Table I between superconductivity and the effective copper valence (calculated from the nominal stoichiometry). Thus, all five compounds have the features believed necessary for high T_c superconductivity: they are copper oxides that have metallic conductivity, effective copper valence between 2+ and 3+, and structures with Cu–O networks, separated by ordered oxygen vacancies. From the data in Figure 3 and Table I, these features may be *necessary* for superconductivity, but they are clearly not sufficient. We conclude that the phenomenon of high T_c superconductivity is a subtle one.

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Note Added in Proof. The title compound has been independently observed by the groups at Caen[19] and Northwestern[20] and its structure solved.[19] We thank B. Raveau and K. Poeppelmeier for communicating their results prior to publication.

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[19] Er-Rakho, L.; Michel, C.; Raveau, B., submitted to *J. Solid State Chem.*

[20] Hahn, J.; Mason, T. O.; Hwu, S. J.; Poeppelmeier, K. R., submitted to *CHEMTRONICS.*

Sequential Insertion by an Extraordinarily Reactive (Cyclopentadienyl)cobalt Anion Complex

Dingneng Wang and Robert R. Squires*

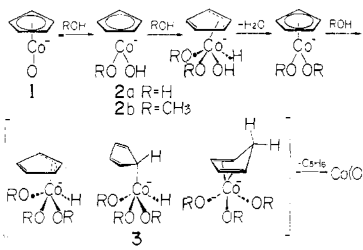
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received August 20, 1987

We recently described the formation of several novel examples of transition-metal oxide and polyoxide negative ions as products of gas-phase reactions between dioxygen and the 17-electron metal carbonylates $Fe(CO)_4^-$, $Cr(CO)_5^-$, and $Mo(CO)_5^-$.[1] In exploring the scope of this oxidation reaction with metal ion complexes possessing larger, polydentate organic ligands, we discovered that certain of the organometallic oxide product ions exhibit an enhanced gas-phase reactivity that is usually found only with highly coordinatively unsaturated species such as atomic ions or small metal ion fragments.[2] We describe here the gas-phase ion-molecule reactions of $CpCoO^-$ (**1**, Cp = η-C_5H_5), formed from oxidation of $CpCo(CO)_2^-$ by O_2, and show how this ion undergoes facile addition and sequential oxidative insertion reactions that are promoted by haptotropic rearrangement ("slippage") of the cyclopentadienyl ligand.

Our experiments were carried out at 298 K in a flowing afterglow apparatus that was recently mated to a triple quadrupole tandem mass spectrometer.[3] Collision-induced dissociation (CID) experiments with negative metal ions generated in the flow reactor (P(He) = 0.40 Torr; $\bar{v}$ = 9400 cm/s; F(He) = 190 STP cm^3/s) were performed in the triple quadrupole analyzer under single-collision conditions with argon target gas ($P(Ar) = 10^{-5}$ Torr). Bimolecular and termolecular reactions of mass-selected ions with neutral reagents in the central quadrupole were carried out under multiple-collision conditions ($P \simeq 10^{-4}$ Torr), with the axial kinetic energy of the reactant ion minimized (KE (c.m.) $\leq$ 0.1 eV).[4]

Scheme I



The $CpCo(CO)_2$ complex forms an abundant molecular anion in the flowing afterglow by thermal electron capture.[5] This ion undergoes a relatively slow reaction with O_2 ($k_{obsd} = 5.7 \pm 0.5 \times 10^{-11}$ cm^3/s; $k_{obsd}/k_{coll} = 0.1$) to yield $CpCoO^-$ (48%), $CpCo^-$ (30%), $CpCo(CO)O^-$ (12%), and $CpCo(CO)O_2^-$ (8%) as the major primary product ions. At higher O_2 flow rates, CoO_n^- and CoO_nH^- (n = 2, 3, 4) ions emerge as secondary and tertiary oxidation products.

The $CpCoO^-$ ion displays extraordinary reactivity for a (formally) 17-electron metal anion complex that distinguishes it from simple metal carbonylates[2b] and the other cyclopentadienylcobalt ions listed above, including $CpCo^-$. While **1** does not react with methane or other alkanes, it does react in a general way with Bronsted acids (HA) such as water, amines, alcohols, thiols, and certain unsaturated hydrocarbons by the stepwise addition–dehydration sequence shown in eq 1. In many cases the $CpCoA_2^-$ product reacts further with HA to yield an adduct and the CoA_3^- ion by displacement of 1,3-cyclopentadiene.

$$CpCoO^- \xrightarrow{HA} CpCo(OH)A^- \xrightarrow[-H_2O]{HA} CpCoA_2^- \xrightarrow[-C_5H_6]{HA} CoA_3^- \qquad (1)$$

$$HA = NH_3, H_2O, ROH, RCO_2H, H_2S, RSH$$

Isotope-labeling and CID experiments show that reactions of **1** with H_2O and alcohols occur by the sequential O–H insertion mechanism outlined in Scheme I. Addition of H_2O to **1** produces a bishydroxide complex ($CpCo(OH)_2^-$, **2a**), as evidenced by the occurrence of two *sequential* H/D exchanges when this ion reacts with D_2O in the middle quadrupole,[6] and by the identical yields for H_2O loss and $H_2{}^{18}O$ loss from CID of the $CpCo^{18}O^-/H_2O$ adduct formed in the flow tube. Interestingly, the reactions of $CpCo^{18}O^-$ with H_2O or $CpCoO^-$ with $H_2{}^{18}O$ do not produce an observable $^{18}O/^{16}O$ exchange.[7] This indicates that once addition of water across the cobalt–oxygen bond occurs, collisional stabilization takes place faster than redissociation of H_2O.

The H/D exchanges described above are actually a result of reversible *hydroxyl* exchange on the metal, rather than protonic exchange on oxygen. Thus, the $CpCo(OH)(^{18}OH)^-$ ion, formed by H_2O addition to $CpCo^{18}O^-$, reacts further with H_2O to yield $CpCo(OH)_2^-$, while the doubly labeled ion $CpCo(OD)(^{18}OD)^-$ (m/z 162) reacts with H_2O to produce $CpCo(OH)(^{18}OD)^-$ (m/z 161) and $CpCo(OD)(OH)^-$ (m/z 159), but *no* $CpCo(OH)(^{18}OH)^-$ (m/z 160) (eq 2).

$$\underset{}{CpCo^{18}O^-} \xrightarrow{D_2O} \underset{m/z\ 162}{CpCo(^{18}OD)(OD)^-} \xrightarrow{H_2O} \underset{m/z\ 161}{CpCo(^{18}OD)(OH)^-} + \underset{m/z\ 159}{CpCo(OH)(OD)^-} \qquad (2)$$

Reversible OH/OCH_3 exchanges are evident in the methanol reactions which also demonstrate that metal insertion into the C–O bond of methanol does *not* occur in this system.[8] For example,

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[1] Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2719.

[2] For reviews, see: (a) Allison, J. *Prog. Inorg. Chem.* **1986**, 627. (b) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623.

[3] (a) Lane, K. R.; Lee, R. E.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 5767. (b) Squires, R. R.; Lane, K. R.; Lee, R. E.; Wright, L. G.; Wood, K. V.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* **1985**, *64*, 185.

[4] (a) Dawson, P. H.; French, J. B.; Buckley, J. A.; Douglas, D. J.; Simmons, D. *Org. Mass Spectrom.* **1982**, *17*, 205. (b) Kinter, M. T.; Bursey, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 1797 and references cited therein.

[5] Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1977**, *16*, 3135.

[6] Similar exchanges in other gas-phase hydroxymetal anions have been observed: McDonald, R. N.; Jones, M. T. *Organometallics* **1987**, *6*, 1991.

[7] (a) Koola, J. D.; Kochi, J. K. *Inorg. Chem.* **1987**, *26*, 908. (b) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671.

[8] (a) McElvany, S. W.; Allison, J. *Organometallics* **1986**, *5*, 416, 1219. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641. Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

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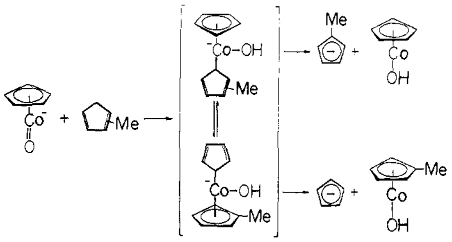
Scheme II



the $CpCo(^{18}OD)(OCH_3)^-$ ion, formed by addition of CH_3OD to $CpCo^{18}O^-$, reacts with H_2O to yield only $CpCo(OH)(OCH_3)^-$, $CpCo(^{18}OD)(OH)^-$, and $CpCo(OH)_2^-$ as primary and secondary products, while $CpCo(OH)(OCH_3)^-$ reacts with CD_3OD to yield $CpCo(OH)(OCD_3)^-$, $CpCo(OCH_3)(OCD_3)^-$, and $CpCo(OCD_3)_2^-$ but no $CpCo(OD)(OCH_3)^-$. Moreover, $CpCo(OCH_3)_2^-$ undergoes consecutive alkoxyl exchanges with CD_3OD to produce $CpCo(OCH_3)(OCD_3)^-$ and $CpCo(OCD_3)_2^-$.

Hydroxyl and alkoxyl group exchange in the reactions of **2** with water or alcohols requires oxidative insertion of cobalt into an O–H bond and formation of a hydridocobalt intermediate **3** possessing equivalent hydroxyl or alkoxyl groups and a "slipped" (η^3 or η^1)-Cp ligand or, alternatively, an η^4-1,3-cyclopentadiene ligand.[9] The stable H_2O adducts formed in the flow reactor with compositions corresponding to **3** are shown to have equivalent hydroxyl groups by the *statistical* yields for H_2O vs $H_2{}^{18}O$ loss from CID of the mixed isotopomers in the triple quadrupole. We also note that the occurrence of H_2O (or CH_3OH) loss as the lowest energy decomposition pathway for these ions argues against an $(\eta^4\text{-}C_5H_6)Co(OR)_3^-$ structure.

Approximately 10% of the reaction between **1** and CH_3OH yields $CpCo(OH)(H)^-$ by dehydrogenation and CH_2O loss. Reaction of $CpCo^{18}O^-$ with CH_3OD in the flow reactor followed by hydroxyl exchange of the dehydrogenation product (*m/z* 145) with H_2O in the middle quadrupole yields *only* $CpCo(OH)(H)^-$ (*m/z* 142) and *no* $CpCo(OH)D^-$ (*m/z* 143) or $CpCo(^{18}OH)H^-$ (*m/z* 144) (eq 3). This indicates that dehydrogenation of CH_3OD occurs by initial O–D addition across the metal–oxygen bond followed by β-elimination of CH_2O.

$$\underset{m/z\ 142}{CpCo^{18}O^-} \xrightarrow{CH_3OD} \underset{m/z\ 145}{CpCo(^{18}OD)(H)^-} \xrightarrow{H_2O} \underset{m/z\ 142}{CpCo(OH)(H)^-} \tag{3}$$

The reaction of **1** with 1,3-cyclopentadiene provides an especially interesting example of the sequence outlined in eq 1. Two primary products are observed corresponding to addition and proton transfer (eq 4). At higher cyclopentadiene flow rates, addition–dehydration occurs to produce a tricyclopentadienylcobalt anion that is best formulated as $(\eta^5\text{-Cp})(\eta^1\text{-Cp})_2Co^-$.[10] Reaction 4a is evidently not just a simple proton transfer, since reaction of **1** with methylcyclopentadiene (MeC_5H_5) yields nearly equal amounts of $MeC_5H_4^-$ and $C_5H_5^-$. Moreover, the mixed adduct $CpCo(OH)(MeC_5H_4)^-$ incorporates a single deuterium when reacted with D_2O and undergoes CID to yield nearly equal amounts of $MeC_5H_4^-$ and $C_5H_5^-$. These observations suggest that the two organic ligands in both the stabilized adduct and the proton transfer intermediate become chemically equivalent, presumably by way of the η^5-to-η^1 haptotropic rearrangement shown in Scheme II.[11] A complete accounting of the reactions of $CpCoO^-$ will be reported in a subsequent publication.

$CpCoO^-$ +  $\xrightarrow{a} C_5H_5^- + CpCoOH$ (4a)

$$\xrightarrow[\text{[He]}]{b} (C_5H_5)_2CoOH^- \xrightarrow[-H_2O]{C_5H_6} (C_5H_5)_3Co^- \tag{4b}$$

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(9) (a) Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Benjenke, V.; Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329. (b) Campbell, A. J.; Cottrell, C. E.; Fyfe, C. A.; Bennett, M. J.; Cotton, F. A.; Davison, A.; Faller, J. W.; Lippard, W. J.; Morehouse, S. M.; Jeffrey, K. R. *Inorg. Chem.* **1976**, *15*, 1326. (c) Bunner, H.; Langer, M. *J. Organomet. Chem.* **1973**, *54*, 221. (d) Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384. (e) Revek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908 and references therein. (f) Merola, J. S.; Kacmarcik, R. T.; Engen, D. V. *J. Am. Chem. Soc.* **1986**, *108*, 329.

(10) (a) Calderon, J. L.; Cotton, F. A.; Legzdins, J. *J. Am. Chem. Soc.* **1969**, *91*, 2528. (b) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238. (c) Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Takats, J. *J. Am. Chem. Soc.* **1971**, *93*, 3592.

(11) (a) Calderon, J. L.; Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1971**, *93*, 3587. (b) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1956**, 3030.

CO Hydrogenation, Deoxygenation, and C–C Coupling Promoted by $[(silox)_2TaH_2]_2$

Robert Toreki, Robert E. LaPointe, and
Peter T. Wolczanski*[†]

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853

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The Fischer–Tropsch (F–T) reaction, considered a potential solution to future energy concerns, has commanded the attention of researchers in both heterogeneous and homogeneous catalysis for the past 15 years.[1-4] The most widely accepted mechanism[2] for this conversion of synthesis gas (CO/H_2) to hydrocarbons and oxygenates incorporates three crucial steps: (1) CO is deoxygenated,[4-10] presumably via dissociative adsorption;[4] (2) H-transfer to surface carbides[2-5] or CO_{ads}[7,11-13] produces surface methylene

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[†] Sloan Foundation Fellow, 1987–1989.

(1) (a) Falbe, J. *Chemical Feedstocks from Coal*; John Wiley and Sons: New York, 1981. (b) Dombeck, B. D. *Adv. Catal.* **1983**, *32*, 325–416. (c) Bell, A. T. *Catal. Rev.-Sci. Eng.* **1981**, *23*, 203–232. (d) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165–216. (e) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447–474.

(2) (a) Fischer, F.; Tropsch, H. *Chem. Ber.* **1926**, *59*, 830–836. (b) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1981**, *103*, 1287–1289. (c) Brady, R. C., III; Pettit, R. *Ibid.* **1980**, *102*, 6182–6184. (d) George, P. M.; Avery, N. R.; Weinberg, W. H.; Tebbe, F. N. *Ibid.* **1983**, *105*, 1393–1394.

(3) (a) Mims, C. A.; McCandlish, L. E. *J. Phys. Chem.* **1987**, *91*, 929–937. (b) Zhang, X.; Biloen, P. *J. Catal.* **1986**, *98*, 468–476. (c) Vannice, M. A.; Sudhaker, C. *J. Phys. Chem.* **1984**, *88*, 2429–2432.

(4) (a) Biloen, P.; Helle, J. N.; Sachtler, W. M. H. *J. Catal.* **1979**, *58*, 95–107. (b) Biloen, P.; Helle, J. N.; van der Berg, F. G. A.; Sachtler, W. M. H. *Ibid.* **1983**, *81*, 450–463.

(5) (a) Bradley, J. S. *Adv. Organomet. Chem.* **1983**, *22*, 1–58. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (c) Tachikawa, M.; Muetterties, E. L.; *Prog. Inorg. Chem.* **1981**, *28*, 203–238. (d) Horwitz, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 8147–8153.

(6) (a) Marsella, J.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chem. Acta* **1985**, *96*, 161–170. (b) Marsella, J. A.; Huffman, J. C.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596–5598. (c) Wood, C. D.; Schrock, R. R. *Ibid.* **1979**, *101*, 5421–5422. (d) Planalp, R. P.; Andersen, R. A. *Ibid.* **1983**, *105*, 7774–7775. (e) Blenkers, J.; de Liefde Meijer, H. J.; Teuben, J. H. *Organometallics* **1983**, *2*, 1483–1484. (f) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Ziller, J. W.; Beanan, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 1144–1145. (g) Jacobsen, E. N.; Trost, M. K.; Bergman, R. G. *Ibid.* **1986**, *108*, 8092–8094.

(7) (a) Erker, G.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251–2257. (b) Kropp, K.; Skibbe, V.; Erker, G.; Kruger, C. *Ibid.* **1983**, *105*, 3353–3354. (c) Erker, G.; Kropp, K.; Kruger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447–2640. (d) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103–109.

(8) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2425–2433, and references therein concerning CH_2O complexes.

(9) (a) Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Smith, C. A. *Organometallics* **1987**, *6*, 1280–1291. (b) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C.; Streib, W. E. *Ibid.* **1985**, 1771–1773.

(10) (a) LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382–6384. (b) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *Ibid.* **1985**, *107*, 3728–3730.

0002-7863/87/1509-7558$01.50/0