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Preparation and Reactivity of an Organometallic Lewis Acid Bearing Two Accessible Coordination Sites

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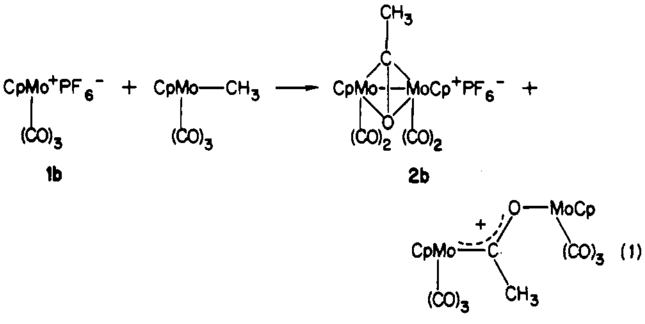
Treatment of the η^3-allyl complex $Cp(CO)_2Mo(CH_2CHCH_2)$ with 1 equiv of HBF_4 generates the η^2-propene compound $Cp(CO)_2Mo(CH_2{=}CHCH_3)(FBF_3)$ (**7**), a covalent molecule containing ligated propene and FBF_3^-, as a rapidly equilibrating mixture (on the NMR time scale) of cis and trans isomers. Carbonylation (1 atm) of **7** thus gives the propene salt $Cp(CO)_3Mo(CH_2{=}CHCH_3)^+BF_4^-$. Of more importance, **7** functions as a labile precursor to the formally 14-electron (or doubly unsaturated) Lewis acid $Cp(CO)_2Mo^+$. For example, both latent coordination sites on **7** are available for selectively forming the disubstituted derivatives $Cp(CO)_2Mo(PPh_3)_2^+$ and $(Cp(CO)_2MoI)_2$ upon treatment with PPh_3 and I^-, respectively, under mild conditions. The corresponding Lewis acid $Cp(CO)_3MoFBF_3$ (**1a**) with only one latent coordination site (ligated FBF_3^-), in contrast, gives only the monosubstituted derivatives $Cp(CO)_3Mo(PPh_3)^+$ and $Cp(CO)_3MoI$ under comparable reaction conditions. A study was also instituted to see if the Lewis acids **7** and **1a** convert $Cp(CO)_3MoCH_3$ and $Cp(CO)_3MoH$ to their bimetallic and symmetric μ-(η^2-*C*,*O*)-acyl complexes $[Cp(CO)_2Mo]_2(COR)^+$, where R = CH_3 and H, respectively. [Note that using **7** instead of **1a** now entails a net conservation of CO ligands in the formal Lewis acid promoted alkyl (or hydride) migration.] Reaction between **7** and $Cp(CO)_3MoCH_3$ indeed gives the known μ-(η^2-*C*,*O*)-acetyl compound (42% yield vs. 36% from **1a**), whereas **7** and $Cp(CO)_3MoH$ afford no discernible reaction products.

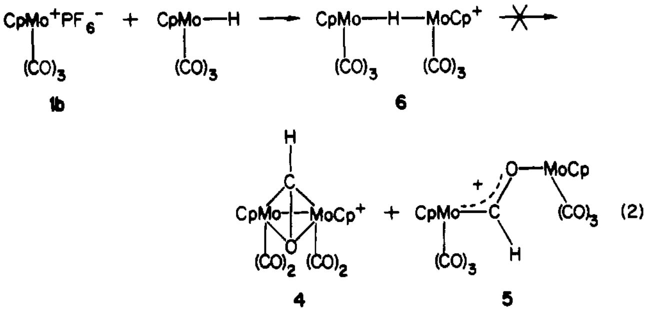
Introduction

The organometallic Lewis acid $(\eta\text{-}C_5H_5)Mo(CO)_3{}^+BF_4^-$ or $-PF_6^-$ (**1a,b**),[1] an extremely reactive electrophile bearing an accessible coordination site, coordinates the acyl ligand on another metal center and forms novel bimetallic μ-acyl complexes. Indeed, **1a** and **1b** even promote methyl–CO migratory insertion to give μ-acetyl complexes. Electrophilic **1b** and $(\eta\text{-}C_5H_5)Mo(CO)_3CH_3$, for example, when mixed at −20 °C, afford mixtures of bimetallic μ-(η^2-*C*,*O*)- (**2**) and μ-(η^1-*C*,*O*)-acetyl (**3**) compounds[2] (eq 1). Beck et al. independently prepared **2a** and determined its structure by X-ray crystallography.[3a]



1b **2b** **3b**

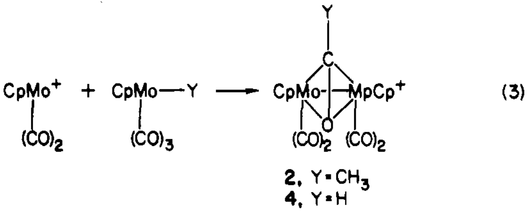
We are also interested in preparing analogous μ-(η^2-*C*,*O*)- (**4**) and μ-(η^1-*C*,*O*)-formyl (**5**) complexes. Several other bimetallic formyl complexes have been characterized by the Bercaw and Schrock groups,[4] although the corresponding monometal formyl compounds were not detected. We attempted to prepare **4** and **5** by reacting **1b** with $(C_5H_5)(CO)_3MoH$ (eq 2).[5] Only the



1b **6** **4** **5**

μ-hydride salt **6**[1] formed, and it resisted further attempts to convert it to **4** and/or **5**.

Another synthetic approach to the (η^2-*C*,*O*)-acetyl (**2**) and -formyl (**4**) complexes entails using a 14-electron or "doubly unsaturated" Lewis acid $(C_5H_5)Mo(CO)_2^+$ in place of $(C_5H_5)Mo(CO)_3^+$ (**1a,b**) in eq 1 and 2. If the first vacant coordination site an $(C_5H_5)Mo(CO)_2^+$ promotes methyl[6]– or hydride[7]–CO migratory insertion [on $(C_5H_5)(CO)_3MoCH_3$ and $(C_5H_5)(CO)_3MoH$, respectively], then the second accessible site could selectively bind the acyl ligand as **2** or **4** (eq 3). Note the net



2, Y = CH_3
4, Y = H

conservation of CO ligands in eq 3, as opposed to the disproportionation reaction (in terms of CO ligand distribution on products) that is implied by eq 2.

This paper concerns $Cp(CO)_2Mo(FBF_3)(\eta^2\text{-}CH_2{=}CHCH_3)$ (**7**), its preparation by protonating $Cp(CO)_2Mo(\eta^3\text{-}CH_2CHCH_2)$

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(1) (a) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214. (b) Schloter, K.; Beck, W. *Ibid.* **1980**, *35B*, 985. (c) Sünkel, K.; Günter, U.; Beck, W. *J. Organomet. Chem.* **1983**, *252*, 187.

(2) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312.

(3) (a) Sünkel, K.; Schloter, K.; Beck, W. *J. Organomet. Chem.* **1983**, *241*, 333. (b) Sünkel, K.; Nagel, U.; Beck, W. *Ibid.* **1983**, *251*, 227.

(4) (a) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc* **1984**, *106*, 5178. Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (b) Belmonte, P. A.; Cloke, F. G. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 2643.

(5) Markham, J.; Cutler, A. *Organometallics* **1984**, *3*, 736.

(6) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093. Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272. Stimson, R. E.; Shriver, D. F. *Organometallics* **1982**, *1*, 787. Labinger, J. A.; Bonfiglio, J. N.; Grimmett, D. L.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* **1983**, *2*, 733.

(7) (a) Attempts at inducing hydride–CO insertion reactions have been thwarted by deleterious side reactions arising from the basicity of the metal hydride in the presence of necessarily strong Lewis acids: Richmond, T. G.; Basolo, F.; Shriver, D. F. *Organometallics* **1982**, *1*, 1624. Grimmett, D. L.; Labinger, J. A.; Bonfiglio, J. N.; Masuo, S. T.; Shearin, E.; Miller, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 6858; *Organometallics* **1983**, *2*, 1325 and references cited therein. (b) For examples of mononuclear formyl complexes derived by carbonylation of a metal hydride, see: Wyland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700. Fagan, P. J.; Moloy, K. G.; Marks, T. J. *Ibid.* **1981**, *103*, 6959. Only in the last example has an intramolecular hydride migration reaction been demonstrated.

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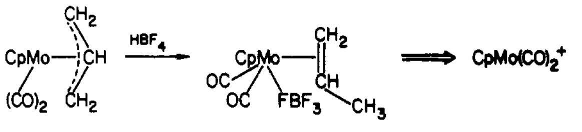
(eq 4), and its use as a labile precursor to the formally 14-electron



(4)

7

Lewis acid $CpMo(CO)_2^+$. We are particularly interested in demonstating that both latent coordination sites on the electrophile **7** are indeed available for selectively forming (1) disubstituted derivatives $Cp(CO)_2MoL_2^+$ and $Cp(CO)_2MoX_2^-$ or $[Cp(CO)_2MoX]_2$ with the appropriate Lewis bases (L = PPh_3; X = I^-) and (2) bimetallic acetyl **2a** and formyl **4a** compounds from the requisite methyl- and hydridomolybdenum species. The reactivities of $Cp(CO)_3MoFBF_3$ (**1a**) [a labile precursor to $CpMo(CO)_3^+$] and of **7** toward iodide, PPh_3, and $Cp(CO)_3MoCH_3$ accordingly will be compared.

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques and glassware suitably modified for inert-atmosphere work.[8] A nitrogen atmosphere was routinely provided for the following four operations: (a) carrying out reactions, (b) handling all solutions of metal complexes, (c) column chromatography, and (d) breaking the vacuum to evacuated vessels, including the Buchi rotovaporator. Solvents for synthetic work and recording of spectral data were deoxygenated by bubbling dinitrogen through the solvent for 20 min. Camag alumina (neutral, activity 3) was used in column chromatography. Carbonylation studies were carried out under conditions of vigorous stirring in Fischer-Porter bottles (85 psig).

Infrared spectra were taken on CH_2Cl_2 solutions in NaCl amalgam-spaced (0.10-mm) solution cells and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The ν(CO) frequencies (2200–1500 cm^{-1}) were calibrated against the polystyrene 1601-cm^{-1} absorption. ^1H NMR spectra of concentrated $CDCl_3$ or CD_3NO_2 solutions were recorded, after insoluble residues were centrifuged off. Varian Model EM-360 and XL-200 NMR spectrometers supplied the NMR spectra, which are reported as δ values downfield from internal Me_4Si. Combustion microanalyses were performed by Baron Consulting Co., Orange, CT.

Reagent grade solvents and reagents were obtained commercially and used as received. Tetrahydrofuran was additionally distilled under nitrogen from sodium benzophenone ketyl; methylene chloride and nitromethane were likewise procured as needed from P_2O_5. Deuterionitromethane was dried by passage through activated alumina. A modification of Dauben's procedure[9] was used to prepare $Ph_3C^+BF_4^-$. Although stored under nitrogen at +5 °C, trityl salts slowly decompose[10] (as evidenced by appearance of acid fumes), which necessitates periodic reprecipitation from CH_2Cl_2–ethyl acetate and vacuum drying. Anhydrous acid etherates $HBF_4{\cdot}OMe_2$ and $HBF_4{\cdot}OEt_2$ were used as received from Aldrich Chemical Co. Metal carbonyl complexes $(C_5H_5)(CO)_3MoH$,[11] $(C_5H_5)(CO)_3MoCH_3$,[12] $(C_5H_5)(CO)_3Mo(\eta^1\text{-}CH_2CH{=}CH_2)$, and $(C_5H_5)(CO)_2Mo(\eta^3\text{-}CH_2CHCH_2)$[13] were prepared by literature procedures and judged pure by IR and NMR spectroscopy.

Preparation of $(C_5H_5)(CO)_2Mo(\eta^2\text{-}CH_2{=}CHCH_3)FBF_3$ (7). $HBF_4{\cdot}O(CH_2CH_3)_2$ (1.50 mL, 1.00 mmol) was added to a yellow solution of $Cp(CO)_2Mo(\eta^3\text{-}CH_2CHCH_2)$ (0.258 g, 1.0 mmol) in 15 mL of CH_2Cl_2 (22 °C). The resulting dark red solution contains **7**: IR (CH_2Cl_2) 2027 (s, 1.0 relative intensity), 1973 (s, 0.9) (CO), 1230–900 (m, br, peak maximum 1148) cm^{-1} (MoFBF$_3$). ^1H NMR spectral data were obtained on solutions of **7** prepared in $CDCl_3$. Interfering ether absorptions accordingly were eliminated both by using $HBF_4{\cdot}O(CH_3)_2$ in place of the diethyl etherate and by removing $CDCl_3$ at 10^{-1} mm and 0 °C (with either etherate) and then redissolving the red gum in $CDCl_3$. These $CDCl_3$ solutions afforded **7** as the only NMR detectable species: ^1H NMR ($CDCl_3$) δ 5.65 (s, 5 H, Cp), 4.95 (m, 1 H, $CH_2{=}CHCH_3$), 3.70 (m, 1 H, (*E*)-*H*—CH=$CHCH_3$), 2.95 (m, 1 H, (*Z*)-*H*—CH=$CHCH_3$), 1.98 (d, *J* = 5 Hz, 3 H, CH_3). Attempts to isolate **7** as a solid were thwarted by its facile decomposition to an insoluble black residue.

Carbonylation of $(C_5H_5)(CO)_2Mo(\eta^2\text{-}CH_2{=}CHCH_3)FBF_3$ (7). Carbon monoxide was bubbled into a CH_2Cl_2 solution (30 mL) of $Cp(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (**7**) (1.0 mmol) for 1 h. This produced a light red supernatant and much tan suspension, which redissolved upon slowly adding CH_3NO_2 with stirring. Filtration of the light red solution (50 mL) through a Celite pad into ether (400 mL) produced a light tannish green precipitate. Spectroscopically pure $Cp(CO)_3Mo(CH_2{=}CHCH_3)^+BF_4^-$ (**8**)[13a] (0.246 g, 65% yield) remained after filtering this precipitate, washing with ether (3 × 20 mL), and vacuum drying (10^{-1} mm): IR (CH_3NO_2) 2053 (s), 1984 (s, br) (CO), 1080–980 (s, sharp peak maximum 1053) cm^{-1} (uncoordinated BF_4^-); ^1H NMR (CD_3NO_2) δ 5.99 (s, 5 H, Cp), 4.95 (m, 1 H, $CH_2{=}CHCH_3$), 3.67 (d, J_{cis} = 9 Hz, 1 H, (*E*)-*H*-CH=$CHCH_3$), 3.57 (d, J_{trans} = 15 Hz, 1 H, (*Z*)-*H*-CH=$CHCH_3$), 1.98 (d, *J* = 6 Hz, 3 H, CH_3). Authentic samples of **8** were also prepared by protonating $Cp(CO)_3Mo(\eta^1\text{-}CH_2CH{=}CH_2)$ in CH_2Cl_2 and reprecipitating the product from CH_3NO_2–ether. One equivalent of iodide (as the tetra-*n*-butylammonium salt) immediately and quantitatively converts $Cp(CO)_3Mo(CH_2{=}CHCH_3)^+BF_4^-$ in CH_3NO_2 solution to $Cp(CO)_3MoI$: IR 2045 (s), 1963 (s, br) cm^{-1}.

Pressurization of a $Cp(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (**7**) CH_2Cl_2 solution (1.0 mmol in 5 mL) at 85 psig CO (1 h) gave a red-orange suspension. A dark orange-brown powder (0.360 g) resulted after adding this suspension to 150 mL of Et_2O, filtering the precipitate, washing with ether, and vacuum drying (0.10 mm, 1 h). This precipitate corresponds to a 1:1 mixture of $Cp(CO)_3Mo(CH_2{=}CHCH_3)^+BF_4^-$ (**8**) and $CpMo(CO)_4^+BF_4^-$. An authentic sample of $CpMo(CO)_4^+BF_4^-$[14] was prepared by carbonylating $Cp(CO)_3MoFBF_3$[1] and working up the reaction according to the above procedure 58% yield): IR (CH_3NO_2) 2121 (s), 2040 (vs, br) (CO), 1080–980 (s, sharp peak maximum 1053) cm^{-1} (uncoordinated BF_4^-); ^1H NMR (CD_3NO_2) δ 6.20 (s, Cp).

Reaction of $(C_5H_5)(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (7) with Iodide. To a solution of $Cp(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (**7**) (0.50 mmol) in 5 mL of CH_2Cl_2 was added (5 min) $(n\text{-}Bu)_4N^+I^-$ (0.185 g, 0.5 mmol) in CH_2Cl_2 (10 mL). An IR spectrum of the resulting brown solution indicated essentially quantitative conversion to $[Cp(CO)_2MoI]_2$[15] (**10**) [IR (CH_2Cl_2) 1961 (vs), 1879 (s) cm^{-1}], with trace amounts (<4%) of $Cp(CO)_3MoI$ (**9**) [IR 2043, 1968 cm^{-1}] and no detectable $Cp(CO)_2MoI_2^-$ [IR 1940, 1842 cm^{-1}]. Slow addition of the brown solution to 200 mL of ether with scratching precipitated $(n\text{-}Bu)_4N^+BF_4^-$, the amount of which further increased upon cooling the mixture to −80 °C (1 h). The supernatant was then transferred with a stainless steel double-ended needle (fitted with a medium-porosity sintered-glass frit) into a second flask. Two ether washings (15 mL) of the $(n\text{-}Bu)_4N^+BF_4^-$ at −80 °C were likewise transferred, and the combined ether phases were stripped. This left 0.145 g (84% yield) of **10** as a brown powder that was spectroscopically pure: NMR ($CDCl_3$) δ 5.45 (s, Cp), with neither $(n\text{-}Bu)_4N^+$ nor **9** (δ 5.64) being evident. Treatment of CH_2Cl_2 solutions of $[Cp(CO)_2MoI]_2$ (**10**) either with 1 equiv of $Bu_4N^+I^-$ or with CO (1 atm, 10 h) effected complete conversion to $Cp(CO)_2MoI_2$ and **9**, respectively.

Reaction of $(C_5H_5)(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (7) and Ph_3P. PPh_3 (0.262 g, 1.0 mmol) was added to a CH_2Cl_2 solution (15 mL) of $Cp(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (**7**) (0.5 mmol). An IR spectrum of the resulting yellowish brown solution was consistent with complete conversion of **7** to $Cp(CO)_2Mo(PPh_3)_2^+$[16a,b] (**12**): IR (CH_2Cl_2) 1976 (s, 0.73 relative intensity), 1900 (s, 1.00) cm^{-1}. Less than 3% of $Cp(CO)_3MoPPh_3^+$ (**11**)[1,16a–c,17] was evident, as ascertained from its IR spectral absorption at 2063 cm^{-1}. Addition of this solution to pentane (200 mL) with scraping produced a tan precipitate, which was filtered off, washed with pentane, and vacuum dried, giving 0.374 g (90% yield)

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[8] (a) Eisch, J. J. "Organometallic Synthesis", Academic Press: New York, 1981; Vol. 2. (b) Brown, H. C. "Organic Synthesis *via* Boranes"; Wiley: New York, 1975. (c) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969. (d) King, R. B. "Organometallic Synthesis"; Academic Press: New York, 1965; Vol. 1.

[9] Dauben, H. J., Jr.; Hoonen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442. Olah, G. A.; Svoboda, J. J.; Olah, J. A. *Synthesis* **1972**, 544.

[10] Lloyd, D.; Walton, D. J.; Declercq, J. P.; Germain, G.; Van Meerssche, M. *J. Chem. Res., Synop.* **1979**, *7*, 249.

[11] King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99. Fischer, E. O. *Ibid.* **1963**, *7*, 136. Reference 8d, pp 156–158.

[12] Reference 8d, p 145. Pruett, R. L. In "Preparative Inorganic Reactions"; Jolly, W. L., Ed.; Wiley-Interscience: New York, 1965; Vol. 2, p 187.

[13] (a) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1963**, 889. (b) Fadel, S.; Weidenhammer, K.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1979**, *453*, 98.

[14] Fischer, E. O.; Fichtell, K.; Öfele, K. *Chem. Ber.* **1962**, *95*, 249. Jetz, W.; Angelici, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3799.

[15] Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23. Curtis, M. D.; Fotinos, N. A.; Han, K. R.; Butler, W. M. *J. Am. Chem. Soc.* **1983**, *105*, 2686.

[16] (a) Triechel, P. M.; Barnett, K. W.; Shubkin, R. L. *J. Organomet. Chem.* **1967**, *7*, 449. (b) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1967**, 94. (c) Nolte, M. J.; Reimann, R. H. *J. Chem. Soc., Dalton Trans.* **1978**, 932. (d) King, R. B.; Pannell, K. H.; Eggers, C. A.; Houk, L. W. *Inorg. Chem.* **1968**, *7*, 2353.

[17] Sünkel, K.; Ernst, H.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 474.

of **12** as a 6:1 mixture of cis and trans isomers: ^1H NMR (CD_3NO_2) δ 5.40 (s, Cp, *cis*-**12**), 5.18 (t, J = 1.5 Hz, Cp, *trans*-**12**), 7.57 (br s, PPh_3). The IR relative intensities for the carbonyl absorptions of this sample registered from 0.64 to 1.0. A CH_2Cl_2 solution of this product was refluxed for 3 h, and **12** was then recollected by precipitating with pentane. Its NMR spectrum in CD_2NO_2 indicated the presence of only *trans*-**12**. No regrowth of the cis isomer occurred after leaving the CD_3NO_2 solution for 12 h (22 °C); the IR spectrum had relative intensities of 0.47–1.0.

Reaction of $(C_5H_5)(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (7) with $Ph_2PCH_2CH_2PPh_2$. A CH_2Cl_2 solution (5 mL) of $Cp(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (**7**) (0.20 mmol) was treated with $Ph_2PCH_2CH_2PPh_2$ (0.078 g, 0.20 mmol). This produced an orange-brown solution that was then added to pentane (100 mL) with scratching to precipitate a tan solid. Filtration, washing with pentane, and vacuum drying left 0.125 g of $Cp(CO)_2Mo(Ph_2PCH_2CH_2PPh_2)^+BF_4^-$ (**13**)[16a,b,d] as a tan solid (88%): IR (CH_2Cl_2) 1984 (s, relative intensity 1.00), 1917 (s, 0.80) cm^{-1}; ^1H NMR (CD_3NO_2) δ 7.60 (m, 20 H, Ph), 4.90 (s, 5 H, Cp), 3.75 (m, 4 H, $-CH_2CH_2-$).

Reaction of $Cp(CO)_2M(CH_2{=}CHCH_3)FBF_3$ (7) and $Cp(CO)_3MoCH_3$. $Cp(CO)_3MoCH_3$ (0.130 g, 0.50 mmol) was added to a red CH_2Cl_2 solution (15 mL) of $Cp(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (**7**) (0.50 mmol). The reaction mixture gradually turned brown over 6 h as fine black particles settled out. (IR spectra monitoring of this reaction had established 6 h as the optimal reaction time.) Filtration of the brown suspension into ether (150 mL) with scratching produced a light brown precipitate, which was collected, washed with ether, and vacuum dried (0.1 mm) for 1 h. This left 0.130 g (42% yield) of $[Cp(CO)_2Mo]_2(\mu\text{-}\eta^2\text{-}COCH_3)^+BF_4^-$ (**2a**):[3] IR (CH_2Cl_2) 2062 (s), 2017 (vs), 1919 (m, br) cm^{-1}; NMR (CD_3NO_2) δ 5.94 (s, 10 H, Cp), 2.98 (s, 3 H, CH_3). No trace of the μ-(η^1-*C*,*O*)-acetyl complex $Cp(CO)_3Mo(\mu\text{-}COCH_3)Mo(CO)_3Cp^+$ (**3a**)[2] was evident in the IR and NMR spectra.

Treatment of $Cp(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (7) with $Cp(CO)_3MoH$. IR monitoring of a CH_2Cl_2 solution (15 mL) containing $Cp(CO)_2Mo(CH_2{=}CHCH_3)FBF_3$ (**7**) (0.50 mmol) and $Cp(CO)_3MoH$ (0.125 g, 0.50 mmol) was supportive of essentially no reaction over 6 h. Trace amounts of $[Cp(CO)_3Mo]_2H^+BF_4^-$ (**6**)[1a,5] [IR (CH_3NO_2) 2071 (m), 2053 (m), 1986 (s, br) cm^{-1}] were sometimes isolated as the ether-insoluble residue after 20-min reaction. The predominant reaction mode (up to 6 h), however, corresponds to degradation of **7** to insoluble brown solids.

Reaction of $(C_5H_5)(CO)_3MoFBF_3$ (1a) and PPh_3. A solution of $Ph_3C^+BF_4^-$ (0.165 g, 0.50 mmol) in 12.5 mL of CH_2Cl_2 (25 °C) was treated with $(C_5H_5)(CO)_3MoH$ (0.123 g, 0.50 mmol). This immediately produced a reddish purple solution of $(C_5H_5)(CO)_3MoFBF_3$ (**1a**)[1] [IR 2074 (s), 1995 (s, br) (CO), 1200–800 (m, br, peak maximum 1070) cm^{-1} ($MoFBF_3$)], which turned clear red upon addition of PPh_3 (0.262 g, 1.0 mmol). IR spectral examination indicated complete conversion to $(C_5H_5)(CO)_3MoPPh_3{}^+BF_4^-$ (**11**)[16] [IR 2061 (s), 1998 (m, sh), 1973 (s, br) cm^{-1}] and a smaller amount (0.08 mmol) of $(C_5H_5)(CO)_2Mo(PPh_3)_2{}^+BF_4^-$ (**12**), ascertained via quantitative IR spectroscopic measurements with the 1898-cm^{-1} absorption. Addition of this solution to ether–pentane (100–10 mL) followed by scraping and sitting at +5 °C (8 h) afforded a yellow precipitate (0.259 g) that was collected, washed with ether, and vacuum dried. Its IR spectrum (CH_2Cl_2) was identical with that recorded previously, and its NMR data confirmed the presence of only $(C_5H_5)(CO)_3MoPPh_3{}^+BF_4^-$ (**11**)[16] (65% yield) [NMR δ (CD_3NO_2) 7.56 (m, 15 H, PPh_3), 5.81 (s, 5 H, Cp)] and $(C_5H_5)(CO)_2Mo(PPh_3)_2{}^+BF_4^-$ (**12**) (16% yield). No additional CpMo compounds were evident in the ether fractions, which had been combined, stripped, and analyzed by IR spectroscopy.

Several experimental modifications of the $(C_5H_5)(CO)_3MoFBF_3$ reaction with PPh_3 afforded different amounts of $(C_5H_5)(CO)_3MoPPh_3{}^+$ (**11**) and $(C_5H_5)(CO)_2Mo(PPh_3)_2{}^+$ (**12**). Substituting 1 equiv of PPh_3 (0.131 g, 0.50 mmol) in the above procedure resulted in a yellow precipitate (0.210 g) containing 65% **11** and less than 8% **12**, as ascertained by quantitative IR spectroscopy. Use of 4 equiv of PPh_3 (0.524 g, 2.0 mmol) realized a yellow precipitate (0.289 g) that had substantially more of the bis(phosphine) salt **12** (26% by IR and 20% by NMR spectroscopic analyses) and less mono(phosphine) salt **11** (52% by IR and 48% by NMR spectroscopy). In a final modification, **1a** was generated at −80 °C and warmed to room temperature (0.5 h) before adding 2 equiv of PPh_3 (0.262 g, 1.0 mmol). The yellow precipitate (0.225 g) that was subsequently isolated corresponds to a 76% yield of **11**. None of the bis(phosphine) salt was detected.

$(C_5H_5)(CO)_3Mo(PPh_3)^+$ (**11**) does not react at 25 °C with PPh_3. The results of IR spectral monitoring of a CH_2Cl_2 solution (5.0 mL) of $(C_5H_5)(CO)_3Mo(PPh_3)^+PF_6^-$ (**11**) (0.130 g, 0.20 mmol) containing PPh_3 (0.313 g, 0.50 mmol) established that no reaction takes place over at least 2 h.

Reaction of $(C_5H_5)(CO)_3MoFBF_3$ (1a) and $(C_5H_5)(CO)_3MoCH_3$. To a reddish purple solution of $(C_5H_5)(CO)_3MoFBF_3$ (**1a**) (1.0 mmol, generated at 22 °C) in 12.5 mL of CH_2Cl_2 was added $(C_5H_5)(CO)_3MoCH_3$ (0.260 g, 1.0 mmol). After 1 h of stirring, the resulting yellow-brown suspension was filtered in order to remove a red precipitate, yield 0.079 g after washing with 2 × 5 mL portions of CH_2Cl_2 and drying with a N_2 flow. This precipitate corresponds to a 1:1 mixture of $(C_5H_5)(CO)_4Mo^+BF_4^-$ [IR (CH_3NO_2) 2120 (s), 2038 (vs) cm^{-1}; ^1H NMR (CD_3NO_2) δ 6.13 (C_5H_5)] and $(C_5H_5)(CO)_3Mo(CH_3NO_2)^+BF_4^-$ [IR (CH_3NO_2) 2070 (s), 1985 (vs) cm^{-1}; NMR (CD_3NO_2) δ 5.92 (C_5H_5)]. The latter product corresponds to a derivative of a presently unidentified byproduct. Treatment of a CH_3NO_2 solution of the red precipitate with excess $(n\text{-}Bu)_4N^+I^-$ immediately converts the CH_3NO_2 adduct to $(C_5H_5)(CO)_3MoI$ [IR 2040 (s), 1960 (vs) cm^{-1}].

The yellowish brown CH_2Cl_2 filtrate, upon adding to ether–pentane (200:20 mL) and scraping, provided an orange-pink precipitate (0.185 g) after filtering, washing with 3 × 20 mL of ether, and vacuum drying. This precipitate is spectroscopically pure $[(C_5H_5)(CO)_2Mo]_2COCH_3{}^+BF_4^-$ (**2a**)[3] (33% yield): IR (CH_2Cl_2) 2062 (s), 2013 (vs), 1920 (m, br) cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.97 (s, 10 H, C_5H_5), 3.02 (s, 3 H, CH_3). IR spectral analysis of the combined ether filtrates, after stripping off solvent and redissolving in CH_2Cl_2, was used to establish a 47% recovery of $(C_5H_5)(CO)_3MoCH_3$: IR (CH_2Cl_2) 2015 (s), 1930 (vs) cm^{-1}. Using a reaction time of 6 h for **1a** and $(C_5H_5)(CO)_3MoCH_3$ also gives **2a** (36% yield) in an otherwise identical workup.

Reaction of $(C_5H_5)(CO)_3MoFBF_3$ (1a) and Iodide. A reddish purple solution containing 0.20 mmol of $(C_5H_5)(CO)_3MoFBF_3$ (**1a**) in 5.0 mL of CH_2Cl_2 was treated with 3 equiv of $(n\text{-}Bu)_4N^+I^-$ (0.222 g, 0.60 mmol). The resulting yellow-brown solution was allowed to stir for 3 h in the dark. This brownish solution corresponds to quantitative conversion to $(C_5H_5)(CO)_3MoI$: IR 2042 (s), 1965 (vs) cm^{-1}. Exposure of these solutions to laboratory lighting (fluorescent) results in gradual conversion (~10% in 4 h) to $(C_5H_5)(CO)_2MoI_2{}^-$, as expected.[18]

Results and Discussion

Organometallic Lewis Acids. Organometallic Lewis acids having available one vacant coordination site short of attaining their thermodynamically favored configuration have found widespread use in organometallic chemistry. Such cationic and 16-electron Lewis acids are generated in solution through dissociation of a labile or weakly associated ligand from a coordinatively saturated precursor (eq 5). Once generated, these extremely reactive

$$M{-}X,\ M{-}S^+ \rightleftarrows M{-}\blacksquare^+ + X^-,\ S \xrightarrow{L'} (M{-}L')^+ \qquad (5)$$

$$X^-:\ FBF_3{}^-,\ OClO_3{}^- \qquad S:\ THF,\ O{=}CMe_2,\ NCCH_3$$
$$L':\ \text{alkene},\ CO,\ PR_3$$

intermediates readily resaturate by binding a nonlabile ligand L′—thus mediating a net disociative ligand substitution reaction.[19]

These cationic organometallic Lewis acids typically fulfill three conditions: (1) Their precursors contain a relatively soft metal center coupled to a potentially hard O-donor ligand or other weakly coordinating anion ($FBF_3{}^-$, $OClO_3{}^-$, $OSO_2CF_3{}^-$), a neutral O donor (THF, CH_3OH, $O{=}CMe_2$), or acetonitrile. These ligands are therefore extremely labile.[20] (2) The resulting Lewis acids, being positively charged and highly electrophilic, irreversibly bind substrate ligands that possess additional π-acceptor character (vide infra). The chief synthetic utility of these Lewis acids then rests in their capability of selectively adding a CO, alkene, etc. to the metal center. (3) The coordinatively unsaturated Lewis acids are not detected. Instead, these hypothetical species are best viewed as transient intermediates, which preferentially bind a wide variety of Lewis bases. Even the "noncoordinating" anions, e.g. BF_4^-,

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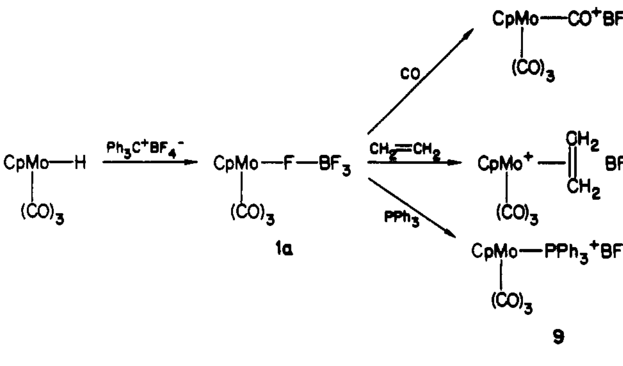
(18) Burkett, A. R.; Meyer, T. J.; Whitten, D. G. *J. Organomet. Chem.* **1974**, *67*, 67. Hughey, J. L., IV; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 947.

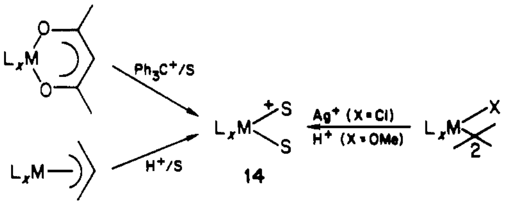
(19) (a) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113. Atwood, J. D.; Workulich, M. J.; Sonnenberger, D. C. *Acc. Chem. Res.* **1983**, *16*, 350. (b) Interchange pathways, either dissociative or associative, may function in some instances.

(20) (a) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 79. (b) The soft metal center originates from the combination of its low formal oxidation state and the symbiotic interaction of softer (i.e., π-acceptor) η-C_5H_5, CO, and phosphine ancillary ligands. An additional hard (O-donor) ligand is therefore expected to be only weakly associated and, in fact, a good leaving group.

Scheme I



Scheme II



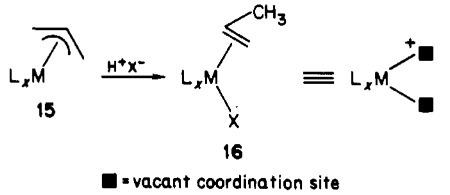
function as Lewis bases in this context.[21]

The reaction chemistry of $Cp(CO)_3Mo^+$ (**1**) exemplifies that of metal Lewis acids supporting a vacant coordination site. Beck et al. thus established **1** as being readily available in CH_2Cl_2 solution from its covalent $Cp(CO)_3MoFBF_3$ (**1a**) and ionic $Cp(CO)_3Mo^+PF_6^-$ (**1b**) derivatives;[1] these in turn are generated by abstracting hydride[22] from $Cp(CO)_3MoH$ with the requisite trityl salt. Electrophilic **1** then readily binds a wide variety of Lewis bases at or below room temperature (Scheme I).

In this study we are interested in generating organometallic Lewis acids that formally at least possess two vacant coordination sites. It is of course unlikely that a doubly unsaturated (14-electron) electrophile would obtain in solution. A more plausible scenario for affording such Lewis acids entails stepwise dissociation of two labile ligands, each occupying a coordination site, from the appropriate precursor. [In this context we operationally define a labile ligand as one that dissociated more readily (faster) than coordinated CO.] Each dissociation step will then immediately be followed by association of other coordinating ligands—for two net ligand substitution processes.

Synthesis of Lewis acid precursors with two accessible coordination sites has precedent. Scheme II in fact depicts three promising procedures that form **14**, where $L_xMS_2^+$ serves as the descriptor of these precursor complexes having two labile ligands; S = CH_3OH, O=CMe_2, or other coordinating solvents. In the first two procedures, electrophiles will either abstract the η^2-acetylacetonato-*O,O′* ligand[23,24] or cleave symmetrical halide or alkoxide bridges[24,25] to give examples of **14** [L_xM = (η^4-diene)Rh, (η^4-diene)Ir, (η^3-allyl)Pd] in weakly solvating media. Protonation of η^3-allyl complexes [L_xM = $Co(P(OMe)_3)_3$,[26] $Mn(CO)_2(P(O\text{-}i\text{-}C_3H_7)_3)_2$,[27] $Ru^{II}(\eta^4\text{-diene})$[28]], as the third procedure, severs the allyl ligand and secures two reactive coordination sites as **14**. In view of the large number of η^3-allyl complexes available as metal carbonyl systems,[29] we felt that this latter procedure offered greater promise for preparing metal carbonyl containing Lewis acid precursors with two labile ligands.

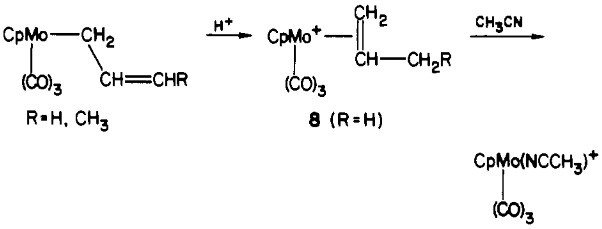
An η^3-allyl complex **15** when protonated in noncoordinating solvents (e.g., CH_2Cl_2) most likely converts to an η^2-propene compound **16**[30] at the same metal oxidation state (eq 6). The



(6)

propene and acid counterion, however, now occupy the two coordination sites originally used by the η^3-allyl ligand; these two latent coordination positions on **16** formally relate to the doubly unsaturated Lewis acid L_xM^+ through stepwise loss of propene and X^-. Complexes of type **16** up to now have not been detected after acid treatment of η^3-allyl compounds: typically only the ligated products $L_xMS_2^+$ were detected in coordinating solvents.

For our initial studies we investigated the protonation sequence outlined in eq 4 for converting $Cp(CO)_2Mo(\eta^3\text{-}C_3H_5)$ to $Cp(CO)_2Mo(\eta^2\text{-}C_3H_6)FBF_3$ (**7**). Complex **7** is set up to readily dissociate both propene and BF_4^- and thus serve as a precursor to the hypothetical doubly unsaturated $Cp(CO)_2Mo^+$ Lewis acid. Certainly $Cp(CO)_3MoFBF_3$ (**1a**) eliminates BF_4^- readily.[1] In addition, the η^2-propene adduct of **1a**, $Cp(CO)_3Mo(CH_2{=}CHCH_3)^+BF_4^-$ (**8**), which results from acid treatment of its η^1-allyl complex (eq 7), preferentially labilizes propene in acetonitrile or



(7)

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(21) (a) Tetrafluoroborate coordinated as a weakly associated ligand to transition organometallic complexes $M{-}F{-}BF_3$ has been well documented by single-crystal X-ray crystallographic,[21b,c] and IR spectroscopic studies[1a,17,21b,d] and in solution by ^{19}F, ^{11}B, and ^{31}P NMR spectroscopic[1c,21e,f] studies. Such coordination of BF_4^- amounts to F^- bridging the M^+ and BF_3 Lewis acids. One diagnostic feature of this complexation mode is the appearance of a broad dissected envelope (of moderate intensity) in the 1200–700-cm^{-1} region of their IR spectra. Plausible assignments include at least six IR-allowed BF_4^- vibrational modes (for ^{10}B and ^{11}B) corresponding to the reduced C_{3v} symmetry of the MBF_3 unit.[21g] (b) Olgemöller, B.; Bauer, H.; Löbermann, H.; Nagel, U.; Beck, W. *Chem. Ber.* **1982**, *115*, 2271. (c) Gaugham, A. P.; Dori, Z.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1657. (d) Raab, K.; Olgemöller, B.; Schloter, K.; Beck, W. *J. Organomet. Chem.* **1981**, *214*, 81. (e) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186. (f) Richter, K.; Fischer, E. O.; Krieter, C. G. *J. Organomet. Chem.* **1976**, *122*, 187. Fischer, E. O.; Waltz, S.; Ruhs, A.; Kreissl, F. R. *Chem. Ber.* **1978**, *111*, 2765. (g) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; Chapter 2.6.

(22) (a) Other examples of hydride abstraction from organometallic hydride complexes using Ph_3C^+ are $Cp(CO)_2PPh_3Mo{-}H$,[17] $(CO)_5Re{-}H$,[21d] $Cp(NO)_2W{-}H$,[22b] $Cp(CO)(NO)Re{-}H$,[22c] $(CO)_4PPh_3Mn{-}H$,[22d] $(PPh_3)_4RuH_2$,[22e] $Cp(CO)_2Os{-}H$,[22f] and $(PPh_3)_3OsH_4$.[22g] (b) Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1979**, *18*, 1250. Harnes, B. W.; Legzdins, P. *Organometallics* **1982**, *1*, 116. (c) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982. (d) Harris, P. J.; Knox, S. A. R.; McKinney, R. J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1009. (e) Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1333; **1973**, 743. (f) Hoyano, J. K.; May, C. J.; Graham, W. A. G. *Inorg. Chem.* **1982**, *21*, 3095. (g) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663.

(23) Johnson, B. F. G.; Lewis, J.; White, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 5186; *J. Chem. Soc. A* **1970**, 1738; **1971**, 2699. Green, M.; Kuc, T. A.; Taylor, S. H. *Ibid.* **1971**, 2334; *J. Chem. Soc., Dalton Trans.* **1972**, 832.

(24) Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 489.

(25) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397, 3089.

(26) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1976**, *98*, 4665; **1978**, *100*, 6978.

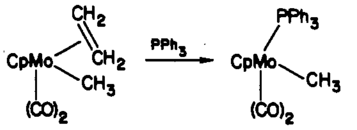
(27) Stuhl, L. S.; Muetterties, E. L. *Inorg. Chem.* **1978**, *17*, 2148.

(28) Schrock, R. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 951.

(29) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; Chapter 27. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

(30) (a) Proton addition may take place initially at the metal center, with subsequent proton transfer from the metal to the allyl ligand. Analogous pathways are extant during acidification of η^4-diene complexes: (η^4-diene)$Fe(CO)_3$[30b] and (η^4-diene)RhCp[30c] complexes evidently protonate to the metal first and then isomerize to the corresponding η^3-allyl compounds. (b) Whitesides, T.; Arhart, R. *J. Am. Chem. Soc.* **1971**, *93*, 5296. Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* **1976**, *15*, 1550. (c) Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2084.

upon treating with iodide.[13] It is also worth noting the facile displacement of alkene in neutral complexes analogous to 7 (eq 8).[31a] Finally, Faller and Rosan have already noted (with no



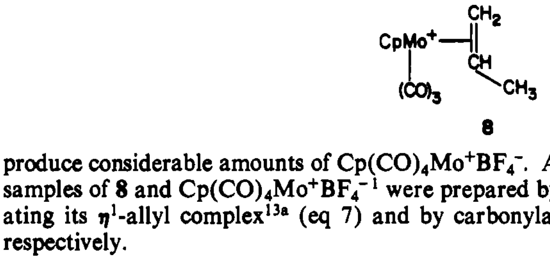
(8)

elaboration) that treatment of $Cp(CO)_2Mo(\eta^3\text{-}C_3H_5)$ with trifluoroacetic acid evolves propene.[32] In this paper we demonstrate that 7 indeed can be characterized, can be used as a Lewis acid, and can be selectively derivatized by replacing both propene and BF_4^- with Lewis bases. Studies in progress are focused on replacing just the BF_4^- ligand from 7 as a nonphotochemical synthesis of additional examples of $Cp(CO)_2Mo(alkyl)(\eta^2\text{-alkene})$ complexes.

Preparation and Characterization of $(\eta\text{-}C_5H_5)(CO)_2Mo(FBF_3)(\eta\text{-}CH_2{=}CHCH_3)$. The η^3-allyl complex $Cp(CO)_2Mo(CH_2CHCH_2)$ in CH_2Cl_2 upon treatment with 1 equiv of HBF_4 etherate quantitatively converts to a single organometallic product 7 as a red solution. Numerous attempts to isolate this material as a solid failed; instead only gums (at lower temperatures) or insoluble decomposition products (at room temperature) resulted. CH_2Cl_2 solutions of 7 also decompose slowly at room temperature and deposit CH_3NO_2-insoluble material. Structural details of 7 were deduced from ^1H NMR and IR spectral data and from the results of carbonylation experiments.

^1H NMR spectral data of crude 7 are consistent with the presence of one organometallic product, as judged by a single Cp resonance at δ 5.65 ($CDCl_3$), and with ligated propene. It is particularly noteworthy that the Cp chemical shift agrees rather closely with that exhibited by the covalent iodide complex $Cp(CO)_3MoI$ at δ 5.63 ($CDCl_3$), while differing considerably from the value expected for a cationic complex, e.g. δ 5.99 (CD_3NO_2) for $Cp(CO)_3Mo(CH_2{=}CHCH_3)^+BF_4^-$ (**8**). Even the high solubility of 7 in $CDCl_3$ also rules out an ionic structure: **8**, for example, is totally insoluble in $CHCl_3$. Remaining NMR absorptions for 7 have chemical shifts and integration ratios corresponding to the six hydrogens on ligated propene (as compared to **8**), even though the limited resolution of these absorptions precluded our discerning detailed spin-coupling information (see Experimental Section).

Further support for ligated propene on 7 derives from the results of carbonylation experiments. One atmosphere of CO thus cleanly converts 7 to **8** (eq 9), although higher pressures (6.6 atm) also



7

8

(9)

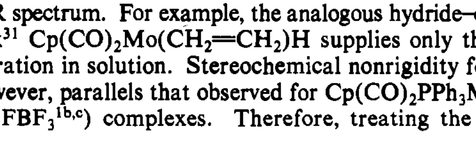
produce considerable amounts of $Cp(CO)_4Mo^+BF_4^-$. Authentic samples of **8** and $Cp(CO)_4Mo^+BF_4^-$[1] were prepared by protonating its η^1-allyl complex[13a] (eq 7) and by carbonylating **1a**,[1] respectively.

The fluoroborate present in 7, as in $Cp(CO)_3MoFBF_3$ (**1a**)[1] or $Cp(CO)_2FeFBF_3$,[21e] is ligated. IR spectral data in the 1200–800-cm^{-1} BF_4^- stretching region support this assignment.[21] Appearance of a broad, dissected BF_4^- absorption for 7 clearly resembles that for **1a**, but differs markedly from the narrow, symmetrical absorption (signifying uncoordinated BF_4^-) for **8**. Taken together, the spectral data and the results of the carbonylation studies on 7 are in accord with a covalent $(\eta\text{-}C_5H_5)Mo(\eta^2\text{-propene})$ complex that also contains ligated FBF_3^-.

The remainder of the coordination environment on 7 corresponds to two CO ligands that engender a cis or trans stereochemical array along the square base of the square-pyramidal Mo center.[33] Its IR spectrum thus exhibits two intense CO stretching frequencies (2027, 1973 cm^{-1}) having band shapes indicative of a $Mo(CO)_2$ moiety. Absorption half-widths (35 and 40 cm^{-1}) of these ν(CO) absorptions thus are more consistent with a dicarbonyl species (e.g., 32 and 35 cm^{-1} for $Cp(CO)_2MoI_2^-(n\text{-}Bu)_4N^+$) than with a tricarbonyl Mo center (e.g., 18 and 45 cm^{-1} for $Cp(CO)_3MoI$ (**9**)). Established IR and NMR spectral guidelines[33a,b,34] were used to discern among four possible stereochemical formulations for the dicarbonyl fragment on 7: *cis*- or *trans*-**7**, a mixture of *cis*- plus *trans*-**7**, and, finally, a rapidly equilibrating mixture (on the NMR time scale) at 25 °C.

In disubstituted $Cp(CO)_2MoLX$ and $Cp(CO)_2MoL_2^+$ complexes the IR ν(CO) bands observed for separate cis and trans stereoisomers often overlap. Nevertheless, the relative intensities of these symmetric and symmetric CO stretches, being a sensitive function of the angle between the carbonyls, differ markedly for the individual isomers. Cis and trans isomers of the 2-oxacyclopentylidene salt $Cp(CO)_2Mo(PPh_3)\overline{COCH_2CH_2CH_2}{}^+BF_4^-$, for example, have been separately characterized:[35] IR cis 1980, 1910 cm^{-1} (1.0/0.5); *trans* 1985, 1910 cm^{-1} (0.5/1.0). (The observed ratios, $I(a)/I(s)$, are indicated in parentheses.) The ^1H NMR spectra of these disbustituted Mo centers, particularly the absorptions for the Cp ligands, also serve as a sensitive probe into the stereochemistry. Such data for Cotton's 2-oxacyclopentylidene salts [cis δ 5.83 (s); trans δ 5.56 (d, J = 1.1 Hz)] are in accord with the expected upfield shift (by ~0.2 ppm) and observable ^{31}P NMR splitting (~1.5 Hz) for the trans isomer. Useful IR and NMR spectral criteria therefore are available to assign cis or trans stereochemistry to disubstituted $Cp(CO)_2MoLX/Cp(CO)_2MoL_2^+$ complexes, as illustrated for the above 2-oxacyclopentylidene salts, by noting the order of the approximately 2:1 (or 1:2) intensity relationship of the two ν(CO) absorptions in the IR spectrum and by noting the singlet or doublet appearance (and perhaps its relative chemical shift) of the NMR absorption for the Cp ligand.

For 7 we observe a 1.0:0.9 intensity ratio for the two carbonyl IR stretching frequencies and a broadened singlet in the ^1H NMR spectrum for the Cp ligand. These data signal a rapidly equilibrating mixture (on the NMR time scale) of cis and trans isomers (eq 10). A simple mixture or relatively slow equilibrium of *cis*- and *trans*-**7** would have afforded separate resonances for the Cp ligands, and either the cis (more likely in view of the singlet character of Cp absorption) or the trans isomer alone would have the expected 2:1 (or 1:2) intensity ratio for ν(CO) absorptions in the IR spectrum. For example, the analogous hydride–ethylene complex[31] $Cp(CO)_2Mo(CH_2{=}CH_2)H$ supplies only the trans configuration in solution. Stereochemical nonrigidity for 7 (eq 10), however, parallels that observed for $Cp(CO)_2PPh_3MoX$ (X = H,[33] FBF_3[1b,c]) complexes. Therefore, treating the η^3-allyl



cis-7 *trans*-7

(10)

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(31) (a) Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005. (b) Mahmoud, K. A.; Rest, A. J.; Alt, H. G.; Eichner, M. E.; Jansen, B. M. *J. Chem. Soc., Dalton Trans.* **1984**, 175. Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *Ibid.* **1984**, 187.

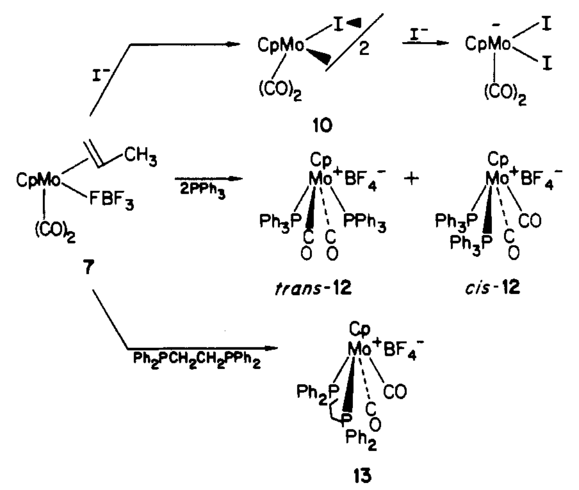
(32) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858.

(33) (a) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852. (b) Barnett, K. W.; Slocum, D. W. *J. Organomet. Chem.* **1972**, *44*, 1. (c) Kubăcek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

(34) Manning, A. R. *J. Chem. Soc. A* **1967**, 1984; **1968**, 6516. Marby, R. J.; Wright, G. *J. Organomet. Chem.* **1970**, *21*, 169. Craig, P. J.; Edwards, J. *Ibid.* **1972**, *46*, 335. Beach, D. L.; Dattilo, M.; Barnett, K. W. *Ibid.* **1977**, *140*, 47.

(35) Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 2672.

Scheme III

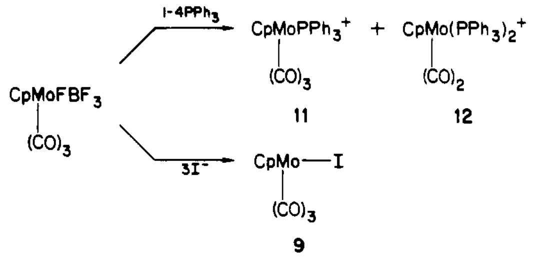


complex $Cp(CO)_2Mo(CH_2CHCH_2)$ with HBF_4 provides a material **7** to which we assign the structure $Cp(CO)_2Mo(FBF_3)(\eta^2\text{-}CH_2{=}CHCH_3)$ as a rapidly equilibrating mixture of *cis*-**7** and *trans*-**7**.

The reactivity of **7** with iodide and phosphine nucleophiles was studied in order to establish the availability of two latent coordination sites at the Mo center (Scheme III). One equivalent of $(n\text{-}Bu)_4N^+I^-$ thus cleanly converts **7** to the known $Cp(CO)_2MoI$ dimer (**10**),[15] with trace amounts of $Cp(CO)_3MoI$ (**9**) as the only other organometallic species detectable by IR and NMR spectroscopy. The addition of more iodide to **10** subsequently affords $Cp(CO)_2Mo_2I_2^-$. Likewise, 2 equiv of PPh_3 immediately consumes **7** (at 22 °C) and replaces both the propene and the BF_4^- ligands by two phosphines, thereby giving $Cp(CO)_2Mo(PPh_3)_2^+$ (**12**)[16a,b] as a 6:1 mixture of trans and cis isomers. The cis isomer has not been previously reported; its assignment rests on the IR and NMR spectral observations detailed in the Experimental Section. In particular, the ^1H NMR spectrum of **12** exhibits two Cp resonances, a triplet (δ 5.18, J = 1.5 Hz) for *trans*-**12** that is upfield of the singlet (δ 5.40) for the cis isomer. Upon warming, this mixture smoothly and irreversibly transformed into *trans*-**12**. *cis*-**12** obviously is a kinetic product that results from intercepting either *cis*-$Cp(CO)_2MoPPh_3(FBF_3)$ or *cis*-$Cp(CO)_2MoPPh_3(CH_2{=}CHMe)^+$, depending on whether propene or BF_4^- is preferentially displaced, with the second equivalent of PPh_3. Of these two intermediates only the former is known.[17] Beck indeed reported that the stereochemically nonrigid $Cp(CO)_2MoPPh_3(FBF_3)$ reacts with additional PPh_3, but apparently only *trans*-**12** was isolated. We also note that either 1 equiv or an excess of $(n\text{-}Bu)_4N^+I^-$ immediately and quantitatively converts a CH_2Cl_2 suspension of $Cp(CO)_3Mo(CH_2{=}CHCH_3)^+BF_4^-$ (**8**) to $Cp(CO)_3MoI$ (**9**), with no evidence for forming $Cp(CO)_2MoI_2^-$. In future studies we will probe the relative lability of propene vs. BF_4^- on **7**; for now, however, we simply note that **7** will afford two cis-coordination sites. As further evidence for availability of these latent cis-coordination sites, the reaction between **7** and the bidentate phosphine $Ph_2PCH_2CH_2PPh_2$ readily affords its cis adduct **13** (88% yield).

Clearly **7** affords two coordination sites for attacking nucleophiles, but does this chemistry really differ significantly from that observed between $Cp(CO)_3MoFBF_3$ (**1a**) and 2 or more equiv of the same nucleophiles? Beck has reported the reaction of **1a** and 1 equiv of PPh_3 at −30 °C to give $Cp(CO)_3MoPPh_3^+$ (**11**) in quantitative yield. We observe that **1a** reacts with from 1 to 4 equiv of PPh_3 at room temperature to produce increasing amounts of $Cp(CO)_2Mo(PPh_3)_2^+BF_4^-$ (**12**) (8–26% yields) along with the expected $Cp(CO)_3MoPPh_3^+BF_4^-$ (**11**) (76–52%) (Scheme IV). Under the conditions of these experiments, **11** is inert to excess PPh_3. Results of the reaction between **1a** and excess iodide (3 equiv), however, are more straightforward: in the dark only $Cp(CO)_3MoI$ forms (in quantitative yield). Therefore, the dominant reactivity mode of $Cp(CO)_3MoFBF_3$ (**1a**) with nucleophiles is to make only one coordination site available through displacement of the labile BF_4^-.

Scheme IV



We have not further investigated the origin of the bis(triphenylphosphine) adduct **12** formed in the reaction of between $Cp(CO)_3MoFBF_3$ (**1a**) and PPh_3. It is, however, worth noting that these disubstituted $Cp(CO)_2MoL_2^+$ complexes commonly persist as minor products during preparation of phosphine-substituted $Cp(CO)_3MoL^+$ complexes from their halide precursors $Cp(CO)_3MoX$, especially when $AlCl_3$-enforced halide abstraction techniques are used[16a] Occurrence of these byproducts can be rationalized through ligand FBF_3^- (or $XAlCl_3^-$) functioning as a cis-labilizing ligand[36] on $Cp(CO)_3MoFBF_3$ (**1a**) (or on $Cp(CO)_3MoXAlCl_3$) to initially generate $Cp(CO)_2PPh_3MoFBF_3$, which subsequently gives **12**.

In conclusion, the propene complex $Cp(CO)_2Mo(CH_2{=}CHCH_3)(FBF_3)$ (**7**), also containing ligated fluoroborate and existing as a stereochemically nonrigid mixture of cis and trans isomers (eq 10), results upon treating the η^3-allyl complex $Cp(CO)_2Mo(CH_2CHCH_2)$ with HBF_4. Labile **7** functions as a precursor to the formally 14-electron or doubly unsaturated Lewis acid $Cp(CO)_2Mo^+$: under extremely mild conditions two coordination sites on **7** are made available to incoming nucleophiles. In contrast, the Lewis acid precursor $Cp(CO)_3MoFBF_3$ (**1a**) reacts predominantly via one latent coordination site (i.e., labile BF_4^-), even with excess nucleophile present.

Reactions of $(\eta\text{-}C_5H_5)(CO)_2Mo(FBF_3)(\eta\text{-}CH_2{=}CHCH_3)$ (7) with $(\eta\text{-}C_5H_5)(CO)_3MoX$ (X = CH_3, H). Organometallic Lewis acids afford a novel group of bimetallic μ-acyl compounds, either by ligating the electron-rich acyl ligand on another complex or by promoting alkyl–CO migratory insertion on an alkyl–metal–carbonyl system. As an example of this latter mode of reactivity, the Lewis acid $CpMo(CO)_3^+$ reacts with $CpMo(CO)_3CH_3$ to give the symmetrical μ-(η^2-*C*,*O*)-acetyl compound $[Cp(CO)_2Mo]_2(COCH_3)^+$ (**2**) in moderate yield. (Beck[3a] reported obtaining **2a** exclusively by using $CpMo(CO)_3FBF_3$ (**1a**) whereas we[2] procured a mixture of **2b** and the unsymmetric bimetallic acetyl salt **3b** (eq 1) with $CpMo(CO)_3^+PF_6^-$.) Significantly, $CpMo(CO)_3^+$ provides two coordination sites in forming **2a,b**.[37] Therefore, the doubly unsaturated Lewis acid $Cp(CO)_2Mo^+$, available through dissociation of BF_4^- and propene from **7**, has the equal optimal ligand array for converting $CpMo(CO)_3CH_3$ to **2**—assuming that the two latent coordination sites on **7** can operate in concert, first to promote methyl–CO migration and then to bind the acetyl ligand as in **2** (eq 3). We also felt that **7** might be used to convert $Cp(CO)_3MoH$ to its analogous μ-(η^2-*C*,*O*)-formyl complex **4** (eq 3), without the deliterious formation of $Cp(CO)_3Mo{-}H{-}Mo(CO)_3Cp^+$ (**6**) (eq 2).

Lewis precursor **7** indeed does react with $Cp(CO)_3MoCH_3$ to give the bimetallic μ-(η^2-*C*,*O*)-acetyl compound **2a**, but the optimal

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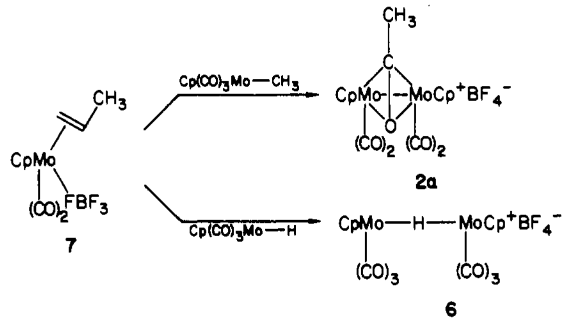
(36) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

(37) We do not imply that $Cp(CO)_3Mo^+$ (**1a,b**) must behave strictly as a Lewis acid in forming **2a,b**. This mechanism, indeed, remains to be established. One alternative mechanism for forming **2**, briefly, entails an initial one-electron oxidation of $Cp(CO)_3MoCH_3$ by $Cp(CO)_3Mo^+$, followed by generation of $Cp(CO)_2Mo(COCH_3)^{+\cdot}$ and then its radical-coupling reaction (and concomitant CO loss) with $Cp(CO)_3Mo\cdot$ to give **2**. We have established that such an electron-transfer/radical-coupling mechanism operates in place of a Lewis acid–base interaction during formation of the μ-(η^1-*C*,*O*)-acetyl complex $Cp(CO)PPh_3FeC(CH_3)OMo(CO)_3Cp^+$: Forschner, T. F.; Menard, K. P.; Cutler, A. R., manuscript in preparation.

Scheme V



yield (42%) does not greatly improve on that obtained when we used $Cp(CO)_3MoFBF_3$ (**1a**) in place of **7** (36%). Both reactions are exceedingly messy (in terms of insoluble decomposition material), and neither produce the unsymmetric μ-(η^1-*C,O*)-acetyl compound **3**. The reaction between **7** and $Cp(CO)_3MoH$ (Scheme V) is even less promising. Essentially no reaction takes place, other than thermal degradation of **7** and generation of small amounts of $Cp(CO)_3Mo\text{-}H\text{-}Mo(CO)_3Cp^+$ (**6**).

We are at a loss to explain the rather disappointing conversion of $Cp(CO)_3MoCH_3$ to **2** by using **7** instead of $Cp(CO)_3MoFBF_3$ (**1a**). Clearly **7** functions as a Lewis acid precursor to $Cp(CO)_2Mo^+$ (as demonstrated by results of the reaction with iodide or PPh_3), but perhaps both ligated BF_4^- and propene are not sufficiently labile during the sequence of alkyl–CO migration and binding of the incipient acyl ligand (as η^2 complexation). We, of course, have no evidence for a metal Lewis acid even promoting hydride–CO insertion. Further mechanistic discussion is unwarranted until answers for at least three questions are forthcoming:

1. What is the mechanism for the reaction of $Cp(CO)_3MoCH_3$ and $Cp(CO)_3Mo^+$?
2. Will **7** interact with stable acetyl complexes and after CO loss give isolable μ-(η^2-*C,O*)-acetyl compounds?
3. Can **7** be altered (e.g., replacement of BF_4^- and propene by PF_6^- and isobutylene, respectively) in order to generate an even more labile/reactive Lewis acid precursor?

These and related questions concerning the reactions of organometallic Lewis acids with coordinated ligands are currently under investigation.

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Contribution from the Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Structural and Spectroscopic Study of $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$, a Compound Containing a Cubane-like Cluster with Six Molybdenum–Molybdenum Bonds

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Refluxing $Mo_2(S_2CN(C_2H_5)_2)_6$ in toluene gave the tetranuclear complex $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$, which usually contains solvent molecules of crystallization. Recrystallization of the complex from chloroform yielded $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4\cdot 2CHCl_3$, which has been characterized by infrared, UV/vis, and NMR spectroscopy and single-crystal structural studies. Its crystals are tetragonal, of space group $P4_12_12$, with $a = 12.442$ (3) Å, $c = 40.30$ (1) Å, $D_o = 1.735$ (8) g cm^{-3}, $D_m = 1.746$ g cm^{-3}, and $Z = 4$. The structure was determined from 1099 reflections and refined by blocked-cascade least squares to an R factor of 0.094. The complex contains a cubane-like Mo_4S_4 cluster. Two of the dithiocarbamate ligands each form a bridge between the two Mo atoms on the opposite sides of the cube; the remaining four each coordinate to a Mo atom in a bidentate mode. The Mo_4S_4 cluster is similar to that of Fe_4S_4, but the four Mo atoms are mutually bonded via Mo–Mo single bonds ranging from 2.732 (5) Å for two Mo atoms bridged via the same dithiocarbamate to an average value of 2.861 (6) Å for the other four Mo–Mo distances.

Introduction

Molybdenum and iron are key metals in nitrogenase, an enzyme responsible for nitrogen fixation. The iron may be present as Fe_4S_4 clusters, yet the state of molybdenum is still to be identified. Over the years, many model studies were carried out to probe the function and state of the molybdenum atoms in the enzyme, and the available literature indicates that the enzyme consists of Fe- and Mo-Fe proteins.[1] Various Mo-Fe-S cubane-like clusters were proposed for the Mo-Fe protein, but no definite conclusion has ever been reached.[2] In our studies on molybdenum chemistry, the compound $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$ was prepared, its crystal structure was determined, and other properties were measured. Although the present results have no direct connection with the study of nitrogenase, the existence of a cubane-like Mo_4S_4 cluster may prove to be highly significant in subsequent research on this enzyme.

The complex $Mo_2(S_2CN(C_2H_5)_2)_6$ was first reported by Brown et al.[3] by the method of oxidative decarbonylation of tricarbonyl(η^6-cycloheptatriene)molybdenum. Later, its preparation was reported by Mitchell and Scarle,[4] who suggested a distorted octahedral geometry around each Mo atom with four bidentate dithiocarbamate groups and two unidentate groups that bridge the Mo atoms. The former report was called into question by some workers.[5,6] One group of workers[7] doubted whether Mo(III) dithiocarbamates can be prepared by the above method, for their preparation always resulted in $Mo(S_2CN(C_2H_5)_2)_4$. Brown, Glass, and Jasim[8] reinvestigated the above system for dithiocarbamates with R = CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9, and they suggested that the complexes may be formulated as dimeric species with

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(1) Herskovitz, T.; Averill, B. A.; Holm, R. H.; Ibers, J. M.; Phillips, W. D.; Weiher, J. F. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 2437.

(2) Averill, B. A. *Struct. Bonding (Berlin)* **1983**, *53*, 59.

(3) Brown, D. A.; Cordon, B. J.; Glass, W. K.; O'Daly, C. J. *Proc. Int. Conf. Coord. Chem., 11th* **1972**, 646.

(4) Mitchell, P. C. H.; Scarle, R. D. *J. Chem. Soc., Dalton Trans.* **1975**, 110.

(5) Nieuwpoort, A.; Classen, H. M.; Van der Linden, J. G. M. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 869.

(6) Willemse, J.; Cras, J. A.; Staggerda, J. J.; Kujzers, C. P. *Struct. Bonding (Berlin)* **1976**, *28*, 83.

(7) Nieuwpoort, A.; Staggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 250.

(8) Brown, D. A.; Glass, W. K.; Jasim, K. S. *Chem. Uses Molybdenum, Proc. Int. Conf., 4th* **1982**, 156.

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