the result is an intermediate that is either identical with the original monoanion or to an open form of the original monoanion. The latter is the intermediate that is postulated in Scheme I, and the two schemes then become very similar. These combined mechanistic possibilities are shown in Scheme III. Equation 1 is

$$\tau^{-1} = (k_2 + k_1[\mathrm{OH^-}])(1 + 1/K[\mathrm{OH^-}]) \qquad (1)$$

derived[1,2] from Scheme III and the line in the figure is a plot of eq 1 with the values $k_1 = 4.1 \times 10^5$ $\mathrm{M^{-1}\,s^{-1}}$, $k_2 = 7.4 \times 10^3$ $\mathrm{s^{-1}}$, and $K = 32.0$ $\mathrm{M^{-1}}$. The value of the equilibrium constant K = [dianion]/[monoanion][OH$^-$] = 32.0 ± 2 $\mathrm{M^{-1}}$ was determined separately by spectrophotometric measurements.[6]

Scheme III is identical with Scheme I except that an additional route to the open form of the monoanion through the conjugate acid is included. Formation of the open form can occur either by direct opening or through the conjugate acid. In order to explain the dependence of reciprocal relaxation time on hydroxide ion concentration and derive eq 1, it is necessary to specify that the upper route in Scheme III occurs by direct attack on the hydrogen-bonded proton and does not proceed through an open form of the monoanion.[7] In this way Scheme III differs from Scheme II, and the data for bis(phenylazo)resorcinol monoanions therefore provide evidence that direct attack by base on the hydrogen-bonded proton is occurring.

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Registry No. 1, 84174-81-2; **2**, 84237-51-4.

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(6) For **1** half-dissociation occurs at [OH$^-$] = 0.0002, and kinetic data were restricted to the range [OH$^-$] = 0.0005–0.004 M. A linear dependence of τ^{-1} on [OH$^-$] was observed, but the gradient and intercept were not compatible with the separately measured equilibrium constant. The data were fitted to eq 1, and it was predicted that the minimum was below the lowest accessible hydroxide ion concentration.

(7) If the upper route in Scheme III occurred through the open form of the monoanion, two of the routes in Scheme III would become identical. The expression derived for the dependence of τ^{-1} on [OH$^-$] from the resulting scheme is not compatible with a minimum in τ^{-1}.

Phosphorus Donor–Crown Ether Hybrid Ligands as a Route to CO Activation: Phosphorus Substituent Effects and the Importance of Strong Cation Binding

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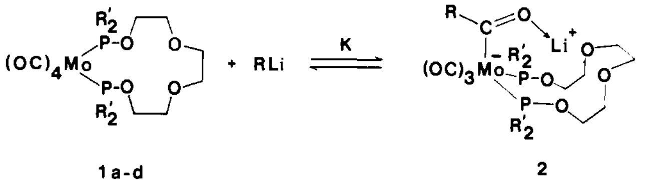
We have recently shown that "selective cation binding by the product molecule" may provide additional stabilization with respect to the addition of a nucleophile to a coordinated carbon monoxide[1] (e.g., reaction 1). In this communication we present data that clearly emphasize the importance of strong Li$^+$ cation binding in promoting nucleophilic addition to coordinated CO.



1a-d **2**

reaction 1

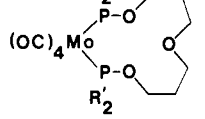
(a) R$'$ = Ph
(b) R$'_2$ = $-\mathrm{OCH_2CH_2O}-$
(c) R$'_2$ = 1,2-$\mathrm{OC_6H_4O}-$
(d) R$'_2$ = $-\mathrm{N(Me)C_2H_4(Me)N}-$

Table I. Infrared Data (ν_{CO} Region) and Selected Equilibrium Constant Data {K = [Mo(CO)$_3$(PhCOLi)P$_2$]/([Mo(CO)$_4$P$_2$][RLi])} As Determined by Infrared Spectroscopy (ν_{CO} Region) for Reaction 1 in THF Solutions (7.25 × 10^{-3} M in Mo) at 25 °C

complex		equilibrium const,[a] L mol^{-1}	
	ν_{CO}, cm^{-1}	$K(\mathrm{PhLi})_{\mathrm{THF}}$	$K(\mathrm{MeLi})_{\mathrm{THF}}$
1a	2024, 1928, 1909, 1899	2700	44000
1b	2039, 1947, 1928	<5	<5
1c	2052, 1966, 1948	<1	<5
1d	2021, 1917, 1907, 1883	3000	100000
3a	2024, 1923, 1910, 1899	500	6700
3b	2041, 1952, 1928	<50	<50
3c	2075, 1990, 1970, 1950	<5	<50
3d	2020, 1918, 1906, 1886	2900	11000

[a] Errors in individual K value vary from ±40% to ±15% depending on the magnitude of K (largest and smallest values have higher percent errors).

Replacing the phenyl substituents on the phosphorus atoms in **1a** with more electron-withdrawing substituents could have two *competing* effects that would influence the magnitude of the equilibrium constant for reaction 1: (i) It would make the coordinated CO in **1** more susceptible to nucleophilic attack (i.e., decrease the electron density on the CO carbon as indicated by slightly higher ν_{CO}'s, and/or (ii) it would result in the product **2** being a poorer ligand for Li$^+$ by decreasing the basicity of the "P–O donor oxygen" (i.e., increased oxygen to phosphorus π-dative bonding). To determine which of these effects is the more important, we have synthesized the tetracarbonyl phosphite–crown ether molybdenum complexes **1b,c** and **3b,c** via previously reported methods.[1,2] Equilibrium constant data for the reaction of these compounds with organolithium reagents (i.e., K, reaction 1) are given in Table I together with those for their diphenylphosphinite analogues **1a** and **3a**. The data indicate that the phosphite systems do not favor nucleophilic addition to a coordinated CO owing to the reduced basicity of the P–O donor oxygen, which makes the products of nucleophilic addition (e.g., **2b,c**) poorer ligands for Li$^+$ as compared to the diphenylphosphinite analogues (e.g., **2a**). Replacement of two of the phosphite oxygens with dialkylamino groups, as in complexes **1d** and **3d**, should lead to an increase in the basicity of the remaining oxygen (NB strong nitrogen to phosphorus π-dative bonding[3]) and hence make **2d** thermodynamically more favorable owing to the stronger Li$^+$ binding by this molecule. The equilibrium constant data (table) indicate that this is so. (N.B. For **1a–d** and **3a–d** it is the complexes with the *lowest* ν_{CO}'s that are most susceptible to nucleophilic addition to a coordinated CO.)



3 a-d

That "strong Li$^+$ binding by the product molecule" is a dominant feature in determining the extent of nucleophilic addition to a coordinated CO in *cis*-(OC)$_4$M(PR$_3$)$_2$ complexes is also illustrated by a study of the molecules **4** and **5**. Complex **4** (Scheme I) is totally unreactive with respect to RLi addition. In contrast **5** reacts sequentially with 2 equiv of RLi in THF to give the highly reactive dilithium salt **6** (may be isolated as a yellow solid). Addition of a third equivalent of RLi results in an orange-red solution, and IR and ^{13}C NMR data are consistent with the formation of the acylate product **7**.[4] Addition of 1 equiv of

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(1) Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941.

(2) Satisfactory infrared and ^{1}H, ^{13}C, and ^{31}P NMR spectra and elemental analyses have been obtained for all the new *cis*-tetracarbonyl complexes reported in this communication.

(3) Grec, D.; Hubert-Pfalzgrat, L. G.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1980**, *102*, 7133 and references therein.

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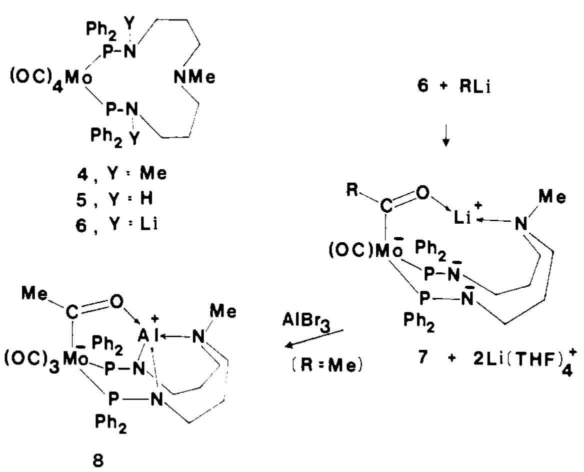
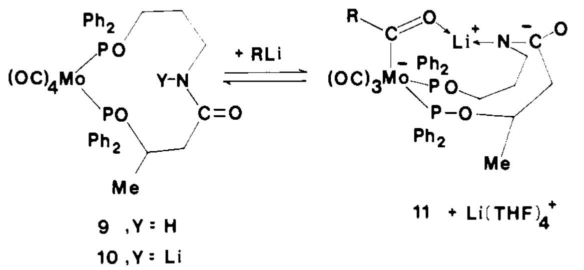
Scheme I



$AlBr_3$ to a solution of **7** (R = CH_3) gives **8** as an isolable orange, crystalline solid.[5] Solution IR studies indicate that the molecules *cis*-$(OC)_4Mo[Ph_2PNH(CH_2)_4NHPPh_2]$, *cis*-$(OC)_4Mo(Ph_2PNH_2)_2$,[6] and *cis*-$\{(OC)_4Mo[(Ph_2PO)_2H]\}Et_3NH$[6] likewise react sequentially with 3RLi to give acylate type products similar to **7**.[7]

A third example of strong Li^+ binding favoring acylate-type products involves RLi reactions with complex **9**, containing an amide function in the pseudo crown ether ring (ν_{NH} 3375, ν_{CO}(amide) 1676 cm^{-1}). Addition of 1 equiv of RLi to **9** gives the lithium amidate **10**, which can be isolated as a highly reactive yellow solid (no ν_{NH}, ν_{CO}(amidate) 1583 cm^{-1}). Addition of excess RLi to **10** gives the benzoylate/acylate products **11**.[8]



The above results indicate that the important feature to be considered when varying P-donor crown ether ligand substituents is *the effect these changes have on Li⁺ binding by the product molecule* with strong Li^+ binding favoring nucleophilic addition to a coordinated CO. The effect(s) that these changes may have on the CO electron distribution in the starting tetracarbonyl is of secondary importance.

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(4) E.g., spectroscopic data for **7** (R = Me): ν_{CO} 1905 (s), 1815 (s), 1725 (s, br) cm^{-1}; ^{31}P NMR (THF) δ 75.8; ^{13}C NMR δ 342.8 (MeCO, 1:2:1, t, $J_{^{31}P-^{13}C}$ - 15 Hz.

(5) Anal. Calcd for $C_{36}H_{38}AlMoN_3O_4P_2$ (**8**) C, 56.8; H, 5.0; N, 5.5; Al, 3.5. Found: C, 56.5; H, 5.2; N, 5.3; Al, 3.3. The postulated structure for **8** is similar to the dimethylamidate derivative $[(OC)_4Fe(Me_2NCO)Al(NMe_2)_2]_2$ derived from the reaction of $Fe(CO)_5$ with $Al_2(NMe_2)_6$: Petz, W.; Schmid, G. *Angew Chem., Int. Ed. Engl.* **1972**, *11*, 934.

(6) Gray, G. M.; Kraihanzel, C. S. *J. Organomet. Chem.* **1978**, *146*, 23. Reference 6 reports that the complex *cis*-$(OC)_4Mo(PPh_2NH_2)_2$ reacts sequentially with RLi to give the dilithium salt *cis*-$(OC)_4Mo(PPh_2NHLi)_2$ as an insoluble yellow solid. Further reaction with RLi was reported to give an orange-red solution, but the structure of this solution species was not elucidated.

(7) A qualitative order for the stability of the acylate/benzoylate products obtained from reaction of RLi with the following: **5** > *cis*-$(OC)_4Mo[Ph_2PNH(CH_2)_4NHPPh_2]$ ~ *cis*-$(OC)_4Mo(PPh_2NH_2)_2$ > *cis*-$(OC)_4Mo[(Ph_2PO)_2H]Et_3NH$. This order reflects a decrease in Li^+ binding by the product molecule.

(8) E.g., **11** (R = Ph) may be isolated as a highly reactive orange oil, ν_{CO} 1933 s, 1855, 1831 cm^{-1}. Reaction of **11** with alcohols or water regenerates the starting tetracarbonyl **9**.

Low-Temperature Photochemistry of $Fe(CO)_4$(ethylene) and $Fe(CO)_4$(propylene). Spectroscopic Observation of Catalytically Significant Intermediates

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We report the low-temperature photochemistry of $Fe(CO)_4$(olefin) (olefin = ethylene, propylene, 1-pentene, 3,3-dimethyl-1-pentene, 1,4-pentadiene) and the IR spectroscopic characterization of several intermediates involved in the $Fe(CO)_5$-photocatalyzed isomerization of alkenes. There are reports of extraordinary catalytic activity for the light-generated catalyst derived from $Fe(CO)_5$ in the presence of 1-pentene,[1,2] and many papers document[3] the thermal and photoinduced catalytic reactions in this system. While a $HFe(CO)_3(\pi\text{-allyl})$ intermediate has been invoked to account for the alkene isomerization,[3g-i] the only Fe species observed under (photo)catalysis conditions is $Fe(CO)_4$(alkene).[3a,4] The $Fe(CO)_4$(alkene) alone is not sufficiently thermally active to account for the high activity found upon photoactivation of $Fe(CO)_5$.

It has been reported[5] that $Fe(CO)_4(C_2H_4)$ undergoes loss of CO upon irradiation in a rigid Ar matrix at low temperature as detected by IR spectroscopy (eq 1). With this result in hand we

$$Fe(CO)_4(C_2H_4) \xrightarrow{h\nu} Fe(CO)_3(C_2H_4) + CO \qquad (1)$$

undertook a study of the reactivity of such species for alkenes having allylic hydrogens. Figure 1 shows a comparison of the IR spectral changes accompanying irradiation of matrix-isolated $Fe(CO)_4(C_2H_4)$ and $Fe(CO)_4(C_3H_6)$ in alkane at 77 K.[6] The spectral changes for the C_2H_4 complex are nearly identical with those found in an Ar matrix[5] and show a feature attributable to the photoejected CO (2132 cm^{-1}) and three bands associated with the 16-electron $Fe(CO)_3(C_2H_4)$ (Table I). In contrast, the spectral changes for $Fe(CO)_4(C_3H_6)$ are consistent with a different product that we suggest is $HFe(CO)_3(\eta^3\text{-}C_3H_5)$. The infrared band pattern is similar to that for $BrFe(CO)_3(\eta_3\text{-}C_3H_5)$.[7] The light-induced loss of CO from the propylene complex is evident in that there is a free CO band at 2132 cm^{-1}, but the three-band

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(1) Mitchener, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 975.

(2) (a) Chase, D. B.; Weigert, F. J. *J. Am. Chem. Soc.* **1981**, *103*, 977. (b) Whetten, R. L.; Fu, K.-J.; Cerant, E. R. *Ibid.* **1982**, *104*, 4270.

(3) (a) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551; *J. Organomet. Chem.* **1977**, *128*, 345. (b) Asinger, F. Y.; Fell, B.; Schrage, K. *Chem. Ber.* **1965**, *98*, 372, 381. (c) Asinger, F.; Fell, B.; Collin, G. *Ibid.*, **1963**, *96*, 716. (d) Carr, M. D.; kane, V. V.; Whiting, M. C. *Proc. R. Chem. Soc. London* **1964**, 408. (e) Howard, J. F.; Chalk, A. J. *Org. Synth. Met. Carbonyls* **1977**, *2*, 680–694. (f) Frankel, E. N.; Emken, E. A. Peters, H. M.; Davison, V. L.; Butterfield, R. O. *J. Org. Chem.* **1964**, *29*, 3292, 3620. (g) Casey, C. P.; Cry, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248. (h) Cowherd, F. G.; von Rosenberg, J. L. *Ibid.* **1969**, *91*, 2157. (i) Barborak, J. C.; Dasher, L. W.; McPhail, A. T.; Nichols, J. B., Oman, K. D. *Inorg. Chem.* **1978**, *17*, 2936.

(4) (a) We note the report of the very labile $Fe(CO)_3(\eta^2\text{-methylacrylate})_2$ formed photochemically at low temperature (−30 °C): Grevels, F.-W.; Schulz, D.; Koerner von Gustorf, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 534. (b) Further, we note the postulate of $HFe(CO)_3(\eta^3\text{-}C_3H_5)$ as an intermediate in the formation of $Fe(CO)_3(\eta^3\text{-}C_3H_5)$ upon photolysis of $Fe(CO)_5$ in the presence of C_3H_6: Krusic, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2131.

(5) Ellerhorst, G.; Gerhartz, W.; Grevels, F.-W. *Inorg. Chem.* **1980**, *19*, 67.

(6) Low-temperature irradiations were carried out with olefin-free methylcyclohexane or 3-methylpentane as the matrix material. $Fe(CO)_4$(olefin) can be prepared in situ by irradiation of $Fe(CO)_5$ in the presence of olefin.[3a] This concentration of $Fe(CO)_4$(olefin) was <10^{-2} M to avoid complications due to lack of site isolation. For olefin = C_2H_4 or C_3H_6 the olefin can be purged from the solution by using an Ar stream to completely remove uncomplexed olefin. For these and other olefins the concentration of olefin was varied to determine the ability to form multiple-substitution products. The irradiation source was a Pyrex-filtered 200W high-pressure Hg lamp. Spectral changes were monitored by using a Nicolet 7199 FT IR employing a variable-temperature cell that serves as the reaction vessel. Full details will be given in the full paper.

(7) An IR of a sample prepared by the literature method was recorded in alkane solution: Mudoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1963**, *45*, 1927.

0002-7863/83/1505-1065$01.50/0