Packard 5993/95 mass spectrometer using the direct insertion probe. Infrared spectra of the carbonyl region (2150–1800 cm^{-1}) were taken of dilute *n*-hexane solutions of the complexes in a 0.2-mm NaCl liquid cell. Multinuclear (^{1}H, ^{13}C, ^{17}O, ^{31}P, ^{95}Mo) NMR spectra were taken of saturated chloroform-d_1 solutions of the complexes in 10-mm quartz tubes using a JEOL FX90Q NMR spectrometer. The operating parameters are summarized in Table II.

Results

Syntheses. The method of Kraihanzel and Bartish[14] shown in eq 1 was used to synthesize the methyl,[1] ethyl,[2]

---

(11) Alyen, E. C.; Lenkinski, R. E.; Somogyvari, A. *Polyhedron* **1982**, *1*, 130.

(12) Masters, A. F.; Brownlee, R. T. C.; O'Conner, M. J.; Wedd, A. G. *Inorg. Chem.* **1981**, *20*, 4183.

(13) Brownlee, R. T. C.; Masters, A. F.; O'Connor, M. J.; Wedd, A. G.; Kimlin, H. A.; Cotton, J. D. Org. Magn. *Reson.* **1982**, *20*, 73.

(14) Kraihanzel, C. S. Bartish, C. M. *J. Organomet. Chem.* **1972**, *43*, 343.

$$\mathrm{Mo(CO)_5(PPh_2Cl) + ROH \xrightarrow{reflux} Mo(CO)_5(PPh_2OR)} \quad (1)$$

and *n*-propyl[3] esters of (diphenylphosphinous acid)-pentacarbonylmolybdenum(0). However, when this method was applied to the synthesis of the isopropyl (**4**) and *sec*-butyl (**6**) esters, a large amount of a second product, identified as $[\mathrm{Mo(CO)_5PPh_2}]_2\mathrm{O}$ (**15**) by its multinuclear NMR spectra, was also obtained. This material may have resulted from the presence of residual water in the alcohols or from thermal degradation of the phosphinite esters. To avoid this problem $\mathrm{Mo(CO)_5(PPh_2Cl)}$ was reacted with the alkoxides of isopropyl alcohol and *sec*-butyl alcohol, which were generated by the reaction of metallic sodium with the alcohol, to yield the corresponding isopropyl (**4**) and *sec*-butyl (**6**) phosphinite esters. This method, which is shown in eq 2, was also used to synthesize the *n*-butyl (**5**) and isobutyl (**7**) esters.

$$\mathrm{Mo(CO)_5(PPh_2Cl) + NaOR \xrightarrow{HOR} Mo(CO)_5(PPh_2OR) + NaCl} \quad (2)$$

The phosphinamides were synthesized by addition of an excess of either the gaseous or liquid amines to a tetrahydrofuran solution of $\mathrm{Mo(CO)_5(PPh_2Cl)}$ as shown in eq 3.

$$\mathrm{Mo(CO)_5(PPh_2Cl) + 2RNH_2 \xrightarrow{THF} Mo(CO)_5(PPh_2NHR) + RNH_3^+Cl^-} \quad (3)$$

The phosphinite esters and phosphinamides synthesized in this study are all colorless, low melting solids which are soluble in ethers, aliphatic, chlorinated and aromatic hydrocarbons, acetone, and alcohols. The complexes gradually decompose in the light but are relatively stable if stored under N_2 in the dark.

^{1}H NMR Results. Proton NMR data for the $\mathrm{Mo(CO)_5(PPh_2XR)}$ complexes are summarized in Table III. The spectra appear to be first order, and the coupling constants observed ($^3J_{HH}$ = 6–7 Hz, $^3J_{PH}$ = 6–14 Hz, and $^2J_{PH}$ = 16–19 Hz) are in agreement with those previously reported for a series of *cis*-$\mathrm{Mo(CO)_4(PPh_2XR)_2}$ complexes.[15]

^{13}C NMR Results. The ^{13}C NMR data for the carbonyl ligands cis and trans to the P-donor ligand in the $\mathrm{Mo(CO)_5(PPh_2XR)}$ complexes are summarized in Table VI. The resonances for both the trans and cis carbonyls are doublets with the less intense trans doublet ($^2J_{PC}$ = 23–29 Hz) found approximately 4.5 ppm downfield of the cis doublet ($^2J_{PC}$ = 9–10 Hz). The trans carbonyl ^{13}C resonances of the alkyl phosphinite complexes are observed 0.43–0.57 ppm upfield of the trans carbonyl ^{13}C resonances of the corresponding phosphinamide complexes while the cis carbonyl ^{13}C resonances of the alkyl phosphinite complexes are found 0.11–0.21 ppm upfield of the cis carbonyl ^{13}C resonances of the corresponding phosphinamide complexes. A second factor which affects the carbonyl ^{13}C chemical shifts of the $\mathrm{Mo(CO)_5(PPh_2XR)}$ complexes is the degree of substitution on the α carbon of the R group.

The ^{13}C NMR data for the phosphorus phenyl groups are summarized in Table IV. The C(1), ortho, and meta carbon resonances are all doublets while the para carbon gives rise to either a doublet or a broad singlet. The magnitudes of the phosphorus–carbon coupling constants may be summarized as follows: $^1J_{PC}$ = 30–40 Hz, $^2J_{PC}$ = 13–15 Hz, $^3J_{PC}$ = 9–10 Hz, $^4J_{PC}$ = 0–1 Hz. An unusual feature of the aromatic ^{13}C NMR spectra of the two Mo-

Table III. ^{1}H NMR Data for Aliphatic Protons in the $\mathrm{Mo(CO)_5(PPh_2XR)}$ Complexes

XR	δ(NH)	$^2J_{PH}$	$^3J_{PH}$	δ(C(1)H$_n$)	$^3J_{PH}$	$^2J_{HH}$	*n*	δ(C(2)H$_n$)	$^3J_{HH}$	*n*		$^3J_{HH}$	*n*	δ(C(4)H$_n$)	$^3J_{HH}$	*n*
OMe (**1**)				3.44 d	13		3									
OEt (**2**)				3.66 dq	7	7	2	1.25 t	7	3						
O-*n*-Pr (**3**)				3.57 dt	6	6	2	1.59 tq	6, 6	2	0.93 t	6	3			
O-*i*-Pr (**4**)				3.41 ds	10	6	1	1.10 d	6	6						
O-*n*-Bu (**5**)				3.60 dt	6	6	2	~1.4 m	*b*	2	~1.4 m	*b*	2	0.86 t	6	3
O-*s*-Bu (**6**)				~4.2 m	*b*	*b*	1	~1.4 m 1.05 d	*b* 6	2 3	0.81 t	6	3			
O-*i*-Bu (**7**)				3.36 dd	7	6	2	1.89 ts	7, 6	1	0.91 d	7	6			
NHMe (**8**)	*c*			2.33 d	12		3									
NHEt (**9**)	2.05 dt	19	6	2.65 ddq	12	6, 6	2	0.98 t	6	3						
NH-*n*-Pr (**10**)	2.08 dt	19	6	2.57 ddt	6	6, 6	2	1.32 tq	6, 6	2	0.78 t	6	3			
NH-*i*-Pr (**11**)	1.90 dd	18	10	~3.1 m	*b*	*b*	1	0.87 d	6	6						
NH-*n*-Bu (**12**)	2.08 dt	19	6	2.61 ddt	6	6, 6	2	~1.3 m	*b*	2	~1.3 m	*b*	2	0.85 t	6	3
NH-*s*-Bu (**13**)	1.97 dd	16	10	~2.9 m	*b*	*b*	1	~1.2 m 0.87 d	*b* 6	2 3	0.71 d	7	3			
NH-*i*-Bu (**14**)	*c*			2.40 ddd	6	6, 6	2	1.43 ds	6, 6	1	0.78 d	6	6			

[a] $\mathrm{CDCl_3}$ solutions measured relative to internal $\mathrm{Me_4Si}$ at 0.00 ppm. Coupling constants in hertz. Multiplicities: d = doublet; t = triplet; q = quartet; m = multiplet; s = septet. [b] Coupling constants not measurable. [c] Resonance obscured.

---

(15) Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1978**, *146*, 23.

Table IV. ^{13}C NMR Data for Aromatic Carbons in the $Mo(CO)_5PPh_2XR$ Complexes[a]

XR	C(1)[b]		C(ortho)[b]		C(meta)[b]		C(para)[c]	
	δ	$^1J_{PC}$, Hz	δ	$^2J_{PC}$, Hz	δ	$^3J_{PC}$, Hz	δ	$^4J_{PC}$, Hz
OMe (**1**)	138.65	35.2	130.76	13.9	128.55	9.5	130.78	1.5
OEt (**2**)	139.12	34.4	130.73	13.9	128.45	9.5	130.61	
O-*n*-Pr (**3**)	139.08	34.4	130.83	13.9	128.45	9.5	130.61	
O-*i*-Pr (**4**)	140.66	36.6	130.91	14.7	128.31	8.8	130.91	
O-*n*-Bu (**5**)	139.07	35.2	130.86	13.9	128.48	9.5	130.65	
O-*s*-Bu (**6**)	141.20	38.8	131.15	13.9	128.29	9.5	130.61	1.5
	140.76	35.2	130.68	14.7				
O-*i*-Bu (**7**)	138.92	34.4	130.89	13.9	128.45	9.5	130.58	
NHMe (**8**)	136.14	39.6	131.30	13.2	128.42	9.5	130.00	
NHEt (**9**)	136.92	39.6	131.23	13.2	128.42	9.5	129.96	
NH-*n*-Pr (**10**)	136.99	39.6	131.30	13.2	128.39	9.5	130.58	
NH-*i*-Pr (**11**)	138.20	40.3	131.33	13.2	128.35	9.5	130.00	1.5
NH-*n*-Bu (**12**)	136.97	40.3	131.33	13.2	128.42	9.5	130.00	
NH-s-Bu (**13**)	138.82	40.3	131.56	13.2	128.35	9.5	129.96	
	138.30	40.3	131.22	13.2				
NH-*i*-Bu (**14**)	136.91	40.3	131.36	13.2	128.35	9.5	129.99	

[a] $CDCl_3$ solutions, Me_4Si internal reference at 0.00 ppm. [b] Resonance is a doublet. [c] Resonance is either a doublet or a broad singlet.

(CO)$_5$(PPh$_2$X-s-Bu) complexes, **6** and **13**, is that two doublets are observed for both the C(1) and ortho carbons' resonances which may result from restricted rotation about the molybdenum–phosphorus bond since these ligands have the largest cone angles of all the ligands studied.

The phosphorus–carbon coupling constants observed in the aliphatic portion of the ^{13}C NMR spectra of the Mo(CO)$_5$(PPh$_2$XR) complexes are unusual in that the magnitude of $^nJ_{PC}$ is strongly dependent upon the nature of the X group. For the alkyl phosphinite complexes $^2J_{PC}$ is between 0 and 4 Hz while $^3J_{PC}$ is between 4 and 9 Hz. In contrast, for the phosphinamide complexes $^2J_{PC}$ is between 7 and 8 Hz while $^3J_{PC}$ is between 3 and 6 Hz. These differences in coupling constants may reflect a significant difference in either the hybridization or the effective nuclear charge of the X group.

^{17}O NMR Results. The ^{17}O NMR spectra of the Mo(CO)$_5$(PPh$_2$XR) complexes consist of two resonances with the lower intensity resonance, due to the trans carbonyl ligand, downfield and partially obscured by the more intense resonance arising from the four cis carbonyl ligands. No significant change in the chemical shift of either resonance was observed as the R group was changed. However, the ^{17}O NMR resonances of the trans and cis carbonyls in the alkyl phosphinite complexes were 1.6 and 1.2 ppm, respectively, downfield of the corresponding resonances of the phosphinamide complexes. That the substitution of the NH group by the more electronegative O causes a downfield shift in the carbonyl ^{17}O NMR resonances and an upfield shift in the carbonyl ^{13}C NMR resonances is consistent with the predictions of the theory of Todd and co-workers[5] which is based upon changes in the electron density in the carbonyl π-antibonding orbitals due to changes in the π-acceptor ability of the P-donor ligand. The ^{17}O NMR data are summarized in Table VI.

^{31}P NMR Results. The ^{31}P NMR spectra of the Mo(CO)$_5$(PPh$_2$XR) complexes, summarized in Table VI, contain a single resonance, making this an excellent method for ascertaining the presence of other phosphorus-containing impurities such as [Mo(CO)$_5$(PPh$_2$)]$_2$O (**15**). The ^{31}P NMR resonances of the alkyl phosphinite complexes are found 66.40 ± 2.22 ppm downfield of the corresponding phosphinamide complexes indicating that replacing an NH group by an O has a nearly identical effect on the ^{31}P chemical shifts of any of the Mo(CO)$_5$(PPh$_2$XR) complexes studied regardless of the identity of the R group.

^{95}Mo NMR Results. The ^{95}Mo NMR chemical shifts and coupling constants are summarized in Table VI. These resonances are doublets with a $^2J_{MoP}$ of 147 Hz for the phosphinamide complexes and a $^2J_{MoP}$ of 158 Hz for the alkyl phosphinite complexes. The ^{95}Mo NMR resonances of the alkyl phosphinite complexes are found 24.23 ± 2.23 ppm upfield of the phosphinamide complexes, and although this behavior is the opposite of what might be expected based upon electronegativity arguments, it is consistent with the results of previous studies on a wide variety of molybdenum complexes.[2,16]

Discussion

Previous workers have demonstrated that changes in both the electronic[1-5] and steric properties[17,18] of P-donor ligands are reflected by changes in the chemical shifts and coupling constants of the multinuclear NMR resonances of their metal carbonyl complexes. Thus it might be expected that a systematic variation in the steric and electronic properties of the XR groups in Mo(CO)$_5$(PPh$_2$XR) complexes would result in corresponding changes in the chemical shifts and coupling constants of the multinuclear NMR resonances of the complexes. Furthermore, if the chemical shifts of various resonances of these complexes are affected similarly by the changes in the XR groups, good correlations should be observed between the chemical shifts similar to those which have been reported previously.[1,3]

The P-donor ligands used in this study are of great utility in relating changes in the electronic and steric properties to the chemical shifts of the ^{13}C, ^{17}O, ^{31}P, and ^{95}Mo nuclei of the complexes. To a first approximation the electronic donor/acceptor properties of the ligands should depend on the nature of the X group (O or NH) while the steric properties should be a function of the R (alkyl) group. Thus, to a certain extent, the steric and electronic changes in these complexes can be controlled and their effect on the multinuclear NMR spectra of the complexes studied independently.

From the data in Tables III–VI it is obvious that, as expected, the change in the X group has a much greater effect upon the chemical shifts of the various resonances than do variations in the R group. A change in the X group affects the chemical shifts of all of the ^{13}C, ^{17}O, ^{31}P,

---

(16) Christensen, K. A.; Miller, P. E.; Minelli, M.; Rockway, T. W.; Enemark, J. H. *Inorg. Chim. Acta* **1981**, *56*, L27.

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

(18) Colquhoun, I. J.; Grim, S. O.; McFarlane, W.; Mitchell, J. D.; Smith, P. H. *Inorg. Chem.* **1981**, *20*, 2516.

Table V. ^{13}C NMR Data for Aliphatic Carbons in the Mo(CO)$_5$(PPh$_2$XR) Complexes[a]

	C(1)[b]		C(2)[c]			
XR	δ	$^1J_{PC}$, Hz	δ	$^2J_{PC}$, Hz	C(3)[d] δ	C(4)[d] δ
OMe (1)	53.58 m3	2.9				
OEt (2)	62.59 m2	2.9	16.19 m3	8.8		
O-*n*-Pr (3)	68.12 m2	4.4	23.98 m2	8.1	10.40 m3	
O-*i*-Pr (4)	72.31 m1		24.03 m3	4.4		
O-*n*-Bu (5)	66.32 m2	3.7	32.63 m2	8.1	19.07 m2	13.69 m3
O-*s*-Bu (6)	77.03 m1		30.55 m2	5.1	9.04 m3	
			20.82 m3	3.7		
O-*i*-Bu (7)	72.54 m2	4.4	29.54 m1	8.1	19.02 m3	
NHMe (8)	30.00 m3	8.1				
NHEt (9)	38.81 m2	8.1	16.97 m3	5.9		
NH-*n*-Pr (10)	45.73 m2	8.1	24.81 m2	5.9	11.18 m3	
NH-*i*-Pr (11)	46.71 m1	6.6	25.64 m3	3.7		
NH-*n*-Bu (12)	43.68 m2	8.1	33.77 m2	5.1	19.87 m2	13.72 m3
NH-*s*-Bu (13)	51.68 m1	6.6	31.82 m2	3.7	9.66 m3	
			22.34 m3	2.9		
NH-*i*-Bu (14)	51.37 m2	8.8	29.90 m1	5.1	19.96 m3	

[a] CDCl$_3$ solutions, Me$_4$Si internal reference at 0.00 ppm. m3 = methyl, m2 = methylene, and m1 = methine. [b] Doublets or broad singlets. [c] Doublets. [d] Singlets.

and ^{95}Mo resonances of the complexes. In contrast, for a given X group, the chemical shifts of the ^{13}C and ^{17}O resonances of the carbonyl ligands are insensitive to changes in the R groups while the chemical shifts of the ^{13}C resonance of the aromatic C(1) carbons and the ^{31}P and ^{95}Mo resonances appear to depend on the degree of substitution at the α carbon of the R group.

Substitution at the α carbon of the R group could affect the electron donor/acceptor properties of the P-donor ligand either electronically via hyperconjugation or sterically through changes in the cone angle of the ligands. If hyperconjugation is the predominant factor in determining the chemical shifts observed for the phosphinamide (X = NH) or phosphinite (X = O) complexes, then changes in the chemical shifts as the electron donor strength of the R group is decreased, i.e., CH$_3$ > CH$_2$R > CHR$_2$, should parallel the changes in the chemical shifts as the electronegativity of the X group is increased, i.e. NH to O. This is observed for the ^{13}C chemical shifts of the aromatic C(1) resonance where both decreasing electron donor ability of the R group and increasing electronegativity of the X group result in a downfield shift of this resonance. However, these two trends cause opposite shifts for the ^{31}P and ^{95}Mo resonances. Decreasing the electron donor ability of the R group causes an upfield shift in the ^{31}P resonance and a downfield shift in the ^{95}Mo resonance while increasing the electronegativity of the X group causes the ^{31}P resonance to move downfield and the ^{95}Mo resonance to move upfield. Thus it does not appear that hyperconjugation can be used to explain the effect of changes in the degree of substitution at the α carbon of the R group on these chemical shifts.

The primary effect of the substitution at the α carbon of the R group on the aromatic C(1) ^{13}C, ^{31}P, and ^{95}Mo chemical shifts appears to be steric in nature. This can be rationalized as follows. As the degree of substitution at the α carbon of the R group increases, the cone angle of the P-donor ligand also increases. The change in cone angle will affect the hybridization of the P-donor ligands[17] which may in turn cause the ligand to become a better π acceptor. This would then result in the observed upfield shift in the ^{31}P resonance and the downfield shifts in the aromatic C(1) ^{13}C and ^{95}Mo resonances. Although no proof can be offered that an increase in the cone angle of the ligands does indeed cause an increase in the π-acceptor ability of the P-donor ligands used, the explanation is consistent with observed trends and is supported by the observation that small changes in the cone angle of P-donor ligands do have significant effects on their ^{31}P NMR spectra.[18,19]

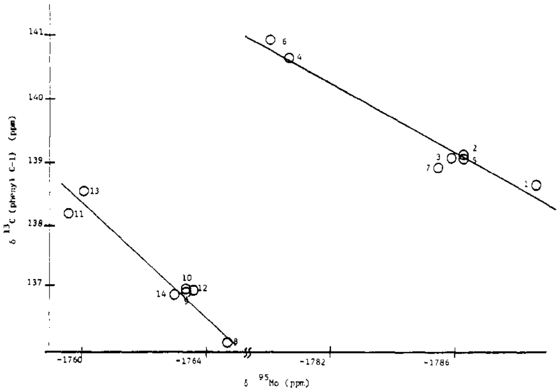

Figure 1. Plot of the phenyl C(1) ^{13}C chemical shift vs. the ^{95}Mo chemical shift.

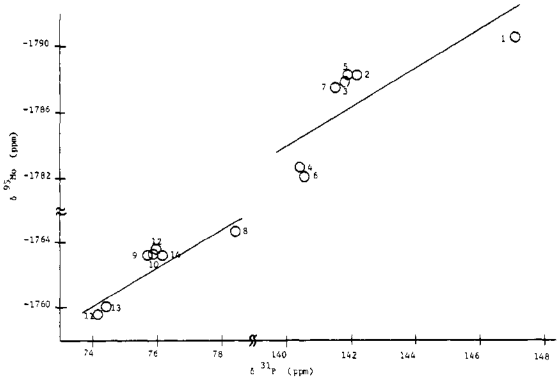

Figure 2. Plot of the ^{95}Mo chemical shift vs. the ^{31}P chemical shift.

Since the aromatic C(1) ^{13}C, ^{31}P, and ^{95}Mo resonances appear to be similarly affected by the degree of substitution at the α carbon of the R group, the correlations between the chemical shifts of these resonances as the R group is varied have been examined and plots of the chemical shifts of these resonances versus one another are given in Figures 1–3. The data for the phosphinite (X = O) and phosphinamide (X = NH) complexes are considered separately as it has previously been noted that the

---

(19) Derencsenyi, T. J. *Inorg. Chem.* **1981**, *20*, 665.

Table VI. Carbonyl, ^{13}C, ^{17}O, ^{31}P, and ^{95}Mo NMR Data for the $Mo(CO)_5(PPh_2XR)$ Complexes^a

	^{13}C(trans CO^b)^c		^{13}C(cis CO^b)^c		^{17}O(trans CO^b)^d δ	^{17}O(cis CO^b)^d δ	^{31}P^e δ	^{95}Mo^f	
XR	δ	J, Hz	δ	J, Hz				δ	J, Hz
OMe (1)	209.81	27.1	205.37	10.3	367.3	362.1	147.11	−1790.6	156
OEt (2)	209.95	23.4	205.44	10.3	366.9	362.1	142.20	−1788.3	159
O-*n*-Pr (3)	209.95	26.4	205.48	9.5	367.3	362.1	141.86	−1787.9	159
O-*i*-Pr (4)	209.98	26.4	205.53	10.3	366.9	362.5	140.45	−1782.7	156
O-*n*-Bu (5)	209.99	26.4	205.50	10.3	366.5	362.1	141.93	−1788.3	159
O-*s*-Bu (6)	209.99	26.4	205.53	10.3	366.9	362.5	140.58	−1782.1	159
O-*i*-Bu (7)	210.01	26.4	205.55	9.5	367.3	362.1	141.56	−1787.5	159
NHMe (8)	210.38	23.4	205.58	9.5	365.3	360.9	78.49	−1764.7	146
NHEt (9)	210.48	23.4	205.64	9.5	365.3	360.9	75.80	−1763.4	146
NH-*n*-Pr (10)	210.47	23.4	205.68	9.5	364.9	360.9	75.90	−1763.4	146
NH-*i*-Pr (11)	210.50	23.4	205.64	9.5	365.3	360.9	74.18	−1759.6	146
NH-*n*-Bu (12)	210.47	23.4	205.68	9.5	365.3	360.9	75.97	−1763.6	149
NH-*s*-Bu (13)	210.54	23.4	205.68	9.5	365.3	360.9	74.42	−1760.1	151
NH-*i*-Bu (14)	210.44	23.4	205.66	10.3	365.3	360.9	76.14	−1763.0	146

[a] $CDCl_3$ solutions. [b] Trans CO refers to the CO's trans to one of the P-donor ligands; cis CO refers to CO's cis to both of the P-donor ligands. [c] Resonance is a doublet. Relative to internal Me_4Si at 0.00 ppm. [d] Relative to the ^{17}O resonance of external H_2O at 0.00 ppm. [e] Relative to the ^{31}P resonance of external 85% aqueous H_3PO_4. [f] Relative to the ^{95}Mo resonance of external 2 M aqueous Na_2MoO_4. These data are reproducible to ±0.04 ppm.

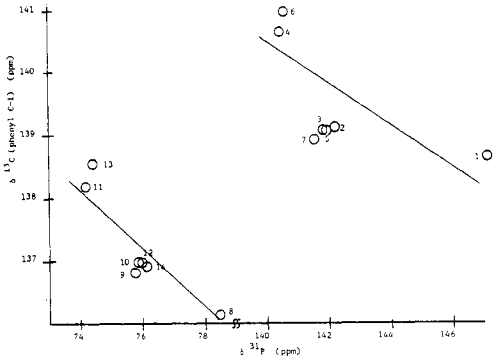

Figure 3. Plot of the phenyl C(1) ^{13}C chemical shift vs. the ^{31}P chemical shift.

changes in the X groups have a different and considerably greater effects on the chemical shifts of these resonances than do changes in the R group. The best correlations are found between the chemical shifts of the aromatic C(1) ^{13}C and ^{95}Mo resonances for both the phosphinite ($R = -0.94$) and phosphinamide ($R = -0.97$) complexes. A good correlation is also observed between the aromatic C(1) ^{13}C and ^{31}P resonances of the phosphinamide complexes ($R = -0.92$) while a poor correlation is found between the chemical shifts of these resonances for the phosphinite complexes ($R = -0.64$). Finally the correlation between the chemical shifts of the ^{31}P and ^{95}Mo resonances for the phosphinamide complexes is only fair ($R = 0.88$) while it is poor ($R = 0.76$) for the phosphinite complexes.

The fact that the best correlations are observed between the ^{95}Mo and aromatic C(1) ^{13}C resonances may be rationalized by examining the basic structure of the complexes. The ^{95}Mo and aromatic C(1) ^{13}C nuclei are separated from the α carbon of the R group by three bonds while the ^{31}P nucleus is only two bonds distant. It is then not unreasonable to conclude that the chemical shift of the closer ^{31}P nucleus may respond differently to changes in the degree of substitution at the α carbon than do the more distant ^{95}Mo and aromatic C(1) ^{13}C nuclei. Thus the best correlations might be expected between the nuclei which are more nearly equidistant from the α carbon of the R group. This does not explain, however, why the correlations between the three types of nuclei are always better for the phosphinamide complexes than they are for the phosphinite complexes. The reason for this behavior is not clear at the present time.

The correlations observed between the various chemical shifts as the alkyl group is changed are limited as the total chemical shift range observed for the ^{95}Mo resonance (8 ppm for X = O and 5 ppm for X = NH), the ^{31}P resonance (7 ppm for X = O and 4 ppm for X = NH) and the aromatic C(1) ^{13}C resonance are small compared to the chemical shift ranges of these resonances. However, these changes in chemical shifts are greater than the precision of the NMR experiments used in their determination, and thus these correlations are valid for limited changes observed. The good correlations observed between the chemical shifts of the ^{95}Mo and aromatic C(1) ^{13}C resonances indicate that when the ^{95}Mo nucleus is maintained in a constant coordination environment and oxidation state, the ^{95}Mo resonance responds to changes in the steric and electronic parameters in a manner similar to that of the aromatic C(1) ^{13}C resonance.

Conclusion

Through studies of the ^{13}C, ^{17}O, ^{31}P, and ^{95}Mo NMR spectra of a series of $Mo(CO)_5(PPh_2XR)$ complexes the steric effect of substitution at the α carbon of the R group on the chemical shifts of the aromatic C(1) ^{13}C, ^{31}P, and ^{95}Mo resonances has been demonstrated. In addition, the good correlation observed between the chemical shifts of the aromatic C(1) ^{13}C and ^{95}Mo resonance are the first involving the ^{95}Mo resonance and indicate that, for the limited series of complexes studied, the ^{95}Mo resonance responds to the same changes in the electronic and steric properties of the P-donor ligands as do some of the other resonances. No correlations were observed for the ^{13}C and ^{17}O resonances. These studies demonstrate that careful control of changes in the steric and electronic properties of P-donor ligands is necessary if good correlations are to be observed between the chemical shifts of the various resonances of their metal complexes.

Acknowledgment. We thank J. T. Baker Chemical Co. for the support of this work.

Registry No. **1**, 37834-18-7; **2**, 38268-60-9; **3**, 38268-61-0; **4**, 38268-62-1; **5**, 85762-05-6; **6**, 85762-06-7; **7**, 85762-07-8; **8**, 38656-46-1; **9**, 85762-08-9; **10**, 85762-09-0; **11**, 85762-10-3; **12**, 85762-11-4; **13**, 85762-12-5; **14**, 85762-13-6; $Mo(CO)_5(PPh_2Cl)$, 23581-74-0.