

Effects of temperature and supporting electrolyte on the electrochemical oxidation of (benzene)tricarbonylchromium and other π -hydrocarbon complexes

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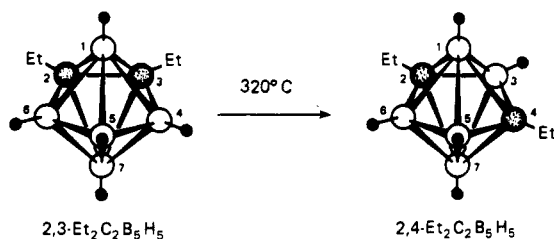
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with Et_3NBH_3 yields $(\text{Et}_3\text{NH}^+)_2\text{B}_{12}\text{H}_{12}^{2-}$ and the reaction⁸ of *arachno*-1,3- $\text{C}_2\text{B}_7\text{H}_{13}$ with B_2H_6 gives *closo*-1,6- $\text{C}_2\text{B}_8\text{H}_{10}$. Onak⁹ has previously examined the reaction of *nido*-2,3- $\text{C}_2\text{B}_4\text{H}_8$ with diborane(6) at 220 °C but found that, due to the rapid decomposition of diborane(6) at these temperatures, no *closo*-carboranes are produced. Indeed, our studies have indicated that a minimum temperature of 140 °C is necessary to activate the 2,3- $\text{Et}_2\text{C}_2\text{B}_4\text{H}_8$ for reaction and that only Lewis base-borane complexes, such as triethylamine-borane, which are stable to decomposition at these temperatures are suitable BH-capping reagents. In the present case it was also found that the *closo*-2,3- $\text{Et}_2\text{C}_2\text{B}_5\text{H}_5$ product undergoes slow attack by triethylamine at 140 °C; therefore, it is necessary to periodically remove the triethylamine which is evolved during the reaction in order to achieve good yields. We have also employed other borane complexes containing less nucleophilic bases, such as $\text{C}_6\text{H}_5\text{N}(\text{Et})_2\text{BH}_3$ and $(n\text{-Bu})_3\text{P}\cdot\text{BH}_3$, and have obtained similar yields without removal of the base during the reaction; however, longer reaction times and higher temperatures were required.

In the present study it was also found that thermolysis of 2,3- $\text{Et}_2\text{C}_2\text{B}_5\text{H}_5$ (0.114 g, 0.81 mmol) in a sealed glass tube in vacuo for 47.5 h at ~ 320 °C gave the nonadjacent carbon isomer 2,4- $\text{Et}_2\text{C}_2\text{B}_5\text{H}_5$ (0.093 g, 0.66 mmol) in high yield¹⁰ (81%). Such thermally induced cage rearrangements, leading to separation of cage carbon atoms, are well-known¹¹ for adjacent carbon carboranes, and this isomerization reaction thus provides a convenient, selective synthetic route to the 2,4-isomer.



The *closo*- $\text{C}_2\text{B}_5\text{H}_7$ cage system is the most stable small carborane and has, in fact, been used¹² as the backbone structure of a number of high-temperature polymers. The development, reported here, of new rational synthetic routes to both the 2,3- and 2,4-isomers promises to result in renewed interest in the chemistry and properties of these carboranes.

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(10) The isomeric purity of the product was again confirmed by spectroscopic and gas chromatographic analysis.⁶ ¹¹B NMR (64.2 MHz, ppm, C_6D_6): 8.25 (d, B3, $J_{\text{BH}} = 166$ Hz), 5.77 (d, B5,6, $J_{\text{BH}} = 169$ Hz), -17.71 (d, B1,7, $J_{\text{BH}} = 177$ Hz); ¹H NMR (200 MHz, ¹¹B spin-decoupled, δ , C_6D_6): 4.60 (s, BH3), 4.26 (s, BH5,6), 2.26 (q, CH_2), 0.93 (t, CH_3), 0.54 (s, BH1,7).

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Effects of Temperature and Supporting Electrolyte on the Electrochemical Oxidation of (Benzene)tricarbonylchromium and Other π -Hydrocarbon Complexes

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Summary: The electrochemical oxidation of $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and other π -hydrocarbon complexes can be made chemically reversible in dichloromethane by using low temperatures or by using tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

The electrochemical oxidation of $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ (1) has been the subject of numerous studies.¹⁻⁷ Normally the one-electron oxidation of 1 at room temperature is followed by rapid decomposition leading to Cr(II) or Cr(III) and free benzene. The stability of (arene) $\text{Cr}(\text{CO})_3^+$ radical cations can be enhanced by alkylation or metalation of the arene ring⁶⁻¹¹ or by using pure trifluoroacetic acid (TFAA) as the solvent.⁴ The success of TFAA in this regard is no doubt due to its low intrinsic nucleophilicity as well as its ability to lower the reactivity of the supporting electrolyte anion via hydrogen bonding.^{4,12-14} Nevertheless, the serious corrosive and toxic properties of TFAA render it inconvenient as a routine solvent for electrochemical studies. We have previously shown¹⁵⁻¹⁷ that cyclic voltammetry at temperatures down to -95 °C in the relatively nonpolar and nonnucleophilic solvent dichloromethane is a convenient procedure for studying reactive metalloporphyrin complexes. Herein we demonstrate that low-temperature cyclic voltammetry (LTCV) in dichloromethane is a useful way to study organometallics such as 1 that display chemically irreversible redox processes at room temperature. Also reported is the surprising observation that the radical cations produced from the room-temperature oxidation of 1 and other π -hydrocarbon complexes are much more persistent when the supporting electrolyte is changed

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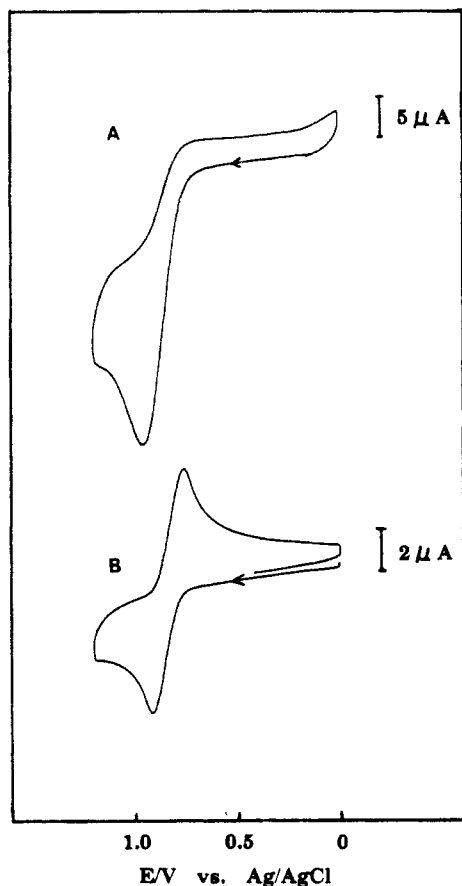


Figure 1. Cyclic voltammograms of 5×10^{-4} M $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in dichloromethane with TBAP = 0.05 M. The working electrode was glassy carbon, and the scan rate was 200 mV/s. The temperature was 19 °C for A and -90 °C for B.

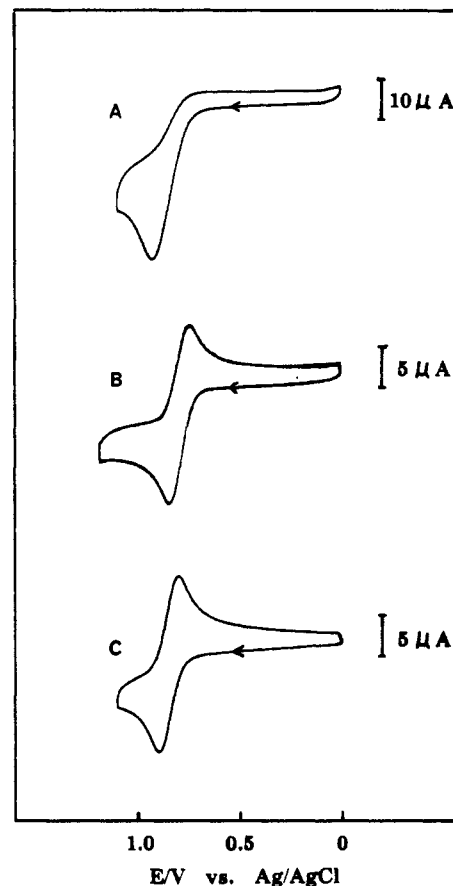


Figure 2. Cyclic voltammograms of 5×10^{-4} M $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in dichloromethane. The working electrode was glassy carbon, and the scan rate was 200 mV/s. The key is as follows: (A), 17 °C, TBAP = 0.1 M; (B), 15 °C, TBAPF₆ = 0.1 M; (C), -30 °C, TBAPF₆ = 0.1 M.

from tetrabutylammonium perchlorate (TBAP) to tetrabutylammonium hexafluorophosphate (TBAPF₆).

LTCV was used to study 1 at temperatures between 22 and -95 °C. The experimental procedure is a very simple one and has been described previously.^{15,16} The working electrodes used were gold, platinum, and glassy carbon disks. The counter electrode was a platinum wire, and the reference electrode was Ag/AgCl in CH₂Cl₂ which was 0.1 M in TBAP and saturated with LiCl. With TBAP, TBABF₄, or TBACF₃SO₃ as the supporting electrolyte 1 was found to undergo a chemically irreversible oxidation at ca. 0.90 V in CH₂Cl₂ at room temperature. While similar electrochemical behavior was observed with platinum, gold, and glassy carbon electrodes, coating of the electrode was least noticeable with glassy carbon as judged from multiple CV scans. Upon lowering the temperature to ca. -90 °C, the oxidation of 1 became chemically reversible in the presence of any of the three supporting electrolytes. This is illustrated in Figure 1. Typical peak separations for 1 (ΔE_p) were 80–200 mV, depending on concentration (IR compensation not applied). By comparison to ferrocene standards, the oxidation of 1 at low temperatures was determined to involve one electron. At a concentration of 0.1 M the supporting electrolyte frequently precipitated at ca. -90 °C. For this reason most experiments at low temperatures were performed with the electrolyte at 0.05 M. Electrolyte precipitation at low temperature was less frequent with TBABF₄ and TBACF₃SO₃ than with TBAP and TBAPF₆.

The results in Figure 1 nicely illustrate the ability of LTCV to simplify the electrochemistry of organometallic systems. Most previous studies at low temperature in-

involved protic or fairly polar aprotic solvents.^{18–22} Low-temperature work in relatively nonpolar solvents like dichloromethane is of much more recent vintage,^{15,16,23,24} probably because of presumed IR drop problems.¹⁸ We find that IR drop, while evident, is not large enough to preclude high quality results even if IR compensation is not applied (vide supra). LTCV in relatively nonpolar and inert solvents like dichloromethane promises to be a valuable tool for the organometallic chemist since the ability to produce persistent radicals means that these important species can be studied and can be utilized in stoichiometric and catalytic transformations.

Surprisingly the electrochemical behavior of 1 was found to depend markedly on the nature of the electrolyte. As Figure 2 shows, the oxidation of 1 is partially chemically reversible ($i_{pc}/i_{pa} \geq 0.75$) at room temperature when TBAPF₆ is substituted for TBAP (or TBABF₄ and TBACF₃SO₃). At -30 °C the oxidation is fully reversible with TBAPF₆. Rotating disk voltammetry on a glassy carbon electrode at room temperature established that the oxidation involves one electron with TBAPF₆ and two electrons with TBAP. The room temperature reversibility of the 1⁺/1 couple with TBAPF₆ was found to be very

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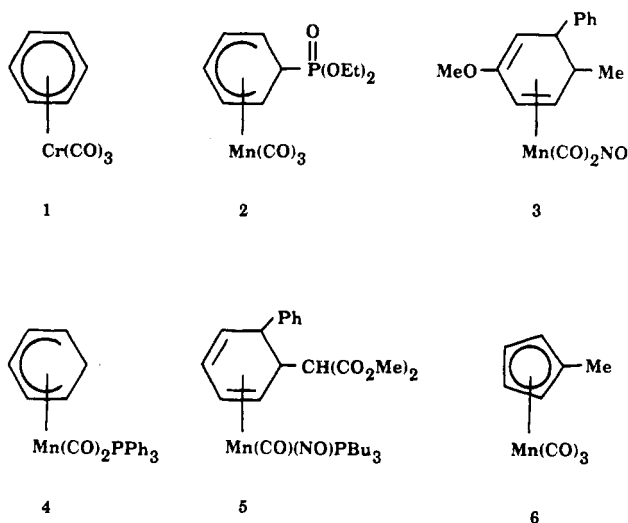
sensitive to small amounts of nucleophilic species such as MeOH, H₂O, MeCN, Me₂CO, and THF. For example, the addition of MeOH or MeCN at <0.1 M completely destroyed the reversibility. The addition of TBAP at only 0.003 M to 1 in CH₂Cl₂ with TBAPF₆ at 0.1 M also resulted in the loss of reversibility. It is likely that the enhanced persistence of 1⁺ in TBAPF₆/CH₂Cl₂ relative to TBAP/CH₂Cl₂ is due to the lower nucleophilicity of PF₆⁻ compared to ClO₄⁻ and not due to any special stabilization of 1⁺ by PF₆⁻. It is possible that simple ion pair formation between 1⁺ and PF₆⁻ serves to protect 1⁺ from attack by nucleophiles. By using careful drying procedures, storing all materials in oven-dried containers and performing Karl Fischer titrations, it was established that the observed behavior was not due to water present as an impurity. The effects described above were independent of the electrode material (platinum, gold, glassy carbon), suggesting that adsorption is not playing a significant role. To verify this point, double-potential-step chronocoulometry was performed on a solution of 1 in CH₂Cl₂ (0.1 M TBAPF₆) at -30 °C. In these experiments the potential was stepped from +0.35 to +1.1 V and back to +0.35 V. The amount of time (τ) at +1.1 V was varied from 0.050 to 5.0 s. Standard plots²⁵ of Q_f vs. $t^{1/2}$ ($t < \tau$) and Q_r vs. θ ($t > \tau$; $\theta = \tau^{1/2} - t^{1/2} + (t - \tau)^{1/2}$) as well as plots of Q_f vs. $t^{1/2}$ for solutions containing only electrolyte gave within error identical intercepts for a given electrode (platinum, gold, glassy carbon). This indicates that adsorption is not significant.

In order to quantify the effect of TBAPF₆ relative to TBAP, CV's obtained at -30 °C were compared to ones calculated²⁶ by digital simulation for an EC mechanism. At this temperature the 1⁺/1 couple was partially reversible with TBAP at scan rates above 100 mV/s; with TBAPF₆ the couple was completely reversible at all scan rates employed (10 to 1000 mV/s). The best fit of the data with TBAP gave a rate constant (k) for the irreversible decomposition of 1⁺ of 1.4 s⁻¹, while in the presence of TBAPF₆ $k < 0.005$ s⁻¹. The conclusion is that TBAPF₆ reduces the rate of decomposition of 1⁺ by at least a factor of 250.

A variety of other π -hydrocarbon complexes (2-6) were briefly investigated in order to test the utility of LTCV in organometallic chemistry and to test the generality of the TBAPF₆ effect noted above. All the complexes 2-6 showed cleaner and more reversible CV's at lower temperatures, and with 2, 3, and 5 completely irreversible oxidations at room temperature were converted to reversible ones at low temperatures. With 3, 5, and 6 the use of TBAPF₆ instead of TBAP was investigated with TBAPF₆ giving much more reversible behavior in each case.

In conclusion, we have shown that LTCV in dichloromethane can be a useful technique in organometallic chemistry and that the use of TBAPF₆ instead of TBAP or other supporting electrolytes may give significantly more persistent radicals in electrochemical oxidations.

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Note Added in Proof: We recently became aware of a study of the electrochemical oxidation of aromatic hydrocarbons in dichloromethane at temperatures down to -70 °C: Byrd, L.; Miller, L. L.; Pletcher, D. *Tetrahedron Lett.* 1972, 2419. In this paper it was shown that the half-lives of aromatic hydrocarbon radical cations can be increased by 10²-10⁴ by lowering the temperature from ambient to -70 °C.

Uranium-Carbon Multiple-Bond Chemistry. 8.¹ The Reaction of W(CO)₆ with Cp₃U=CHP(Ph)(R)(Me) To Form (OC)₅WC(OUCp₃)CHP(Ph)(R)(Me) and Its Isomerization to Cp₃UOCH=CHP(Ph)(R)CH₂W(CO)₅

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Summary: The reaction of W(CO)₆ with Cp₃U=CHP(Ph)(R)(Me) yields the tungstaenolate (OC)₅WC(OUCp₃)CHP(Ph)(R)(Me) (3a, R = Me; 3b, R = Ph) which upon heating at 90 °C isomerizes to Cp₃UOCH=CHP(Ph)(R)CH₂W(CO)₅ (4a, R = Me; 4b, R = Ph). This exchange of W(CO)₅ and hydrogen establishes a third type of carbonyl activation for Cp₃U=CHP(Ph)(R)(Me). The crystal structures of 3b·¹/₂C₇H₈ (space group *P*2₁/*c*, unit-cell parameters $a = 8.669$ (1) Å, $b = 10.576$ (2) Å, $c = 39.63$ (2) Å, $\beta = 98.38$ (2)°, and $V = 3595$ (2) Å³; $R = 5.85\%$, $R_G = 6.83\%$) and 4b (space group *P*2₁/*c*, unit-cell parameters $a = 17.176$ (4) Å, $b = 11.804$ (2) Å, $c = 17.588$ (2) Å, $\beta = 114.49$ (1)°, and $V = 3245$ (1) Å³; $R = 4.19\%$, $R_G = 4.59\%$) have been determined.

We have shown²⁻⁴ that carbon monoxide which is co-

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