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Communications

Frontier Orbital Control of Ligand Addition to $Mo(CO)_2(S_2CNR_2)_2$

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Summary: The moderate electrophilicity of $Mo(CO)_2(S_2CNR_2)_2$ (**1**), a 16-electron complex, has been established by measuring equilibrium constants for a series of ligand addition reactions. Initial ligand addition opposite to the carbonyl ligands in **1** is predicted by molecular orbital theory, and the structure of a tetrahydrothiophene adduct of **1** is in accord with this frontier orbital hypothesis.

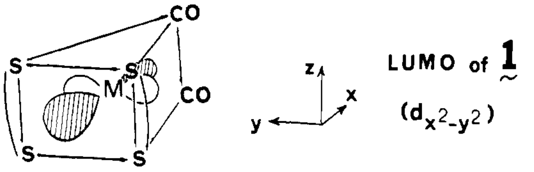
Only rarely have the implications of frontier orbital theory[1] for organometallic reactions[2] been confirmed by structurally characterizing a series of compounds representative of a reaction coordinate.[3] Reaction 1 is facile

$$\underset{2}{M(CO)_3(S_2CNR_2)_2} + L \rightleftharpoons \underset{3}{M(CO)_2L(S_2CNR_2)_2} + CO(g) \tag{1}$$

for numerous ligands L (M = Mo, W).[4] Unsaturated $M(CO)_2(S_2CNR_2)_2$ complexes (**1**) have been isolated (eq 2),[5] and an unusual trigonal-prismatic structure has been reported for **1b** (M = Mo; R = *i*-Pr).[6] A molecular orbital

$$\underset{2}{M(CO)_3(S_2CNR_2)_2} \rightleftharpoons \underset{1}{M(CO)_2(S_2CNR_2)_2} + CO(g) \tag{2}$$

rationale for the properties of 1 has been published.[7] Ligand attack at the LUMO of 1, localized in the open cavity defined by the 135° dihedral angle between the two chelating ligands, would be predicted by frontier orbital theory.



The coordination geometries of **2a** (M = W; R = Et)[8] and **3a** (M = W; R = Et; L = PPh_3)[4c] are related by a simple L for CO substitution. The structural feature most germane to the reaction coordinate for eq 1 is the mutually *cis*-$ML(CO)_2$ fragment for both L = CO and PPh_3. This ground-state geometry does not preclude frontier orbital control during the initial stages of addition reactions of **1a** since intramolecular rearrangements, common for seven-coordinate complexes, could convert any initially formed isomer to the thermodynamic product. Note that in 1 the methylene chloride of solvation caps the trigonal prism with one chloride trans to both carbonyls, 4.3 Å from the metal atom, and that a dimeric hydrazine adduct has been characterized with unusually long Mo–N bonds (2.40 Å)[9] directed into the LUMO of the parent $M(CO)_2(S_2CNR_2)_2$ fragments.

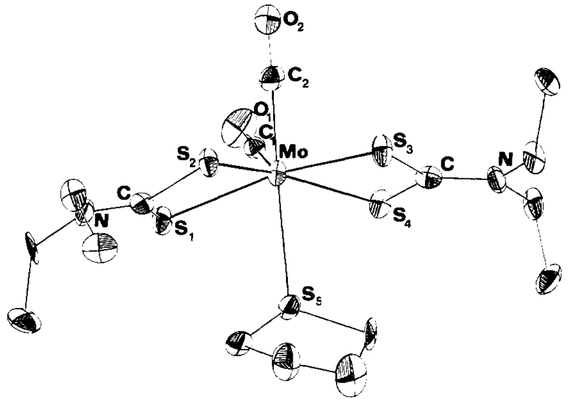
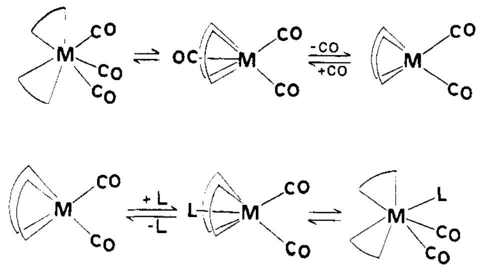


Figure 1. An ORTEP view of $Mo(CO)_2(tht)(S_2CNEt_2)_2$ showing the atomic labeling scheme.

Scheme I



The properties of 1 presented a unique opportunity to measure equilibrium constants (K_3) for eq 3 directly for

$$\underset{\mathbf{1b}}{Mo(CO)_2(S_2CNEt_2)_2} + L \rightleftharpoons \underset{3}{Mo(CO)_2L(S_2CNEt_2)_2} \tag{3}$$

cases where substantial amounts of the 16-electron complex remain in the presence of L ($K_3 \leq 1000\ M^{-1}$) and indirectly from K_1 (eq 1) for larger values of K_3 once K_2 (eq 2) had been determined ($K_3 = K_1/K_2$, see Table I). Although the relative errors in K_3 are large, the change in free energy for reaction 3 as a function of L is clearly indicated and the surprisingly moderate electrophilicity of 1 is placed on a quantitative basis by these studies.

The modest value of K_3 for L = SC_4H_8 (**tht**) (**3b**) coupled with retention of the carbonyl infrared frequencies and intensities of 1 in spectra of **3b** and rapid loss of **tht** from **3b** in vacuo suggested that this weakly associated adduct of 1 might reflect the site of incipient M–L bond formation for ligand addition to 1. The molecular structure

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Table I. Equilibrium Constants (K_3) for Addition of L to $Mo(CO)_2(S_2CNEt_2)_2$ (1b)

ligand (L)	Br^- [a]	*trans*-stilbene[a]	Cl^- [a]	tht[a]	py[a]	$P(OPh)_3$ [b]	PPh_3 [b]	CO(g)[b]
K_3, M^{-1}	0.5 (1)[c,d]	0.7 (1)[e]	3.0 (6)[d]	45 (5)[e]	440 (40)[e]	49 (3) × 10^3 [f]	49 (3) × 10^3 [f]	350 (20)[g]

[a] Measurements conducted in CH_2Cl_2 at 22 °C. [b] Measurements conducted in o-$C_6H_4Cl_2$ at 22 °C. [c] The estimated error in the last figure is indicated in parentheses. [d] Determined by quantitative infrared absorption spectroscopy. [e] Determined by quantitative electronic absorption spectroscopy. [f] K_1 was determined by infrared techniques and K_3 was calculated from K_1 and K_2 (see text). [g] The units for L = CO are atm^{-1}; $K_3(CO) \equiv K_2$.

Table II. Selected Bond Distances and Angles for $Mo(CO)_2(SC_4H_8)(S_2CNEt_2)_2$ (3b)

Bond Distances, Å			
Mo-S1	2.524 (3)	Mo-C1	1.901 (11)
Mo-S2	2.517 (3)	Mo-C2	1.901 (11)
Mo-S3	2.538 (3)	C1-O1	1.197 (11)
Mo-S4	2.537 (3)	C2-O2	1.160 (10)
Mo-S5	2.701 (3)		
Bond Angles, Deg			
S1-Mo-S2	68.2 (1)	C2-Mo-S5	173.2 (3)
S3-Mo-S4	68.2 (1)	C1-Mo-C2	73.5 (5)
C1-Mo-S5	113.2 (3)		

of **3b** is depicted in Figure 1, and selected bond distances and angles are listed in Table II.[10] The two structural features of **3b** most relevant to the frontier orbital reaction hypothesis are (1) the gross coordination geometry with L capping the quadrilateral S_4 face opposite both carbonyl ligands and (2) the Mo–S(**tht**) length (2.70 Å) which exceeds nominal single-bond expectations.[11] The location of L in the seven-coordinate adducts may reflect the π-acceptor ability of the ligand (CO and PPh_3 cis to both carbonyls and **tht** opposite the carbonyls), but the present data base is insufficient to confirm this hypothesis.

The stepwise substitution mechanism shown in Scheme I incorporates the structural features of "intermediates" **3b** and **1a**. To the extent that **tht** and N_2H_4 are representative of other donor ligands, these results suggest that nucleophiles attack opposite the carbonyls in **1** prior to adopting the final isomeric form, e.g., *cis*-$ML(CO)_2$ for L = CO or PPh_3. It follows from the principle of microscopic reversibility that $M(CO)_2L(S_2CNR_2)_2$ adopts a geometry with L over the S_4 face prior to dissociation of L.

This system illustrates several important mechanistic points. (1) The structure of 16-electron intermediates need not bear a close relationship to saturated reagents or products. (2) Electron-deficient species may adopt geometries which are unprecedented for related 18-electron complexes. (3) Even when ligand substitution occurs with retention of the original coordination geometry, the reaction pathway may be mapped more accurately by a series of reversible structural rearrangements accompanying ligand dissociation and addition than by a principle of least motion reaction scheme. (4) Access to unsaturated intermediates may involve prior rearrangement of the reagent rather than ligand dissociation followed by reorganization of the electron-deficient intermediate. This final point is in accord with Hammond's postulate[12] since the transition state for ligand dissociation would resemble the unsaturated intermediate rather than the reagent.

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Registry No. 1b, 74807-43-5; **3b**, 81830-95-7; Br^-, 24959-67-9; *trans*-stilbene, 103-30-0; Cl^-, 16887-00-6; tht, 110-01-0; py, 110-86-1; $P(OPh)_3$, 101-02-0; PPh_3, 603-35-0; CO, 630-08-0.

Supplementary Material Available: A table of positional and thermal parameters for **3b** (2 pages). Ordering information is given on any current masthead page.

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(10) The crystal selected was monoclinic, space group $P2_1/n$, with unit cell dimensions of a = 8.289 (7) Å, b = 17.956 (5) Å, c = 15.913 (6) Å, β = 102.77 (5)°, and Z = 4. Of the 5291 reflections monitored, 1647 independent reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement which converged to 0.061 and 0.044 for R and R_w, respectively. The final difference Fourier map was featureless with the highest residual electron equal to 0.40 e/Å^3.

(11) Compare with the following M–S distances (M = Mo or W). (a) W–S(tht) = 2.57 Å in $[WCl_2(tht)]_2(\mu\text{-}S)(\mu\text{-}SEt)_2$: Boorman, P. M.; Kerr, K. A.; Patel, V. D. *J. Chem. Soc., Dalton Trans.* **1981**, 506. (b) W–S(dithiohexane = dth) = 2.54, 2.58 Å in $(OC)_3W(dth)Cl(SnCl_2Me)$: Elder, M.; Hall, D. *Inorg. Chem.* **1969**, *8*, 1273. (c) Mo-S(S-PPh_3) 2.46 Å in $MoOCl_3(SPPh_3)$: Boorman, P. M.; Garner, C. D.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1974**, 663.

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Heterobimetallic Phosphido-Bridged Complexes Containing Coordinatively Unsaturated Rhodium(I) and Iridium(I) Centers

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Summary: A series of new phosphido-bridged heterometallic dinuclear complexes $FeM(\mu\text{-}PPh_2)(CO)_x(L)_2$ (M = Rh, L = PEt_3, x = 4, 5; M = Ir, L = PPh_3, x = 4–6) have been synthesized by the reaction of $Li[Fe(CO)_4(PPh_2)]$ with the appropriate *trans*-$MCl(CO)L_2$ complex. Each of the new compounds undergoes a series of reversible addition/elimination reactions with CO, and the Fe–Ir compounds react with H_2 to give new H_2 adducts.

Although a very large number of heterobimetallic complexes have been prepared and characterized, nearly all are coordinatively saturated with a high percentage of carbonyls and other ligands that are reluctant to undergo dissociation.[1-3] Thus, most of these complexes have shown relatively low reactivity toward reversible addition and exchange of ligands. The latter are particularly desirable properties if such complexes are to be used as bimetallic catalysts. Ideal complexes would appear to be those which link traditional monomeric homogeneous catalysts of the group 8 metals to another metal center, preferably with a bridging ligand to assist in holding the metals together. Reported herein are the syntheses and preliminary re-

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