

## ***ansa*-Metallocene derivatives**

### **XIV \*. Electrochemical reactions of unbridged and of tetramethylethanediy-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 ethanediy- or silanediy-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].

\* 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  $0^\circ C$  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)/ $0.1 M TBA^+ PF_6^- / THF$  ( $25^\circ C$ ) 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  $0^\circ C$  under an atmosphere of Ar we observed uncomplicated cyclic voltammograms 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

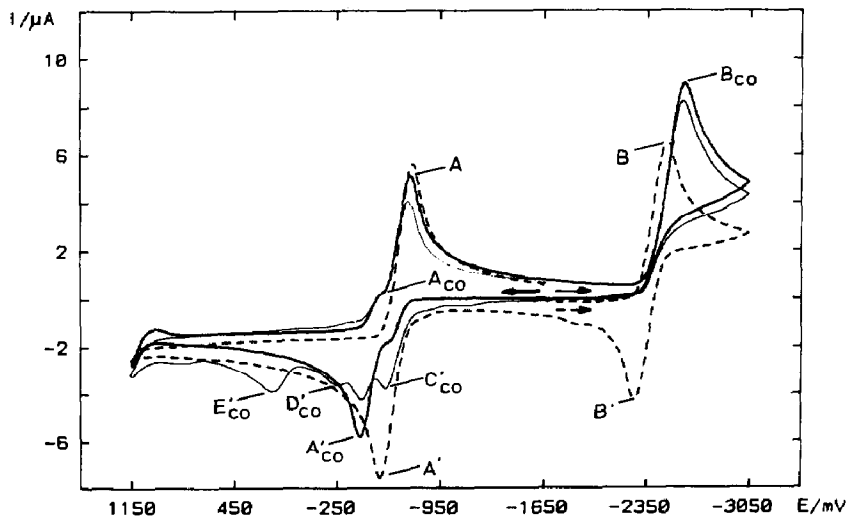


Fig. 1. Cyclic voltammograms of  $(C_5H_5)_2Cr$ , ca.  $10^{-3} M$  in THF with  $0.1 M TBA^+ PF_6^-$ , at  $0^\circ C$ , under Ar (dashed line) and under CO (solid lines). Sweep rate  $0.1 V/s$ .

\* 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 \*\*\*.

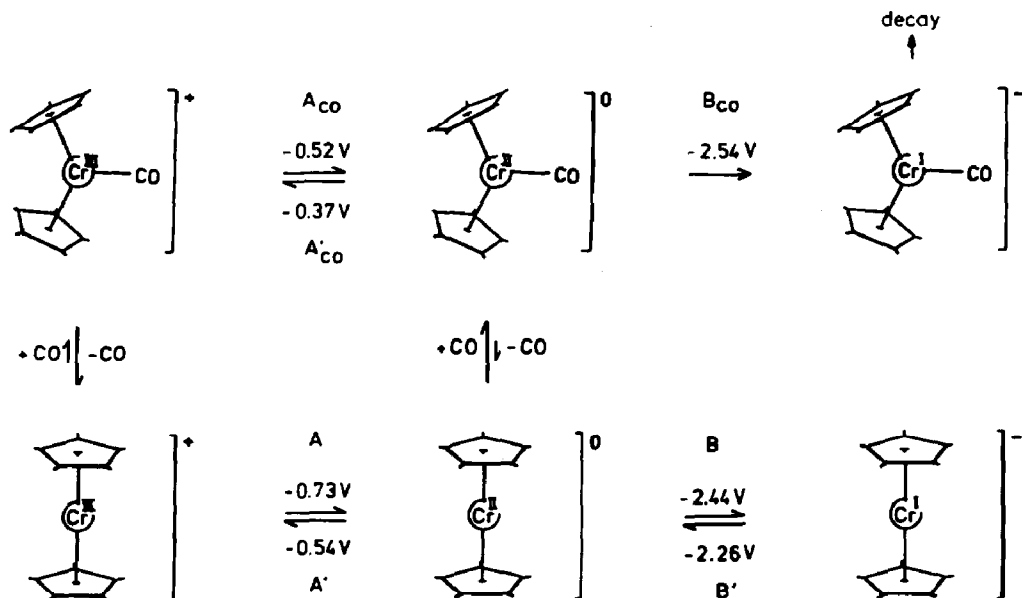
Additional differences between  $(C_5H_5)_2Cr$  and  $(C_5H_5)_2Cr(CO)$  concern the oxidation waves around  $-0.5$  V. Instead of the anodic peak  $A'$  at  $E_p(A') -0.54$  V observed before, a slightly more positive peak  $A'(CO)$  appears under CO at  $E_p(A'(CO)) -0.37$  V. The potential of the 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  $1\text{ s}^{-1}$  for the loss of CO from  $(C_5H_5)_2Cr(CO)^+$ . Scheme 1 summarizes these interconversion reactions involving the chromocene carbonyl complex  $(C_5H_5)_2Cr(CO)$ .

\* From data given in ref. 5 one can estimate a complex formation constant  $K \approx 50\text{ atm}^{-1}$  for  $(C_5H_5)_2Cr(CO)$  at  $0^\circ\text{C}$  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  $(C_5H_5)_2Cr(CO) + 2\text{CO} \rightarrow (C_5H_5)Cr(CO)_3^- + (C_5H_5)_2Cr^+ + C_5H_5$ .

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



Scheme 1

*Tetramethylethanediybridged carbonyl complex*  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$ . In THF/TBA<sup>+</sup>PF<sub>6</sub><sup>-</sup> under an Ar atmosphere the *ansa*-chromocene carbonyl complex  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$  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  $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{CO})$ , 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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^+$  undergoes a second one-electron oxidation at  $E_p(C'_b) + 1.04$  V; no comparable peak was observed for  $(\text{C}_5\text{H}_5)_2\text{Cr}$  or  $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{CO})$  up to the oxidation threshold of THF.

The oxidation of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^+$  to  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^{2+}$  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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^{2+}$  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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^{2+}$  (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

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

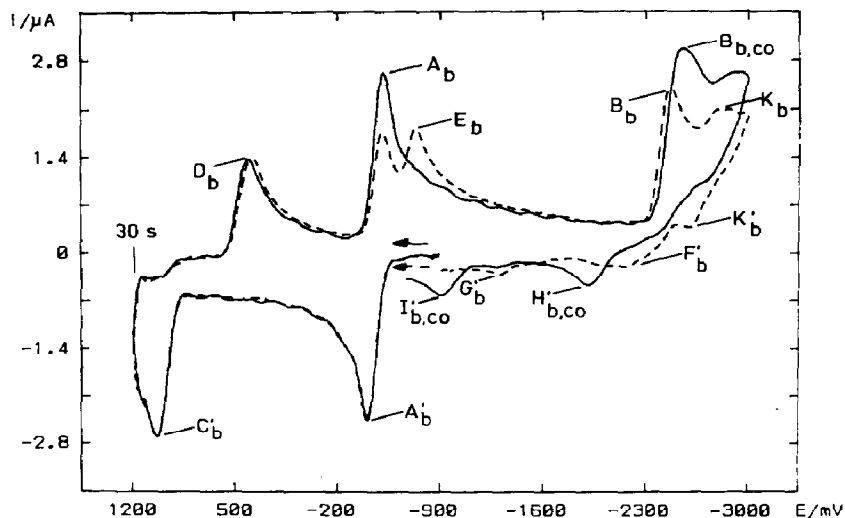


Fig. 2. Cyclic voltammograms of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$ , ca.  $10^{-3}$  M in THF with 0.1 M TBA<sup>+</sup> PF<sub>6</sub><sup>-</sup>, at 0°C, under Ar (dashed line) and under CO (solid line). Sweep rate 0.5 V/s.

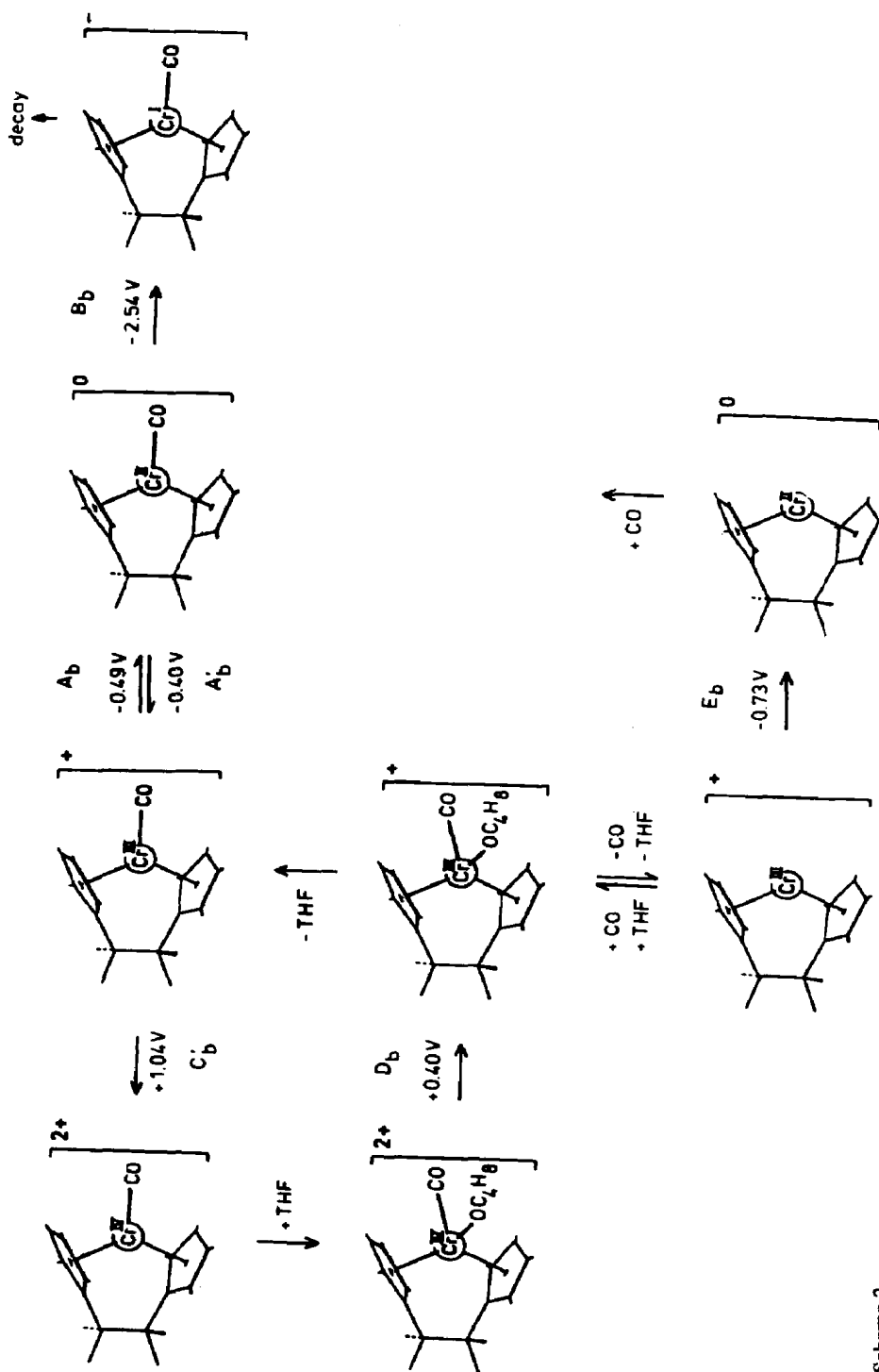
reduction peak  $A_b$  is restored to its original peak current, i.e. to  $i_p(A_b)/i_p(A'_b) = 1$  (see Fig. 2).

The complete lack of a conjugate reduction peak  $C_b$  for the dication  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^{2+}$  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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})(\text{THF})^{2+}$  at peak  $D_b$  occurs at a potential which is about 0.6 V more negative than that required for oxidation of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^+$  at peak  $C'_b$ . Dissociation of the unstable 19-electron product arising at peak  $D_b$  (probably the cation  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})(\text{THF})^+$ )

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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^+$ , we assume, from the coincidence of peak  $E_b$  with peak  $A$  of  $(\text{C}_5\text{H}_5)_2\text{Cr}^+$ , that the CO-free cation  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}^+$  is reduced to  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}$  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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^+$  at peak  $A_b$  to its full current, i.e. to  $i_p(A_b)/i_p(A'_b) = 1.0$ . Thus, oxidation of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$  to its dication  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^{2+}$  is reversible in an overall sense if loss of CO from some unstable intermediate, e.g. from the solvent adduct  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})(\text{THF})^+$ , is suppressed relative to the competing regeneration of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^+$ , by excess CO.

One-electron reduction of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$  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

\* Alternatively, a complex  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})\text{X}^+$  could be formed by uptake of an anionic species  $\text{X}^-$ , such as PF<sub>6</sub><sup>-</sup> or F<sup>-</sup>.



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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$  is only partly regenerated from the products arising by its one-electron reduction at peak  $B_b$  \*.

In the presence of CO, reduction peak  $B_b(\text{CO})$  at  $E_p(B_b(\text{CO})) - 2.66$  V (0.5 V/s) is slightly shifted relative to  $B_b$ , and increased to a peak current ratio of  $i_p(B_b(\text{CO}))/i_p(A_b)$  1.0; the associated, broad reoxidation peaks, which formerly appeared at  $-2.1$  and  $-1.3$  V, are now shifted to more positive potentials,  $E_p(H'_b(\text{CO})) - 1.9$  V and  $E_p(I'_b(\text{CO})) - 0.9$  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  $B_b(\text{CO})$ ; this indicates that  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$  is partly decomposed after its reduction, with or without excess CO.

The redox and ligand exchange reactions of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$  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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$ .

## Conclusions

The oxidations of  $(\text{C}_5\text{H}_5)_2\text{Cr}$  and of  $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{CO})$  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  $(\text{C}_5\text{H}_5)_2\text{Cr}$  and of  $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{CO})$  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  $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{CO})$  which is non-bonding rather than bonding with respect to the CO ligand. The axially symmetric, high-spin  $d^3$  complex  $(\text{C}_5\text{H}_5)_2\text{Cr}^+$  [16] appears to be a sufficiently favoured species, at any rate, to make loss of CO from  $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{CO})^+$  a facile process.

Oxidation of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$  occurs at practically the same potential as that of unbridged  $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{CO})$ . In contrast to  $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{CO})^+$ , however, the *ansa*-cation  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^+$ , 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  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})^+$  with its 17-electron configuration would undoubtedly be more prone to undergo further oxidation than the 15-electron cation  $(\text{C}_5\text{H}_5)_2\text{Cr}^+$ .

While an interannular bridge can thus extend the range of accessible chromocene derivatives to the  $\text{Cr}^{\text{IV}}$  oxidation state, no stabilisation of the metallocene framework is evident for electron uptake by  $\text{Cr}^{\text{II}}$  derivatives. The extra electron appears to enter an orbital which is antibonding with respect to the  $(\text{C}_5\text{H}_5)$  ligands, so making them susceptible to facile replacement by other ligands.

\* 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.

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