Synthesis of the Paramagnetic μ-Cyclopentadienylidene Dicobalt Complexes [$(C_5R_5)Co(\mu\text{-}C_5H_4)Co(X)(C_5R_5)$] (X = Cl, Br). X-Ray Crystal Structure of [$(C_5Me_5)Co(\mu\text{-}C_5H_4)Co(Br)(C_5Me_5)$]

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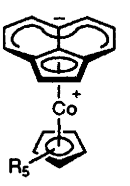
Careful chemical oxidation of the dinuclear carbene complexes [$(\eta\text{-}C_5R_5)Co(\mu\text{-}C_5H_4)Co(\eta\text{-}C_2H_4)(\eta\text{-}C_5R_5)$] gives the novel paramagnetic halide derivatives [$(\eta\text{-}C_5R_5)Co(\mu\text{-}C_5H_4)Co(X)(\eta\text{-}C_5R_5)$] (R = H, Me; X = Cl, Br) which have $\eta^5 : \eta^1$-cyclopentadienylidene bridges.

A novel class of organometallic complexes has been defined which derives considerable stabilisation from intramolecular charge transfer leading to a zwitterionic structure.[1] This is driven by the formation of substructures which correspond to the very stable cobaltocinium ion. Examples are the mononuclear acenaphthylene complexes **1**,[2] the dinuclear μ-cyclopentadienylidene complexes **2**–**5**[3] and the 'cobaltapentalene' complexes **6**.[1]

As expected from their zwitterionic nature the complexes **2**–**5** are very sensitive to oxidation. For example reversible electrochemical one-electron oxidation takes place at −0.41 V for **2a** (L = C_2H_4), −0.48 V for **2b** (L = CO) and −0.91 V for **2c** [L = $P(OMe)_3$].† Upon dissolution of **2a** in dichloromethane the colour changed from turquoise–green to deep-blue. At ambient temperature the blue solution decomposed within a few seconds. We suspected that chemical oxidation of **2a** by CH_2Cl_2 had taken place leading to the blue chloride derivative **7a** which, however, seemed to have a rather limited lifetime at room temperature. More stable paramagnetic blue solutions could be obtained by dissolving **5a** (L = C_2H_4) in CH_2Br_2 at −60 °C. However, no product could be isolated from these extremely sensitive solutions.

In one particular attempt to generate the trimethylphosphine derivative of **5** from **5a** and PMe_3 a small amount of dark-blue single crystals was obtained. An X-ray crystal structure analysis‡ revealed that the isolated material did not contain trimethylphosphine but rather was the bromide derivative **8b**. The presence of bromide, proved by reaction with silver ions, was traced back to the sample of [$(C_5Me_5)Co(C_2H_4)_2$] which had been used to synthesise **5a**. Presumably some $CoBr_2\cdot$dme (dme = 1,2-dimethoxyethane), from which [$(C_5Me_5)Co(C_2H_4)_2$] is prepared,[4] was carried over to [$(C_5Me_5)Co(C_2H_4)_2$] and to **5a**, then acting as a mild oxidising agent. Indeed reaction of **5a** with an equimolar amount of $CoBr_2\cdot$dme in toluene led to a deep-blue solution from which crystalline **8b** could be obtained in 15% yield. A practical route to the chloride derivatives **7a** and **8a** was the reaction of the ethylene complexes **2a** and **5a** with tetrachloroethylene. Generated *via* this route **7a** and **8a** proved to be reasonably stable in solution even at room temperature.

The molecular structure of **8b**, shown in Fig. 1, consists of a (μ-cyclopentadienylidene)-dicobalt core. The coordination geometry of the C_5H_4 bridge is μ-η^5(Co1) : η^1(Co2). However, the C_5-ring is slightly folded along C(2)···C(5) (folding angle 3°) with the carbene carbon atom C(1) pointing away from Co(1). This causes the distance Co(1)–C(1) to be somewhat longer [2.151(7) Å] than the bonds Co(1)–C(2)···C(5) [1.979(8)···2.044(8) Å]. The sandwich-like arrangement of ligands at Co(1) is completed by an η^5-C_5Me_5 ring which is nearly parallel to the 'diene' part [C(2) to C(5)] of the bridging C_5H_4 ligand. The Co(2)(Br)C_5Me_5 unit is connected to C(1) by a short [1.919(8) Å] bond. The plane defined by Co(2), Br(1) and the centroid of the C_5Me_5 ring is rotated around C(1)–Co(2) so as to form an angle of 30° to the mean plane of the cyclopentadienylidene ring.



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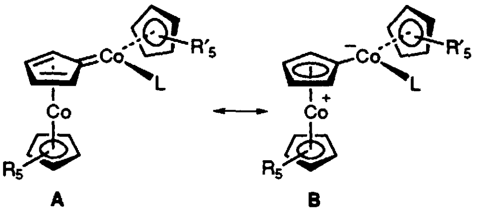
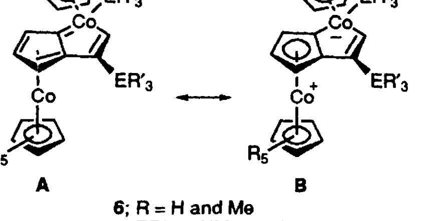
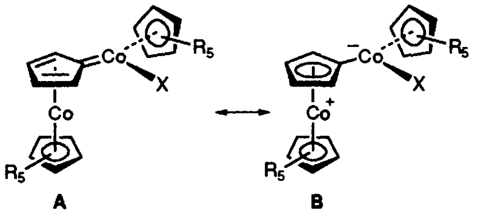


2; R = R′ = H
3; R = H, R′ = Me
4; R = Me, R′ = H
5; R = R′ = Me

a; L = C_2H_4
b; L = CO
c; L = $P(OMe)_3$



6; R = H and Me
ER′3 = SiMe3 and / or GeMe3



7a; R = H, X = Cl
7b; R = H, X = Br
8a; R = Me, X = Cl
8b; R = Me, X = Br

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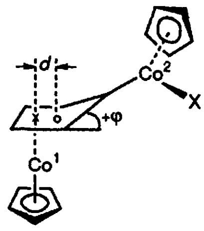
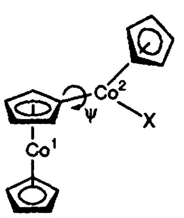
† Electrode potentials are given with respect to the standard calomel electrode.

‡ *Crystal data* for [$(C_5Me_5)Co(\mu\text{-}C_5H_4)Co(Br)(C_5Me_5)$]: $C_{25}H_{34}BrCo\cdot0.5C_7H_8$, M = 578.384, monoclinic, a = 11.359(6), b = 15.818(7), c = 15.559(10) Å, β = 107.25(4)°, V = 2672 Å^3, space group $P2_1/c$, Z = 4, μ = 27.4 cm^{-1}, crystal size 0.3 × 0.4 × 0.4 mm, STOE-Siemens four-circle diffractometer, Mo-Kα radiation (graphite monochromator), ω-scan, $2\theta_{min}$ = 3°, $2\theta_{max}$ = 48°, *hkl* range ±12, 16, 17. Reflexions measured: 4358, unique: 4358, observed: 1984 [$I > 2\sigma(I)$]; empirical absorption correction (T_{min} = 0.36, T_{max} = 0.52). The structure was solved by the heavy atom method and refined by blocked-matrix least-squares. Hydrogen atoms were inserted at calculated positions, methyl groups were refined as rigid groups. Final R-factors were R = 0.051, R_w = 0.045, $w = \sigma^{-2}(F)$ (SHELX-76, G. M. Sheldrick, University of Cambridge, 1976). The atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



C



D

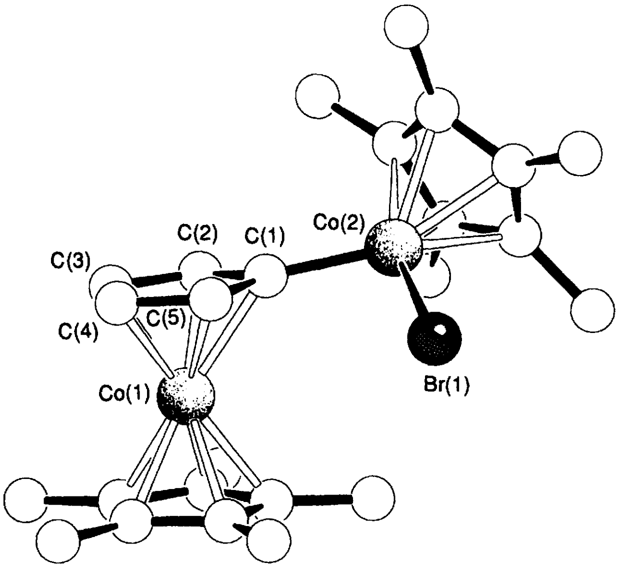


Fig.1 A view of the structure of **8b**. Selected bond lengths (Å) and angles (°): Co(1)–C(1) 2.151(7), Co(1)–C(2) 2.025(8), Co(1)–C(3) 1.979(8), Co(1)–C(4) 2.012(9), Co(1)–C(5) 2.044(8), C(1)–C(2) 1.43(1), C(1)–C(5) 1.46(1), C(2)–C(3) 1.41(1), C(3)–C(4) 1.41(1), C(4)–C(5) 1.41(1), Co(2)–C(1) 1.919(8), Co(2)–Br(1) 2.371(1), C(2)–C(1)–C(5) 102.7(7), C(2)–C(1)–Co(2) 131.9(6), C(5)–C(1)–Co(2) 125.2(6), C(1)–Co(2)–Br(1) 98.4(2).

In contrast to most dinuclear complexes with a cyclopentadienylidene bridge[5] there is no direct interaction between the two metal atoms in **2**–**8**. In analogy to **2**–**5** (**A**, **B**) two resonance structures **7**, **8** (**A**, **B**) can also be drawn for the paramagnetic halide derivatives. Formally, there is Co^{I}/Co^{I} (**A**) or Co^{III}/Co^{I} (**B**) in **2**–**5**. The actual electronic situation was found to depend on the donor–acceptor properties of the two electron ligand L.[3] Within certain limits various intermediate bonding situations between the extremes $\eta^4:\eta^1$-C_5H_4 (**A**) and $\eta^5:\eta^1$-C_5H_4 (**B**) are encountered. In **7** and **8** there is Co^{I}/Co^{II} (**A**) or Co^{III}/Co^{II} (**B**). Hence, our simple model predicts a formal oxidation of Co(2) in going from **2**–**5** to **7** and **8**.

To establish the electronic structure of **7** and **8** extended Hückel (EH) and Fenske–Hall SCF (FH) molecular orbital calculations§ were carried out on the model complex **7b**. Initially, the asymmetric geometry **C** with all C–C bonds fixed at 1.40 Å was assumed. We then varied the folding angle φ and the displacement *d* of Co(1) with respect to the position below the centroid of the (initially planar) C_5H_4 ring. The EH total energy varied only little; a *minimum* was found at $\varphi = -2°$, $d = 0.05$ Å. The total energy was further decreased when the bonds which connect the carbene carbon atom to the diene part of the cyclopentadienylidene were set to 1.45 Å (minimum energy for $\varphi = 0°$, $d = 0.0$ Å). This clearly corresponds to an $\eta^5:\eta^1$-C_5H_4 ligand in accord with the solid-state structure of **8b**. Rotation of the Co(Br)Cp fragment by an angle ψ around the bond from Co(2) to the carbene carbon atom in the direction of the C_s structure **D** ($\psi = 90°$) does not have a significant influence on the EH total energy up to $\psi = 40°$. At larger values of ψ steric interactions between the bromide and the hydrogens of the cyclopentadienyl ligand on Co(1) cause the energy to increase considerably. The negligible electronic energy barrier for the mutual rotation of the two parts of the molecule can be explained by the presence of two energetically close orthogonal π-orbitals on the Co(X)Cp fragment,[6] which are available for π-bonding with the p_π-orbital on the carbene carbon atom. For the five examples of **2**–**4** which have been studied by X-ray crystallography the unsymmetrical structure **C** was found in the solid state.[1,7] However NMR data of **2**–**5** indicate a low rotational barrier around Co(2)–C(14) in solution.[3] We therefore believe that the particular conformation found in crystalline **8a** is due to steric hindrance of the bulky C_5Me_5 and Br ligands.

The FH SCF-MO calculations of **7b** result in a HOMO which is nearly exclusively (>85%) centred on the Co(Br)Cp fragment. This singly occupied orbital has a large LCAO amplitude at Co(2) [*ca.* 61% Co(2) 3d, 4p]. Thus our picture with oxidation taking place at Co(2) is qualitatively justified.

Experimental information on the singly occupied MO should be available from EPR spectroscopy. However, **8b** only gives a broad EPR signal with $g = 2.14$ both in liquid solution and in solvent glass at 110 K. This could be due to unresolved hyperfine coupling to the bromine, which has two spin-active isotopes ($I = 3/2$). The EPR spectra of **7a** and **8a** at 110 K ($g = 2.16$) are also broad but show signs of hyperfine structure. Although a detailed analysis of the EPR spectra has not been possible, their general appearance is similar to those of 17-valence electron Co^{II} radicals.[8]

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§ EH calculations were carried out with CACAO (C. Mealli and D. M. Proserpio, *J. Chem. Educ.*, 1990, **67**, 399) using parameters supplied with the package. The wavefunctions used for the FH calculations (M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 1972, **11**, 768) were the same as in earlier work (H. Wadepohl and L. Zhu, *J. Organomet. Chem.*, 1989, **376**, 115). Idealised geometries were used in all cases. The distances Co(1)–(C_5H_5), Co(1)–(C_5H_4) and Co(2)–(C_5H_5) were set to 1.63, 1.64 and 1.74 Å, respectively. CH distances were fixed at 1.08 Å. The FH calculations were carried out with all bond lengths close to the experimental values.

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