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Oxygen Atom Transfer Reaction to Metal Carbonyls. Kinetics and Mechanism of CO-Substitution Reactions of $Mo(CO)_5L$ in the Presence of $(CH_3)_3NO$

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Kinetic data are reported for the reactions of $Mo(CO)_5L$ (where L[1] = $P(c\text{-}Hx)_3$, $P(n\text{-}Bu)_3$, NMe_3, py, PPh_3, $AsPh_3$, $P(OEt)_3$, or $P(OMe)_3$) with L in the presence of Me_3NO to form *cis*-$Mo(CO)_4L_2$. The rates of reactions are second order: first order in $Mo(CO)_5L$ concentration, first order in Me_3NO concentration, and zero order in L concentration. For ligand L with cone angles less than 135°, the rates of reaction increase with increasing stretching frequency of the CO bands in the IR. This supports the proposed mechanism, which involves attack by the O atom of Me_3NO on a C of a CO cis to L in $Mo(CO)_5L$. For L = PPh_3 or $AsPh_3$, the reactions are faster than expected on the basis of their ν_{CO} values, and this is discussed in terms of steric effects.

Introduction

Recently[2] we reported the results of a kinetic study for the reaction of $M(CO)_6$ (M = Cr, Mo, W) complexes with Me_3NO, in the absence (eq 1) and in the presence of another entering ligand (eq 2). It was found the rates of reaction of the metal carbonyls

$$M(CO)_6 + Me_3NO \rightarrow M(CO)_5NMe_3 + CO_2 \qquad (1)$$

$$M(CO)_6 + Me_3NO + L \rightarrow M(CO)_5L + Me_3N + CO_2 \qquad (2)$$

toward this oxygen atom transfer reagent varied in the order W > Mo $\gtrsim$ Cr. A mechanism was proposed where the rate-determining step involves an attack by Me_3NO at the C atom of CO. Support for this associative mechanism was found in earlier reports,[3] which showed that the C atoms have a partial positive charge (0.23), while the O atom[4] of Me_3NO bears a partial negative charge (−0.504). The observed reactivities of the different metal complexes were attributed both to the greater σ donicity of CO to the metal centers (W > Mo > Cr), and to the size of the metal atom (Cr < Mo $\lesssim$ W). The greater σ donation of CO makes the C atoms more susceptible to nucleophilic attack, and the larger metal atoms form less crowded (more favorable) transition states during the course of the associative substitution reactions.

An earlier investigation[5] of the reactions of $Fe(CO)_4L$ complexes with $PhCH_2MgBr$ showed that the rates of nucleophilic attack at the C atoms of CO by the benzyl nucleophile are controlled by electronic factors. The electronic character of L controls the amount of electron density transferred to the CO's by Fe → CO π back-bonding. As the amount of back-bonding increases, the electron density on the C atoms increases, and the C atoms become less susceptible to nucleophilic attack.

Unlike the $Fe(CO)_4L$ compounds, the rates of reaction of $M(CO)_5L$ (M = Cr, Mo, W) complexes with $PhCH_2MgBr$ were reported[5] to be controlled by the steric nature of L. Yet another investigation for similar reactions of $M(CO)_5L$ compounds with MeLi reported[6] that the rates of reaction showed no preference for either steric factors or electronic factors.

In this paper we report the role of electronic factors and steric factors in the reactions of $Mo(CO)_5L$ complexes with Me_3NO. We find that electronic effects at the C atoms of CO are more important than steric effects in these reactions for complexes where L has a cone angle less than 135°.

Experimental Section

Compounds and Solvents. Manipulations involving the metal carbonyls were routinely carried out under a N_2 atmosphere. The solvents dichloromethane, acetonitrile, hexane, and tetrahydrofuran were dried and purified by published[7] procedures, and these solvents were distilled under a N_2 atmosphere prior to use. The phosphorus nucleophiles were obtained from Strem Chemicals. The nucleophiles $P(c\text{-}Hx)_3$,[1] PPh_3, and $AsPh_3$ were purified by recrystallization from ethanol. The compounds $P(n\text{-}Bu)_3$, $P(OEt)_3$, and $P(OMe)_3$ were distilled over Na under a N_2 atmosphere prior to use. Pyridene (Aldrich) was distilled from BaO under a N_2 atmosphere prior to use. The oxide Me_3NO was obtained as the dihydrate (Aldrich) and was purified by sublimation.

Table I. Values of ν_{CO} for $Mo(CO)_5L$ in Hexane and Observed Rate Constants for the Reaction (Eq 3) in 1:1 (v/v) CH_2Cl_2:CH_3CN Solution at 26.0 °C

no.[a]	L	ν_{CO}, cm^{-1}	ref	k_{obsd},[b] s^{-1}
1	$P(c\text{-}Hx)_3$	2066, 1989, 1941, 1937	9a	$\sim 6 \times 10^{-6}$
2	$P(n\text{-}Bu)_3$	2070, 1943, 1938	9b	3.3×10^{-5}
3	NMe_3	2072, 1941, 1921	8	9.9×10^{-5}
4	py	2074, 1943, 1922	9b	1.53×10^{-4}
5	PPh_3	2075, 1989, 1950, 1945	9b	9.1×10^{-4}
6	$AsPh_3$	2076, 1989, 1952, 1945	9b	6.1×10^{-4}
7	$P(OEt)_3$	2080, 1995, 1966, 1952	9b	2.35×10^{-4}
8	$P(OMe)_3$	2082, 1997, 1970, 1956	9b	3.18×10^{-4}

[a] The $Mo(CO)_5L$ compound numbers as used in Figures 3 and 4. [b] Concentrations: $[Mo(CO)_5L] = 5.7 \times 10^{-3}$ M, [L] = 0.23 M, $[Me_3NO] = 0.0842$ M.

The $Mo(CO)_5L$ compounds were synthesized by a published procedure[8] from $Mo(CO)_6$ (Strem), the appropriate ligand (L) and Me_3NO. The infrared ν_{CO} bands of these complexes are contained in Table I, and these bands are identical with reported[9] values. The PCl_3 complex could not be prepared by this route due to the rapid formation of $OPCl_3$. Likewise, the $P(OPh)_3$ complex was prepared in very low yield by the above method, because $OP(OPh)_3$ was formed.

Instrumentation. Infrared spectra were recorded on a Nicolet 7199 FT-IR spectrophotometer using either a 0.1-mm CaF_2 cell or a Specac P/N 20.500 variable-temperature IR cell with 0.5-mm AgCl windows. Constant temperature was maintained by immersing a hollow copper coil into the solvent chamber of the variable-temperature IR cell. The liquid from the constant temperature bath (Neslab RTE-8) circulated through the copper coil, and the temperature of the cell was determined from a copper thermocouple attached to the interior of the cell. A Varian 400 FT-NMR instrument was used to collect ^{13}C NMR data.

Kinetic Measurements. Because of solubility problems, all kinetic reactions were carried out in 1:1 (vol/vol) CH_2Cl_2:CH_3CN solutions. Rate data for the disappearance of reactant metal complexes were obtained by monitoring spectra changes of the A_1 ν_{CO} IR band, which corresponds to the highest energy bands listed in Table I. In a typical experiment, a CH_2Cl_2 stock solution of $Mo(CO)_5L$ was syringed into a flask, and a 40-fold excess of the appropriate nucleophile (L) was syr-

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(1) Abbreviations: $P(c\text{-}Hx)_3$ = tricyclohexylphosphine, PPh_3 = triphenylphosphine, $AsPh_3$ = triphenylarsine, $P(n\text{-}Bu)_3$ = tri-*n*-butylphosphine, $P(OEt)_3$ = triethyl phosphite, $P(OMe)_3$ = trimethyl phosphite, CH_2Cl_2 = dichloromethane, CH_3CN = acetonitrile, THF = tetrahydrofuran, Me_3NO = trimethylamine oxide, py = pyridine.
(2) Shi, Y. L.; Gao, Y.-C.; Shi, Q.-Z.; Kershner, D. L.; Basolo, F. *Organometallics* **1987**, *6*, 1528–1531.
(3) Caulton, K. G.; Fenske, R. F. *Inorg. Chem.* **1968**, *7*, 1273.
(4) Nelson, S. D.; Kollman, P. A.; Trager, W. F. *J. Med. Chem.* **1973**, *16*, 1034.
(5) Darensbourg, M. Y.; Condor, H. L.; Darensbourg, D. J.; Hosday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919–5924.
(6) Dobson, G. R.; Paxson, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5925–5930.
(7) Gordon, A. J.; Ford, R. A. *The Chemists Companion*; Wiley-Interscience: New York, 1972.
(8) Koelle, U. *J. Organomet. Chem.* **1977**, *133*, 53–58.
(9) (a) Grim, S. O.; Wheatland, D. A.; McFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573–5577. (b) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959–966.

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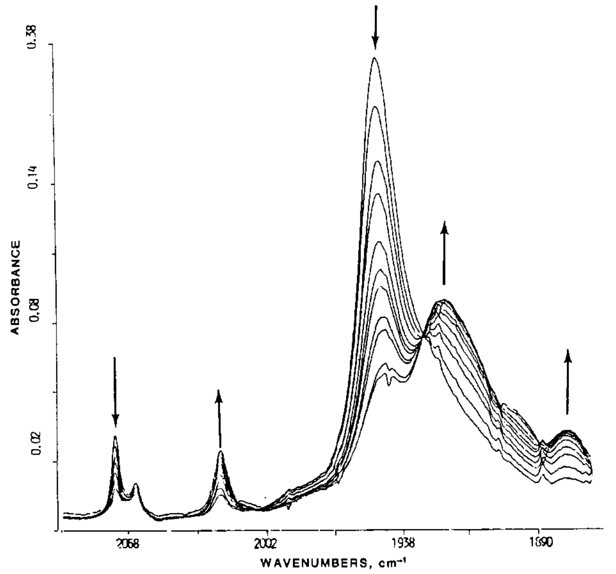

Figure 1. Infrared ν_{CO} absorbance changes with time for the reaction $Mo(CO)_5AsPh_3 + AsPh_3 + Me_3NO \rightarrow$ *cis*-$Mo(CO)_4(AsPh_3)_2 + NMe_3 + CO_2$ in 1:1 (vol/vol) $CH_2Cl_2{:}CH_3CN$ solution at 26 °C.

Table II. Values of ν_{CO} for the *cis*-$Mo(CO)_4L_2$ Products from the Reaction (Eq 3) in 1:1 (v/v) $CH_3Cl_2{:}CH_3CN$ Solution

L	ν_{CO}, cm^{-1}
P(c-Hx)	2007, 1863
P(*n*-Bu)$_3$	2011, 1917, 1890, 1868
NMe$_3$	2017, 1921, 1916, 1906
py	2034, 1922, 1918, 1910
PPh$_3$	2021, 1912, 1906
AsPh$_3$	2024, 1915
P(OEt)$_3$	2031, 1917, 1914
P(OMe)$_3$	2034, 1923, 1918

inged into the flask (neat or from a CH_3CN stock solution). Appropriate volumes of CH_3CN and CH_2Cl_2 were syringed into the flask to obtain a 1:1 (vol/vol) $CH_3CN{:}CH_2Cl_2$ solution, and a 1:1 (vol/vol) $CH_3CN{:}CH_2Cl_2$ stock solution of Me_3NO was syringed into the flask. After the flask was vigorously shaken, an aliquot was removed by syringe, the aliquot was syringed into an IR cell flushed with N_2 and sealed with rubber septa, and the resultant spectral changes were monitored.

Results

The rates of reaction (eq 3) were monitored by following changes in the IR absorption spectra with time. Spectral changes

$$Mo(CO)_5L + L + Me_3NO \rightarrow cis\text{-}Mo(CO)_4L_2 + Me_3N + CO_2 \quad (3)$$

for a typical reaction are shown in Figure 1, suggesting a good stoichiometric reaction yielding a cis bis-substituted product (Table II). In all cases, the reaction products had IR spectra in agreement with reported[10] spectra of known cis bis-substituted compounds.

Plots of $-\ln A$ vs time for the reaction (eq 3) were linear over 2–3 half-lives. A representative plot of k_{obsd} vs [Me_3NO] for the $Mo(CO)_5P(OMe)_3$ complex shows (Figure 2) a first-order dependence on [Me_3NO]. Reaction rates were independent of the concentration of $P(OMe)_3$ (Table III).

Kinetic data for the reaction (eq 3) are given in Table I, and the second-order rate constants and activation parameters are contained in Table IV.

Discussion

The reactions of $Mo(CO)_5L$ complexes with Me_3NO in the presence of excess L (eq 3) yield cis-$Mo(CO)_4L_2$, as established by their IR spectra in the ν_{CO} region (Table II). At lower concentrations of L, $Mo(CO)_4(L)(NMe_3)$ compounds are also formed as minor products.

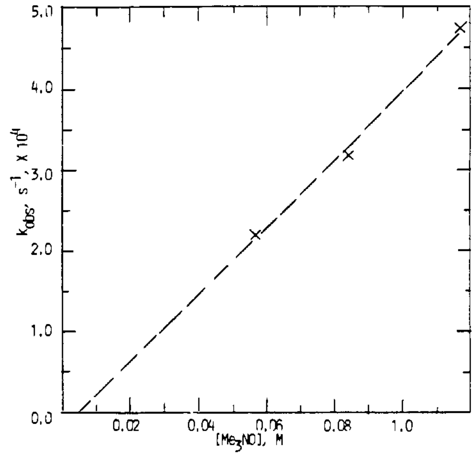

Figure 2. Plot of k_{obsd} vs Me_3NO concentration for the reaction $M(CO)_5P(OMe)_3 + P(OMe)_3 + Me_3NO \rightarrow$ *cis*-$Mo(CO)_4[P(OMe)_3]_2 + NMe_3 + CO_2$ in 1:1 (vol/vol) $CH_2Cl_2{:}CH_3CN$ solution at 26 °C.

Table III. Observed Rate Constants, k_{obsd}, for the Reaction (Eq 3) at Different Concentrations of $P(OMe)_3$ and of Me_3NO in 1:1 (v/v) $CH_2Cl_2{:}CH_3CN$ Solution at 26.0 °C

[P(OMe)$_3$], M	[Me$_3$NO], M	k_{obsd}, s^{-1}
0.113	0.0185	8.04×10^{-5} [a]
0.240	0.0185	7.00×10^{-5} [a]
0.480	0.0185	6.59×10^{-5} [a]
0.240	0.0576	2.19×10^{-4} [b]
0.240	0.0842	3.18×10^{-4} [b]
0.240	0.117	4.73×10^{-4} [b]

[a] [$Mo(CO)_5P(OMe)_3$] = 5.7×10^{-3} M. [b] [$Mo(CO)_5P(OMe)_3$] = 9.6×10^{-4} M.

Table IV. Second-Order Constants and Activation Parameters for the Reactions (Eq 3) of $Mo(CO)_5L$ Complexes in 1:1 (v/v) $CH_2Cl_2{:}CH_3CN$ Solution

L	*T*, °C	*k*,[a] M^{-1} s^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/(deg mol)
P(OMe)$_3$	9.0	7.00×10^{-6}	20.3 ± 1.9[b]	−4.9 ± 6.5
	21.0	4.07×10^{-5}		
	34.0	1.46×10^{-4}		
PPh$_3$	10.0	1.77×10^{-4}	15.3 ± 1.1	−16.4 ± 3.6
	26.0	9.13×10^{-4}		
	36.0	1.87×10^{-3}		

[a] Concentrations: [$Mo(CO)_5L$] $\simeq 5.7 \times 10^{-3}$, [L] = 0.230 M, [$Me_3NO$] = 0.0842 M. [b] Calculated errors of two standard deviations.

Results of our kinetic study show that the reactions (eq 3) obey a second-order rate law, first order in metal complex concentration, first order in Me_3NO concentration, and zero order in concentration of L (Table III). Activation parameters for these reactions (Table IV) are typical of an associative mechanism for ligand substitution. The low values of $\Delta H^\ddagger$ and the negative values of $\Delta S^\ddagger$ suggest a process in which both bond making and bond breaking contribute to the activation energy for reaction, whereas dissociative mechanism would have large values of $\Delta H^\ddagger$ and positive values of $\Delta S^\ddagger$.

Like some previous investigators,[5,11] we find that the degree of M → CO π back-bonding in $Mo(CO)_5L$ complexes influences the reactivity of the C atoms of CO toward nucleophilic attack. The relative degree of M → CO π back-bonding in analogous metal carbonyls is indicated by the frequencies of their IR ν_{CO} bands. As electron density is transferred to the CO π^* orbitals by π back-bonding, the ν_{CO} bands decrease in energy. This increased M → CO π back-bonding increases the electron density

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(10) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702–711. Chatt, J.; Leigh, G. J.; Thankarajan, N. *J. Organomet. Chem.* **1971**, *29*, 105–110. Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, *47*, 2996–3021. Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680–2682.

(11) Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *8*, 1754–1758.

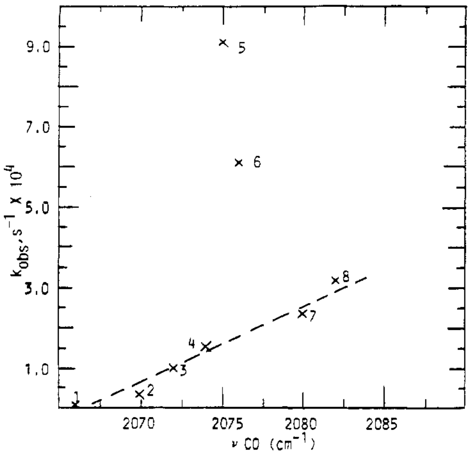
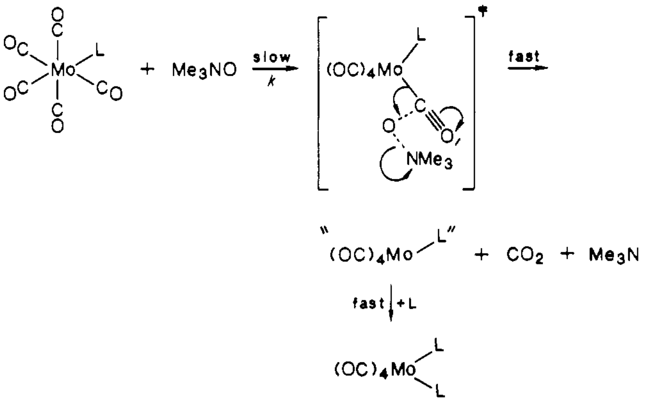


Figure 3. Plot of k_{obsd} values for the reaction (eq 3) vs the A_1 ν_{CO} bands of the $Mo(CO)_5L$ compounds. See Table I for compound numbers.

Scheme I



on the C atoms and renders them less susceptible to nucleophilic attack. That such a correlation exists between reactivity and ν_{CO} is shown (Figure 3) by a plot of k_{obsd} values vs. the highest energy ν_{CO} bands in Table I. Except for PPh_3 and for $AsPh_3$ complexes (vide infra), a general correlation factor of 0.98 is obtained between the values of ν_{CO} and the rates of reaction. A similar plot using the CO stretching force constants (F_{CO}) is not reported, because F_{CO} values are not known for all of the compounds studied.

The steric properties of L appear to be less important than its electronic character. No correlation is seen between the observed reaction rates and the cone angles[12] of L. This is in contrast to the steric dependence for reactions between $Mo(CO)_5L$ and $C_6H_5CH_2MgBr$.[5] This electronic control of reactions of $Mo(CO)_5L$ with Me_3NO compared with steric control for reactions with $C_6H_5CH_2MgBr$ can perhaps be attributed to the smaller size of Me_3NO compared to $C_6H_5CH_2MgBr$. That rates of substitution reactions of $Fe(CO)_4L$ complexes are also more sensitive to electronic effects than to steric effects[5] may be due to the lower coordination number of the Fe complex compared to the Mo complex, which means there is less of a steric requirement for the Fe system in an associative pathway.

The overall reaction (eq 3) is believed to take place by the rate-determining attack of Me_3NO on a C atom of a CO cis to L in $Mo(CO)_5L$, followed by the rapid loss of CO_2 and the uptake of L to form cis-$Mo(CO)_4L_2$ (Scheme I). This mechanism is in accord with the previously proposed[2] mechanism for the corresponding reactions of $M(CO)_6$. That Me_3NO attacks one of the four COs cis to L in $Mo(CO)_5L$ seems plausible both on the basis of theory and of experiment.[5,6,11] Theory[13] tells us that the CO trans to L in $Mo(CO)_5L$ competes directly with L for π back-bonding. Since L is not a good π acid relative to CO, it follows that the CO trans to L will be more strongly π bonded to Mo than are the four CO's trans to another CO (and cis to L). Thus, the greater electron density on the CO trans to L will retard its attack by the nucleophile Me_3NO relative to the more positive CO's cis to L in $Mo(CO)_5L$.

Table V. ^{13}C NMR Chemical Shifts[a] in $CDCl_3$ and Cone Angles[b] of L for $Mo(CO)_5L$ Complexes

no.	L	$\delta(^{13}CO_{cis})$	$\delta(^{13}CO_{trans})$	θ, deg
1	P(c-Hx)	207.4	210.9	170
2	$P(n\text{-}Bu)_3$	206.3	209.7	132
3	NMe_3	203.7[c]	213.8[c]	114[d]
4	py	204.2[c]	214.3[c]	105[e]
5	PPh_3	205.7	210.2	145
6	$AsPh_3$	205.3	210.3	~145[f]
7	$P(OEt)_3$	204.7	208.6	109
8	$P(OMe)_3$	204.3	208.2	107

[a] Reference 16c. [b] Reference 12. [c] This work. [d] Calculated from the X-ray structure of Me_3NBF_3 given in ref 17. [e] Value given for C_6H_5 in ref 12. [f] Value given for PPh_3 in ref 12.

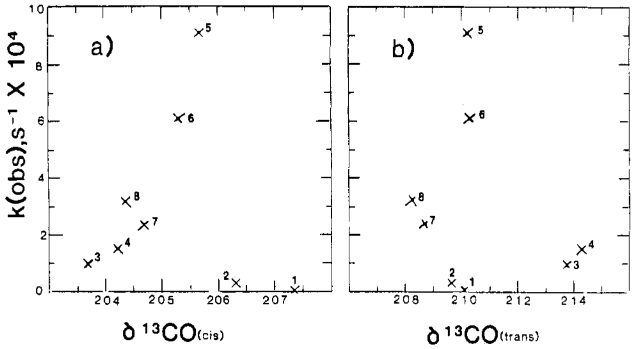


Figure 4. Observed rate constants for the reaction (eq 3) vs $\delta(^{13}CO)$ values: (a) cis; (b) trans. See Table I for compound numbers.

Experiment[5,6,11] also suggests nucleophilic attack on a CO cis to L in $Mo(CO)_5L$. Reactions of $M(CO)_5L$ with nucleophiles that do not result in M–C bond cleavage shows the nucleophile on a carbonyl cis to L. This has been observed for reactions of $M(CO)_5L$ with CH_3Li[6] to give *cis*-$[Mn(CO)_4L(C(=O)CH_3)]^-$, with $C_6H_5CH_2MgBr$[5] to give *cis*-$[M(CO)_4L(C(=O)CH_2C_6H_5)]^-$, and with RNH_2[11] to give *cis*-$[M(CO)_4L(C(=O)NHR)]^-$.

Finally, it should be mentioned that the formation of a *cis*-$M(CO)_4L_2$ product is no assurance this results from attack on a CO cis to L in $Mo(CO)_5L$. The five-coordinate active intermediate in Scheme I may have a trigonal-bipyramid structure (instead of the tetragonal pyramid shown), which could then readily generate either *cis*- or *trans*-$Mo(CO)_4L_2$ products. Alternatively, if the five-coordinate active intermediate is fluxional on a time scale shorter than that of L addition it follows that either cis or trans products could result. That the reactions (eq 3) give exclusively cis products is in accord with the Atwood and Brown[14] cis effect and with low-temperature matrix studies[15] which suggest that transition states or active intermediates of the type $M(CO)_4L$ direct entering ligands into a cis position.

Further support for a cis attack is found by comparing the observed rate constants of the reaction (eq 3) with the $\delta(^{13}CO)$ NMR chemical shifts of $Mo(CO)_5L$. As the L group becomes a stronger σ donor or a poorer π acceptor, the $\delta(^{13}CO)$ values (Table V) are shifted to lower field. This is attributed[16] to paramagnetic effects caused by the increase in the M → CO π back-bonding interaction. Therefore, as more electron density is returned to the CO ligand by π back-bonding the $\delta(^{13}CO)$ values

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[12] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

[13] Basolo, F.; Pearson, R. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967.

[14] Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160–3166.

[15] Dobson, G. R. *Acc. Chem. Res.* **1976**, *9*, 300–306, and references therein.

[16] (a) Braterman, P. S.; Milne, D. W.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Dalton Trans.* **1973**, 1027–1031. (b) Bodner, G. M. *Inorg. Chem.* **1975**, *14*, 2694–2698. (c) Bodner, G. M.; May. M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951–1958.

[17] Geller, S.; Hoard, J. L. *Acta Crystallogr.* **1951**, *4*, 399–405.

increase. Since the $\delta(^{13}\mathrm{CO}_{\mathrm{cis}})$ value for a given complex is less than the $\delta(^{13}\mathrm{CO}_{\mathrm{trans}})$ value, the C atoms of the cis CO's are expected to be more susceptible to nucleophilic attack than is the C atom of the trans CO. Figure 4 shows plots of k_{obsd} vs $\delta(^{13}\mathrm{CO})$ for the reaction (eq 3). There is no correlation with $\delta(^{13}\mathrm{CO}_{\mathrm{trans}})$, and the correlation with $\delta(^{13}\mathrm{CO}_{\mathrm{cis}})$ is not nearly as good as was obtained for a similar plot using the ν_{CO} values (Figure 3). Yet the $\delta(^{13}\mathrm{CO})$ NMR results qualitatively support attack on a CO cis to L over the trans CO. Again, the PPh_3 and $AsPh_3$ derivatives react faster than expected on the basis of their $\delta(^{13}\mathrm{CO}_{\mathrm{cis}})$ values (vide infra).

Since the rates of reaction of the PPh_3 and the $AsPh_3$ derivatives of $Mo(CO)_5L$ are much faster than expected on the basis of their A_1 ν_{CO} bands and their $\delta(^{13}\mathrm{CO}_{\mathrm{cis}})$ values, this suggests their rates of reaction, unlike the other ligands studied, are not controlled by electronic effects. One is then left with steric factors, and clearly the cone angles (Table V) of PPh_3 and of $AsPh_3$ are larger than for the other ligands used except for $P(c\text{-}Hx)_3$. This greater bulk of the PPh_3 or $AsPh_3$ ligands may impose an enhanced cis effect on adjacent COs, rendering weaker M–C bonds both in the ground and in the transition states for reaction. Such a bond-weakening effect is supported by the small value of $\Delta H^{\ddagger}$ of reaction for the reaction of $Mo(CO)_5PPh_3$ compared with the reaction of $Mo(CO)_5P(OMe)_3$ (Table IV). Also the PPh_3 system has a more negative $\Delta S^{\ddagger}$ than does the ($P(OMe)_3$ system, indicative of more steric strain for reaction. One drawback to this discussion is that the largest ligand $P(c\text{-}Hx)_3$ (Table V) system is then expected to be the fastest to react, but it is found to be the slowest to react. It may be that this ligand, notorious for its huge size, has retarded an associative pathway for reaction sufficiently to just inadvertently give it a rate that seems to correlate the ν_{CO} values (Figure 3). Clearly more detailed study and comprehension of steric and electronic factors influencing transition-metal–phosphorus(III) bonding are needed if we are to better understand experimental facts of the type reported here. For example, QALE[18] (quantitative analysis of ligand effects) is a recent attempt to quantify the heats of reaction of phosphorus ligands with organometallic compounds in terms of σ-electronic, π-electronic, and steric properties of the ligands.

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Registry No. $Mo(CO)_5P(c\text{-}hx)_3$, 15603-94-8; $Mo(CO)_5P(n\text{-}Bu)_3$, 15680-62-3; $Mo(CO)_5NMe_3$, 15152-84-8; $Mo(CO)_5py$, 14324-76-6; $Mo(CO)_5PPh_3$, 14971-42-7; $Mo(CO)_5AsPh_3$, 19212-22-7; $Mo(CO)_5P(OEt)_3$, 15603-75-5; $Mo(CO)_5P(OMe)_3$, 15631-20-6; $P(c\text{-}hx)_3$, 2622-14-2; $P(n\text{-}Bu)_3$, 998-40-3; NMe_3, 75-50-3; py, 110-86-1; PPh_3, 603-35-0; $AsPh_3$, 603-32-7; $P(OEt)_3$, 122-52-1; $P(OMe)_3$, 121-45-9; Me_3NO, 1184-78-7.

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(18) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650–658.

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Destabilizing dπ–pπ Orbital Interactions and the Alkylation Reactions of Iron(II)–Thiolate Complexes[1]

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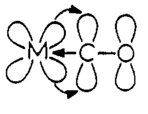
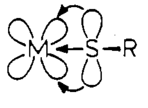
For $CpFe(CO)_2SR$ (**1**) (R = C_6H_4-*p*-Z; Z = OMe, H, Cl, CF_3, NO_2) the π-type interaction between formally occupied metal d orbitals and the sulfur lone pair that is principally 3p in character has been modeled with Fenske–Hall molecular orbital calculations and experimentally investigated by gas-phase photoelectron spectroscopy. A calculation for **1** (R = H) predicts that the highest occupied molecular orbital (HOMO) is metal–sulfur antibonding and largely sulfur in character. The observed HOMO ionization energies of **1** correlate with several chemical properties, including the rate of reaction of the thiolate ligand with alkyl halides. Solvent and substituent effects on the reaction rate favor a mechanism involving nucleophilic displacement of the halide by the coordinated thiolate ligand. The nucleophilicity of the coordinated thiolate ligand of **1** is related to the metal–sulfur dπ–pπ antibonding interactions.

Introduction

The Dewar–Chatt–Duncanson model[2] has proven useful for rationalizing the stability of transition-metal complexes of π-acceptor ligands (e.g. carbon monoxide) and for explaining the



a



b

reactivity of such ligands (a). For example, π-acceptor ligands bound to transition metals in high oxidation states are generally more susceptible to nucleophilic attack than are π-acceptor ligands bound to low-valent, electron-rich metals.[3] However, π-donor ligands have received much less attention. Thiolate ligands (b) possess a σ-donor orbital and a lone-pair orbital that is principally sulfur 3p in character. The latter orbital has the correct symmetry for π interactions with metal d orbitals.[4] If the metal d orbitals are formally occupied, the thiolate ligand may effectively serve as a four electron donor (2σ + 2π). Recently, the stabilities of a highly oxidized transition-metal–carbonyl complex, $Ru^{IV}(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4(CO)$,[5] and of a coordinatively unsaturated

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(2) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Dewar, M. J. S. *Annu. Rep. Prog. Chem.* **1951**, *48*, 112. (c) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2339.

(3) (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 298. (b) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985; p 313. (c) Wong, D. K.; Madhavarac, M.; Marten, D. F.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2823.

(4) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Kamata, M.; Hirotsu, K.; Higuchi, T.; Tasumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772. (c) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kito, M.; Tatsumi, K.; Hoffmann, R. *Organometallics* **1982**, *1*, 227. (d) Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730.

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