of the five-membered ring is bonded to a metal atom; thus, the ligand loses the ability to polymerize, which in turn makes the Friedel–Crafts reaction possible. Moreover, in each case of the reactions of complexes 1–4, only one substituted complex is isolated, which might imply the high selectivity of the reaction. Further investigation of the reactivity of the acylated cluster complexes is in progress in order to find out the possibility of synthetic utility of the acylation reactions of these clusters.

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Registry No. 1, 38979-81-6; 2, 67265-50-3; 3, 109464-89-3; 4, 85159-47-3; 5, 123358-57-6; 6, 123358-58-7; 7, 123358-59-8; 8, 123358-60-1; 9, 123358-61-2; 10, 123358-62-3; 11, 123380-76-7.

Reactivity of Coordinated Carbon Dioxide: Reactions of $(C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ with Electrophiles

Jing-Cherng Tsai, Masood Khan,[1] and Kenneth M. Nicholas*

Department of Chemistry and Biochemistry
University of Oklahoma, Norman, Oklahoma 73019

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Summary: The title complex **1** reacts with a variety of electrophilic reagents to afford products derived from O-centered electrophilic attack on coordinated CO_2. In the case of Me_3SiCl, $^tBuMe_2SiCl$, and HCl complete oxygen transfer occurs, producing $[(C_5H_5)_2Mo(CO)Cl]Cl$ (**2a**) and $R_3SiOSiR_3$ or H_2O. The reaction of **1** with $Me_3SiOSO_2CF_3$ in THF affords the unusual dicationic complex $[(C_5H_5)_2Mo(CO)(THF)](OSO_2CF_3)_2$ (**3**), whose structure has been established by X-ray diffraction.

The prospects for useful transition-metal-mediated reactions of carbon dioxide have stimulated widespread interest in the coordination chemistry of this typically unreactive molecule.[2] Although a number of discrete metal–CO_2 complexes have been characterized,[3] the reactivity of coordinated carbon dioxide, particularly in η^2 complexes, remains virtually unknown.[4] For a few η^1 complexes reductive disproportionation and O-centered electrophilic attack have been observed.[5,6] Following our recent discovery of the first photoinduced reaction of coordinated CO_2 in $(C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ (1),[7] we present here our findings on the *dark* reactions of this η^2 complex with several electrophilic and oxophilic reagents, which result in reduction of coordinated CO_2 via O-transfer to the attacking reagent.

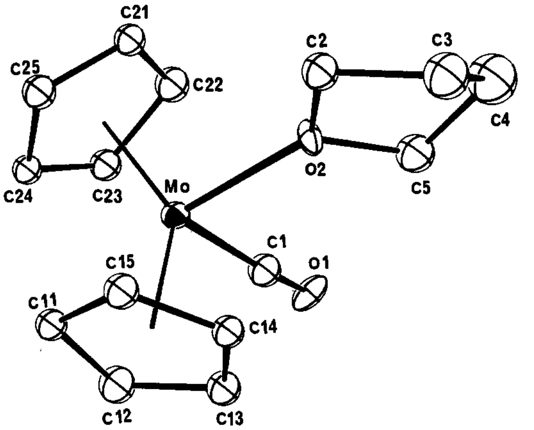
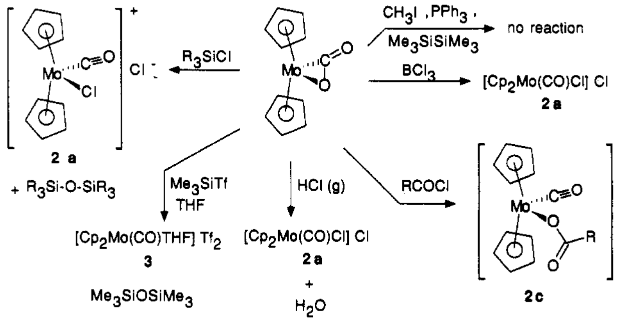


Figure 1. ORTEP diagram for the cation of $[(\eta^5\text{-}C_5H_5)_2Mo(CO)(C_4H_8O)](CF_3SO_3)_2$ (**3**). Selected bond lengths (Å) and angles (deg): Mo–Cp(1) = 1.99 (2), Mo–Cp(2) = 1.98 (2), Mo–O(2) = 2.14 (1), Mo–C(1) = 2.03 (2), C(1)–O(1) = 1.17 (2); Cp(1)–Mo–Cp(2) = 137.2 (8), O(2)–Mo–C(1) = 89.3 (7).

Scheme I



Treatment of a THF solution of 1 with 2 equiv of Me_3SiCl at −78 °C results in the immediate precipitation of a pale orange solid identified as $[(C_5H_5)_2Mo(CO)Cl]Cl$ (**2a**, 97%[8]) on the basis of its spectroscopic properties[9] (Scheme I). Analysis of the reaction solution by ^1H NMR and GC/MS methods revealed the presence of an approximately equal amount of $Me_3SiOSiMe_3$.[10] The reaction between 1 and $^tBuMe_2SiCl$ proceeded analogously, albeit more slowly, also giving **2a** (92%) and $^tBuMe_2SiOSiMe_2Bu^t$.[11] Complex 1 also reacts rapidly with 2 equiv of $Me_3SiOSO_2CF_3$ in THF at −78 °C to quantitatively afford the cationic carbonyl complex 3 (ν_{CO} 2060 cm^{-1}) and $Me_3SiOSiMe_3$. Since spectroscopic and analytical data[12] for 3 did not allow an unambiguous structural

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(1) Address inquiries regarding X-ray diffraction results to this author.

(2) Reviews: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, West Germany, 1988. (b) Ito, T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Halstead Press: New York, 1982; Chapter 3, pp 79–151. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

(3) Reference 2a, pp 15–25.

(4) Protonation of $(Cy_3P)_2Ni(\eta^2\text{-}CO_2)$ by RSH and HCl to produce $(Cy_3P)_2Ni(CO)_2$ has been reported recently: Aresta, M.; Quaranta, E.; Tommasi, I. *J. Chem. Soc., Chem. Commun.* **1988**, 450.

(5) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *104*, 6796. Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

(6) Harlow, R. L.; Kinney, J. B.; Herskovitz, T. *J. Chem. Soc., Chem. Commun.* **1980**, 813. For O-alkylation/silylation of other η^1-CO_2 complexes see: Forschner, T.; Menard, K.; Cutler, A. R. *J. Chem. Soc., Chem. Commun.* **1984**, 121. Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970. Senn, D. R.; Gladysz, J. A.; Emerson, K.; Larsen, R. D. *Inorg. Chem.* **1987**, *26*, 2737.

(7) Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004.

(8) IR (KBr): 2040 cm^{-1}. ^1H NMR (DMSO-d_6): δ 6.39. MS (FAB): *m/e* 291 ($Cp_2{}^{98}MoCOCl^+$), 263 ($Cp_2{}^{98}MoCl^+$), 256 ($Cp_2{}^{98}MoCO^+$). The IR and NMR data coincide with those of $\{Cp_2Mo(CO)Cl\}AlCl_4$.[9]

(9) Bell, L. G.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *135*, 173.

(10) MS (EI, 12 eV) of $(CH_3)_3SiOSi(CH_3)_3$: *m/e* 147 ($M^+ - CH_3$, 100), 73 ($Si(CH_3)_3{}^+$, 2). The ratio of *m/e* 147/148/149 peaks (100:17:8) was identical with that for authentic $(CH_3)_3SiOSi(CH_3)_3$.

(11) MS (EI, 12 eV) of $(CH_3)_3CSi(CH_3)_2OSi(CH_3)_2C(CH_3)_3$: *m/e* 246 ($M^+$, 1), 231 ($M^+ - CH_3$, 1), 189 ($M^+ - C(CH_3)_2$, 20), 147 ($M^+ - 2C(CH_3)_2$, 100).

(12) Analytical and spectroscopic data for **3** are as follows. IR (KBr): 2060 cm^{-1}. ^1H NMR (acetone-d_6): δ 6.96 (s, C_5H_5, 10 H), 4.01 (apparent t, J = 6.6 Hz, 4 H), 1.98 (m, 4 H). ^{19}F NMR (acetone-d_6): δ −89.6 (vs, CF_3CO_2H). MS (FAB): *m/e* 405 ($Cp_2{}^{98}Mo(CO)OSO_2CF_3{}^+$), 377 ($Cp_2{}^{98}MoOSO_2CF_3{}^+$), 328 ($Cp_2{}^{98}MoCO(C_4H_8O)$), 256 ($Cp_2{}^{98}MoCO^+$). Anal. Calcd for $[(C_5H_5)_2Mo(CO)(C_4H_8O)](CF_3SO_2)_2$: C, 32.7; H, 2.9; F, 18.3. Found: C, 33.2; H, 2.9; F, 20.2.

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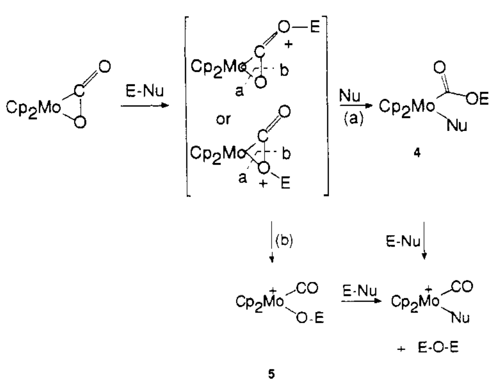
Scheme II



assignment, its X-ray crystal structure was determined[13] and is presented in Figure 1. Besides the expected cyclopentadienyl and carbonyl ligands of **3**, a THF molecule was found to be coordinated in place of the weakly donating triflate, providing the first example of a dicationic $Cp_2M(CO)L$ complex.[14] In each of these reactions of **1** cleavage of coordinated CO_2 to CO has occurred with oxygen transfer to the electrophilic silicon atom.

Similar CO_2 "splitting" resulted from the interaction of **1** with H^+ as the electrophile. Thus, when a CH_2Cl_2 solution of **1** was treated with excess HCl(g) at −78 to −20 °C, the chloro carbonyl complex **2a** was again produced (>50%) in addition to H_2O, which could be detected by ^1H NMR spectroscopy (Scheme I) and verified by spiking. This reaction constitutes a stoichiometric "reverse" water-gas shift reaction, i.e. $CO_2 + 2e^- + 2\,H^+ \rightarrow CO + H_2O$, with the electrons being supplied by Mo.

The reactivity of **1** toward some carbon electrophiles also was briefly surveyed. No reaction was observed when **1** was treated with CH_3I in THF at 0 °C. On the other hand, $CH_3OSO_2CF_3$ (2 equiv) reacts rapidly with **1** under the same conditions to afford an inseparable mixture of products, including CO_2-cleavage $[(C_5H_5)_2Mo(CO)Z]^+$ derivatives **2b** (ν_{CO} 2050 cm^{-1}). Carboxylic acid chlorides, including oxalyl, acetyl, and 4-nitrobenzoyl chlorides (2 equiv), were found to react slowly with **1** in CH_2Cl_2 during warming from −78 to 0 °C. The major product isolated (30%) from the reaction with oxalyl chloride proved to be the carbonyl chloride salt **2a**. On the other hand, addition of pentane to the $1/CH_3C({=}O)Cl$ reaction mixture caused precipitation of a mixture of **2a**, $CpMoCl_2$, and the acetato carbonyl complex **2c** (Scheme I) as judged by IR, ^1H NMR, and MS analysis.[15]

The Lewis acids $BF_3{\cdot}Et_2O$ and BCl_3 also were found to induce (rapid) CO_2 splitting in **1** (2 equiv, −78 °C, CH_2Cl_2 or THF), producing cationic carbonyl salts. The product from the reaction with BCl_3 (79%) was identified once again as the carbonyl chloride salt **2a**. The nature of the inner- and outer-sphere ions of the very sensitive BF_3-derived product, however, cannot be identified with certainty at present.[16]

Finally, some oxophilic but less electrophilic reagents were found to be unreactive toward **1**. Thus, neither $Me_3SiSiMe_3$ nor PPh_3 reacted with **1** below 0 °C; at higher temperatures decomposition of **1** to the recently characterized $(C_5H_5)_2Mo(\eta^2\text{-}CO_3)$[7] occurred.

Two mechanisms that account for the observed electrophilic cleavage of coordinated CO_2 in **1** are suggested in Scheme II. Initial attack by the electrophile (i.e. R_3Si^+, H^+, R^+, RCO^+, BX_3) could occur on either the coordinated or noncoordinated oxygen atom of CO_2. Subsequent scission of the Mo–O bond (pathway a) would give the metallocarboxylate derivative **4**, whereas C–O scission would lead to the cationic carbonyl species **5**. Either **4** or **5** then could react rapidly with a second equivalent of the reagent to produce the final product **2**. At present we cannot unambiguously distinguish between pathways a and b. Use of 1 equiv of reagent (e.g. with R_3SiX) generally afforded only product complex **2** and starting CO_2 complex **1**. Furthermore, IR monitoring at room temperature of several reactions failed to detect any intermediate species. However, low-temperature (−30 °C) ^1H NMR (CD_2Cl_2) monitoring of the reaction between **1** and $^tBuMe_2SiCl$ revealed transient C_5H_5– (5.15 ppm), $(CH_3)_3C$– (0.75 ppm), and $(CH_3)_2Si$– (0.07 ppm) resonances, which are appropriately positioned for a neutral intermediate such as **4** (E = $^tBuMe_2Si$). Efforts are underway to identify these intermediates and to explore further the reactions of **1** with external reagents.

Acknowledgment. We are grateful for support provided by the U.S. Department of Energy under Grants DE-FG01-87FE61146 and DE-FG05-89ER13997 (Office of Basic Energy Sciences, Division of Chemical Sciences).

Supplementary Material Available: Listings of atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and torsion angles for **3** (7 pages); a listing of structure factors (7 pages). Ordering information is given on any current masthead page.

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(13) X-ray crystal data for **3**: molecular formula $C_{17}H_{18}F_6MoO_8S_2$; M_r = 624.38; orthorhombic space group $P2_12_12_1$; a = 18.518 (4) Å, b = 15.773 (4) Å, c = 7.353 (2) Å, V = 2147.7 Å^3; Z = 4; μ(Mo Kα) = 7.89 cm^{-1}; R = 0.086, R_w = 0.096 for 1672 unique relections, ρ_{max} in the final difference map 7.6 e Å^{-3}. Data were collected at 160 ± 2 K with an Enraf-Nonius CAD4 diffractometer with monochromated Mo Kα (0.71069 Å) radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method. Poor crystal quality, however, limited the data quality, the main reason for the high R factor and the low accuracy of the structural parameters. Unusually, the highest peak in the difference map (7.6 e Å^{-3}) was found at 0.95 Å from the Mo atom. The location of this peak is too close to Mo and O(2) to be a bonded atom. Because of its unusual height the possibility of a disordered Mo position was checked, but it did not lead to a meaningful refinement. All of the interionic contacts are normal, the shortest (3.03 (2) Å) being between F(3) of $CF_3SO_3^-$ and C(5). Despite this peculiarity the gross molecular structural features of **3** are secure.

(14) A small number of $[Cp_2MoLL']^{2+}$ salts have been prepared, all of which have L and L′ as N- or P-donors: Calhorda, M. J.; Diaz, A. R. *Rev. Port. Quim.* **1981**, *23*, 12. Calhorda, M. J.; Diaz, A. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1443. Aviles, T.; Green, M. L. H.; Diaz, A. R.; Romao, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1367. Forder, R. A.; Gale, G. D.; Prout, K. *Acta Crystallogr., Sect. B* **1975**, *31*, 297.

(15) Spectroscopic data for $[Cp_2Mo(CO)OCOCH_3]Cl$ (**2c**, admixed with Cp_2MoCl_2 and **2a**): IR (KBr) 2050, 1645 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.46 (s, 10 H), 2.09 (s, 3 H); MS (FAB) m/e 351.0 ($Cp_2{}^{98}Mo(CO)OCOCH_3^+$, 54), 286.9 ($Cp_2{}^{98}MoOCOCH_3^+$, 86), 255.9 ($Cp_2{}^{98}MoCO^+$, 14), 228.0 ($Cp_2{}^{98}Mo^+$, 37).

(16) Spectroscopic data for the product from **1** + $BF_3{\cdot}Et_2O$: IR (KBr) 2070 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.53 (C_5H_5); ^{19}F NMR (acetone-d_6, CF_3CO_2H reference) δ −103.7; MS (FAB) m/e 434.9, 403.1, 337.0, 256.0 ($Cp_2{}^{98}MoCO$), 244.0 ($Cp_2{}^{98}MoO$), 228.0 ($Cp_2{}^{98}Mo$, 100).

Nucleophilic Addition to Coordinated Imines: Diastereoselective Synthesis of the Ruthenium Amide Complexes $(\eta^6\text{-}C_6Me_6)RuN(Ph)CRR'C_6H_4(PMe_3)$

Gaines C. Martin and James M. Boncella*

Department of Chemistry
University of Florida, Gainesville, Florida 32611

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Summary: The complex $(\eta^6\text{-}C_6Me_6)Ru(PMe_3)Cl_2$ reacts with 2 equiv of benzylideneaniline and 2 equiv of $[Ag][BF_4]$ to give the cationic ortho metalated imine complex