

Communications

Electrochemical Studies of the Preparation and One-Electron Reduction of Half-Sandwich Cobalt-Arene Cations

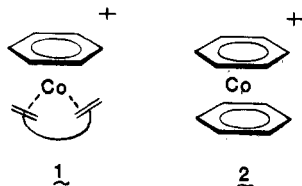
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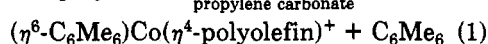
Summary: The half-sandwich compounds $[(\eta^6\text{-C}_6\text{Me}_6)\text{-Co}(\eta^4\text{-polyolefin})][\text{PF}_6]$, polyolefin = 1,5-cyclooctadiene or norbornadiene, have been prepared by reaction of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Co}]^+$ with polyolefin in propylene carbonate. Cyclic voltammetry was used to find the optimum reaction conditions and to demonstrate the reversibility of one-electron reductions of the half-sandwich cations.

In contrast to the rich chemistry of compounds containing the CpCo (Cp = $\eta^5\text{-C}_5\text{H}_5$) moiety, complexes of the isoelectronic $(\eta^6\text{-arene})\text{Co}^+$ group are rare,¹ exceptions being the sandwich compounds $(\eta^6\text{-C}_6\text{R}_6)\text{Co}(\eta\text{-C}_n\text{R}_n)^{m+}$, with $m = 1$ when $n = 4$, $m = 2$ when $n = 5$, and $m = 2$, 1, or 0 when $n = 6$.² We now report a method of preparation of the half-sandwich cationic compounds $(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-polyolefin})^+$, **1**, by reaction of $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Co}^+$,



2, with the appropriate polyolefin. The reaction may be accomplished by electrochemical or chemical reduction of $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Co}^{2+}$ in the presence of diene or by direct reaction of $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Co}^+$ with the diene in propylene carbonate. The half-sandwich cations **1** undergo reversible one-electron reductions to persistent neutral radicals.

The choice of solvent in the ligand-exchange reaction (1) is crucial, for **2** is stable in the presence of polyolefins for days in CH_2Cl_2 and undergoes rapid decomposition to $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Co}^+ + \text{polyolefin}$



non-arene-containing complexes in strongly coordinating solvents like acetone and acetonitrile. However, the reaction proceeds quantitatively when pure propylene car-

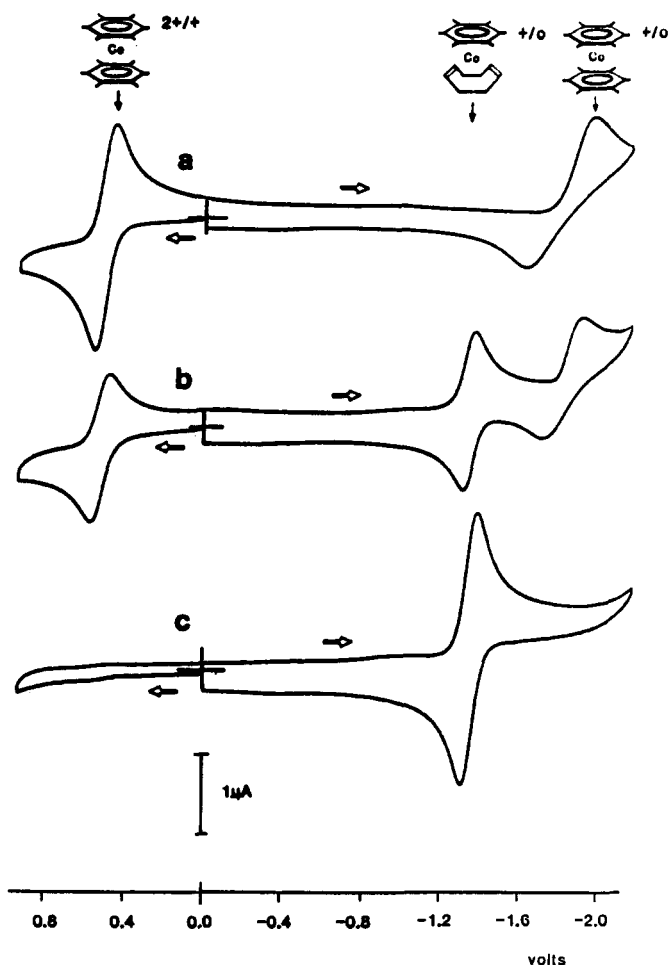


Figure 1. Cyclic voltammograms of a 5×10^{-4} mM solution of **2** in propylene carbonate/0.1 M Bu_4NPF_6 at a Pt electrode using a scan rate of 200 mV/s: (a) **2** alone; (b) 20 min after addition of ca. 100-fold excess of 1,5-cod; (c) 100 min after addition of 1,5-cod.

bonate or a 3–5% solution of acetone or propylene carbonate in CH_2Cl_2 is employed as the reaction medium. Optimum conditions were found by monitoring the reaction using cyclic voltammetry (CV). Figure 1 shows CV scans of a solution of 0.5 mM **2** in propylene carbonate³ before (top) and after (center and bottom) addition of a 100-fold excess of 1,5-cyclooctadiene (cod). The two reversible waves for the bis(arene) complex **2** (top trace) are due to the processes $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Co}^{2+/+}$ ($E^0 = +0.52$ V) and $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Co}^{+/0}$ ($E^0 = -1.73$ V). The electrochemistry of this compound has been previously reported.^{2f} Starting about 5 min after addition of 1,5-cod, a new reversible wave appeared at $E^0 = -1.30$ V. This wave continued to grow at the expense of those of **2** (middle trace), until the conversion was complete after 2 h (bottom trace).

The complex **1**, polyolefin = 1,5-cod, responsible for the wave at $E^0 = -1.30$ V, was isolated through a nonelectro-

(3) Supporting electrolyte was 0.1 M Bu_4NPF_6 , and a Pt bead electrode was employed. Propylene carbonate was used as received from Burdick and Jackson Laboratories. Potentials are referred to the saturated calomel electrode.

(1) Kemmitt, R. D. W.; Russell, D. R. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 5.

(2) $(\eta^6\text{-arene})\text{Co}(\eta^4\text{-C}_4\text{R}_4)^+$: (a) Efraty, A.; Maitlis, P. *J. Am. Chem. Soc.* **1967**, *89*, 3744. $(\eta^6\text{-arene})\text{CoCp}^{2+}$: (b) Fischer, E. O.; Fisher, R. D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *16B*, 556. (c) Fairhurst, G.; White, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1531. (d) Lai, Y.-H.; Tam, W.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *216*, 97. (e) Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Dalton Trans.* **1979**, 355. (f) $(\eta\text{-C}_6\text{R}_6)_2\text{Co}^{m+}$: Koelle, U.; Fuss, B.; Rajasekharan, B. L.; Ramakrishna, B. L.; Ammeter, J. H.; Böhm, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 4152. $(\eta\text{-C}_6\text{R}_6)_2\text{Co}^{m+}$: (g) Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964**, *2*, 222. (h) *J. Organomet. Chem.* **1964**, *1*, 307. (i) Thompson, M. R.; Day, C. S.; Day, V. W.; Mink, R. I.; Muettterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2979.

chemical preparation. When 0.78 mmol of $2\cdot[\text{PF}_6]$ and 8.3 mmol of 1,5-cod were stirred under nitrogen for 2 h in 2.5 mL of propylene carbonate, the solution turned from yellow-green to red-orange with precipitation of the displaced hexamethylbenzene. Addition of diethyl ether resulted in separation of a brown oil that was crystallized after adding more ether (about 80 mL in total). Filtration and twice repeated crystallization from CH_2Cl_2 /ether gave 0.69 mmol (88% yield) of red-orange crystals of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-1,5-cod})][\text{PF}_6]^4$. Yellow crystals of the corresponding norbornadiene complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-C}_7\text{H}_8)][\text{PF}_6]$ have been similarly isolated,⁵ and reactions with several other cyclic polyolefins, including cyclohexadiene, cycloheptadiene, cycloheptatriene and cyclooctatetraene, have been monitored electrochemically.

2 is a formally 20-electron species. However, unlike the isoelectronic $(\eta\text{-C}_6\text{Me}_6)_2\text{Ru}$, which relieves its electronic strain by having one η^4 arene,⁶ it has two planar η^6 -arenes.⁷ Replacement of one arene by a diene thus results in the stable 18-electron complexes 1. Apparently, a key intermediate in the ligand-exchange process is the solvento-species $(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\text{solv})_n^+$, where $n = 2$ (or possibly 3).

The complexes 1 are of interest as cationic analogues of $\text{CpCo}(\eta^4\text{-polyolefin})$ complexes, which can undergo isomerizations of the polyolefin when reduced.⁸ The new (hexamethylbenzene)cobalt cationic complexes are very well-behaved electrochemically, showing one-electron reductions in nonaqueous media. Their E^0 potentials are shifted by a volt or more positive of the corresponding $\text{CpCo}(\text{polyolefin})$ reductions, befitting the positive charge on the arene complexes. Cyclic voltammetry studies of 1 (polyolefin = 1,5-cod or norbornadiene) show that the reduction to the neutral 19-electron radical $(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-polyolefin})$ is fully reversible and diffusion controlled. In propylene carbonate at a scan rate of 100 mV/s, separation of the anodic and cathodic peak potentials is 60 mV and the anodic to cathodic current ratio is 1.0. The cathodic current function ($i_{pc}/v^{1/2}$) is constant ($\pm 1\%$) over an order of magnitude change in scan rate.⁹

We are currently investigating other reactions of 2 and the structure and reactions of the radicals derived from the electroreduction of 1.

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Registry No. $2\cdot[\text{PF}_6]$, 53382-65-3; $[(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-1,5-cod})][\text{PF}_6]$, 92694-81-0; $[(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-C}_7\text{H}_8)][\text{PF}_6]$, 92694-83-2; $(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-1,5-cod})$, 92694-84-3; $(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-C}_7\text{H}_8)$, 92694-82-1; $(\eta^6\text{-C}_6\text{Me}_6)_2\text{Co}^{2+}$, 53382-66-4; cyclohexadiene, 29797-09-9; cycloheptadiene, 29828-02-2; cycloheptatriene, 544-25-2; cyclooctatetraene, 629-20-9.

(4) Data for $[(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(1,5\text{-cod})][\text{PF}_6]$: $^1\text{H NMR}$ (CD_2Cl_2) δ 3.19 (br s, 4 H), 2.51 (m, 4 H), 2.18 (s, 18 H), 1.80 (m, 4 H). Calcd for $\text{C}_{20}\text{H}_{30}\text{CoPF}_6$: C, 50.64; H, 6.38. Found: C, 50.48; H, 6.52.

(5) Data for $[(\eta^6\text{-C}_6\text{Me}_6)\text{Co}(\eta^4\text{-C}_7\text{H}_8)][\text{PF}_6]$: $^1\text{H NMR}$ (CD_2Cl_2) δ 3.36 (m, 2 H), 2.97 (dd, 4 H), 2.24 (s, 18 H), 1.03 (t, 2 H). Calcd for $\text{C}_{19}\text{H}_{26}\text{CoPF}_6$: C, 49.79; H, 5.72. Found: C, 49.50; H, 5.87.

(6) (a) Fischer, E. O.; Elschenbroich, Ch. *Chem. Ber.* 1970, 103, 162.

(b) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* 1972, B28, 2049.

(7) Thompson, M. R.; Day, C. S.; Day, V. W.; Mink, R. I.; Muetterties, E. L. *J. Am. Chem. Soc.* 1980, 102, 2979.

(8) (a) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* 1981, 103, 4779. (b) Albright, T. A.; Geiger, W. E.; Moraczewski, J.; Tulyathan, B. *J. Am. Chem. Soc.* 1983, 105, 1772.

(9) The significance of these observations is as follows. The 60-mV peak separation (independent of scan rate) is consistent with an electrochemically reversible (fast electron transfer) one-electron process. The value of unity for the current ratio shows that the electrode product (the neutral radical) is stable over the cyclic voltammetry time scale (ca. 10 s here), and the constant current function (peak cathodic current divided by square root of scan rate) is indicative of a diffusion-controlled process.

Thermolysis Reactions of Iron and Ruthenium Metallo-carboxylic Acids

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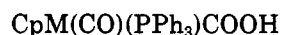
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Summary: A new synthesis of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COOH}$ is described as is the preparation of a new metallo-carboxylic acid, $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{COOH}$. Upon heating, the iron acid provided $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{PPh}_3)$, as the first isolable product, which resulted from reaction of the acid with its decarboxylation product $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{H}$. The ruthenium acid decarboxylated to the hydride in acetone, but it was stable to thermolysis in benzene. The ruthenium acid is not reactive toward $\text{CpM}(\text{CO})(\text{PPh}_3)\text{H}$ ($\text{M} = \text{Fe}, \text{Ru}$). Thermolyses in chlorinated solvents take place wholly (iron acid) or in part (ruthenium acid) by redox paths; both acids were also readily oxidized by Ag^+ .

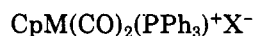
Studies of metallo-carboxylic acids are of interest because of the proposed intermediacy of such complexes in metal carbonyl catalyzed water gas shift reactions.¹ Although relatively few metallo-carboxylic acids have been isolated and studied thoroughly,² one of the reactions that has been thought to be characteristic of this class of compounds is decarboxylation, induced by heating and, in some instances, catalyzed by base.

A preliminary account of the preparation of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COOH}$ (1a) and several of its derivatives appeared several years ago.^{2c} The thermal instability was noted, but, although decarboxylation was suggested, the thermolysis products were not identified. As part of a general study of metallo-carboxylic acids,^{2e,j} we have prepared 1a and its ruthenium analogue 1b and studied the thermolysis reactions of these two acids.



1a, M = Fe

1b, M = Ru

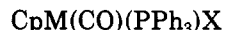


2a, M = Fe, X = BF_4

2b, M = Ru, X = BF_4

2c, M = Fe, X = Cl

2d, M = Ru, X = Cl



3a, M = Fe, X = H

3b, M = Ru, X = H

3c, M = Fe, X = Cl

3d, M = Ru, X = Cl

(1) Pettit, R.; Mauldin, C.; Cole, T.; Kang, H. *Ann. N.Y. Acad. Sci.* 1977, 295, 151. (b) For a recent review of the WGS reaction see: Ford, P. C. *Acc. Chem. Res.* 1981, 14, 31.

(2) Although widely invoked as probable intermediates in reactions involving OH^- and metal carbonyls, few examples of these complexes have been observed: (a) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* 1969, 443. (b) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* 1979, 103, 741 [see also: Sweet, J. R.; Graham, W. A. G. *Organometallics* 1982, 1, 982. (c) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* 1979, 103, 1627. (d) Catellini, M.; Halpern, J. *Inorg. Chem.* 1980, 19, 566. (e) Gibson, D. H.; Hsu, W.-L.; Ahmed, F. U. *J. Organomet. Chem.* 1981, 215, 379. (f) Tam, W.; Lin, G.-Y.; Wong, W. K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* 1982, 104, 141. (g) Alton, J. G.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* 1983, 246, C23. (h) Barrientos-Penna, C. F.; Gilchrist, A. B.; Sutton, D. *Organometallics* 1983, 2, 1265. (i) Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* 1973, 55, C88. (j) Gibson, D. H.; Owens, K.; Ong, T.-S. *J. Am. Chem. Soc.* 1984, 106, 1125.