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New class of mixed sandwich cycloheptatrienylchromium complex: crystal structures of the redox pair $[Cr(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_6C_6H_4Me\text{-}4)][PF_6]_n$ ($n = 1$ or 2)†

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The mixed sandwich complex $[Cr(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_6C_6H_4\text{-}Me\text{-}4)][PF_6]$ **1** underwent a reversible one-electron oxidation to the radical dication $[Cr(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_6C_6H_4\text{-}Me\text{-}4][PF_6]_2$ **2**; X-ray crystallographic studies on the redox pair revealed that the principal structural alteration resulting from oxidation is a small increase in the metal-to-ring distances.

The mixed sandwich complex $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ has long been the focus of a series of synthetic,[1] physical[2–5] and theoretical[6,7] investigations directed towards elucidation of the structure and bonding. However other cycloheptatrienylchromium sandwich systems[8,9] have been neglected notwithstanding the development of an extensive reaction chemistry of molybdenum analogues such as the cycloheptadienyl[10,11] and arene[12,13] derivatives $[Mo(\eta\text{-}C_7H_9)(\eta\text{-}C_7H_7)]$ and $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]^+$. This communication presents our initial findings on the structure, bonding and reactivity of the cationic arene derivatives $[Cr(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_6C_6H_4Me\text{-}4)][PF_6]_n$ (n = 1 or 2) and, in addition to providing a new impetus for physical and theoretical studies, this work has potential for applications in synthesis, *via* arene displacement, or in non-linear optical materials[14] through the provision of a cationic cycloheptatrienylchromium centre which can support reversible redox activity.

Although the reaction of $[Cr(CO)_3(\eta\text{-}C_7H_7)][PF_6]$ with refluxing toluene undoubtedly yields $[Cr(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ in a synthesis directly analogous to that of the molybdenum derivative, the product was formed in low yield and purity. However, reflux of the ring-substituted derivative $[Cr(CO)_3(\eta\text{-}C_7H_6C_6H_4Me\text{-}4)][PF_6]$[15,16] led to the isolation of $[Cr(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_6C_6H_4Me\text{-}4)][PF_6]$ **1**,‡ as a green solid in good yield and purity. The sandwich arrangement of **1** was confirmed by an X-ray structural investigation§ (Fig. 1) and important molecular parameters are summarised in Table 1. A key structural feature of **1** is the close comparability of average metal-to-ring bond lengths for the six- and seven-membered rings. The slight elongation in metal–arene bond distances by comparison with metal–cycloheptatrienyl distances becomes more distinct in the related molybdenum sandwich complex $[Mo(\eta\text{-}C_6H_5BPh_3)(\eta\text{-}C_7H_7)]$[18] and this structural difference may underlie the contrasting reactivity and redox properties of analogous chromium and molybdenum systems (see later).

Investigations on the structure and bonding in $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ have been facilitated by an extensive redox chemistry[3,5] and therefore the cyclic voltammetry of complex **1** was probed in MeCN. In contrast with the molybdenum analogues $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_6R)]^+$ (R = H, Me or C_6H_4F-4),[16] which undergo irreversible oxidation processes, the chromium complex **1** exhibits a reversible one-electron oxidation [E°(MeCN) 0.49 V *vs.* SCE] with the normal criteria for reversibility satisfied. Chemical oxidation of **1** with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2 resulted in the precipitation of a yellow-orange product which was identified as the radical

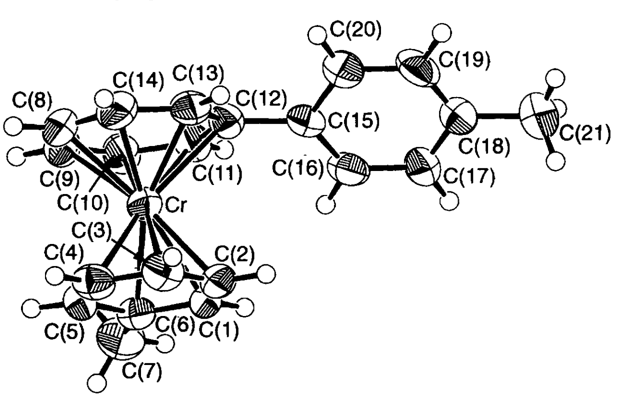

Fig. 1 Molecular structure of complex **1**; hydrogen atoms and PF_6 counter anion omitted

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† *Non-SI unit employed:* G = 10^{-4} T.

‡ Complex **1** was prepared in 53% yield from $[Cr(CO)_3(\eta\text{-}C_7H_6C_6H_4Me\text{-}4)][PF_6]$ (0.81 g) refluxed in toluene for 2 h (Found: C, 54.0; H, 4.3. Calc.: C, 53.6; H, 4.5%). Cyclic voltammetry at a carbon working electrode, 0.2 mol dm^{-3} $[NBu^n{}_4][BF_4]$ supporting electrolyte in MeCN, $E^\circ = 0.49$ V *vs.* saturated calomel electrode, SCE (for ferrocene–ferrocenium couple, $E^\circ = 0.43$ V under identical conditions). ^1H NMR (CD_2Cl_2, −80 °C): δ 7.34 (d, 2 H, C_6H_4Me-4); 6.90 (d, 2 H, C_6H_4Me-4); 6.18 (d, 2 H), 5.94 (br, 2 H), 5.78 (br, 2 H) ($C_7H_6C_6H_4$-Me-4); 5.17 (br, 5 H, C_6H_5Me); 1.93 (s, 3 H, $C_6H_4CH_3$); and 1.71 (s, 3 H, $C_6H_5CH_3$). Complex **2**, prepared in 26% yield from **1** (0.05 g) and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.04 g) in CH_2Cl_2 (Found: C, 41.3; H, 3.5. Calc.: C, 41.0; H, 3.4%), is totally insoluble in CH_2Cl_2 so driving the reaction to completion despite unfavourable redox potentials; cyclic voltammetry, E° (MeCN) 0.49 V *vs.* SCE; FAB mass spectrum, m/z 325 (M^+).

§ Crystal data. Complex **1**: $C_{21}H_{21}CrF_6P$, $M = 470.36$, orthorhombic, space group *Pbca* (no. 61), crystal dimensions 0.13 × 0.27 × 0.45 mm, $T = 295$ K, $a = 13.019(3)$, $b = 27.297(8)$, $c = 11.095(5)$ Å, $U = 3943(1)$ Å^3, $Z = 8$, $D_c = 1.584$ g cm^{-3}, $F(000) = 1920$, μ(Mo-Kα) 7.21 cm^{-1}, 2173 reflections with $I > 3.00\sigma(I)$ used in refinement. Solution by Fourier techniques, non-hydrogen atoms refined anisotropically, hydrogen atoms included but not refined; $R = 0.062$, $R' = 0.045$. Complex **2**: $C_{21}H_{21}CrF_{12}P_2$, $M = 615.32$, monoclinic, space group $P2_1/n$ (no. 14), crystal dimensions 0.15 × 0.25 × 0.40 mm, $T = 296$ K, $a = 12.747(5)$, $b = 12.697(4)$, $c = 14.317(5)$ Å, $\beta = 93.22(3)°$, $U = 2313(1)$ Å^3, $Z = 4$, $D_c = 1.766$ g cm^{-3}, $F(000) = 1236$, μ(Mo-Kα) 7.39 cm^{-1}, 3115 reflections with $I > 3.00\sigma(I)$ used in refinement. Solution by direct methods, non-hydrogen atoms refined anisotropically, hydrogen atoms included but not refined; $R = 0.045$, $R' = 0.043$. Data in common: Rigaku AFC5R diffractometer, Mo-Kα radiation (λ = 0.710 69 Å); calculations performed using the TEXSAN package.[17] Empirical absorption correction based on azimuthal scans (transmission factors: 0.85–1.0 for **1**, 0.90–1.0 for **2**), data also corrected for Lorentz-polarisation effects. Refinement based on F; $w = [\sigma_c{}^2(F_o) + (p^2/4)F_o{}^2]^{-1}$ where $\sigma_c(F_o)$ = esd based on counting statistics and $p = 0.0000$ for **1** and 0.0050 for **2**. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/263.

Table 1 Metal-to-ring distances in mixed sandwich cycloheptatrienyl complexes $[M(\eta\text{-}C_nH_{n-1}R')(\eta\text{-}C_7H_6R)]^z$ (n = 5 or 6)

	Complex			
	1	**2**	$[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]^a$	$[Mo(\eta\text{-}C_6H_5BPh_3)(\eta\text{-}C_7H_7)]^b$
M–C(average) ($C_nH_{n-1}R'$)	2.182(3)	2.206(2)	2.18	2.34
M–C(average) (C_7H_6R)	2.145(3)	2.166(2)	2.16	2.275(5)
M–C_n (M to ring plane)	1.688	1.709		1.887
M–C_7 (M to ring plane)	1.429	1.446		1.596

[a] Data from ref. 7. [b] Data from ref. 18.

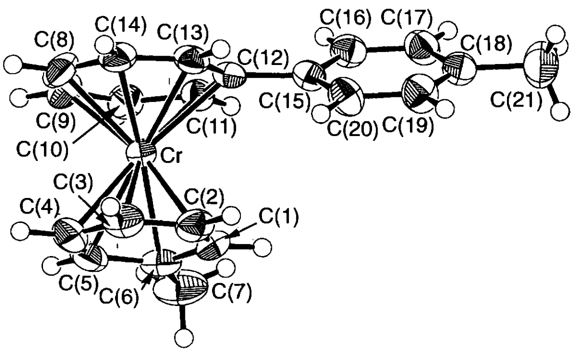

Fig. 2 Molecular structure of complex **2**; hydrogen atoms and PF_6 counter anions omitted

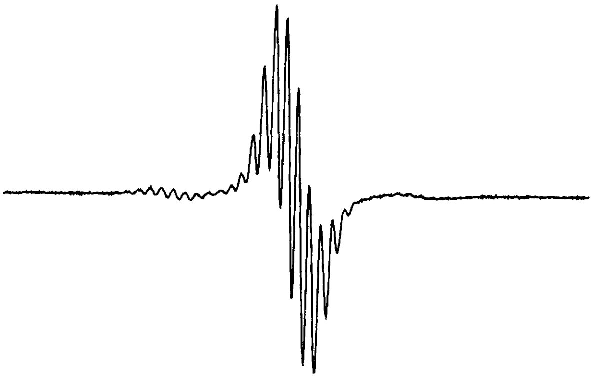

Fig. 3 Room temperature X-band solution ESR spectrum of complex **2**

dication $[Cr(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_6C_6H_4Me\text{-}4)][PF_6]_2$ **2**,‡ by microanalytical, spectroscopic and complementary cyclic voltammetric data. Further to confirm the identity of **2** and to elucidate the structural effects of one-electron oxidation, the crystal structure of **2**§ (Fig. 2) was determined; no corresponding investigation has been undertaken for $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]^z$ ($z = 0$ or $+1$). The principal structural modification associated with the one-electron oxidation of **1** to **2** is a small but consistent increase in all chromium-to-ring bond lengths (Table 1) with no clear distinction between the behaviour of metal–arene and –cycloheptatrienyl distances. Other changes include a small decrease in the dihedral angle between best ring planes [{C(1)–C(6)} – {C(8)–C(14)}; **1**, 1.9; **2**, 1.5°]. The limited change in metal–ring distances associated with one-electron oxidation of **1** suggests that, consistent with simple molecular orbital schemes for mixed sandwich complexes of this type,[19] the highest occupied molecular orbital (HOMO) is of a_1 symmetry and is essentially non-bonding with respect to the chromium-ring interaction.

A further probe of electronic structure is provided by the X-band, acetone solution ESR spectrum of complex **2** (Fig. 3); ESR investigations have been applied with some success to $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]^z$ ($z = +1$[3] or -1[4]) and the results stand comparison with those for **2**. The isotropic $<g>$ value for **2** (1.984) compares closely with that of $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]^+$ (1.988)[3] and is compatible with a singly occupied HOMO of mainly $3d_{z^2}$ character.[4] Yet more informative are the hyperfine coupling constants, determined for **2** with the aid of spectral simulation [$a(^{53}Cr)$ 23.2, $a(C_6H_5Me)$ 3.0, $a(C_7H_6R)$ 2.8 G]. Comparison with corresponding data for $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]^+$ [$a(^{53}Cr)$ 19.0, $a(C_5H_5)$ 2.16, $a(C_7H_7)$ 3.62 G][3] suggests a reduced anisotropy in spin-density distribution in **2**, consistent with the effect of an increase in ring size from cyclopentadienyl to arene.[2]

The successful syntheses of complexes **1** and **2** prompted investigations on the arene substitution chemistry of these complexes in an attempt to develop a route to half-sandwich cycloheptatrienylchromium chemistry analogous to that established for $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]^+$. However, so far, attempts to displace the arene ring from either **1** or **2** have been unsuccessful and we suggest that the difference in metal–arene bond lengths noted for **1** and $[Mo(\eta\text{-}C_6H_5BPh_3)(\eta\text{-}C_7H_7)]$ is also reflected in bond strengths and consequent reactivity. Further studies on complexes **1**, **2** and related derivatives are in progress.

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