Carborane-Stabilized M(III) Complexes of Mononuclear and Dinuclear Arene Complexes (M = Fe, Ru)

Jon M. Merkert,[†] William E. Geiger,*,[†]
James H. Davis, Jr.,[‡] Martin D. Attwood,[‡] and
Russell N. Grimes*,[‡]

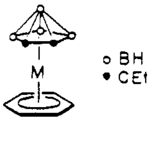
Departments of Chemistry, University of Vermont
Burlington, Vermont 05405
and University of Virginia
Charlottesville, Virginia 22901

Received December 15, 1988

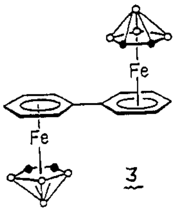
Summary: The complexes $(\eta^6\text{-}C_6H_6)M(Et_2C_2B_4H_4)$, where M = Fe or Ru, undergo reversible one-electron oxidation to the corresponding M(III) monocations, as determined by cyclic voltammetry measurements. The $E°$ values are 0.54 and 0.85 V vs $Cp_2Fe^{0/+}$ for the Fe and Ru complexes, respectively. A bis(ferracarborane) complex of biphenyl shows two reversible oxidations ($E°$ = 0.55 and 0.84 V). This is the first evidence that Fe(II) or Ru(II) arene complexes can be reversibly oxidized and further establishes the ability of *nido*-$R_2C_2B_4H_4^{2-}$ ligands to stabilize arene–transition-metal π-complexes.

The reversible oxidation of π-arene complexes of Fe(II) or Ru(II) has been the goal of a number of investigations. However, except for the report of a frozen solution ESR signal attributed to Fe(III) when (arene)FeCp cations are oxidized in $SbCl_5/CH_2Cl_2$,[1] these efforts have been unsuccessful.[2] Fe(II) arene complexes have been generally shown to be inert to oxidation either at an electrode[3] or by chemical oxidants.[4–6] Analogous Ru(II) arene complexes have been reported to undergo irreversible electrochemical oxidation.[7,8] In this communication we show by cyclic voltammetry experiments that metal carborane complexes of arenes undergo reversible M(II)/M(III) processes.

The *nido*-carborane dianion $(R_2C_2B_4H_4)^{2-}$ forms sandwich complexes that are electronically and structurally analogous to those of the cyclopentadienyl anion,[9] and a number of air-stable divalent carboranyl metal arene complexes have recently been described.[10] Since small carborane ligands are known to strongly stabilize high metal oxidation states,[11] we decided to investigate the electrochemical oxidation of Fe and Ru arene complexes containing the ligand $(Et_2C_2B_4H_4)^{2-}$. Reversible one-electron processes are observed for complexes $[(\eta^6\text{-}C_6H_6)M(Et_2C_2B_4H_4)]^{0/+}$ [M = Fe (1) or Ru (2)] in dichloromethane solutions.



1, M=Fe 2, M=Ru



3

Cyclic voltammetry scans are shown in Figure 1 for $(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_4)$ (solid line) and for the ruthenium analogue $(\eta^6\text{-}C_6H_6)Ru(Et_2C_2B_4H_4)$ (open circles). Both M(II) complexes undergo diffusion-controlled one-electron oxidation processes. The one-electron nature of the oxidation was established through comparison of the wave heights with that of a 1e standard (ferrocene) and by exhaustive coulometry of the Fe complex. Separations of about 70–80 mV were observed for the cathodic and anodic peak currents, close to those observed for ferrocene under similar conditions and scan rates (ca. 0.1–0.2 V/s).

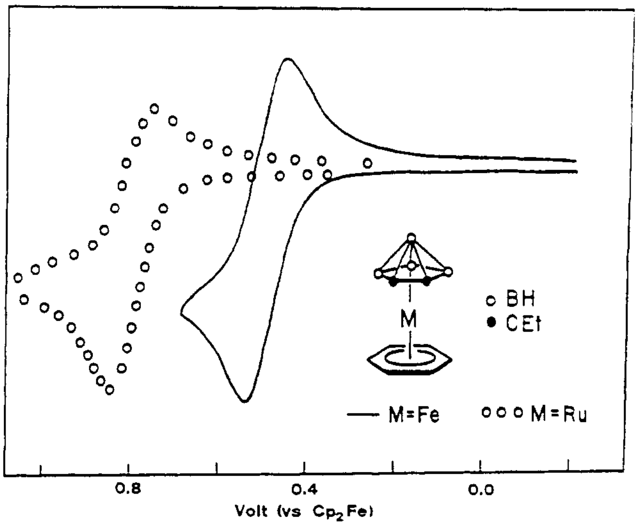


Figure 1. Cyclic voltammograms of Fe complex 1 (solid line) and Ru complex 2 (open circles) in CH_2Cl_2/0.1 M Bu_4NPF_6 at Pt electrode. Conditions: ambient temperature; scan rate = 200 mV/s; concentration = 0.56 mM. Full scale on the *y* axis is 4.5 μA.

The chemical reversibility of the Fe(II)/Fe(III) couple is complete at 298 K when the scan rate is at least 0.1 V/s. The stability of the Ru(III) complex is slightly lower, as indicated by the lower chemical reversibility of the Ru(II)/Ru(III) couple. At 298 K and a scan rate of 0.2 V/s, the ratio of i_c to i_a is only 0.67 for the Ru complex (this ratio increased to 0.93 at a scan rate of 0.5 V/s). The $E°$ of the Fe complex is 0.54 V vs $Cp_2Fe^{0/+}$ (+1.01 V vs SCE) and that of the Ru complex is +0.85 V vs $Cp_2Fe^{0/+}$. In earlier work, substitution of a Cp^- ligand by $R_2C_2B_4H_4^{2-}$ (R = H, Me) was shown to shift a Fe(II)/Fe(III) wave negative by about 0.8 V.[11] This stabilization is much larger than the shifts in potential (either positive or negative) that have been achieved through substitution within the cyclopentadienyl group.[12] Therefore, where synthetically

---

[†] University of Vermont.
[‡] University of Virginia.

(1) Skolodovnikov, S. P.; Nesmeyanov, A. N.; Vol'kenau, N. A.; Kotova, L. S. *J. Organomet. Chem.* **1980**, *201*, C45.
(2) Astruc, D. *Tetrahedron* **1983**, *39*, 4027.
(3) Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 500.
(4) Nesmeyanov, A. N.; Vol'kenau, N. A.; Sirotkina, E. I.; Deryabin, V. V. *Dokl. Akad. Nauk SSR* **1967**, *177*, 1110.
(5) Nesmeyanov, A. N.; Vol'kenau, N. A.; Sirotkina, E. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 1170.
(6) Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3603.
(7) Robertson, I. W.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1982**, *228*, 171.
(8) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981.
(9) Recent review: Grimes, R. N. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenburg, A., Williams, R. E., Eds.; VCH Publishers: New York, 1988; Chapter 11, p 235.
(10) (a) Fe complexes: Spencer, J. T.; Grimes, R. N. *Organometallics* **1987**, *6*, 328 and references therein. (b) Ru complexes: Davis, J. H., Jr.; Sinn, E.; Grimes, R. N., submitted for publication.
(11) Geiger, W. E.; Brennan, D. E. *Inorg. Chem.* **1982**, *21*, 1963.

0276-7333/89/2308-1580$01.50/0

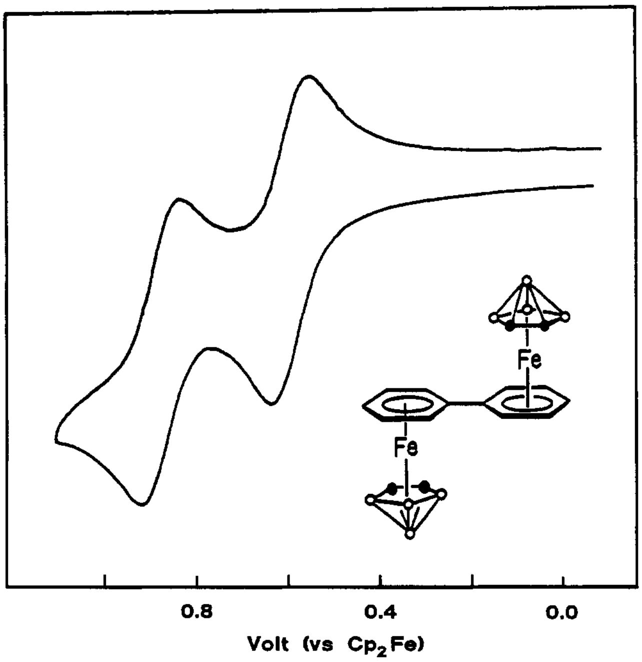


Figure 2. Cyclic voltammogram of biphenyl diiron complex **3** in CH_2Cl_2/0.1 M Bu_4NPF_6 at Pt electrode. Conditions: ambient temperature; scan rate = 200 mV/s; concentration = 1.0 mM. Full scale on the *y* axis is 13 μA.

feasible, substitution of a cyclopentadienyl ligand by a carboranyl ligand should be considered when stabilization of a Fe(III) or Ru(III) complex is desired.

The reduction of dinuclear iron(II) arene complexes, linked either through the arenes[13] or through cyclopentadienyl units,[14] or in cyclophane complexes,[15] has received attention owing to questions concerning mixed valency and electronic delocalization in the formal Fe(II)/Fe(I) species. However, lack of a suitable oxidation process has precluded studies of mixed valency for Fe(II)/Fe(III) systems with arene linkages.[3] The use of the carborane capping ligand in place of Cp^- allows oxidation of dinuclear iron complexes to be observed. Therefore, the biphenyl complex **3** undergoes two reversible one-electron oxidations (Figure 2) at $E°$ = +0.55 and +0.84 V vs $Cp_2Fe^{0/+}$. The separation of the successive $E°$ values (290 mV) is slightly less than those reported for the successive oxidations of biferrocene (330–350 mV).[16,17] A study of mixed valency in the cations derived from **3** and other diiron systems is underway.

Acknowledgment. We appreciate the generous support of the National Science Foundation (NSF CHE86-03728 to W.E.G. and CHE87-21657 to R.N.G.) and the Army Research Office (R.N.G.). We thank Kevin Chase (University of Virginia) for the sample of (η^6-C_6H_6)Ru($Et_2C_2B_4H_4$).

---

(12) Comparison may be made with shifts of +0.32 V for substitution of H by CF_3 in a cyclopentadienyl group [Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228] and −0.37 V for the substitution of H by NH_2 [Britton, W. E.; Kashyap, R.; El-Hashash, M.; El-Kady, M.; Herberhold, M. *Organometallics* **1986**, *5*, 1029].

(13) (a) Lacoste, M.; Varret, F.; Toupet, D. A.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504. (b) Reference 2.

(14) Astruc, D., personal communication to W.E.G.

(15) Bowyer, W. J.; Geiger, W. E.; Boekelheide, V. *Organometallics* **1984**, *3*, 1079.

(16) Morrison, W. H., Jr.; Hendrickson, D. N. *J. Chem. Phys.* **1973**, *59*, 380.

(17) LeVanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700.

The Utility of Ceric Ammonium Nitrate Derived Alkoxide Complexes in the Synthesis of Organometallic Cerium(IV) Complexes: Synthesis and First X-ray Crystallographic Determination of a Tetravalent Cerium Cyclopentadienide Complex, $(C_5H_5)_3Ce(OCMe_3)$

William J. Evans,* Timothy J. Deming, and Joseph W. Ziller

Department of Chemistry, University of California, Irvine Irvine, California 92717

Received February 23, 1989

Summary: $Ce(OCMe_3)_2(NO_3)_2(THF)_2$ reacts with 2 equiv of NaC_5H_5 to form $(C_5H_5)_2Ce(OCMe_3)_2$ in 90% yield. The reaction of $Ce(OCMe_3)(NO_3)_3(THF)_2$ with NaC_5H_5 forms a mixture of $(C_5H_5)_2Ce(OCMe_3)_2$ and $(C_5H_5)_3Ce(OCMe_3)$. The latter product can be isolated by recrystallization from hexane at −34 °C. It crystallizes in space group *Pnma* with unit cell parameters at 183 K of *a* = 14.8351 (17) Å, *b* = 13.3467 (14) Å, *c* = 8.9677 (9) Å, *V* = 1775.6 (3) Å^3, and D_{calcd} = 1.53 g cm^{-3} for *Z* = 4. Least-squares refinement of the model based on 1661 reflections converged to a final R_F of 5.1%. The three C_5H_5 ring centroids and the alkoxide oxygen atom form a distorted tetrahedron around the Ce(IV) center with a 2.76 (2) Å average Ce–C distance and a 2.045 (6) Å Ce–O length.

A fundamental question that has persisted for many years in the organolanthanide area is whether or not organometallic complexes of tetravalent cerium can exist.[1-4] There is good reason to question the existence of organometallic Ce(IV) complexes, since Ce(IV) is strongly oxidizing and the anionic ligands typically found in organolanthanide complexes (e.g., $C_5H_5^-$, $C_8H_8^{2-}$, and R^-) are strongly reducing. Skepticism increased when some early syntheses[5-12] of organometallic cerium(IV) complexes were found to be irreproducible or to form cerium(III) complexes.[13-17] In 1985, the synthesis of $Ce(C_8H_8)_2$[15] was

---

(1) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21.

(2) Forsberg, J. H.; Moeller, T. In *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Moeller, T., Kruerke, U., Schleitzer-Rust, E., Eds.; Springer-Verlag: Berlin, 1983; Part D6, pp 137–282.

(3) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474–493.

(4) Evans, W. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Chapter 12.

(5) Kalsotra, B. L.; Anand, S. P.; Multani, R. K.; Jain, B. D. *J. Organomet. Chem.* **1971**, *28*, 87–89.

(6) Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *Isr. J. Chem.* **1971**, *9*, 569–572.

(7) Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *J. Inorg. Nucl. Chem.* **1973**, *35*, 311–313.

(8) Kapur, S.; Multani, R. K. *J. Organomet. Chem.* **1973**, *63*, 301–303.

(9) Kapur, S.; Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1689–1691.

(10) Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2679–2680.

(11) Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *J. Organomet. Chem.* **1971**, *31*, 67–69.

(12) Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *Chem. Ind.* (*London*) **1972**, 339–340.

(13) Deacon, G. B.; Tuong, T. D.; Vince, D. G. *Polyhedron* **1983**, *2*, 969–970.

(14) Schumann, H. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; Reidel: Dordrecht, 1979; pp 81–112.

(15) Greco, A.; Cesca, S.; Bertolini, G. *J. Organomet. Chem.* **1976**, *113*, 321–330.

(16) Streitwieser, A., Jr.; Kinsley, S. A.; Rigsbee, J. T. *J. Am. Chem. Soc.* **1985**, *107*, 7786–7788.

0276-7333/89/2308-1581$01.50/0