

Furthermore, curve 5^b of the same figure may be called on as a witness to the case in point—a big dose of borate ions simply wrecks the catalysis assembly lines. Finally, as our second witness, curve 5^a and 6^a show that carbonate ions will do nothing of this sort. Thus we conclude that intrasupramolecular catalysis for the hydrolysis of some long-chain esters can be damaged and even nullified by perturbation of their helical conformations.

Registry No. 1, 9005-82-7; 2, 830-03-5; 3, 1956-07-6; 4, 1956-10-1; 5, 1956-11-2; 6, 1492-30-4.

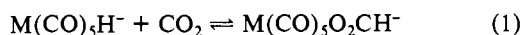
Reduction of Carbon Dioxide and Carbonyl Sulfide by Anionic Group 6B Metal Hydrides and Alkyls. Carbon-Hydrogen and Carbon-Carbon Bond Formation Processes and the Structure of [PNP][Cr(CO)₅SC(O)H]

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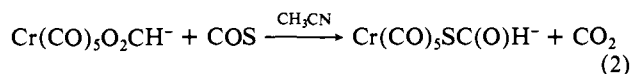
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Considerable interest is being shown in the development of C₁ chemistry, e.g., Fischer-Tropsch (F-T) technology. Recently, we reported on the facile reduction of CO₂ by anionic group 6B metal hydrides to afford metalloformate derivatives (reaction 1).¹



Because of the great potential for employing not only carbon monoxide but carbon dioxide as a feedstock in the production of reduced carbon containing molecules such as alcohols and hydrocarbons, an investigation on CO₂ insertion processes into metal-carbon bonds has been initiated.² Further, in an effort to more fully explore and assimilate the mechanistic aspects of these reactions, as well as to extend their applicability, we have utilized carbonyl sulfide as the substrate in these processes. In this communication we compare and contrast reactions of CO₂ and COS with anionic group 6B metal carbonyl hydrides and alkyls and describe the X-ray structural characterization of the product of carbonyl sulfide insertion into the chromium-hydride bond.

The synthesis of the Cr(CO)₅SC(O)H⁻ anion was achieved by either exchange of COS for carbon dioxide in the (formato)-pentacarbonylmetalate or by direct reaction of COS with Cr(CO)₅H⁻. The [PNP]⁺ or [Et₄N]⁺ salts of Cr(CO)₅O₂CH⁻, prepared from Cr(CO)₅Cl⁻ and TiO₂CH in CH₂Cl₂,¹ reacted cleanly over a 12-h period with COS in CH₃CN at 200 kPa to afford Cr(CO)₅SC(O)H⁻ (reaction 2). Alternatively, [K(Crypt-222)]-



[HCr(CO)₅], synthesized from Cr(CO)₆ and 2 equiv of Crypt 222³

(1) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223.

(2) For a review of other insertion reactions of CO₂ into transition-metal-carbon bonds, see: Kolomnik, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev.* **1978**, *47*, 334.

(3) 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Crypt 222, Kryptofix 222). Supplied by Parish Chemicals, Provo, UT 84601.

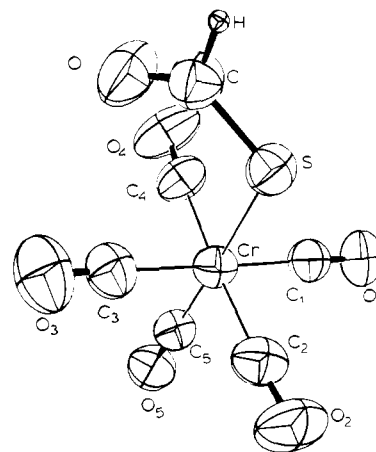


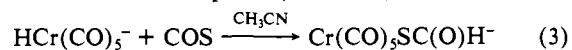
Figure 1. Perspective drawing of the Cr(CO)₅SC(O)H⁻ anion. Some bond lengths are as follows: Cr-S, 2.447 (1); Cr-C(eq)_{av}, 1.894 (4); Cr-C(ax), 1.837 (4); S-C, 1.725 (5); O-C, 1.206 (6); C-H, 1.06 (4) Å.

Table I. Reaction Conditions of CO₂ Insertion into CH₃W(CO)₅^{-a}

no.	additive	time, h	temp, °C	extent of the reaction, ^b %
1	none	24	ambient	~30
2	none	46	ambient	~46
3	none	24	52	100
4	Li salts ^c	20	ambient	100
5	LiCl ^d	6	ambient	100
6	Na ⁺ ^e	<25	ambient	100 ^f

^a CH₃W(CO)₅⁻PNP⁺, 0.01 M solution in THF, CO₂ pressure 100-300 kPa. ^b By IR spectroscopy of carbonyl region. ^c LiCl, LiBr, LiO₂CCH₃ as byproducts of the CH₃Li-LiBr + ClW(CO)₅⁻ → CH₃W(CO)₅⁻ reaction pressurized in situ with CO₂. ^d 1.1 molar excess with respect to CH₃W(CO)₅⁻. ^e NaBPh₄ 4-fold molar excess with respect to CH₃W(CO)₅⁻. ^f Determined as W(CO)₆.

solubilized KOH in CH₃CN,¹ reacted instantaneously with COS to provide the thioformate species (reaction 3).⁴ Both reactions



gave quantitative spectroscopic yields of the desired product.⁵ Since Cr(CO)₅O₂CH⁻ readily undergoes decarboxylation (i.e., reaction 1 run in the reverse direction), reaction 2 probably proceeds via the HCr(CO)₅⁻ anionic species as well. On the other hand, because the Mo and W formate analogues are more inert toward CO₂ extrusion, the thioformate derivatives in these instances were prepared according to reaction 3.

Infrared and ¹³C NMR spectral comparisons of these thioformate complexes with the products arising from CO₂ and CS₂ insertion processes with HM(CO)₅⁻ species are suggestive of binding of the thioformate ligand to the M(CO)₅ moiety through the sulfur atom.^{1,6} This mode of binding was confirmed in the [PNP][Cr(CO)₅SC(O)H] derivative by X-ray crystallography.⁷ The structural results for the anion are depicted in Figure 1.⁸ The disposition of the ligands about the chromium atom is that of a

(4) For preparative scale syntheses of hydridopentacarbonylmetalates, see: Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644. Darensbourg, M. Y.; Slater, S. J. *Am. Chem. Soc.* **1981**, *103*, 5914.

(5) Anal. Calcd for [PNP][Cr(CO)₅SC(O)H]: C, 63.72; H, 3.95; S, 4.05. Found: C, 63.66; H, 4.11; S, 4.13.

(6) For example, the ν(CO) infrared and ¹³C NMR spectral properties of [K(Crypt-222)][Cr(CO)₅SC(O)H] in acetonitrile are 2050 w, 1920 s, and 1861 m cm⁻¹ and δ(C_{ax}) 225.7, δ(C_{eq}) 219.1, and δ(SC(O)H) 198.8, respectively.

(7) Single crystals of [PNP][Cr(CO)₅SC(O)H] were grown from CD₃CN. They belong to the triclinic space group P1 with a = 12.671 (5) Å, b = 12.880 (5) Å, c = 15.356 (6) Å, α = 108.01 (3)°, β = 119.61 (3)°, γ = 97.48 (3)°, Z = 2. R = 4.0% for 5811 reflections with I > 3σ(I). Crystallographic analysis was carried out by Dr. Cynthia S. Day at Crystalitics Co., Lincoln, NE.

(8) The [PNP]⁺ counterion was found to be a well behaved group and contained dimensions which are expected for it. The average P-N bond length is 1.582 (3) Å, and the P-N-P angle is 140.1 (2)°.

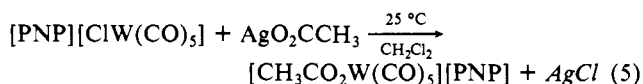
regular octahedron where the average C(ax)-Cr-C(eq) angle is 90.7°. The Cr-SC(O)H bond distance is 2.447 (1) Å and the Cr-C(ax) bond length is 0.057 Å shorter than the average Cr-C(eq) distance.⁹ The thioformate ligand resides in a position above the C(3)-Cr-C(4) quadrant and is contained in a plane which is almost perpendicular to and bisects the C(3)-Cr-C(4) angular arrangement.

The carbon monoxide ligands are quite labile in both Cr(CO)₅O₂CH⁻ and Cr(CO)₅SC(O)H⁻, where 63 and 75% CO exchange with ¹³CO in solution (40 kPa) is observed after only 10 min at ambient temperature. Nevertheless, although CO loss constitutes a necessary step in the extrusion of CO₂ from M(CO)₅O₂CH⁻ with concomitant M(CO)₅H⁻ formation or the reverse process of carboxylation,¹⁰ because of the added strength of the M-S bond the M(CO)₅SC(O)H⁻ derivatives showed no tendency toward COS expulsion.¹¹ Consistent with this observation Cr(CO)₅SC(O)H⁻ did not undergo exchange reactions with CO₂ or CS₂ to afford the formate or dithioformate complexes, e.g., reaction 2 was irreversible.

In a manner dissimilar to its hydrido analogue, W(CO)₅CH₃⁻ exhibits no propensity for dissociative CO loss at ambient temperature; nonetheless, the insertion reaction depicted in reaction 4 occurs under mild conditions in THF solution pressurized with



CO₂ (100-300 kPa). Reaction conditions and yields are summarized in Table I.^{12,13} Runs 1-3 afforded a product with $\nu(\text{CO})$ infrared (THF solution: 2059 w, 1955 w, 1907 s, and 1842 m) and ¹³C NMR (CD₃CN solution: 205.0 (axial CO), 200.3 (equatorial CO), 175.7 (carboxylic carbon), and 22.1 ppm (methyl carbon); the corresponding values in CDCl₃ are 206.4, 200.5, 177.4, and 23.7 ppm) spectral properties identical with that observed for the (acetato)pentacarbonyltungsten species obtained from reaction 5.^{9,14}



The presence of lithium salts was found to accelerate the rate of CO₂ insertion into the methyl-tungsten bond (see runs 4 and 5 in Table I). Although there were no apparent changes in the solution $\nu(\text{CO})$ infrared spectrum of the CH₃W(CO)₅⁻ anion upon addition of LiCl, the once formed acetate derivative in the presence of lithium salts exhibited slightly shifted $\nu(\text{CO})$ and ¹³C NMR spectral characteristics from that of pure [PNP][CH₃CO₂W(CO)₅]. The $\nu(\text{CO})$ infrared bands in THF were found at 2060 w, 1955 w, 1910 s, and 1846 m, and ¹³C NMR resonances in CDCl₃ were observed at 202.9, 198.8, 173.8, and 25.8 ppm. Although these spectral shifts are small, they were reproducible and are indeed significant. Hence, the electron-donating ability of the acetate ligand in the presence of the lithium cation is decreased, as indicated by the direction of the shift of both the $\nu(\text{CO})$ and ¹³C NMR spectral parameters. This most likely is indicative of complexation of the lithium cation at the nonbonding oxygen atom of the acetate group.¹⁵ Presumably an ion-pairing

(9) A similar observation was noted in the (acetato)pentacarbonylmetalates. Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398.

(10) The rate of decarboxylation of the M(CO)₅O₂CH⁻ (M = Cr and W) derivatives is greatly retarded when carried out under an atmosphere of carbon monoxide. Darensbourg, D. J.; Rokicki, A., unpublished results.

(11) For example, the Cr(CO)₅SC(O)H⁻ anion did not expel COS at temperatures ranging from ambient to 83 °C. The reaction of Cr(CO)₅O₂CH⁻ was incorrectly reported in ref 1 to reversibly add CS₂ with concomitant formation of Cr(CO)₅S₂CH⁻. The reaction is *not* reversible under the conditions studied. This oversight will be corrected in a full paper in preparation describing these insertion processes.

(12) [PNP][W(CO)₅CH₃] was prepared according to the published procedure.¹³

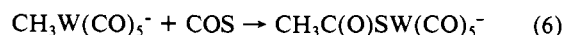
(13) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565.

(14) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudarski, R. *Inorg. Chem.*, in press.

(15) The interaction of alkali cations with carboxyl oxygens of metal carbonyl acyl anions is well-known: Darensbourg, M. Y.; Burns, D. *Inorg. Chem.* **1974**, *13*, 2970. Collman, J. P.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 5905.

interaction of this type in the transition state lowers the barrier of CO₂ insertion into the alkyl-tungsten bond.¹⁶ Independent experiments employing ¹³CO demonstrated that lithium salts neither accelerate the reactivity of CH₃W(CO)₅⁻ toward methyl migration nor labilize the complex anion toward CO dissociation. The sodium cation has an even more dramatic effect on the nature of the CO₂ reaction (see run 6 in Table I). In addition to enhancing the reactivity of the CH₃W(CO)₅⁻ anion toward CO₂, the thus formed CH₃CO₂W(CO)₅⁻ readily decomposes in the presence of sodium ion to afford W(CO)₆.

In contrast to reaction 4 the analogous process involving COS as a substrate to yield the sulfur-bonded (thioacetato)pentacarbonyltungsten derivative takes place much more readily (reaction 6). That is, reaction 6 is completed in less than 3 h at



room temperature at COS pressures between 100-200 kPa. This observation is probably indicative of metal-sulfur bond formation, a process more favorable than metal-oxygen bond formation, concurrent with or prior to carbon-carbon bond formation. Studies into the scope and intimate mechanism of CO₂ and COS insertions into group 6B metal alkyl bonds, along with subsequent CO₂ reduction processes, are currently under way. For example, the acetate derivatives are smoothly and quantitatively alkylated by alkyl halides to provide alkyl acetates and the precursors to metal-alkyl complexes, metal pentacarbonylhalide anions.¹⁷

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 80-09233) is greatly appreciated.

Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-squares refinements (6 pages). Ordering information is given on any current masthead page.

(16) This cation effect is not a reflection of reaction 4 involving an equilibrium process, since control experiments starting with CH₃CO₂W(CO)₅⁻ revealed no CH₃W(CO)₅⁻ and CO₂ formation.

(17) Darensbourg, D. J.; Kudarski, R., unpublished results.

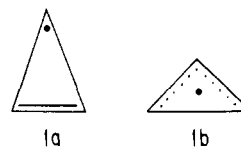
Structure and Dynamics of the Trimethylcyclopropenyl Radical As Determined by Electron and Nuclear Magnetic Resonance¹

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The structure of the simplest cyclic conjugated radical, cyclopropenyl radical, is of considerable theoretical interest. Theory predicts that the molecule will deviate from D_{3h} symmetry because of the Jahn-Teller effect. The simplest distortion compatible with the Jahn-Teller theorem yields a molecule with C_{2v} symmetry as represented by either **1a** or **1b**, with **1a** being the more likely structure. However, it is likely that the molecule has only C_s



symmetry because the substituent at the smallest angle of the isosceles triangle **1a** may be located substantially away from the ring plane. In addition to the structural problem, there exists the interesting problem regarding the barrier height in the threefold

(1) Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.