Acknowledgment. We wish to thank the M. H. Wrubel Computing Center for computational facilities and the National Science Foundation for generous financial support.

Registry No. $[Et_4N][CH_3COW(CO)_5]$, 59610-08-1; $[Et_4N][C_6H_5COW(CO)_5]$, 68866-92-2; $[Et_4N][C_3H_5COW(CO)_5]$, 75112-12-8; $[Et_4N][CH_3COCr(CO)_5]$, 75112-13-9; $[Et_4N][C_6H_5COCr(CO)_5]$, 54817-05-9; $[Et_4N][p\text{-}CH_3C_6H_4COCr(CO)_5]$, 59610-10-5; $[Et_4N][p\text{-}FC_6H_4COCr(CO)_5]$, 75112-15-1; $[Et_4N][p\text{-}CH_3OC_6H_4COCr(CO)_5]$, 75112-17-3; $[Et_4N][Me_3SiCH_2COCr(CO)_5]$, 51447-06-4; $PhCOCr^I(CO)_5$, 46933-82-8; $Ph(HO)C{=}Cr(CO)_5$, 50507-79-4; $CH_2{=}CH_2$, 74-85-1; $(CO)_5Cr{=}C(OH)Ph{\cdot}NCCH_3$, 75112-18-4; $Cr(CO)_4(NCCH_3)_2$, 16800-44-5; benzene, 71-43-2.

Supplementary Material Available: Complete listings of anisotropic thermal parameters (Table VIII), observed and calculated structure factors (Table IX), and bond distances and angles (Table X) (15 pages). Ordering information is given on any current masthead page.

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Metallocene Electrochemistry. 2. Reduction–Oxidation Behavior of Nickelocene in the Room-Temperature Alkylpyridinium Chloride–Aluminum Chloride Melt System

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In neutral 1:1 molar ratio mixtures of $AlCl_3$–1-butylpyridinium chloride, at 40 °C, nickelocene undergoes a reversible 1-electron charge-transfer reaction, with $E_{1/2} = -0.165$ V vs. Al (2:1) reference. Evidence is presented to show that both nickelocene and the nickelocenium(III) ion are unstable in chloride ion rich solvents. Spontaneous oxidation to the nickelocenium cation occurs in acidic (>1:1) melts, and a stable dication is formed reversibly at $E_{1/2} = +0.912$ V vs. Al (2:1) reference. Electronic spectra of nickelocene species in the II, III, and IV oxidation states have been recorded in these melts. The spectrum of the dication species contains bands at 412, 438, 532 nm.

Introduction

Although the electrochemistry of the transition-metal metallocenes, particularly the effects of derivatized ferrocenes, has been investigated fairly thoroughly in both aqueous[2] and nonaqueous organic solvents,[3] only ferrocene and decamethylferrocene had been studied previously in the room-temperature $AlCl_3$–1-butylpyridinium chloride (BPC) molten salt. Chum et al.[4] were the first to study the electrochemistry of organometallic compounds in these aprotic Lewis acid solvents, and, in addition to ferrocene, they have reported the redox behaviors for two aliphatic diimine complexes of iron(II) and for six metal carbonyls, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_6$, $Re_2(CO)_{10}$, and $Mn_2(CO)_{10}$.[5] Robinson and Osteryoung[6] observed that the ferrocene oxidation potential was independent of the melt acidity (cyclic voltammetric $E_{p/2} = 0.24$ V vs. Al (2:1) reference), and they determined the values of the diffusion coefficient as a function of the temperature in the range 30–175 °C. Singh et al.[7] have demonstrated the existence of appreciable photoeffects at the semiconductor anode of the $n\text{-GaAs}|Cp_2Fe^+/Cp_2Fe;\ AlCl_3\text{–BPC}|$ vitreous C cell. Our interest in the electrochemistry of metallocenes in these molten salts has arisen from an assessment of redox systems for photovoltaic devices, in particular because it appears that uncommon oxidation states of certain metallocenes may be stable in these strong Lewis acid, aprotic solvents.[8]

Results and Discussion

Electrochemical Investigations. Cyclic voltammograms illustrated in Figure 1A show that nickelocene (Cp_2Ni) dissolved in a 1:1 molar ratio $AlCl_3$–BPC melt at 40 °C undergoes a reversible 1-electron charge-transfer reaction to the nickelocenium cation (Cp_2Ni^+) at $E_{1/2} \approx -0.165$ V vs. Al (2:1) reference. The potential shift from the value for the Cp_2Fe/Cp_2Fe^+ couple of approximately −400 mV is consistent with the difference between the two corresponding polarographic waves in 90% ethanolic $HClO_4$ solutions at mercury electrodes.[2a,c] Calculated values for the diffusion coefficient were scattered, probably because of electrode roughness variations ($D = 2.5 \times 10^{-7}$ cm^2 s^{-1} from cyclic voltammetry (Nicholson–Shain constants); $D = 2.9 \times 10^{-7}$ cm^2 s^{-1} from chronoamperometry (40 °C)).

When the red-brown solution of Cp_2Ni in a 1:1 molar ratio melt was adjusted to the 0.95:1 $AlCl_3$:BPC ratio the cyclic voltammograms at low sweep rates (<50 mV s^{-1}) could be interpreted by invoking a slow chemical reaction following charge transfer (Figure 1). The value for the forward anodic oxidation current was unaffected during the course of this experiment (vide infra). Assuming a simple EC mechanism, we estimated the mean reaction rate of the chemical step from theoretical response curves of the i_p^c/i_p^a ratio[9] to be $k_f = 0.030 \pm 0.005$. This reaction was too slow to be measured conveniently by the double-pulse chronoamperometric technique, and the nature of the follow-up process has not been investigated further by us. Addition of butylpyridinium chloride, to adjust the melt to 0.8:1 molar ratio, caused the formation of a green solution and chemical modification to a Cp_2Ni species which exhibited an irreversible oxidation wave at ∼+0.16 V (Figure 2). Readjusting the melt composition to

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(2) See, for example: (a) Page, J. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6149. (b) Cotton, F. A.; Whipple, R. O.; Wilkinson, G. *Ibid.* **1953**, *75*, 3586. (c) Wilkinson, G.; Pauson, P. L.; Cotton, F. A. *Ibid.* **1954**, *76*, 1970. (d) Wilkinson, G.; Birmingham, J. M. *Ibid.* **1954**, *76*, 4281. (e) Tirouflet, J.; Laviron, E.; Dabard, R.; Komenda, J. *Bull. Soc. Chim. Fr.* **1963**, 857.

(3) See, for example: (a) Bublitz, D. E.; Hoh, G.; Kuwana, T. *Chem. Ind. (London)* **1959**, 635. (b) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811. (c) Biegler, T.; Parsons, R. *J. Electroanal. Chem.* **1970**, *27*, 314. (d) Gubin, S. P.; Smirnova, S. A.; Denisovitch, L. I.; Lubovich, A. A. *J. Organomet. Chem.* **1971**, *30*, 243. (e) Holloway, J. D. L.; Bowden, W. L.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 7089.

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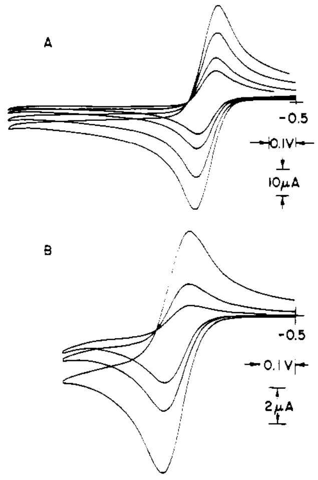

Figure 1. Cyclic voltammograms: A, 16.2 mM Cp_2Ni in 1:1 melt, 40 °C, ν = 10, 20, 50, and 100 mV s^{-1}; B, 5.1 mM Cp_2Ni in 0.95:1 melt, 40 °C, ν = 10, 20, and 50 mV s^{-1}.

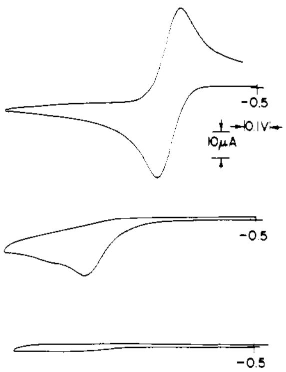

Figure 2. Cyclic voltammogram of 9.6 mM nickelocene in 1:1 melt with its composition adjusted to 0.8:1 and then to 1:1 by addition of 1-BPC and $AlCl_3$, respectively (ν = 100 mV s^{-1}, 40 °C).

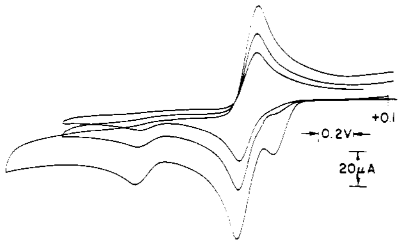

Figure 3. Cyclic voltammetry of 15.3 mM Cp_2Ni^+ ion in 1.1:1 melt, 40 °C, at ν = 50, 100, and 200 mV s^{-1}.

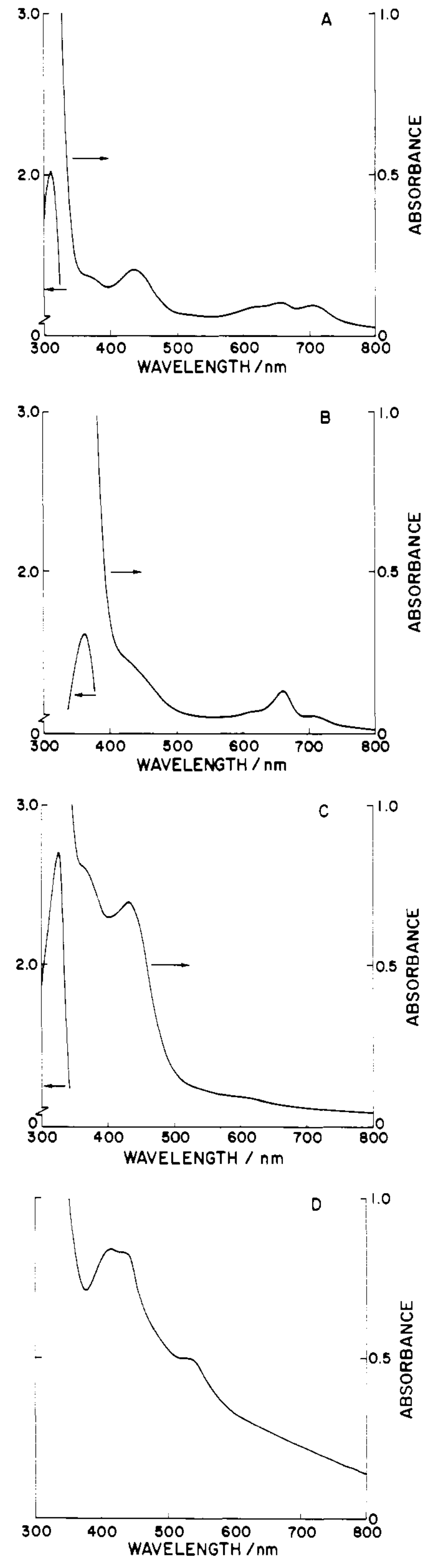

Figure 4. Electronic absorbance spectra of nickelocene species: A, 0.43 mM Cp_2Ni in 1:1 melt; B, 0.22 mM Cp_2Ni in 0.8:1 melt; C, 0.50 mM Cp_2Ni^+ in 1.1:1 melt; D, 0.46 mM Cp_2Ni^{2+} ion in 1.1:1 melt.

the 1:1 molar ratio restored a brown color but little if any electrochemical activity. These results suggest that both Cp_2Ni^+ ion and neutral Cp_2Ni react irreversibly with the excess chloride ion in the basic molten salts (<1:1 $AlCl_3$:BPC).

Since the half-wave potential for the Cp_2Ni^+/Cp_2Ni couple lies negative of the Al reference electrode, adjusting the melt acidity to the acidic compositions (>1:1 $AlCl_3$:BPC) will cause spontaneous oxidation of Cp_2Ni to Cp_2Ni^+ ion (cf. decamethylferrocene[8]). This Ni(III) ion with a formal d^7 electronic configuration can be further oxidized in a reversible manner to a stable Cp_2Ni^{2+} ion species in an acidic 1.1:1 melt, at a half-wave potential $E_{1/2} \approx +0.912$ V vs. Al (2:1) reference (Figure 3). The potential difference, $\Delta E \approx 1.08$ V, between the Ni(II)/Ni(III) and Ni(III)/Ni(IV) couples compares to $\Delta E \approx +0.76$ V or +0.86 V for these couples at Pt electrodes/CH_3CN solvent.[10,11] An additional irreversible oxidation wave was present at ~1.54 V, and the reversible wave is complicated by a prewave only on the forward sweep, at scan rates, ν, $\gtrsim$100 mV s^{-1}, which could be caused by complex equilibria complicated by adsorption. The nature of this effect has not been investigated further. Constant-potential coulo-

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metry at +1.1 V confirmed that the reversible oxidation is a one-electron process and that the dication is stable for several hours at least. Other workers[11,12] have been able to obtain the dication Ni(IV) species in highly purified acetonitile, and their results show that the Cp_2Ni^{2+} ion is a highly reactive entity undergoing rapid nucleophilic attack by water. The strictly anhydrous nature of the acidic $AlCl_3$-BPC melt precludes the presence of water as a nucleophilic scavenger.

Spectral Investigations. Visible absorption spectra of nickelocene species in the II, III, and IV oxidation states are shown in Figure 4. Although the major features of the spectra were reproducible (in the 1:1 region), a slight deviation from the neutral point toward either the acidic or basic compositions caused the spectra to contain features appropriate for the oxidized Cp_2Ni^+ ion or for the basic melt species, respectively. The d^6 metallocenes such as ferrocene commonly exhibit two low-intensity bands in the visible region which are generally assigned to d-d transitions.[13] Nickelocene in the neutral melt region has a spectrum that resembles the electronic spectra for Cp_2Ni in isooctane solution;[14] however, the d-d transitions at ca. 660 nm are resolved into three bands and the peak at ~435 nm has similar intensity to a shoulder at ~365 nm. In the basic melt, the spectrum of nickelocene is similar to that in the neutral region for the visible frequencies but a strong peak which appears in each of the other spectra at 320 ± 5 nm is shifted to ~360 nm. In aqueous chloride solutions, the Cp_2Ni^+ ion has absorption bands at approximately 300, 358, and 389 nm,[15] whereas Cp_2Ni^+ ion in ethanolic $HClO_4$ has two broad peaks at 300 and 434 nm.[16] This latter result more closely resembles the spectrum of Cp_2Ni^+ ion in the acidic molten salt. The 300-400-nm regions of these spectra seem to be sensitive to solvent interactions or chloride complex charge-transfer transitions,[16] and the interpretation of these spectra will be restricted to this general comparison. A spectrum of the dication Cp_2Ni^{2+} has not been reported previously and bands at 412, 438, and 532 nm are resolved (in an acidic melt composition).

Experimental Section

Nickelocene was prepared by a modification of the method of Cordes,[17] entailing a 3-h reflux in THF and extraction with petroleum ether (bp 30-60 °C). It was stored under argon at 0 °C. The preparation of $AlCl_3$-1-butylpyridinium chloride was similar to that described earlier.[6] All electrochemical experiments were done in a drybox under purified argon atmosphere. Cyclic voltammetry and chronoamperometry were performed with use of a PAR 175 Universal Programmer, PAR 173 potentiostat and Model 179 digital coulometer, a PAR RE0074 X-Y recorder, and a Tektronix 561A oscilloscope. Working electrodes were polished vitreous carbon (Atomergic Chemetals) of areas 0.0573 and 0.0855 cm^2, and an Al wire comprised the reference electrode in the 2:1 molar ratio $AlCl_3$-BPC melt, respectively (+0.15 V vs. SCE). Visible spectra were recorded in quartz 1-cm path length cells (filled and sealed in the drybox) on a Varian Techtron Model 635 spectrometer.

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Registry No. Cp_2Ni, 1271-28-9; Cp_2Ni^+, 11091-00-2; Cp_2Ni^{2+}, 75365-53-6; 1-BPC, 1124-64-7; $AlCl_3$, 7446-70-0.

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Metallocene Electrochemistry. 3. Reduction-Oxidation Study of Dicyclopentadienyl Compounds of Ruthenium and Titanium in Lewis Acid-Base Molten Salts

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Voltammetry at vitreous C electrodes of $Ru(\eta^5\text{-}C_5H_5)_2$ and $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ in the 0.8:1 molar ratio $AlCl_3$-1-butylpyridinium chloride melt reveals an irreversible oxidation ($E_{p/2}$ = +0.68 V, 100 mV s^{-1}) and a reversible 1e reduction ($E_{1/2}$ = -0.65 V vs. SCE), respectively. These electrode potentials are comparable to those found for each species in nonaqueous, organic electrolytes. In the acidic melts (excess $AlCl_3$), $Ru(\eta^5\text{-}C_5H_5)_2$ is oxidized by multistep pathways sensitive to the melt composition, while the $Ti(\eta^5\text{-}C_5H_5)^{2+}$ dication is reduced by a reversible 1e step ($E_{1/2}$ = +0.67 V vs. SCE, 2:1 mole ratio melt) in a pCl^- dependent process. Electrochemical behavior of each of these metallocenes in neutral 1:1 molar ratio melts is complicated.

Introduction

The electrochemistry and photochemistry of the metallocenes recently have been attracting attention because they represent well-characterized organometallic model compounds and because they have possible applications in solar energy conversion systems.[2-5] Our studies of their electrochemistry in the room temperature $AlCl_3$-1-butylpyridinium chloride melts have been pursued for four reasons in particular: (i) redox potentials of couples may be determined in the absence of polar solvent molecules, (ii) uncommon oxidation states of the metal center can be stabilized in the highly aprotic, ionic environment,[6] (iii) nucleophilic attack by chloride ion or the formation and stability of anionic complexes may be investigated, e.g., ref 7, and (iv) metal electrodeposition processes may be possible via cyclopentadienyl metal complexes, e.g., Zr and V.[8]

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