Communications

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

Joseph Edwin and William E. Geiger*

Department of Chemistry, University of Vermont
Burlington, Vermont 05405

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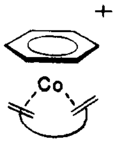
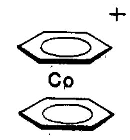
Summary: The half-sandwich compounds $[(\eta^6\text{-}C_6Me_6)\text{-}Co(\eta^4\text{-polyolefin})][PF_6]$, polyolefin = 1,5-cyclooctadiene or norbornadiene, have been prepared by reaction of $[(\eta^6\text{-}C_6Me_6)_2Co]^+$ with polyolefin in propylene carbonate. Cyclic voltammetry was used to find 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 = $\eta^5\text{-}C_5H_5$) moiety, complexes of the isoelectronic $(\eta^6\text{-arene})Co^+$ group are rare,[1] exceptions being the sandwich compounds $(\eta^6\text{-}C_6R_6)Co(\eta\text{-}C_nR_n)^{m+}$, 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 $(\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-polyolefin})^+$, 1, by reaction of $(\eta^6\text{-}C_6Me_6)_2Co^+$, 2, with the appropriate polyolefin. The reaction may be accomplished by electrochemical or chemical reduction of $(\eta^6\text{-}C_6Me_6)_2Co^{2+}$ in the presence of diene or by direct reaction of $(\eta^6\text{-}C_6Me_6)_2Co^+$ with the diene in propylene carbonate. The half-sandwich cations 1 undergo reversible one-electron reductions to persistent neutral radicals.



1



2

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

$$(\eta^6\text{-}C_6Me_6)_2Co^+ + \text{polyolefin} \xrightarrow[\text{propylene carbonate}]{} (\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-polyolefin})^+ + C_6Me_6 \quad (1)$$

non-arene-containing complexes in strongly coordinating solvents like acetone and acetonitrile. However, the reaction proceeds quantitatively when pure propylene carbonate 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 carbonate[3] 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 $(\eta^6\text{-}C_6Me_6)_2Co^{2+/+}$ ($E^0 = +0.52$ V) and $(\eta^6\text{-}C_6Me_6)_2Co^{+/0}$ ($E^0 = -1.73$ 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).

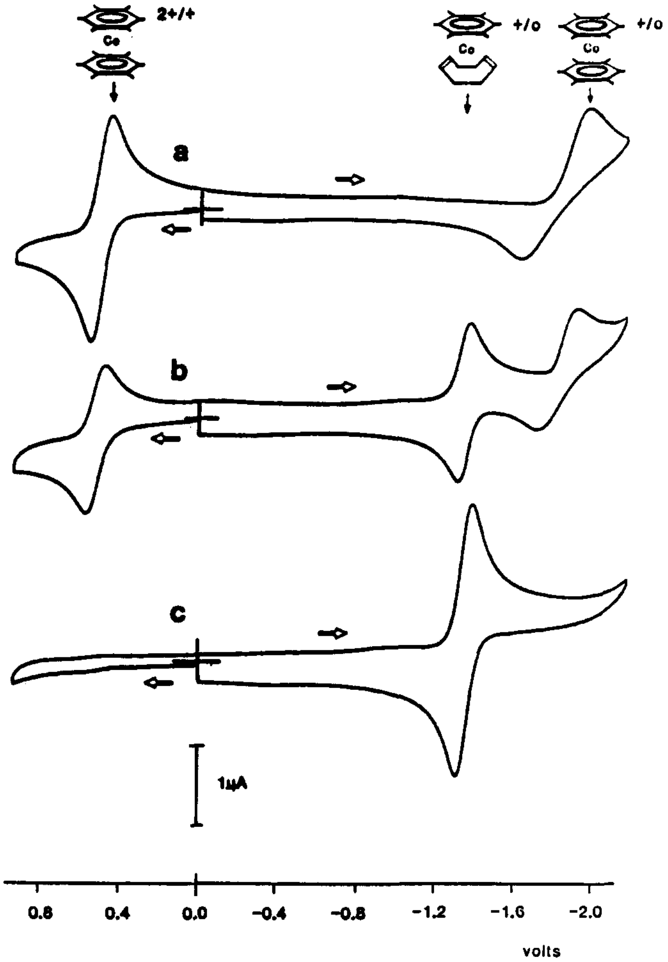


Figure 1. Cyclic voltammograms of a 5×10^{-4} mM solution of 2 in propylene carbonate/0.1 M Bu_4NPF_6 at a Pt electrode using a scan rate of 200 mV/s: (a) 2 alone; (b) 20 min after addition of ca. 100-fold excess of 1,5-cod; (c) 100 min after addition of 1,5-cod.

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

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[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] $(\eta^6\text{-arene})Co(\eta^4\text{-}C_4R_4)^+$: (a) Efraty, A.; Maitlis, P. *J. Am. Chem. Soc.* **1967,** *89,* 3744. $(\eta^6\text{-arene})CoCp^{2+}$: (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) $(\eta\text{-}C_6R_6)_2Co^{m+}$: Koelle, U.; Fuss, B.; Rajasekharan, B. L.; Ramakrishna, B. L.; Ammeter, J. H., Böhm, M. C. *J. Am. Chem. Soc.* **1984,** *106,* 4152. $(\eta\text{-}C_6R_6)_2Co^{m+}$: (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.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980,** *102,* 2979.

[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.

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chemical preparation. When 0.78 mmol of 2·[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 crystalization from CH_2Cl_2/ether gave 0.69 mmol (88% yield) of red-orange crystals of [(η^6-C_6Me_6)Co(η^4-1,5 cod)][PF_6][4]. Yellow crystals of the corresponding norbornadiene complex [(η^6-C_6Me_6)Co(η^4-C_7H_8)][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 (η-C_6Me_6)$_2$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 solventospecies (η^6-C_6Me_6)Co(solv)$_n^+$, where $n = 2$ (or possibly 3).

The complexes 1 are of interest as cationic analogues of CpCo(η^4-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 CpCo(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 (η^6-C_6Me_6)Co(η^4-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 (±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**·[PF_6], 53382-65-3; [(η^6-C_6Me_6)Co(η^4-1,5-Cod)][PF_6], 92694-81-0; [(η^6-C_6Me_6)Co(η^4-C_7C_8)][PF_6], 92694-83-2; (η^6-C_6Me_6)Co(η^4-1,5-Cod), 92694-84-3; (η^6-C_6Me_6)Co(η^4-C_7H_8), 92694-82-1; (η^6-C_6Me_6)$_2$Co^{2+}, 53382-66-4; cyclohexadiene, 29797-09-9; cycloheptadiene, 29828-02-2; cycloheptatriene, 544-25-2; cyclooctatetraene, 629-20-9.

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(4) Data for [(η^6-C_6Me_6)Co(1,5-cod)][PF_6]: ^{1}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 $C_{20}H_{30}CoPF_6$: C, 50.64; H, 6.38. Found: C, 50.48; H, 6.52.

(5) Data for [(η^6-C_6Me_6)Co(η^4-C_7H_8)][PF_6]: ^{1}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 $C_{19}H_{26}CoPF_6$: 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 Metallocarboxylic Acids

Dorothy H. Gibson* and Tek-Sing Ong

Department of Chemistry, University of Louisville
Louisville, Kentucky 40292

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Summary: A new synthesis of CpFe(CO)(PPh_3)COOH is described as is the preparation of a new metallocarboxylic acid, CpRu(CO)(PPh_3)COOH. Upon heating, the iron acid provided $Cp_2Fe_2(CO)_3(PPh_3)$, as the first isolable product, which resulted from reaction of the acid with its decarboxylation product CpFe(CO)(PPh_3)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 CpM(CO)(PPh_3)H (M = Fe, 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 metallocarboxylic acids are of interest because of the proposed intermediacy of such complexes in metal carbonyl catalyzed water gas shift reactions.[1] Although relatively few metallocarboxylic 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 CpFe(CO)(PPh_3)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 metallocarboxylic acids,[2e,j] we have prepared **1a** and its ruthenium analogue **1b** and studied the thermolysis reactions of these two acids.

CpM(CO)(PPh_3)COOH
1a, M = Fe
1b, M = Ru

CpM(CO)$_2$(PPh_3)$^+$X$^-$
2a, M = Fe, X = BF_4
2b, M = Ru, X = BF_4
2c, M = Fe, X = Cl
2d, M = Ru, X = Cl

CpM(CO)(PPh_3)X
3a, M = Fe, X = H
3b, M = Ru, X = H
3c, M = Fe, X = Cl
3d, M = Ru, X = Cl

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(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.

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