(11) M. J. Weaver and F. C. Anson, *J. Electroanal. Chem.*, **65**, 711 (1975).
(12) See for example, R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969, p 145.
(13) The ligand 2_B:2:1 is like the 2:2:1 (**1**) except that the central dioxyethylene of one of the $m = 1$ strands is replaced by the analogous catechol.[1]
(14) A. Aziz and S. J. Lyle, *Anal. Chim. Acta*, **47**, 49 (1969).

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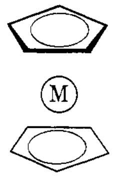
Unusual Electron-Transfer Processes Involving Electron-Rich and Electron-Deficient Metallocenes

Sir:

We wish to report measurements which establish that highly electron-deficient or electron-rich metallocene ($(\eta_5\text{-}C_5H_5)_2M$ or Cp_2M) ions can be generated by electrochemical methods. Although these ions are generally very reactive, cyclic voltammetry (CV) data allow us to draw inferences concerning structural changes involved in the electron-transfer reactions. Included in our discoveries are a 21-electron metallocene (Cp_2Ni^-), which appears to be the most electron-rich metallocene yet detected, the anions of vanadocene (Cp_2V) and chromocene (Cp_2Cr), and a vanadocene cation in which the Cp rings are apparently coplanar.

Working under high-vacuum conditions with an electrochemical cell to be described in a subsequent publication,[1] we have performed electrochemical experiments (CV, dc polarography, coulometry) on the bis(cyclopentadienyl) complexes of V, Cr, and Ni (**1**, $z = 0$). Remarkably, in spite of the obvious importance of oxidation/reduction process in the reactivity (and catalytic properties) of d^2 to d^4 metallocenes,[2-4] no electrochemical studies on neutral Cp_2Cr or Cp_2V have been reported.[5-7] This situation may well have arisen because of the difficulty of handling dilute solutions of these pyrophoric materials, for the redox processes of more air-stable metallocenes such as Cp_2Fe, Cp_2Co^+, and Cp_2Ni have received a great deal of attention.[8]



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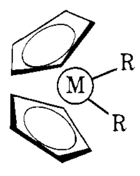

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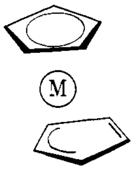

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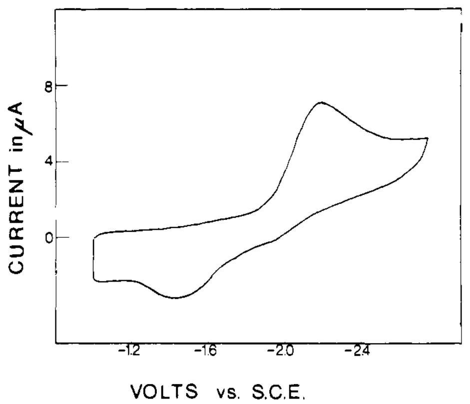

Figure 2. Cyclic voltammogram of the reduction Cp_2Ni in DMF at a platinum electrode, scan rate ~50 V/s.

The electron-transfer reactions of Cp_2Cr appear to be the simplest of the three metals being reported. In either THF or CH_3CN, Cp_2Cr undergoes an electrochemically reversible oxidation to Cp_2Cr^+ and reduction to Cp_2Cr^-, as shown by CV (Figure 1). Salts of the chromocene cation, such as Cp_2CrI, are well known,[9] and the cation probably retains the symmetric coplanar ring structure **1**. The reduction of chromocene is more interesting, for the anion of Cp_2Cr, like all other metallocenes except Co,[8,10,11] has not been previously reported. CV measurements of this reduction show that the anion undergoes follow-up reactions to as yet unspecified products, but the CV peak heights, as well as bulk coulometry measurements, show that a one-electron process is involved in THF.

Cp_2V is reduced just before solvent discharge (ca. −3 V). Polarographic and CV data are consistent with a reversible one-electron change to give the vanadocene anion, a species isoelectronic with Cp_2Cr. The anion is stable enough to be monitored by slow CV, but no bulk electrolyses have been performed as yet.

The electrochemical oxidation of Cp_2V at a platinum electrode allow us to probe the effects of metal oxidation state on the metallocene structure, since the V(III) and V(IV) species derived from Cp_2V, such as Cp_2VX or Cp_2VX_2,[7,12] are believed to have the "bent" structure **2**.[13] Our results confirm that the oxidation of Cp_2V in a relatively inert medium like THF occurs in two discrete steps, yielding first Cp_2V^+ and then Cp_2V^{2+}. The first oxidation, at about −0.7 V, is reversible, and apparently involves no important structural distortions. The second oxidation is irreversible, with an anodic peak potential which is highly dependent on scan rate. The slow electron transfer in the second oxidation is to be expected for a redox process which involves severe structural changes,[14] such as from the planar to the bent structure, **1** → **2**. Presumably,

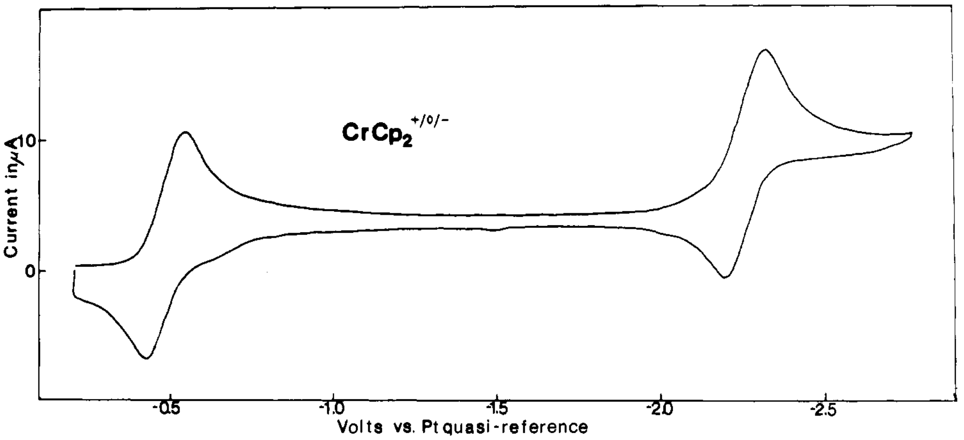

Figure 1. Cyclic voltammogram of Cp_2Cr in THF at a platinum electrode at a scan rate of ~100 mV/s, showing the reversible oxidation to Cp_2Cr^+ and reduction to Cp_2Cr^-.

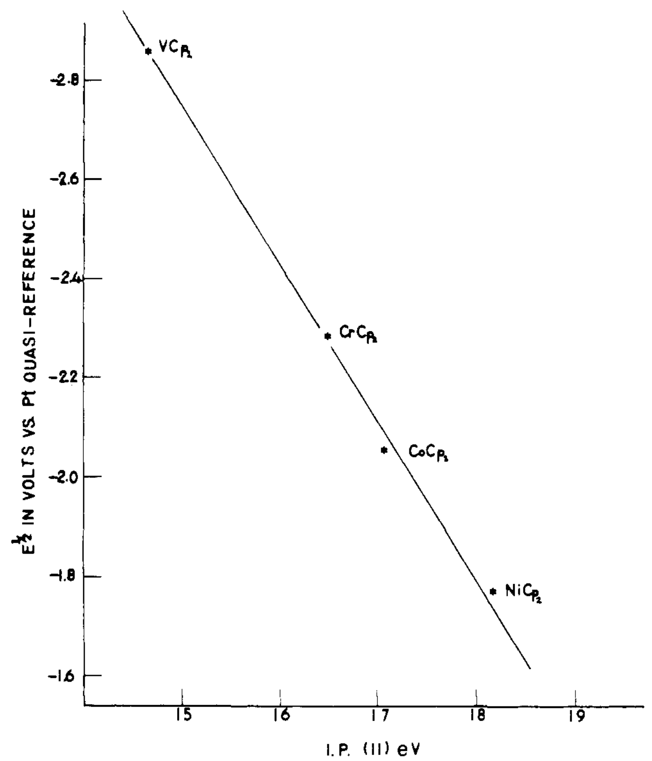

Figure 3. Plot of the polarographic half-wave potentials of the metallocene reductions as a function of second metal ionization potential.

solvent molecules would occupy the extra coordination sites in Cp_2V^{2+}. The apparently ring-parallel Cp_2V^+ is isoelectronic and isostructural with the elusive[15,16] d^2 "titanocene".

Nickelocene, which is already electron rich, can be further reduced in THF or DMF, and the anion Cp_2Ni^- can be detected by CV (Figure 2). Cp_2Ni^- has a half-life of ~1 s at room temperature. The formal Ni(I) complex, a 21-electron compound, appears to be the most electron-excessive metallocene known, since Cp_2Cu has not been reported. The anion proceeds to other electroactive products, which may include $CpNiC_5H_7$.[17]

The reduction of nickelocene ($Cp_2Ni \rightleftarrows Cp_2Ni^-$) is abnormally slow, as shown by the large peak separations in CV measurements (Figure 2), suggesting that a structural change, possibly leading to the "slipped sandwich" structure **3**, occurs to relieve the high electron density around the metal. Such structures are well known for electron-rich metallocarboranes,[18,19] and have been predicted[20] on theoretical grounds for electron-rich metal π hydrocarbons as well.

The trend in reduction potentials of the four metallocenes known to produce simple anions (V, Cr, Co, Ni) is worth noting in that the more electron-rich metallocenes are easier to reduce. In fact a plot of $E_{1/2}$ potentials vs. the second metal ionization potential (Figure 3), is linear, as would be expected for a M(II) $\rightleftarrows$ M(I) process. This and other points will be elaborated on in subsequent publications.

Acknowledgment. The authors are grateful to The National Science Foundation for the support of this work.

References and Notes

(1) Electrochemical apparatus and procedures are similar to those reported previously (W. E. Geiger, T. E. Mines, and F. C. Senftleber, *Inorg. Chem.*, **14**, 2141 (1975)) except that the vacuum electrochemical cell has undergone a number of modifications, including one which allows loading of air-sensitive samples into the cell.
(2) D. L. Kepert, "The Early Transition Metals", Academic Press, New York, N.Y., 1972.
(3) P. C. Wailes, R. S. P. Coutts, and H. Weigold, "Organometallic Chemistry of Titanium, Zirconium, and Hafnium", Academic Press, New York, N.Y., 1974.
(4) R. J. H. Clark, "The Chemistry of Titanium and Vanadium", Elsevier, Amsterdam, 1968.
(5) The electrochemical reduction of "bent" vanadocene derivatives like Cp_2VCl_2 (**2**, R = Cl) has been reported by R. E. Dessy, R. B. King, and M. Waldrop, *J. Am. Chem. Soc.*, **88**, 5112 (1966).
(6) A recent report by G. Fachinetti and C. Floriani (*J. Chem. Soc., Chem. Commun.*, 578 (1975)) suggests that the Cp_2V^{2+}/Cp_2V^+ couple reported for the vanadocene dication[7] in aqueous solution actually involved $Cp_2V(H_2O)^+$.
(7) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).
(8) For leading references, the reader is referred to W. E. Geiger, *J. Am. Chem. Soc.*, **96**, 2632 (1974).
(9) E. O. Fischer and K. Ulm, *Chem. Ber.*, **95**, 692 (1962).
(10) N. El Murr, R. Dabard, E. Laviron, *J. Organomet. Chem.*, **47**, C13 (1973).
(11) N. El Murr and E. Laviron, *Can. J. Chem.*, **54**, 3350 (1976).
(12) H. J. deLiefde Meijer, M. J. Janssen, and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, **80**, 831 (1961).
(13) J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976).
(14) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965).
(15) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **94**, 1219 (1972).
(16) H. Alt and M. D. Rausch, *J. Am. Chem. Soc.*, **96**, 5936 (1974).
(17) That $CpNiC_5H_7$ is a reduction product was originally hypothesized by S. P. Gubin, S. A. Smirnova, and L I. Denisovich, *J. Organomet. Chem.*, **30**, 257 (1971); mechanistic studies and attempts at product identification are underway.
(18) R. M. Wing, *J. Am. Chem. Soc.*, **89**, 5599 (1967).
(19) R. M. Wing, *J. Am. Chem. Soc.*, **90**, 4828 (1968).
(20) K. Wade, *Adv. Inorg. Radiochem.*, **18**, 1 (1976).

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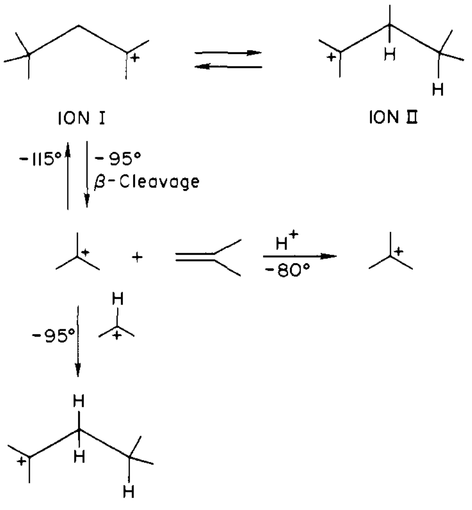
Reversible Addition of a Carbonium Ion to a Double Bond

Sir:

Addition of carbonium ions to double bonds leading to molecular adducts or ring closure is a common mechanistic step. However, detailed examination of the addition step itself has not previously been described. We report here the reaction of *tert*-butyl cation with isobutylene at −115 °C to yield dimethylneopentyl carbonium ion (**I**). On warming to −80 °C, **I** undergoes β-cleavage to the initial cation and olefin which may be trapped by the addition of a proton acid or isopropyl cation.



The addition of *tert*-butyl cation to isobutylene was accomplished via a modification of the molecular beam method of cation preparation.[1] The apparatus was altered so that *three* beams, one each of *tert*-butyl chloride, SbF_5, and isobutylene in a ratio of 5:10:1, impinge on the liquid nitrogen cooled surface of the evacuated apparatus. The intimate mixture formed