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A Fourier Transform Carbon-13 Nuclear Magnetic Resonance Study of Group 6B Transition Metal Carbonyl Complexes

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^{13}C NMR spectra have been obtained for a series of $L_nM(CO)_{6-n}$ derivatives, (n = 0, 1, 2; M = Cr, Mo, W; L = CO, PCl_3, $P(OPh)_3$, $P(OMe)_3$, PH_3, PPh_3, $AsPh_3$, $SbPh_3$, PEt_3, PBu_3, $NH_2C_6H_{11}$, NHC_5H_{10}, Cl^-). For all derivatives studied to date (n = 1, 2, 3) where L is formally a two-electron donor the resonance for the carbonyl trans to L is deshielded relative to the resonance for the carbonyls cis to L, while the converse has been observed when L is formally a one-electron donor. The effect of the sequential replacement of carbonyl ligands by phosphine or phosphite ligands would appear to be additive. A monotonic shielding of the carbonyl resonance in $L_nM(CO)_{6-n}$ derivatives is observed upon the replacement of Cr by Mo and W, which is suggestive of a contribution to the chemical shift from neighboring diamagnetic screening. A linear correlation is observed between the cis carbonyl chemical shifts for $LM(CO)_5$ derivatives and both the k_2 stretching force constants and the carbonyl chemical shifts for analogous $LNi(CO)_3$ derivatives; these data are interpreted in terms of the relative σ-donor/π-acceptor character of the ligands. Data are presented for the $^2J_{^{13}C^{31}P}$ through-metal coupling constants in these derivatives, which suggest a close relationship to the previously reported $^2J_{^{31}P^{31}P}$ coupling constants. The magnitude of the trans $^2J_{^{13}C^{31}P}$ coupling constant for Mo and W derivatives is significantly larger than the magnitude of the cis $^2J_{^{13}C^{31}P}$ coupling constant, whereas the converse is true for Cr derivatives. The relative signs of the trans and cis $^2J_{^{13}C^{31}P}$ coupling constants in *cis*-$(H_3P)_2Cr(CO)_4$ appear to be the same.

Introduction

Darensbourg and Darensbourg[1] have suggested that an increase in the carbonyl mode stretching force constant in transition metal carbonyl complexes, whether the result of an increase in the σ-donor ability or a decrease in the π-acceptor ability of the carbonyl, is a reflection of an increase in the positive character of the carbonyl carbon. Thus, if variations in the ^{13}C NMR carbonyl chemical shifts in $L_nM(CO)_m$ derivatives are dominated by changes in the magnitude of the contribution from either *local* diamagnetic shielding[2] or the dependence of the *local* paramagnetic shielding[3] upon electron density, one should observe a linear correlation between the carbonyl chemical shifts and the infrared stretching force constants, such that an increase in the carbonyl force constant is reflected by a *deshielding* of the carbonyl resonance. Linear correlations have indeed been observed for a number of complexes containing equivalent carbonyls, including η-$(C_5H_5)Fe(CO)_2X$,[4] η-$(C_6H_5X)Cr(CO)_3$,[5] η-$(C_5H_5)Mn(CO)_2L$,[6] and $LNi(CO)_3$[7] derivatives. Unfortunately, in these derivatives and others, an increase in the carbonyl stretching force constant is reflected by a *shielding* of the carbonyl resonance, which we[5-8] and others[9] have attributed to a decrease in the magnitude of the separation between the ground state and the lowest lying electronic excited states with increasing transition metal → carbonyl π back-donation.

^{13}C NMR data have been reported for $LM(CO)_5$ derivatives of Cr, Mo, and W[9-12] which suggest that a correlation exists between the cis carbonyl chemical shifts and the k_2 stretching force constants, whereas the correlation between the trans carbonyl chemical shifts and the k_1 stretching force constants is questionable. Recently Webb and Graham[13] have reported similar behavior for $XRe(CO)_5$ derivatives. We wish to report herein the results of a study of the ^{13}C NMR spectra of a series of $L_nM(CO)_{6-n}$ derivatives (n = 0, M = Cr, Mo, W; n = 1, M = Cr, L = $P(OPh)_3$, $P(OMe)_3$, PH_3, PPh_3, $AsPh_3$, $SbPh_3$, PEt_3, PBu_3, $NH_2C_6H_{11}$, NHC_5H_{10}, Cl^-; n = 1, M = Mo, L = PCl_3, $P(OPh)_3$, $P(OMe)_3$, PPh_3, $AsPh_3$, $SbPh_3$, PBu_3, $NH_2C_6H_{11}$, NHC_5H_{10}; n = 1, M = W, L = $P(OPh)_3$, PPh_3, PBu_3, $NH_2C_6H_{11}$, NHC_5H_{10}; n = 2, M = Cr, Mo, W, L = PBu_3; n = 2, M = Cr, L = $P(OPh)_3$, $P(OMe)_3$, PH_3).

Experimental Section

Materials. $Cr(CO)_6$ and $W(CO)_6$ were purchased from the Pressure Chemical Co. and $Mo(CO)_6$ was obtained as the generous gift of the Climax Molybdenum Co. The hexacarbonyls were used without further purification. All ligands were obtained from commercial sources and used without further purification.

$LM(CO)_5$ complexes were synthesized by the reaction of an excess of the hexacarbonyl with the respective ligand in refluxing diglyme solution (M = Cr, L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OPh)_3$, $P(OMe)_3$, PEt_3, PBu_3; M = W, L = PPh_3, $P(OPh)_3$, PBu_3),[14] by the reaction of the hexacarbonyl with the respective ligand in refluxing methylcyclohexane solution (M = Mo, L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OPh)_3$, $P(OMe)_3$, PBu_3, PCl_3),[15] by the photolysis of the hexacarbonyl with a high-pressure mercury lamp in the presence of the respective ligand in hexane solution (M = Cr, Mo, W, L = $NH_2C_6H_{11}$, NHC_5H_{10}),[16] or by the reaction of the hexacarbonyl with Et_4NCl (M = Cr, L = Cl^-).[17] Excess metal hexacarbonyl was then removed by vacuum sublimation or by fractional recrystallization. *trans*-$L_2M(CO)_4$ derivatives (M = Cr, L = $P(OPh)_3$, $P(OMe)_3$, and PBu_3; M = W, L = PBu_3) were prepared by the reaction of the hexacarbonyl with a large excess of the respective ligand in a minimal volume of diglyme at reflux, while *trans*-$(Bu_3P)_2Mo(CO)_4$ was prepared by the reaction of $Mo(CO)_6$ with excess tributylphosphine in a minimal volume of methylcyclohexane solution at reflux. Samples of $H_3PCr(CO)_5$ and $(H_3P)_2Cr(CO)_4$ were obtained from Dr. U. Klabunde, Central Research Department, E. I. du Pont de Nemours and Co. The preparations of $(CO)_5MC(OMe)Ph$ and $(CO)_5MC(NH_2)Ph$ complexes of Cr and W have been described elsewhere.[10] All complexes were characterized by a combination of melting points (when possible), infrared spectroscopy, mass spectroscopy, and microanalysis.

Instrumentation. ^{13}C NMR spectra were obtained in chloroform solution on a Fourier transform pulsed NMR spectrometer operating at 15.08 MHz as described previously[18] or in deuteriochloroform solution on a Varian Associates XL-100-FT spectrometer operating at 25.16 MHz equipped with an internal deuterium lock. The ^{13}C NMR spectra of the pure $L_nM(CO)_m$ derivatives were recorded, hexacarbonyl was added, and a second series of spectra was obtained in which the ^{13}C NMR carbonyl chemical shifts could be measured relative to an internal $M(CO)_6$ reference. The ^{13}C NMR chemical shifts are reported in ppm *downfield* from TMS using the conversions

$$\delta_{TMS} = \delta_{Cr(CO)_6} - 211.28 \text{ ppm}$$
$$\delta_{TMS} = \delta_{Mo(CO)_6} - 200.77 \text{ ppm}$$
$$\delta_{TMS} = \delta_{W(CO)_6} - 191.40 \text{ ppm}$$

All data are the result of at least two independent measurements with a precision of ±0.06 ppm or better.

Infrared spectra were obtained in cyclohexane solution on Perkin-Elmer 621 and Beckman IR-12 spectrometers with a 10-fold abscissa expansion and a scan speed of 20 cm^{-1}/min. Spectra were calibrated above 2000 cm^{-1} with CO gas at 150 mm pressure and below 2000 cm^{-1} with ambient water vapor.

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Table I. ^{13}C NMR Chemical Shifts and Coupling Constants for $LM(CO)_5$ Derivatives of Cr, Mo, and W

		Cr		Mo		W	
No.	Ligand	Trans CO	Cis CO	Trans CO	Cis CO	Trans CO	Cis CO
1	CO	-211.2_8[a]		-200.7_7		-191.4_0	
2	PCl_3			-206.0_2 (66)	-200.7_8 (11)[b]		
3	$P(OPh)_3$	-218.2_1 (0)[c]	-213.8_7 (20)	-206.9_2 (46)	-203.0_9 (13)	-196.2_3 (44)	-193.7_5 (10)
4	$P(OMe)_3$	-219.1_8 (4)	-215.1_7 (21)	-208.1_6 (40)	-204.3_7 (14)		
5	PH_3	-219.7_1 (7)	-215.2_4 (13.5)				
6	PPh_3	-221.3_4 (7)	-216.5_3 (13.5)	-210.2_1 (23)	-205.6_6 (9)	-199.3_9 (22)	-197.5_0 (7)
7	$AsPh_3$	-222.1_0	-216.6_5	-210.2_6	-205.2_9		
8	$SbPh_3$	-222.3_9	-217.0_2	-209.5_6	-205.6_2		
9	PEt_3	-221.1_7 (8)	-217.2_4 (14.5)				
10	PBu_3	-221.1_1 (8)	-217.3_6 (14.5)	-209.6_5 (21)	-206.3_2 (9)	-199.0_2 (19)	-197.1_2 (6)
11	$NH_2C_6H_{11}$	-219.8_9	-213.9_5	(...)	-204.0_7	-201.3_8	-198.4_8
12	NHC_5H_{10}	-220.0_7	-214.0_5	-206.9_4	-203.9_7	-201.9_0	-198.9_1
13	*i*-PrNC[d]	-218.2	-216.3				
14	C(OMe)Ph[e]	-224.1_5	-216.1_1			-203.6_0	-197.2_2
15	$C(NH_2)Ph$[e]	-223.5_5	-217.0_8			-203.8_3	-198.2_1
16	Cl^-	-223.5_9	-216.1_6				

[a] Chemical shifts in ppm downfield from TMS, ±0.06 ppm, chloroform solution. [b] $^2J_{^{13}C^{31}P}$ nuclear spin-spin coupling constants, ±1 Hz. [c] This chemical shift was erroneously reported as −217.57 ppm: G. M. Bodner and L. J. Todd, *Inorg. Chem.*, 13, 1335 (1974). Substituting the value of −218.21 substantially improves the correlation presented in Figure 3 of this reference. [d] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J. Chem. Soc. A*, 1246 (1972). [e] G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, 12, 1071 (1973).

Table II. ^{13}C NMR Chemical Shifts and $^2J_{^{13}C^{31}P}$ Coupling Constants for $L_2M(CO)_4$ and $L_3M(CO)_3$ Derivatives

	Chem shift		
Complex	Exptl	Calcd	
trans-$[(PhO)_3P]_2Cr(CO)_4$	-216.7_5[a] (20.5)[b]	-216.4_6 (20)	$2\Delta^{cis}$[c]
trans-$[(MeO)_3P]_2Cr(CO)_4$	-218.8_5 (21)	-219.0_6 (21)	$2\Delta^{cis}$
trans-$[Bu_3P]_2Cr(CO)_4$	-223.7_6 (14)	-223.4_4 (14.5)	$2\Delta^{cis}$
cis-$[H_3P]_2Cr(CO)_4$ equatorial CO	-224.0_8 (8)	-223.6_7 (7, 14)	$\Delta^{cis} + \Delta^{trans}$
axial CO	-218.4_8 (14)	-219.2_0 (14)	$2\Delta^{cis}$
trans-$[(MeO)_3P]_2Mo(CO)_4$[d]	-210.3 (13.4)	-210.8 (14)	$2\Delta^{cis}$
trans-$[Bu_3P]_2Mo(CO)_4$	-212.5_5 (9)	-211.8_7 (9)	$2\Delta^{cis}$
trans-$[Et_3P]_2W(CO)_4$[e]	-204.7 (5)	-205.1 (6)	$2\Delta^{cis}$
cis-$[Et_3P]_2W(CO)_4$[e] equatorial CO	-204.7 (15.2)	-206.8 (6, 19)	$\Delta^{cis} + \Delta^{trans}$
axial CO	-204.4 (6.3)	-205.1 (6)	$2\Delta^{cis}$
fac-$[Et_3P]_3W(CO)_3$[e]	-212.4 (5, 14)	-213.4 (6, 19)	$2\Delta^{cis} + \Delta^{trans}$
trans-$[Bu_3P]_2W(CO)_4$	-203.9_4 (6)	-202.8_4 (6)	$2\Delta^{cis}$

[a] Chemical shifts in ppm downfield from TMS, ±0.06 ppm, chloroform solution, with the exception of data obtained from other authors. [b] $^2J_{^{13}C^{31}P}$ nuclear spin-spin coupling constants, ±1 Hz. [c] Δ^{cis} is defined to be the difference between the chemical shifts of the carbonyl resonance of the cis carbonyls in $LM(CO)_5$ and $M(CO)_6$. [d] P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 1027 (1973). [e] B. E. Mann, *ibid.*, 2012 (1973).

Results

The ^{13}C NMR spectra of $LM(CO)_5$ derivatives of Cr, Mo, and W are characterized by two sharp resonances at low field of relative intensity 1:4, which may be split by $^2J_{^{13}C^{31}P}$ nuclear spin–spin coupling, corresponding to the trans and cis carbonyl ligands in these octahedral complexes and a pattern of resonances at high field analogous to those observed for the free ligand, L[19] (see Figure 1). In $XRe(CO)_5$ derivatives, where X is formally a one-electron donor, the trans carbonyl resonance is shielded relative to the cis carbonyl.[13] In $LM(CO)_5$ derivatives of Cr, Mo, and W and in $LRe(CO)_5^+$ derivatives, where L is formally a two-electron donor, the trans carbonyl resonance is deshielded relative to the cis carbonyl. $^2J_{^{13}C^{31}P}$ through-metal nuclear spin–spin coupling is observed to range in magnitude from approximately 0 for the trans carbonyl resonance in $(PhO)_3PCr(CO)_5$ to 66 Hz for the cis carbonyl resonance in $Cl_3PMo(CO)_5$. Chemical shift and coupling constant data for $LM(CO)_5$ derivatives of Cr, Mo, and W are given in Table I.

trans-$L_2M(CO)_4$ and *fac*-$L_3M(CO)_3$ derivatives exhibit a single sharp carbonyl resonance which may be split into an apparent triplet or a doublet of doublets, respectively, by coupling with ^{31}P. *cis*-$L_2M(CO)_4$ derivatives exhibit two distinct carbonyl resonances for the axial and equatorial carbonyl environments, both of which are split into apparent triplets by coupling with ^{31}P. Table II contains the chemical shift and coupling constant data for a series of $L_2M(CO)_4$ and $L_3M(CO)_3$ derivatives of Cr, Mo, and W whose stereochemistry was assigned on the basis of their infrared spectra.

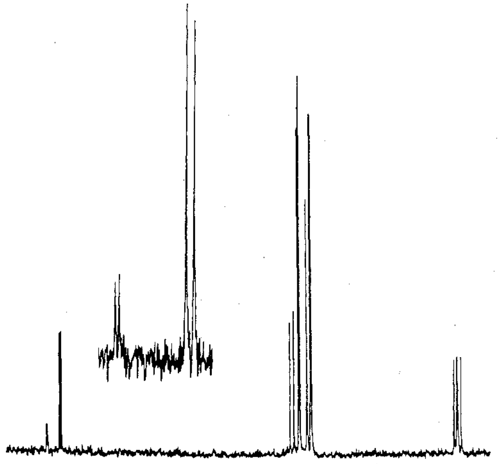

Figure 1. Proton-decoupled Fourier transform ^{13}C NMR spectrum of $Ph_3PCr(CO)_5$; deuteriochloroform solution, approximately 1000 scans, 10-sec pulse delay between scans, 45° flip angle, 200-ppm window. A fivefold expansion of the carbonyl region is also shown.

In a previous paper we suggested that the effect of substitution of carbonyl by phosphine ligands in $L_nNi(CO)_{4-n}$

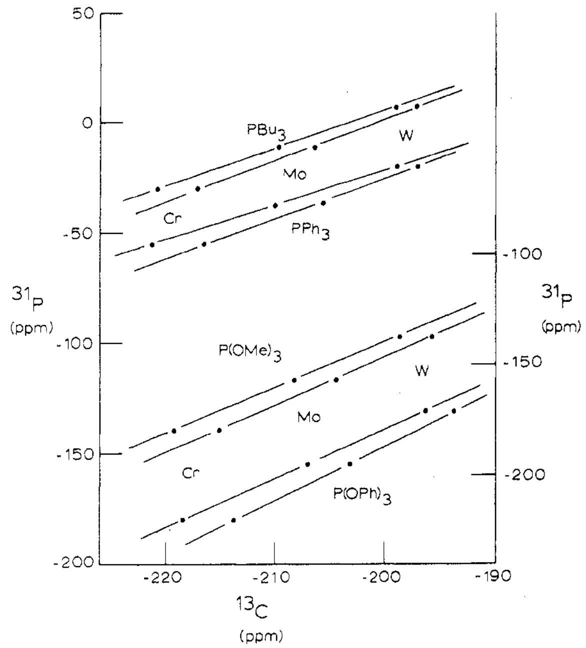

Figure 2. Plot of the ^{31}P NMR chemical shifts in ppm downfield from H_3PO_4 for the phosphorus resonance vs. the ^{13}C NMR chemical shifts in ppm downfield from TMS for the cis and trans carbonyl resonances in $LM(CO)_5$ derivatives (M = Cr, Mo, W; L = PBu_3, PPh_3, $P(OMe)_3$, $P(OPh)_3$). The left ordinate scale is used for L = PBu_3, PPh_3, and $P(OMe)_3$; the right ordinate scale is used when L = $P(OPh)_3$.

derivatives was only slightly less than additive.[7] If we define Δ^{cis} to be the difference between the carbonyl chemical shift for the cis carbonyl resonance in $LM(CO)_5$ and the chemical shift of the respective hexacarbonyl, we would predict that the carbonyl resonance in *trans*-$L_2M(CO)_4$ derivatives would be deshielded by ($2\Delta^{cis}$) relative to the hexacarbonyl. In a similar fashion the carbonyl chemical shifts for the axial and equatorial carbonyls in *cis*-$L_2M(CO)_4$ and the equivalent carbonyls in *fac*-$L_3M(CO)_3$ can be predicted. It would appear that the agreement between experimental and calculated chemical shifts presented in Table II is excellent.

Discussion

^{13}C NMR Carbonyl Chemical Shifts. ^{13}C NMR chemical shifts for the carbonyl resonance in $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in dichloromethane solution have been reported previously,[20] where a shielding of the carbonyl resonance by 10.5 and 20.4 ppm is obtained upon the replacement of Cr by Mo and W. Data presented in Table I suggest that a shielding of the same order of magnitude is operant in the ^{13}C NMR spectra of $LM(CO)_5$ derivatives, while an analogous shielding of approximately twice this magnitude has been observed in the ^{31}P NMR spectra of these derivatives.[21-23] The excellent agreement between the ^{31}P and ^{13}C NMR chemical shifts shown in Figure 2 is consistent with the suggestion that the shielding of the contiguous carbonyl resonance in transition metal carbonyl complexes as one proceeds down a column of the periodic table is the result of a contribution from neighboring diamagnetic circulations.[8]

In those transition metal carbonyl complexes studied to date wherein a single carbonyl resonance is observed for the geometrically equivalent carbonyl ligands, a reasonable correlation has been obtained between the ^{13}C NMR carbonyl chemical shifts and the infrared stretching force constants for the carbonyl mode. Webb and Graham[13] have suggested that this correlation is valid for the cis carbonyl resonance in $XRe(CO)_5$ derivatives but not for the trans carbonyl resonance. An analysis of the data presented to date for $LW(CO)_5$ derivatives[20] would suggest that the agreement between the infrared force constants and the ^{13}C NMR chemical shifts for the cis carbonyl resonance is significantly better than that obtained for the trans carbonyl resonance. Infrared stretching force constants for a series of $LM(CO)_5$ complexes of Cr and Mo are given in Table III, and a plot of the ^{13}C NMR chemical shifts for the trans and cis carbonyl resonances vs. the k_1 and k_2 stretching force constants is shown in Figure 3. As one might expect from preliminary data a correlation exists between the cis carbonyl chemical shifts and the k_2 stretching force constants, while any correlation between the

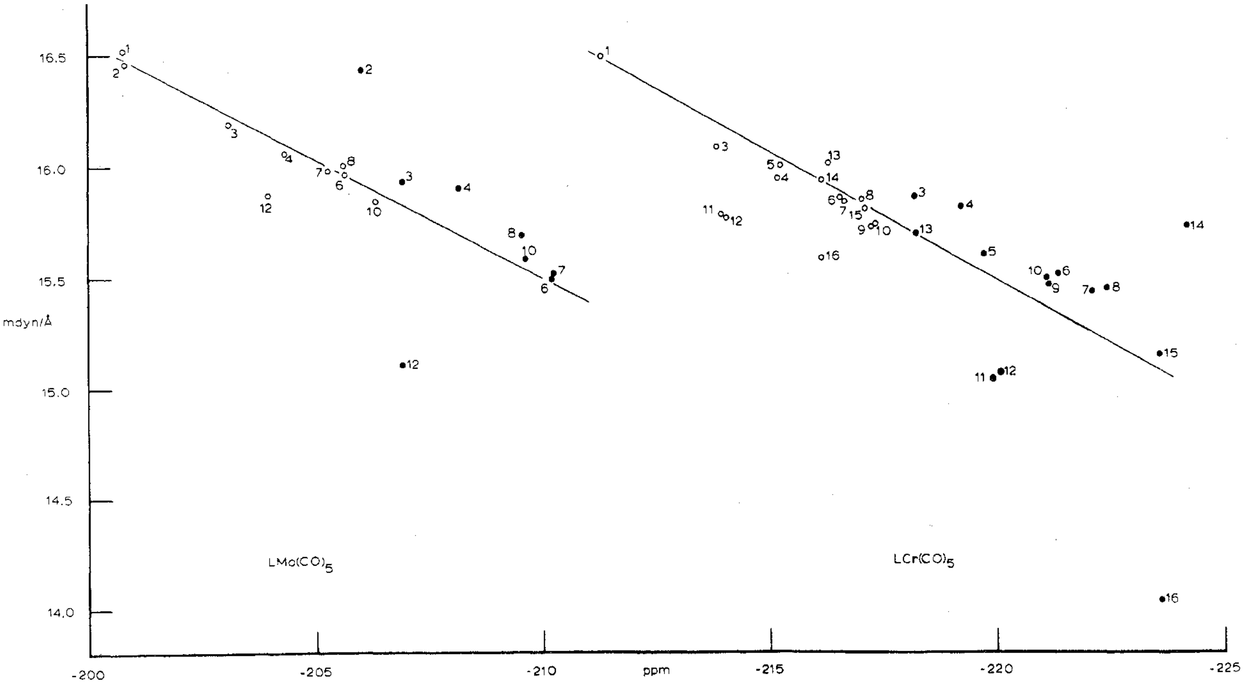

Figure 3. Plot of the ^{13}C NMR chemical shifts in ppm downfield from TMS for the cis (○) and trans (●) carbonyl resonances in $LM(CO)_5$ derivatives of Cr and Mo versus the infrared stretching force constants in mdyn/Å for the carbonyl modes. The precision of the carbonyl chemical shifts is approximately equal to the size of the circles.

Table III. Infrared Stretching Force Constants for the Carbonyl Mode in $LM(CO)_5$ Complexes of Cr and Mo[a]

		Cr		Mo	
No.	Ligand	k_1	k_2	k_1	k_2
1	CO	$16.4_9{}^{b}$		$16.5_2{}^{h}$	
2	PCl_3			16.4_3	$16.4_6{}^{h}$
3	$P(OPh)_3$	15.8_6	16.0_8	15.9_3	$16.1_9{}^{h}$
4	$P(OMe)_3$	15.8_1	15.9_4	15.9_0	$16.0_6{}^{h}$
5	PH_3	15.6_0	$16.0_0{}^{c}$		
6	PPh_3	15.5_1	$15.8_5{}^{b}$	15.4_9	$15.9_6{}^{h}$
7	$AsPh_3$	15.4_3	$15.8_3{}^{c}$	15.5_1	$15.9_8{}^{h}$
8	$SbPh_3$	15.4_4	$15.8_4{}^{c}$	15.6_9	$16.0_0{}^{h}$
9	PEt_3	15.4_6	15.7_2		
10	PBu_3	15.4_9	15.7_3	15.5_8	$15.8_4{}^{i}$
11	$NH_2C_6H_{11}$	15.0_3	$15.7_8{}^{d}$		
12	NHC_5H_{10}	15.0_6	$15.7_6{}^{d}$	15.1_0	$15.8_7{}^{d}$
13	*i*-PrNC	15.6_9	$16.0_2{}^{e}$		
14	C(OMe)Ph	15.7_2	$15.9_3{}^{f}$		
15	$C(NH_2)Ph$	15.1_4	$15.8_0{}^{f}$		
16	Cl^-	14.0_7	$15.5_8{}^{g}$		

[a] Stretching force constants calculated on the basis of the Cotton–Kraihanzel approximations: F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962). k_1 corresponds to the stretching force constant for the trans carbonyl; k_2 is the force constant for the cis carbonyl. [b] D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, 9, 1691 (1970). [c] E. O. Fischer, W. Bathelt, and J. Mullter, *Chem. Ber.*, **103**, 1815 (1970). [d] R. J. Dennenberg and D. J. Darensbourg, *Inorg. Chem.*, **11**, 72 (1972). [e] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1246 (1972). [f] E. O. Fischer and H. J. Kollmeier, *Chem. Ber.*, **104**, 1339 (1971). [g] E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963). [h] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968). [i] W. A. G. Graham, *ibid.*, **7**, 315 (1968).

trans carbonyl chemical shifts and the k_1 stretching force constants would appear to be strictly fortuitous. This behavior, coupled with the realization that the signal-to-noise ratio for the trans carbonyl resonance was relatively low (see Figure 1), led us to question the validity of these data. A duplicate series of measurements of the carbonyl chemical shifts was thus performed which indicated a precision for the trans carbonyl chemical shift of approximately ±0.06 ppm. The close agreement between the ^{13}C NMR chemical shift data for $LM(CO)_5$ complexes of Cr and Mo shown in Figure 4 also suggests that the chemical shift data for the trans carbonyl resonance are well behaved.

Figure 5 would suggest that a linear correlation is observed between the cis carbonyl chemical shifts of $LM(CO)_5$ derivatives of Cr, Mo, and W and the carbonyl chemical shifts of their $LNi(CO)_3$ analogs, whereas a similar plot for the trans carbonyl resonance in $LM(CO)_5$ derivatives yields only marginal agreement. We have suggested previously that the carbonyl chemical shifts in $LNi(CO)_3$[7] and η-$(C_6H_5X)Cr(CO)_3$[3] derivatives were dependent upon variations in the magnitude of the transfer of electron density from the ligand to the transition metal carbonyl moiety which results from variations in the relative magnitude of the σ-donor vs. π-acceptor character of the ligands. Thus, the cis carbonyl chemical shift data for $LM(CO)_5$ derivatives would indicate a net donation of electron density from the ligand to the $M(CO)_5$ moiety, or a σ-donor:π-acceptor ratio, which increases in the order $CO \cong PCl_3 << P(OPh)_3 < NH_2C_6H_{11} < NHC_5H_{10} << P(OMe)_3 \leq PH_3 << C(OMe)Ph \leq Cl^- <$ CN-*i*-Pr $< PPh_3 < AsPh_3 < SbPh_3 \leq C(NH_2)Ph < PEt_3 < PBu_3$. The sequence $CO \cong PCl_3 < P(OPh)_3 < P(OMe)_3 \leq PH_3 < PPh_3 < PEt_3 < PBu_3$, is in accord with the order of decreasing π-acceptor character: $CO \cong PCl_3 > P(OPh)_3 > PH_3 > PPh_3 > PBu_3$, from X-ray crystallographic[24-26] and infrared data, and the suggested order of increasing σ basicity for phosphorus ligands: $P(OPh)_3 < PH_3 < P(OMe)_3 < PPh_3 < PEt_3 < PBu_3$.[27-30] These data are also consistent with the suggestion that the σ-donor:π-acceptor ratio for $C(NH_2)Ph$ is greater than C(OMe)Ph[10,31] and that CN-*i*-Pr is a stronger σ donor than π acceptor.[32] The location of cyclohexylamine and piperidine relative to tributylphosphine in this series would indicate that amines are weaker σ donors than phosphines toward $M(CO)_5$,[33] in accord with the relative rate of ligand

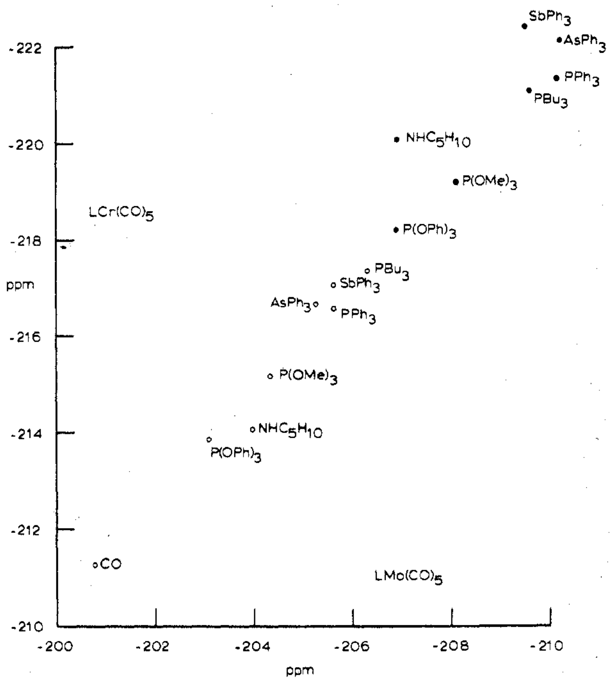

Figure 4. Plot of the ^{13}C NMR chemical shifts in ppm downfield from TMS for the cis (○) and trans (•) carbonyl resonances in $LCr(CO)_5$ derivatives vs. the ^{13}C NMR chemical shifts for the carbonyl resonances in $LMo(CO)_5$ derivatives.

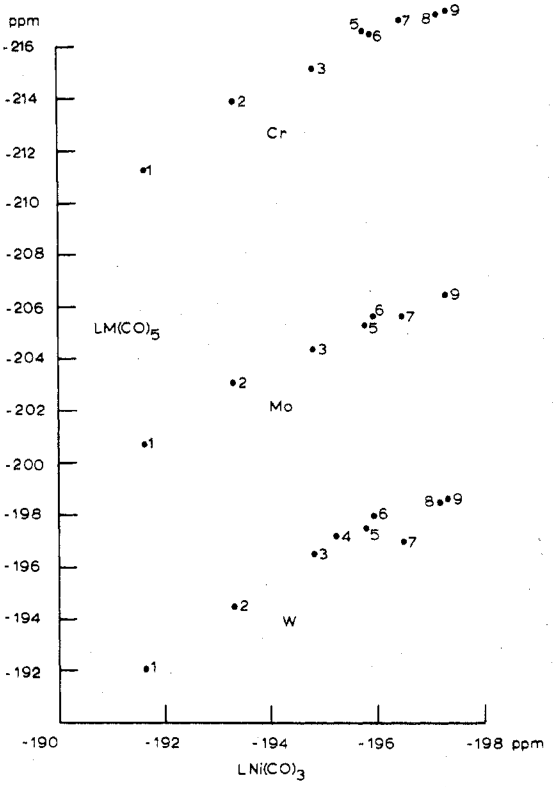

Figure 5. Plot of the ^{13}C NMR chemical shifts in ppm downfield from TMS for the cis carbonyl resonance in $LM(CO)_5$ derivatives of Cr, Mo, and W vs. the ^{13}C NMR chemical shifts in ppm downfield from TMS for the analogous $LNi(CO)_3$ derivatives.

dissociation in these complexes,[34] although it is worth noting that the relative rates of ligand dissociation may be a reflection of the presence of transition metal → phosphine π back-donation which is absent in transition metal–amine complexes.

${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ Nuclear Spin–Spin Coupling Constants. There has been considerable interest to date in both the sign and magnitude of ${}^1J_{^{31}\mathrm{PM}}$ and ${}^2J_{^{31}\mathrm{PMX}}$ coupling constants in octahedral and square-planar transition metal complexes.[29,35,36] The ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling constant data presented in Tables I and II are consistent with several trends. First, the magnitude of the cis and trans ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling in $\mathrm{L_2M(CO)_4}$ and $\mathrm{L_3M(CO)_3}$ derivatives is approximately equal to the magnitude of these couplings in $\mathrm{LM(CO)_5}$ derivatives. Second, the cis ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling constant in $\mathrm{LM(CO)_5}$ derivatives decreases in the order $\mathrm{Cr} > \mathrm{Mo} > \mathrm{W}$, while the trans coupling constant decreases in the order $\mathrm{Mo} \geq \mathrm{W} >> \mathrm{Cr}$. For Mo and W derivatives the trans coupling constant is significantly larger than the cis coupling constant, whereas for Cr derivatives the converse is true. Third, for Cr, Mo, and W derivatives the cis-coupling constant increases upon the substitution of phosphite for phosphine ligands, while for Mo and W the trans coupling constant increases in the order $\mathrm{PR_3} < \mathrm{PPh_3} < \mathrm{P(OMe)_3} < \mathrm{P(OPh)_3}, < \mathrm{PCl_3}$. Thus it would appear that the absolute magnitude of both coupling constants increases with increasing electronegativity of the substituents on phosphorus, as noted previously for η-$\mathrm{(C_5H_5)Mn(CO)_2L}$ derivatives.[6]

It is of interest to note that these trends are mirrored exactly by the behavior of ${}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}}$ coupling constants for *cis*- and *trans*-$\mathrm{L_2M(CO)_4}$ derivatives of Cr, Mo, and W.[29] In fact a reasonable correlation exists between the magnitudes of the ${}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}}$ and ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling constants, such that ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling is not observed for those derivatives wherein ${}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}}$ coupling is approximately equal to zero.[7] The signs of the ${}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}}$ coupling constants have been reported for a number of $\mathrm{L_2M(CO)_4}$ derivatives, and these data suggest that ${}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}}$ coupling in *trans*-$\mathrm{L_2M(CO)_4}$ derivatives of Mo and W is consistently positive, while the coupling in *cis*-$\mathrm{L_2M(CO)_4}$ derivatives of Cr, Mo, and W is negative except when the ${}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}}$ coupling constant for the free ligand is abnormally large. We might expect similar behavior for the ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling constants in $\mathrm{LM(CO)_5}$ derivatives.

The ^{13}C NMR spectrum of *cis*-$\mathrm{(H_3P)_2Cr(CO)_4}$ should exhibit $\mathrm{(X_3M)_2A}$ and $\mathrm{X_3MAM'X'_3}$ patterns for the axial and equatorial carbonyl resonances, respectively, which simplify under conditions of complete proton decoupling to $\mathrm{AX_2}$ and $\mathrm{AXX'}$, respectively. The ^{13}C NMR spectrum for the equatorial carbonyl resonance will appear to be a deceptively simple triplet *except* when $0 < |{}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}}| < |{}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}(\mathrm{trans}) - {}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}(\mathrm{cis})|$. Since $|{}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}}|$ is typically 20 Hz or larger, the observation of a doublet of doublets for this resonance will be rare. Calculated spectra have been generated using the ITRCAL program available from Nicolet Instrument Corp., assuming ${}^2J_{^{31}\mathrm{P}^{31}\mathrm{P}} = -26.2$ Hz[37] and $|{}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}| = 7$ and 14 Hz for the trans and cis coupling constants. When the two ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling constants are assumed to have the same sign (either positive or negative), a five-line pattern is obtained for the equatorial carbonyl resonance, relative intensities 0.01:1.0:2.0:1.0:0.01, with a splitting of the apparent triplet equal to 11 Hz [$(J_{\mathrm{AX}} + J_{\mathrm{AX'}})/2$]. When the signs of these coupling constants are assumed to differ, a five-line pattern is obtained, relative intensities 0.15:1.0:1.7:1.0:0.15, with a splitting of the apparent triplet equal to 3 Hz. The observed spectrum, with a signal-to-noise ratio in excess of 60:1, exhibits a triplet, relative intensities 1.0:2.0:1.1, with a splitting of 8.3 Hz. We must therefore conclude that the signs of the two ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling constants in this complex are the same. Studies are under way at the present time to determine the absolute signs of these coupling constants.

Conclusion

Although we have seen that the carbonyl chemical shifts and ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling constants in $\mathrm{L_2M(CO)_4}$ and $\mathrm{L_3M(CO)_3}$ derivatives may be predicted on the basis of data obtained for $\mathrm{LM(CO)_5}$ derivatives, the inversion in the relative magnitude of the cis and trans carbonyl chemical shifts in $\mathrm{LM(CO)_5}$ derivatives as L is changed from a two-electron donor to a one-electron donor, coupled with the inversion in the relative magnitude of the cis and trans ${}^2J_{^{13}\mathrm{C}^{31}\mathrm{P}}$ coupling constant as Mo and W are replaced by Cr, would suggest that the use of substituent parameters to assign the ^{13}C NMR carbonyl spectra of transition metal carbonyl cluster derivatives must be done with extreme care.

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Registry No. $\mathrm{Cr(CO)_6}$, 13007-92-6; $\mathrm{P(OPh)_3Cr(CO)_5}$, 18461-39-7; $\mathrm{P(OMe)_3Cr(CO)_5}$, 18461-34-2; $\mathrm{PH_3Cr(CO)_5}$, 18116-53-5; $\mathrm{PPh_3Cr(CO)_5}$, 14917-12-5; $\mathrm{AsPh_3Cr(CO)_5}$, 29742-98-1; $\mathrm{SbPh_3Cr(CO)_5}$, 29985-15-7; $\mathrm{PEt_3Cr(CO)_5}$, 21321-30-2; $\mathrm{PBu_3Cr(CO)_5}$, 18497-59-1; $\mathrm{NH_2C_6H_{11}Cr(CO)_5}$, 15134-57-3; $\mathrm{NHC_5H_{10}Cr(CO)_5}$, 15710-39-1; $\mathrm{ClCr(CO)_5^-}$, 14911-56-9; $\mathrm{Mo(CO)_6}$, 13939-06-5; $\mathrm{PCl_3Mo(CO)_5}$, 19212-18-1; $\mathrm{P(OPh)_3Mo(CO)_5}$, 15711-66-7; $\mathrm{P(OMe)_3Mo(CO)_5}$, 15631-20-6; $\mathrm{PPh_3Mo(CO)_5}$, 14971-42-7; $\mathrm{AsPh_3Mo(CO)_5}$, 19212-22-7; $\mathrm{SbPh_3Mo(CO)_5}$, 19212-21-6; $\mathrm{PBu_3Mo(CO)_5}$, 15680-62-3; $\mathrm{NHC_5H_{10}Mo(CO)_5}$, 19456-57-6; $\mathrm{NH_2C_6H_{11}Mo(CO)_5}$, 21199-57-5; $\mathrm{W(CO)_6}$, 14040-11-0; $\mathrm{P(OPh)_3W(CO)_5}$, 23306-41-4; $\mathrm{PPh_3W(CO)_5}$, 15444-65-2; $\mathrm{PBu_3W(CO)_5}$, 17000-19-0; $\mathrm{NH_2C_6H_{11}W(CO)_5}$, 16969-84-9; $\mathrm{NHC_5H_{10}W(CO)_5}$, 31082-68-5; *trans*-$\mathrm{[(PhO)_3P]_2Cr(CO)_4}$, 35039-06-6; *trans*-$\mathrm{[(MeO)_3P]_2Cr(CO)_4}$, 21370-42-3; *trans*-$\mathrm{[Bu_3P]_2Cr(CO)_4}$, 20957-93-1; *cis*-$\mathrm{[H_3P]_2Cr(CO)_4}$, 21676-58-4; *trans*-$\mathrm{[Bu_3P]_2Mo(CO)_4}$, 17650-79-8; *trans*-$\mathrm{[Bu_3P]_2W(CO)_4}$, 21246-25-3; ^{13}C, 14762-74-4; ^{31}P, 7723-14-0.

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(Cyclopentadienyl)dinitrosylcarbonylmolybdenum and -tungsten Cations and Related Complexes

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Reaction of $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ with $NOPF_6$ at −78° affords the reactive green $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ complexes in ~90% yields (M = Mo, W). These complexes undergo facile carbonyl substitution reactions with neutral (L) or anionic (X^-) Lewis bases to yield $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ and $(\eta^5\text{-}C_5H_5)M(NO)_2X$, respectively (L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$; X = Cl, Br, I). The $[(\eta^5\text{-}C_5H_5)Mo(NO)_2L]PF_6$ complexes were also prepared by direct reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$ with $NOPF_6$ and L. The carbonyl group in the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]^+$ cations is rapidly replaced by the coordinating solvents acetonitrile and acetone, in contrast to the behavior of the corresponding chromium cation and the related $[(\eta^5\text{-}C_5H_5)M'(CO)_2NO]^+$ cations (M' = Mn, Re).

Introduction

Numerous (cyclopentadienyl)dinitrosylchromium derivatives have been prepared since the initial synthesis[1] of the halides $(\eta^5\text{-}C_5H_5)Cr(NO)_2X$ (X = Cl, Br, I) almost 20 years ago. Such derivatives include the cation $[(\eta^5\text{-}C_5H_5)Cr(NO)_2CO]^+$,[2] the dimer $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$,[3] and compounds of the type $(\eta^5\text{-}C_5H_5)Cr(NO)_2Y$, which involve metathetical replacement of X by other one-electron ligands (Y = NCO,[4] CN,[5] NCSe,[5] SCF_3,[6] alkyl,[1,7] aryl[1]). In marked contrast the related chemistry of molybdenum and tungsten has remained largely unexplored.[8] This is particularly surprising in the case of molybdenum, for which there exists an extensive chemistry of monomeric and dimeric cyclopentadienyl *mono*nitrosyls.[8] In the course of work intended to expand this area we have now prepared molybdenum and tungsten derivatives of the types $(\eta^5\text{-}C_5H_5)M(NO)_2X$ (X = Cl, Br, I), $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$, and $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ (L = group 5A Lewis base), where M = Mo, W. Except for $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$,[9,10] no other (cyclopentadienyl)dinitrosylmolybdenum or -tungsten compounds were known prior to this work. Certain aspects of this work have been reported in a preliminary form.[11]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen using Schlenk-type apparatus. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were taken in capillaries sealed under nitrogen using a Thomas-Hoover melting point apparatus and are uncorrected. These data are summarized in Table I.

Materials. All solvents (reagent grade) were dried by appropriate methods and were saturated with nitrogen prior to use. Tungsten hexacarbonyl (Pressure Chemical Co.) and nitrosyl hexafluorophosphate (Ozark-Mahoning Co.) were purchased from the indicated commercial sources. Molybdenum hexacarbonyl was a generous gift from the Climax Molybdenum Co. Other chemicals were of reagent grade. $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$ was prepared by the method of Piper and Wilkinson.[1]

Spectra. Infrared spectra (Table II) were obtained on a Perkin-Elmer 180 spectrometer calibrated with carbon monoxide, polystyrene, and indene. Solution spectra were run in NaCl or KBr cells using dichloromethane as solvent. Mull spectra were recorded in Nujol between flat Irtran-2 plates. Mulls of the $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ complexes were carefully prepared in a dry nitrogen-filled glove bag.

Proton NMR spectra (Table II) were recorded at 60 MHz on a JEOL C-60-H instrument using internal TMS as reference and chloroform-d_1 or acetone-d_6 as solvents. Mass spectra were obtained on a Perkin-Elmer Hitachi RMU-5 mass spectrometer at 70 eV with a chamber temperature of 200° and a sample temperature of 100–150°.

Preparation of $(\eta^5\text{-}C_5H_5)W(CO)_2NO$. This compound was prepared by a modification of the preparation reported[1] for the molybdenum derivative. A solution of $(\eta^5\text{-}C_5H_5)W(CO)_3H$, prepared from 50.5 g (143 mmol) of $W(CO)_6$ according to the published procedure,[12] and 34.1 g (159 mmol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ("Diazald") in ether (400 ml) was refluxed for 24 hr. Filtration, followed by removal of solvent, gave an orange crystalline residue which was chromatographed on a Florisil column (6 × 25 cm) using 5:1 hexane–dichloromethane. The broad orange band was collected and concentration of this solution on the rotary evaporator afforded 37.1 g of orange crystalline $(\eta^5\text{-}C_5H_5)W(CO)_2NO$ (77% yield based upon $W(CO)_6$), identified by infrared and NMR spectroscopy.[13]

Preparation of $[(\eta^5\text{-}C_5H_5)M(NO)_2CO]PF_6$ (M = Mo, W). Solid $NOPF_6$ (5.90 g, 34.7 mmol) was added in several portions with stirring to a cooled (−78°) solution of $(\eta^5\text{-}C_5H_5)W(CO)_2NO$ (10.5 g, 31.4 mmol) in dichloromethane (70 ml) and acetonitrile (40 ml). A green precipitate immediately formed, accompanied by rapid gas evolution. The solution was stirred for an additional 30 min at −78° and then 400 ml of cold (−78°) ether was added to complete precipitation. Filtration gave $[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$ as a green powder (yield 13.9 g, 92%).

The molybdenum analog was prepared in comparable yield by a similar procedure involving $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$.

Preparation of $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ (M = Mo, W; L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$). (a) Solid $[(\eta^5\text{-}C_5H_5)W(NO)_2CO]PF_6$ (1.35 g, 2.80 mmol) and PPh_3 (0.77 g, 2.93 mmol) were heated for 1 hr in refluxing dichloromethane. The solution was then filtered, heptane was added, and the resulting mixture was slowly concentrated on the rotary evaporator without external heating. Green crystalline $[(\eta^5\text{-}C_5H_5)W(NO)_2PPh_3]PF_6$ (1.49 g, 74%) was collected by filtration.

The other $[(\eta^5\text{-}C_5H_5)M(NO)_2L]PF_6$ complexes were prepared by