Ersch. in: Journal of Organometallic Chemistry ; 356 (1988), 3. - S. 307-314

http://dx.doi.org/10.1016/0022-328X(88)83148-6

ansa-Metallocene derivatives

XIV *. Electrochemical reactions of unbridged and of tetramethylethanediyl-bridged chromocene carbonyl complexes

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Abstract

$(C_5H_5)_2Cr(CO)$, formed from chromocene and CO gas in THF solution at 0 °C, loses its CO ligand upon one-electron oxidation. No CO loss is observed, on the other hand, when the *ansa*-chromocene carbonyl complex $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ is oxidised to its monocation. Formation of a dication $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^{2+}$, for which there is no unbridged analogue, is irreversible owing to its fast conversion to a solvent adduct; its reduction under CO, however, quantitatively regenerates the neutral carbonyl complex. One-electron reduction of either of the carbonyl complexes, $(C_5H_5)_2Cr(CO)$ or $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$, induces a fast, irreversible decay of the chromocene framework.

Introduction

Interconnection of the ring ligands of metallocene derivatives can substantially alter the electrochemical reactivity of these species. Studies on several group 6 metallocene derivatives have recently shown, for example, that reduction to the bivalent oxidation state occurs at significantly more negative potentials with ethanediyl- or silanediyl-bridged than with unbridged titanocene complexes [2–4]. We now report on a related study concerning the effects of an interannular bridge on redox reactions of the group 6 metallocene carbonyl complexes $(C_5H_5)_2Cr(CO)$ [5] and $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ [6].

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* For part XIII see ref. 1.

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Experimental

$(C_5H_5)_2Cr$ [7] and $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ [6] were prepared as previously described; these compounds and their THF solutions were handled with strict exclusion of air. Electrochemical measurements were conducted with 10^{-3} *M* solutions in anhydrous tetrahydrofuran containing 0.1 *M* tetrabutylammonium hexafluorophosphate (TBA^+ PF_6^-) at 0 °C by use of an electrochemical cell with internal drying column [8], as previously described [3,9]. Potentials were measured, with IR compensation against an $Ag/AgNO_3$ (sat)/0.1 *M* $TBA^+PF_6^-$/THF (25 °C) reference electrode and referred to SCE by adding 0.60 V.

Results and discussion

Unbridged chromocene and its carbonyl complex $(C_5H_5)_2Cr(CO)$. In agreement with earlier reports by Geiger and coworkers [10], for solutions of $(C_5H_5)_2Cr$ in THF/TBAPF$_6$ at 0 °C under an atmosphere of Ar we observed uncomplicated cyclovoltammograms which indicate a quasi-reversible oxidation to the chromocenium cation $(C_5H_5)_2Cr^+$ ($E_p(A)$ -0.73 V, $E_P(A')$ -0.54 V at 0.1 V/s; $i_P(A')/i_P(A) = 1.0$), and a quasi-reversible reduction to $(C_5H_5)_2Cr^-$ ($E_P(B)$ -2.45 V, $E_P(B')$ -2.26 V at 0.1 V/s; see Fig. 1). For this reduction wave there is a peak current ratio of $i_P(B')/i_P(B) = 1.0$ even at relatively low sweep rates of 0.1 V/s, indicating that the anionic species $(C_5H_5)_2Cr^-$ is persistent on the CV time scale *.

Exposure of these solutions to an atmosphere of CO, which causes practically

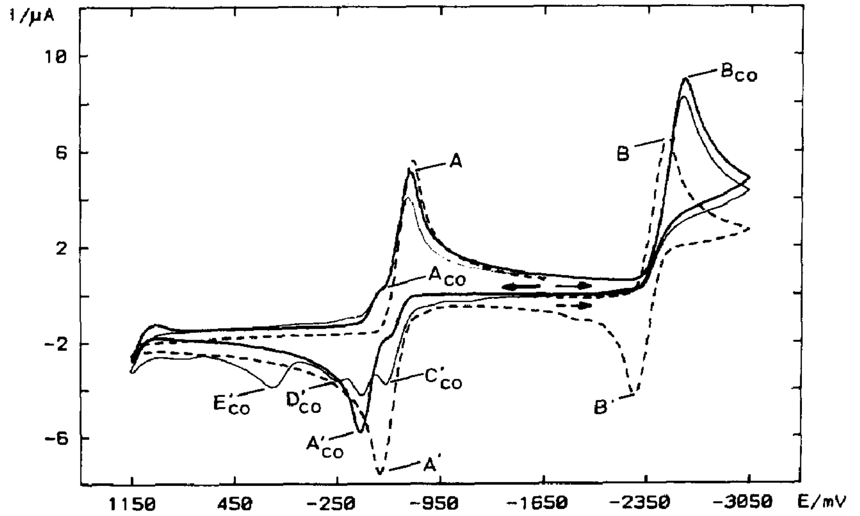

Fig. 1. Cyclic voltammograms of $(C_5H_5)_2Cr$, ca. 10^{-3} *M* in THF with 0.1 *M* TBA^+ PF_6^-, at 0 °C, under Ar (dashed line) and under CO (solid lines). Sweep rate 0.1 V/s.

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* We ascribe this observation, which contrasts with earlier reports [10], to the rigorous exclusion of traces of water from the electrolyte solutions by the cell design employed.

complete conversion of $(C_5H_5)_2Cr$ into its carbonyl complex $(C_5H_5)_2Cr(CO)$ [5] *, leads to a number of changes in the cyclovoltammograms: the reduction peak B(CO) is shifted, by ca. 0.1 V, to a more negative potential than that observed for peak B in the absence of CO. Apparently, reduction of $(C_5H_5)_2Cr(CO)$ to $(C_5H_5)_2Cr(CO)^-$ is slightly more demanding than that of $(C_5H_5)_2Cr$ to its monoanion.

The corresponding reoxidation peak, which was observed before at ca. −2.26 V, is absent in the presence of CO. This, and the appearance of new oxidation peaks, C'(CO), D'(CO) and E'(CO) ($E_P(C'(CO)$ −0.58 V, $E_P(D'(CO))$ −0.27 V and $E_P(E'(CO)$ +0.19 V, at 0.1 V/s; see Fig. 1), suggest that $(C_5H_5)_2Cr(CO)^-$ is rapidly decomposed by CO. The close coincidence of oxidation peak C'(CO), which is particularly pronounced after 30 s of reductive electrolysis at −3 V, with the oxidation peak of $(C_5H_5)Cr(CO)_3^-$ [11] **, suggests that an exchange of one $(C_5H_5)^-$ ligand for three CO ligands occurs at these low potentials ***.

Additional differences between $(C_5H_5)_2Cr$ and $(C_5H_5)_2Cr(CO)$ concern the oxidation waves around −0.5 V. Instead of the anodic peak A′ at $E_P(A')$ −0.54 V observed before, a slightly more positive peak A'(CO) appears under CO at $E_P(A'(CO))$ −0.37 V. The potential of the main reduction peak at −0.73 V, however, is still identical with that of peak A, which was observed for $(C_5H_5)_2Cr$ at $E_P(A)$ −0.73 V in the absence of CO. In addition, and closely adjacent to this reduction peak A, a shoulder A(CO) at $E_P(A(CO)) \approx -0.52$ V appears in the reductive back-sweep after an oxidative sweep up to +1.0 V. The current at this shoulder, which appears to be the counterpart of oxidation peak A'(CO), increases with sweep rate: At rates of 0.1 and 1.0 V/s we estimate current ratios $i_P(A(CO))/i_P(A)$ of ca. 0.3 and ca. 0.9, respectively.

These observations indicate that the cation $(C_5H_5)_2Cr(CO)^+$ arises at the anodic peak A'(CO) and decays rapidly to $(C_5H_5)_2Cr^+$, which is then reduced at the cathodic peak A. The potential difference of 0.17 V between oxidation peaks A' and A'(CO) implies that the equilibrium constant K^+ for the formation of the carbonyl cation $(C_5H_5)_2Cr(CO)^+$ in the equilibrium $(C_5H_5)_2Cr^+ + CO \rightleftharpoons (C_5H_5)_2Cr(CO)^+$ is smaller by about 3 orders of ten than the corresponding constant K for the neutral complexes, and that, hence, only a very small fraction of the carbonyl cation $(C_5H_5)_2Cr(CO)^+$ remains in the equilibrium with $(C_5H_5)_2Cr^+$ under 1 atm of CO. From the sweep-rate dependence of the reduction currents for $(C_5H_5)_2Cr(CO)^+$ and $(C_5H_5)_2Cr^+$ at shoulder A(CO) and peak A, respectively, we estimate a rate constant of the order of 1 s^{-1} for the loss of CO from $(C_5H_5)_2Cr(CO)^+$. Scheme 1 summarizes these interconversion reactions involving the chromocene carbonyl complex $(C_5H_5)_2Cr(CO)$.

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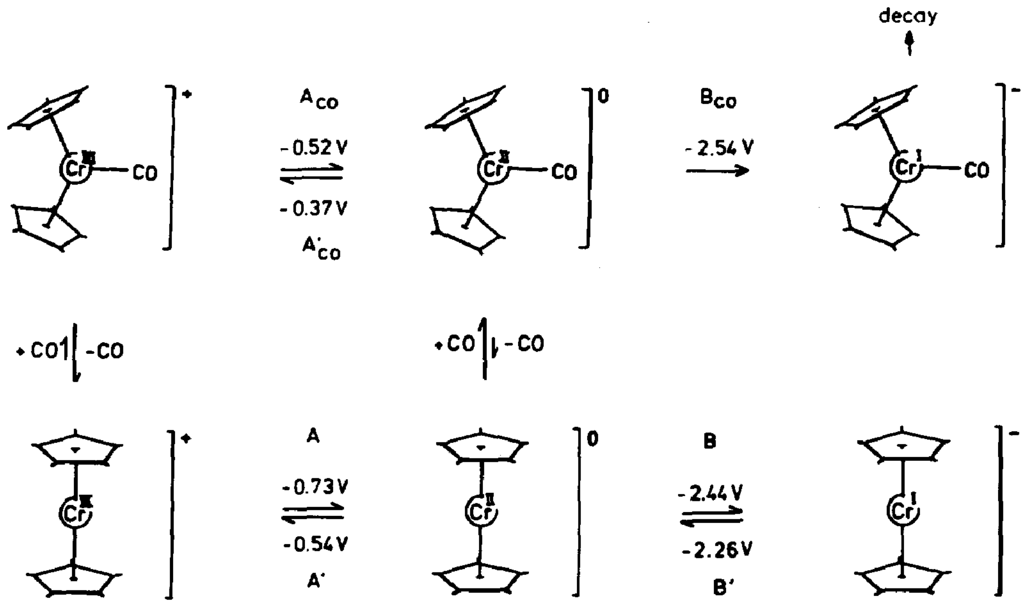
* From data given in ref. 5 one can estimate a complex formation constant $K \approx 50$ atm^{-1} for $(C_5H_5)_2Cr(CO)$ at 0 °C and, hence, a fraction of uncomplexed $(C_5H_5)_2Cr$ of ca. 2% at 1 atm of CO.

** In separate experiments, the oxidation peak of $(C_5H_5)Cr(CO)_3^-$ was found to occur at a potential of −0.53 V vs. SCE. This quasi-reversible oxidation wave almost coincides with that of $(C_5H_5)_2Cr$. A small anodic shoulder occurring at −0.5 V under CO, while possibly due in small parts to uncomplexed $(C_5H_5)_2Cr$, is thus more likely to be caused by a slow formation of $(C_5H_5)Cr(CO)_3^-$ in these solutions, e.g. by a CO-induced decay of $(C_5H_5)_2Cr(CO)$, such as $(C_5H_5)_2Cr(CO) + 2\,CO \rightarrow (C_5H_5)Cr(CO)_3^- + (C_5H_5)_2Cr^+ + C_5H_5^{\cdot}$.

*** Displacement of $(C_5H_5)^-$ from $(C_5H_5)_2Cr$ under reducing conditions has been documented by Jonas and coworkers (ref. 12).



Scheme 1

Tetramethylethanediyl-bridged carbonyl complex $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$. In THF/$TBA^+PF_6^-$ under an Ar atmosphere the *ansa*-chromocene carbonyl complex $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ gives rise to a quasi-reversible oxidation wave ($E_P(A'_b)$ -0.40 V, $E_P(A_b)$ -0.49 V at 0.5 V/s). While these potentials are close to those observed previously for $(C_5H_5)_2Cr(CO)$, a peak current ratio $i_P(A_b)/i_P(A'_b)$ of 1.0, which is now independent of sweep rates between 0.1 and 1.0 V/s, indicates that loss of CO from the *ansa*-chromocene carbonyl cation does not occur on the CV time scale, even in the absence of an excess of CO *.

Furthermore, in contrast to the behaviour observed for the unbridged chromocene, we observe, that the cation $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^+$ undergoes a second one-electron oxidation at $E_P(C'_b)$ $+1.04$ V; no comparable peak was observed for $(C_5H_5)_2Cr$ or $(C_5H_5)_2Cr(CO)$ up to the oxidation threshold of THF.

The oxidation of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^+$ to $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^{2+}$ is obviously irreversible; no conjugate reduction peak is apparent near $+1.0$ V in the reductive back sweep. Instead, a reductive back sweep after generation of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^{2+}$ produces a new reduction peak D_b at $E_P(D_b) = +0.40$ V (0.5 V/s) with a peak current ratio $i(D_b)/i(C'_b)$ of 0.67; a second, weaker reduction peak E_b appears at $E_P(E_b)$ -0.73 V, next to reduction peak A_b. These features are particularly pronounced if the sweep is halted for 30 s at $+1.2$ V to increase production of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^{2+}$ (see Fig. 2); peak A_b is now decreased to a peak current ratio $i_P(A_b)/i_P(A'_b)$ of 0.6.

When the same CV experiment is conducted under an atmosphere of CO, peak currents at oxidation peaks A'_b and C'_b and at reduction peak D_b remain essentially unchanged. Reduction peak E_b, however, is now completely suppressed, while

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* Attempts to isolate salts of this cation were unsuccessful [6].

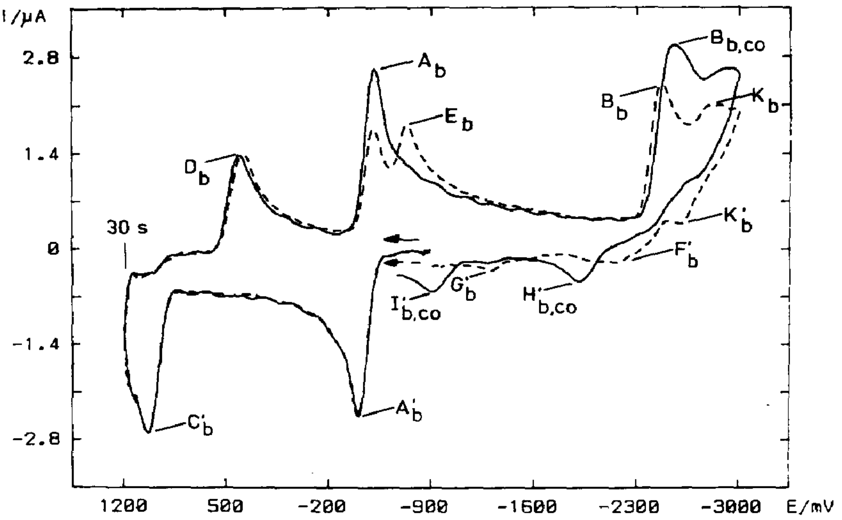

Fig. 2. Cyclic voltammograms of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$, ca. 10^{-3} M in THF with 0.1 M TBA^+ PF_6^-, at 0 ° C, under Ar (dashed line) and under CO (solid line). Sweep rate 0.5 V/s.

reduction peak A_b is restored to its original peak current, i.e. to $i_P(A_b)/i_P(A'_b) = 1$ (see Fig. 2).

The complete lack of a conjugate reduction peak C_b for the dication $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^{2+}$ generated at C'_b indicates that this coordinatively unsaturated species takes up another ligand, probably a THF molecule *. Reduction of the resulting 18-electron complex $(CH_3)_4C_2(C_5H_4)_2Cr(CO)(THF)^{2+}$ at peak D_b occurs at a potential which is about 0.6 V more negative than that required for oxidation of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^+$ at peak C'_b. Dissociation of the unstable 19-electron product arising at peak D_b (probably the cation $(CH_3)_4C_2(C_5H_4)_2$-$Cr(CO)(THF)^+$) could then generate the complexes which are further reduced at peaks A_b and E_b. While that reduced at A_b must be the carbonyl cation $(CH_3)_4C_2$-$(C_5H_4)_2Cr(CO)^+$, we assume, from the coincidence of peak E_b with peak A of $(C_5H_5)_2Cr^+$, that the CO-free cation $(CH_3)_4C_2(C_5H_4)_2Cr^+$ is reduced to $(CH_3)_4$-$C_2(C_5H_4)_2Cr$ at peak E_b. In accord with this is our observation that a CO atmosphere suppresses reduction peak E_b while restoring the reduction of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^+$ at peak A_b to its full current, i.e. to $i_P(A_b)/i_P(A'_b) =$ 1.0. Thus, oxidation of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ to its dication $(CH_3)_4C_2(C_5H_4)_2$-$Cr(CO)^{2+}$ is reversible in an overall sense if loss of CO from some unstable intermediate, e.g. from the solvent adduct $(CH_3)_4C_2(C_5H_4)_2Cr(CO)(THF)^+$, is suppressed relative to the competing regeneration of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^+$, by excess CO.

One-electron reduction of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ occurs at $E_P(B_b)$ −2.54 V (0.5 V/s). The cathodic current at B_b is somewhat smaller than that at A_b, the peak current ratio being $i(B_b)/i(A_b) \approx 0.8$. Reduction at B_b is chemically irreversible: instead of a conjugate reoxidation peak B'_b, two new broad oxidation peaks F'_b and G'_b are observed at $E_P(F'_b)$ −2.1 V and at $E_P(G'_b)$ −1.3 V. A decrease in current

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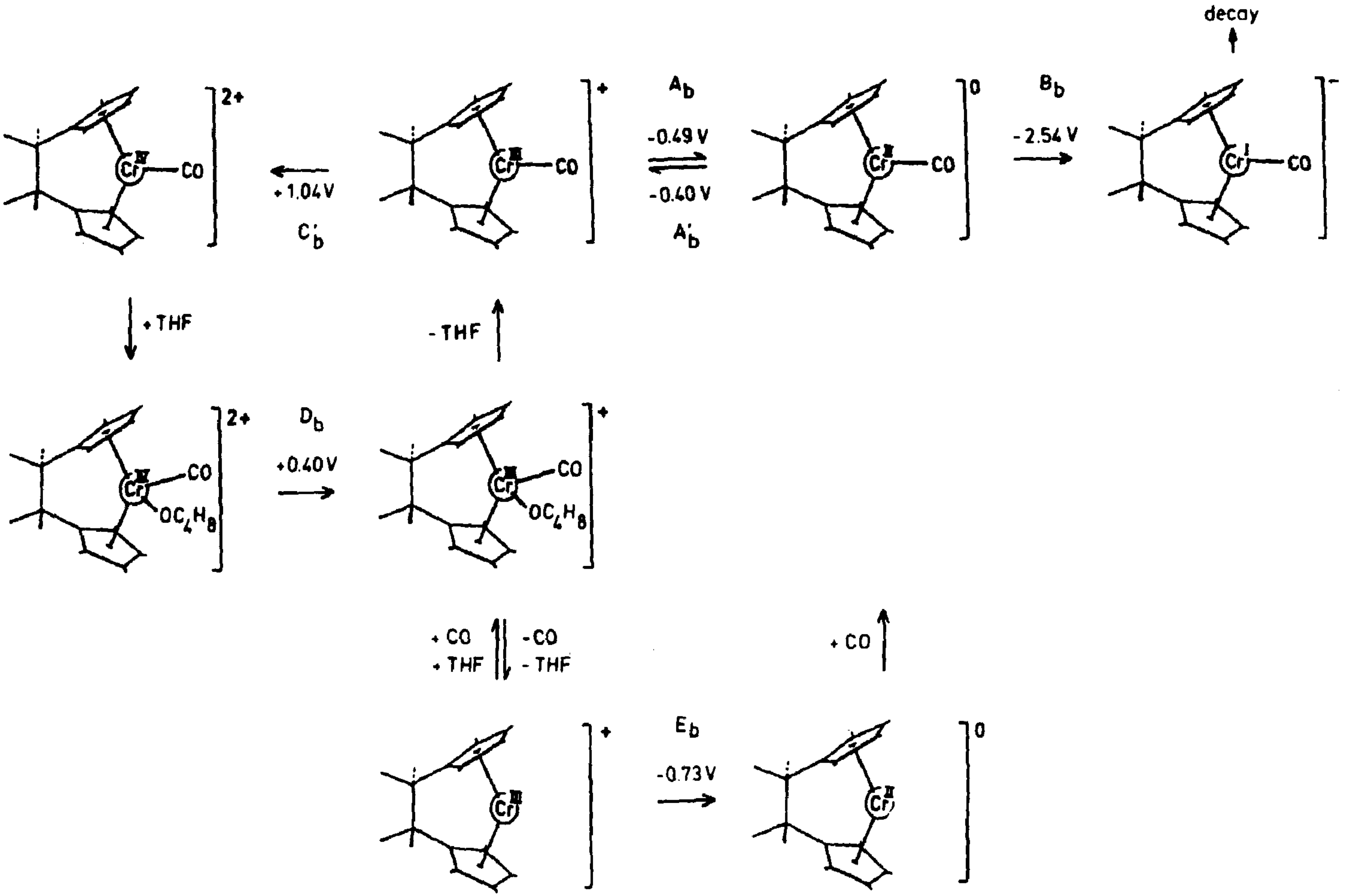
* Alternatively, a complex $(CH_3)_4C_2(C_5H_4)_2Cr(CO)X^+$ could be formed by uptake of an anionic species X^-, such as PF_6^- or F^-.


decay
2+
+
0
−
A_b
-0.49 V
-0.40 V
A'_b
B_b
-2.54 V
+1.04 V
C'_b
Cr III
Cr IV
Cr II
Cr I
CO
+THF
-THF
D_b
+0.40 V
OC_4H_8
+CO
+THF
-CO
-THF
+CO
E_b
-0.73 V

Scheme 2

at oxidation peak A'_b, after previous reduction at peak B_b, to peak current ratios of $i_P(A'_b)/i_P(A_b) \approx 0.8$–$0.9$ indicates that $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ is only partly regenerated from the products arising by its one-electron reduction at peak B_b *.

In the presence of CO, reduction peak $B_b(CO)$ at $E_P(B_b(CO))$ −2.66 V (0.5 V/s) is slightly shifted relative to B_b, and increased to a peak current ratio of $i_P(B_b(CO))/i_P(A_b)$ 1.0; the associated, broad reoxidation peaks, which formerly appeared at −2.1 and −1.3 V, are now shifted to more positive potentials, $E_P(H'_b(CO))$ −1.9 V and $E_P(I'_b(CO))$ −0.9 V. Reoxidation current at peak A'_b is still diminished to a peak current ratio $i_P(A'_b)/i_P(A_b) \approx 0.8$ after reduction at $B_b(CO)$; this indicates that $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ is partly decomposed after its reduction, with or without excess CO.

The redox and ligand exchange reactions of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ derived from the CV observations discussed above are summarized in Scheme 2. Comparison with Scheme 1 shows that the range of accessible positive oxidation states is extended by the presence of the interannular bridge in $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$.

Conclusions

The oxidations of $(C_5H_5)_2Cr$ and of $(C_5H_5)_2Cr(CO)$ occur at rather similar potentials, that for the latter being more positive by 0.17 V. Removal of an electron from related, largely non-bonding, metal *d*-orbitals [13–16] (and similar solvation energies for the arising cations) might explain this similarity: the first vertical ionisations of $(C_5H_5)_2Cr$ and of $(C_5H_5)_2Mo(CO)$ were found to occur at energies of 5.7 and 5.9 eV from doubly occupied, non-bonding e_{2g} and a_1 orbitals, respectively [17,18]. By analogy, an electron would probably be removed from an orbital of $(C_5H_5)_2Cr(CO)$ which is non-bonding rather than bonding with respect to the CO ligand. The axially symmetric, high-spin d^3 complex $(C_5H_5)_2Cr^+$ [16] appears to be a sufficiently favoured species, at any rate, to make loss of CO from $(C_5H_5)_2Cr(CO)^+$ a facile process.

Oxidation of $(CH_3)_4C_2(C_5H_4)_2Cr(CO)$ occurs at practically the same potential as that of unbridged $(C_5H_5)_2Cr(CO)$. In contrast to $(C_5H_5)_2Cr(CO)^+$, however, the *ansa*-cation $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^+$, is stable towards loss of CO on the CV time scale, probably owing to the fixation of its wedge-shaped geometry by the interannular bridge. The increased stability of this cation appears to be essential for the second one-electron oxidation which the *ansa*-chromocene complex undergoes at +1 V: A cationic carbonyl adduct $(CH_3)_4C_2(C_5H_4)_2Cr(CO)^+$ with its 17-electron configuration would undoubtedly be more prone to undergo further oxidation than the 15-electron cation $(C_5H_5)_2Cr^+$.

While an interannular bridge can thus extend the range of accessible chromocene derivatives to the Cr^{IV} oxidation state, no stabilisation of the metallocene framework is evident for electron uptake by Cr^{II} derivatives. The extra electron appears to enter an orbital which is antibonding with respect to the (C_5H_5) ligands, so making them susceptible to facile replacement by other ligands.

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* Changes in peak currents at increased sweep rate (5 V/s) at F'_b (increased) and at G'_b (decreased) indicate that formation of the product oxidized at F'_b precedes that which is oxidized at G'_b. The absence, at this higher sweep rate, of the small peaks K_b and K'_b indicates that these are also due to degradation products.

Acknowledgements

Financial support by Deutsche Forschungsgemeinschaft (grants Bri 510 and Ki 294), by Fonds der Chemischen Industrie and by funds of the University of Konstanz is gratefully acknowledged.

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