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FULL PAPER

Synthesis, redox chemistry and EPR spectroscopy of the mixed-sandwich complexes (η-arene)(η-cycloheptatrienyl)metal(z+) (M = Cr or Mo; z = 1 or 2): crystal structures of the redox pair $[\mathrm{Cr}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})(\eta\text{-C}_7\mathrm{H}_6\mathrm{C}_6\mathrm{H}_4\mathrm{Me}\text{-}4)][\mathrm{PF}_6]_n$ (n = 1 or 2)

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The mixed sandwich complexes $[\mathrm{M}(\eta\text{-arene})(\eta\text{-C}_7\mathrm{H}_6\mathrm{R}')]^+$ (M = Cr, R′ = H, arene = $\mathrm{C}_6\mathrm{H}_4\mathrm{Me}_2$-1,4, **1a**; or $\mathrm{C}_6\mathrm{H}_3\mathrm{Me}_3$-1,3,5, **2a**; R′ = $\mathrm{C}_6\mathrm{H}_4\mathrm{Me}$-4, arene = $\mathrm{C}_6\mathrm{H}_5\mathrm{Me}$, **3a**; M = Mo, R′ = H, arene = $\mathrm{C}_6\mathrm{H}_3\mathrm{Me}_3$-1,3,5, **4a**) were prepared by reflux of $[\mathrm{M(CO)}_3(\eta\text{-C}_7\mathrm{H}_6\mathrm{R}')]^+$ in the appropriate arene solvent. Reflux of $[\mathrm{Mo}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})(\eta\text{-C}_7\mathrm{H}_7)]^+$ with an excess of $\mathrm{HC{\equiv}CBu^t}$ in acetone affords $[\mathrm{Mo}(\eta\text{-C}_6\mathrm{H}_3\mathrm{Bu^t}_3\text{-}1,3,5)(\eta\text{-C}_7\mathrm{H}_7)]^+$, **5a**. Cyclic voltammetric studies in NCMe reveal that each of **1a**, **2a**, **3a** and **5a** undergoes reversible one-electron oxidation processes to give the corresponding, isolable 17-electron radical dications, **1b**, **2b**, **3b** and **5b** which have been characterised by EPR spectroscopy. NMR data for the 18-electron monocations suggest an enhanced electron density at the arene ring in the chromium derivatives by comparison with molybdenum analogues and this is reflected in the stability of complexes **1a**, **2a** and **3a** towards arene displacement reactions. The crystal structure of **3a** reveals only a small asymmetry in the average chromium-to-ring carbon bond lengths for the arene and cycloheptatrienyl rings. One-electron oxidation of **3a** to give **3b** results in a small increase in metal-to-ring distances (*ca.* 0.02 Å) consistent with a HOMO which is essentially non-bonding with respect to the metal–ring interaction.

Mixed-sandwich cycloheptatrienyl complexes of the chromium triad metals have a distinguished history of investigations centred on physical[1–6] and theoretical[7,8] issues. In addition to the classical system (η-cycloheptatrienyl)(η-cyclopentadienyl)-metal (M = Cr,[9] Mo[10] or W[11,12]), two further important types of cycloheptatrienyl sandwich complexes have been developed for these metals, *i.e.* (η-cycloheptadienyl)(η-cycloheptatrienyl)-metal (M = Cr,[13] Mo[10] or W[12]) and (η-arene)(η-cycloheptatrienyl)metal(1+) (M = Cr[14] or Mo[15]) and it is with the latter system that this paper is concerned. Known complexes of this type are restricted almost exclusively to M = Mo and the primary focus of the majority of reports has been in the application of $[\mathrm{Mo}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})(\eta\text{-C}_7\mathrm{H}_7)]^+$ and related derivatives as a source of the cycloheptatrienylmolybdenum fragment.[15–17] In fact, prior to our preliminary account of the work described in this paper,[18] little attention had been given to the physical and structural properties of these complexes or indeed to the synthesis and chemistry of derivatives other than those of molybdenum.

The main objectives of the work described in this paper were therefore to develop synthetic routes to chromium and tungsten analogues of the known molybdenum systems and to investigate the chemical reactivity and physical properties of the new complexes. In particular related sandwich systems are known to exhibit a rich redox chemistry yet the redox chemistry of (η-arene)(η-cycloheptatrienyl)metal(1+) systems is almost unexplored. This paper describes the synthesis of the first well defined examples of (η-arene)(η-cycloheptatrienyl)-chromium(1+) complexes and of a molybdenum derivative which, in contrast to $[\mathrm{Mo}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})(\eta\text{-C}_7\mathrm{H}_7)]^+$, is resistant to arene displacement. The new complexes exhibit reversible one-electron oxidations to the isolable radical dications (η-arene)-(η-cycloheptatrienyl)metal(2+) and, in common with (η-cycloheptatrienyl)(η-cyclopentadienyl)metal(1+), the 17-electron radical dications provide well resolved and informative EPR spectra. These data, together with X-ray structural studies, highlight a contrast between the chromium and molybdenum systems in respect of the metal–arene bonding interaction.

Results and discussion

Synthetic studies

Two synthetic routes to mixed sandwich complexes of the type (η-arene)(η-cycloheptatrienyl)molybdenum(1+) have been reported.[19,20] The most direct of these[19] involves reflux of a suspension of $[\mathrm{Mo(CO)}_3(\eta\text{-C}_7\mathrm{H}_7)]^+$ in the required arene as solvent and using this strategy syntheses of $[\mathrm{Mo}(\eta\text{-arene})(\eta\text{-C}_7\mathrm{H}_7)]^+$ (arene = benzene, toluene or mesitylene) and the cycloheptatrienyl ring-substituted complexes $[\mathrm{Mo}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})(\eta\text{-C}_7\mathrm{H}_3\mathrm{Me}_4\text{-}1,2,4,6)]^+$ and $[\mathrm{Mo}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})(\eta\text{-C}_7\mathrm{H}_6\mathrm{Me})]^+$ have been described.[19,21,22] The objective of the synthetic studies was to exploit the direct reaction between $[\mathrm{M(CO)}_3(\eta\text{-C}_7\mathrm{H}_6\mathrm{R}')]^+$ (M = Cr, Mo or W, R′ = cycloheptatrienyl ring substituent) and arene solvent to obtain an extended series of mixed-sandwich systems (η-arene)(η-cycloheptatrienyl)metal(1+).

The kinetics of the reaction between $[\mathrm{M(CO)}_3(\eta\text{-C}_7\mathrm{H}_7)]^+$ and the arene solvent is dependent upon the boiling point of the arene and for M = Mo the more rapid formation of the toluene complex $[\mathrm{Mo}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})(\eta\text{-C}_7\mathrm{H}_7)][\mathrm{PF}_6]$ by comparison with the benzene derivative $[\mathrm{Mo}(\eta\text{-C}_6\mathrm{H}_6)(\eta\text{-C}_7\mathrm{H}_7)][\mathrm{PF}_6]$ has been documented.[19] In the case of M = Cr there appears to be a delicate balance between the rate of formation of $[\mathrm{Cr}(\eta\text{-arene})(\eta\text{-C}_7\mathrm{H}_7)]^+$ and the thermal decomposition of $[\mathrm{Cr(CO)}_3(\eta\text{-C}_7\mathrm{H}_7)]^+$

Table 1 Microanalytical and mass spectroscopic data

Complex	Analysis (%)[a]		Mass spectral data[b]
	C	H	
1a [Cr(η-$C_6H_4Me_2$-1,4)(η-C_7H_7)][PF_6]	45.7 (45.7)	4.5 (4.3)	249 ([M]$^+$), 159 ([$M - C_7H_7$]$^+$), 143 ([$M - C_6H_4Me_2$]$^+$)
2a [Cr(η-$C_6H_3Me_3$-1,3,5)(η-C_7H_7)][PF_6]	47.0 (47.1)	4.7 (4.7)	263 ([M]$^+$), 172 ([$M - C_7H_7$]$^+$), 143 ([$M - C_6H_3Me_3$]$^+$)
3a [Cr(η-C_6H_5Me)(η-$C_7H_6C_6H_4Me$-4)][PF_6]	54.0 (53.6)	4.3 (4.5)	325 ([M]$^+$), 233 ([$M - C_6H_5Me$]$^+$)
4a [Mo(η-$C_6H_3Me_3$-1,3,5)(η-C_7H_7)][PF_6]	42.1 (42.5)	4.0 (4.2)	309 ([M]$^+$)
5a [Mo(η-$C_6H_3Bu^t_3$-1,3,5)(η-C_7H_7)][PF_6]	52.1 (51.9)	6.5 (6.4)	435 ([M]$^+$)
1b [Cr(η-$C_6H_4Me_2$-1,4)(η-C_7H_7)][PF_6]$_2$	33.4 (33.4)	3.3 (3.2)	249 ([M]$^+$)
2b [Cr(η-$C_6H_3Me_3$-1,3,5)(η-C_7H_7)][PF_6]$_2$	34.2 (34.7)	3.5 (3.4)	263 ([M]$^+$)
3b [Cr(η-C_6H_5Me)(η-$C_7H_6C_6H_4Me$-4)][PF_6]$_2$	41.3 (41.0)	3.5 (3.4)	325 ([M]$^+$), 233 ([$M - C_6H_5Me$]$^+$)
5b [Mo(η-$C_6H_3Bu^t_3$-1,3,5)(η-C_7H_7)][PF_6]$_2$	41.4 (41.5)	5.1 (5.1)	435 ([M]$^+$)

[a] Calculated values in parentheses. [b] By FAB mass spectroscopy, m/z values based on ^{52}Cr, ^{98}Mo.

Table 2 ^1H and ^{13}C-{^1H} NMR data for [M(η-$C_6H_{6-n}R_n$)(η-C_7H_7)]$^+$ [a]

Complex	n	R	^1H NMR data			^{13}C-{^1H} NMR data		
			C_7H_7	$C_6H_{6-n}R_n$	R	C_7H_7	$C_6H_{6-n}R_n$	R
1a[b]	2	Me	6.19	5.73	2.31	91.5	92.0 (CH) 105.3 (CMe)	18.4
2a	3	Me	6.33	5.99	2.03	90.8	92.2 (CH) 105.5 (CMe)	16.4
4a	3	Me	5.73	6.62	2.40	87.6	102.0 (CH) 116.1 (CMe)	19.9
5a	3	Bu^t	5.78	6.54	1.36	86.9	93.2 (CH) 131.7 (CBu^t)	37.1 (*C*Me_3) 31.5 (C*Me_3*)
3a[c]	1	Me	C_7H_6R'[d] 6.18, d, 2H; 5.94, br, 2H; 5.78, br, 2H	5.17	1.71	*C_7H_6R'*[e] and *C_6H_5R* 108.1, 107.6, 93.3, 91.7, 91.6, 91.5, 90.8, 90.5		20.1

[a] 300 MHz ^1H NMR spectra, 75 MHz ^{13}C-{^1H} NMR spectra; all signals singlets unless stated otherwise, d = doublet, m = multiplet, br = broad. Chemical shifts downfield from $SiMe_4$, spectra recorded in acetone-d_6 unless stated otherwise. [b] In CD_2Cl_2. [c] In CD_2Cl_2 at −80 °C. [d] R′ = C_6H_4Me-4: δ 7.34, d, 2H; 6.90, d; 2H, 1.93, 3H (Me). [e] R′ = C_6H_4Me-4: δ 140.2, 137.7, 130.7, 129.4, 22.1.

and/or the product sandwich system. Thus, our attempts to prepare the previously reported but unsubstantiated[14] [Cr(η-C_6H_5Me)(η-C_7H_7)][PF_6] from [Cr(CO)$_3$(η-C_7H_7)][PF_6] refluxed in toluene resulted in very low yields of the impure product which was identified by mass spectroscopy. However reflux of [Cr(CO)$_3$(η-C_7H_7)][PF_6] in the higher boiling solvents *p*-xylene or mesitylene led to isolation of moderate yields of [Cr(η-arene)(η-C_7H_7)][PF_6] (arene = $C_6H_4Me_2$-1,4, **1a**; or $C_6H_3Me_3$-1,3,5, **2a**). Although we were not successful in attempts to obtain a toluene derivative of the Cr(η-C_7H_7) system, the ring-substituted cycloheptatrienyl complex [Cr(CO)$_3$(η-$C_7H_6C_6H_4Me$-4)][PF_6] appears to be activated to carbonyl substitution and reflux of a suspension of [Cr(CO)$_3$(η-$C_7H_6C_6H_4Me$-4)][PF_6] in toluene for 2 hours afforded good yields of pale green [Cr(η-C_6H_5Me)(η-$C_7H_6C_6H_4Me$-4)][PF_6] **3a**. In contrast with the molybdenum sandwich system [Mo(η-C_6H_5Me)(η-C_7H_7)]$^+$, which acts as a source of the Mo(η-C_7H_7)$^+$ fragment *via* arene displacement in refluxing acetone or NCMe, each of the chromium derivatives **1a**, **2a**, and **3a** was stable under these conditions suggesting an enhanced interaction between chromium and the arene ring by comparison with the known molybdenum analogues.

To extend comparison between related chromium and molybdenum complexes, our synthetic studies on the molybdenum system were directed towards isolation of derivatives which are resistant to arene displacement and to this end poly-alkyl substituted arenes were investigated. Reflux of [Mo(CO)$_3$(η-C_7H_7)][PF_6] in mesitylene for 3 hours afforded good yields of the previously reported,[19,20] pale green [Mo(η-$C_6H_3Me_3$-1,3,5)(η-C_7H_7)][PF_6] **4a** which, by comparison with the toluene derivative [Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6], exhibits enhanced stability towards arene displacement in refluxing acetone. However the definitive molybdenum complex with respect to resistance to arene displacement was obtained serendipitously from our investigations on the application of the [Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6]–acetone system as an alkyne polymerisation catalyst. Reflux of [Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6] in acetone in the presence of HC≡CBu^t results in the formation of high yields of white HC≡CBu^t polymer. A mechanism for terminal alkyne polymerisation initiated by a molybdenum or tungsten centre has been proposed[23,24] and pertinently we have previously demonstrated the capacity of the cycloheptatrienylmolybdenum system to effect terminal alkyne to vinylidene transformations.[15,16] Depending on the reaction conditions and identity of the alkyne substituent, both polymerisation and cyclotrimerisation may be observed and the product of cyclotrimerisation was detected in the complex [Mo(η-$C_6H_3Bu^t_3$-1,3,5)(η-C_7H_7)][PF_6] **5a** which was isolated in low yield from the reaction mother liquors. Complex **5a** is stable to arene displacement in refluxing acetone as evidenced by its generation under such conditions. Furthermore, attempts to produce it directly from [Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6] and $C_6H_3Bu^t_3$-1,3,5 in refluxing acetone were unsuccessful so supporting the view that **5a** is formed as an intimate part of a metal-assisted cyclotrimerisation process. All attempts to synthesize complexes of the type (η-arene)(η-cycloheptatrienyl)-tungsten(1+) by direct reaction of [W(CO)$_3$(η-C_7H_7)]$^+$ with an arene solvent were unsuccessful.

Details of the characterisation of **1a** to **5a** and other new complexes described in this paper are presented in Tables 1 (microanalytical and mass spectroscopic data) and 2 (^1H and ^{13}C-{^1H} NMR spectroscopic data). The principal feature of interest in the spectroscopic information is the NMR chemical shift data. Table 3 presents a comparison of ^{13}C-{^1H}

Table 3 Carbon-13 NMR data for $[M(\eta\text{-}L)(\eta\text{-}C_7H_7)]^{z+}$ ($z = 0$, L = C_5H_5; $z = 1$, L = $C_6H_3Me_3$-1,3,5)

Compound	C_7H_7	L		Solvent	Ref.
		*C*H	*C*Me		
$[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$	86.9	75.4		CS_2	5
$[Mo(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$	80.0	83.8		C_6D_6	5
$[W(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$	73.8	82.5		C_6D_6	12
$[Cr(\eta\text{-}C_6H_3Me_3)(\eta\text{-}C_7H_7)]^+$ **2a**	90.8	92.2	105.5	Acetone-d_6	This work
$[Mo(\eta\text{-}C_6H_3Me_3)(\eta\text{-}C_7H_7)]^+$ **4a**	87.6	102.0	116.1	Acetone-d_6	This work

NMR data for the mesitylene derivatives $[M(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta\text{-}C_7H_7)]^+$ (M = Cr **2a** or Mo **4a**) and the cyclopentadienyl complexes $[M(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ (M = Cr, Mo or W). The data for the latter have been interpreted[5,12] to suggest that the distribution of electron density between the C_5 and C_7 rings changes substantially on proceeding down the triad from Cr to W. Thus in $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ the C_5 ring resonance is situated to higher field whereas for Mo and W the high field resonance originates from the C_7 ring. It has been suggested that in the chromium derivative the electron density at the carbon atoms of the C_5 ring is larger than that at the C_7 ring whereas the reverse is true for Mo and W. A similar trend is observed for the arene complexes **2a** and **4a**. The most significant change is a shift to low field of the arene ring carbons from Cr to Mo; there is a corresponding shift in the C_7 resonance to high field but this is much smaller than in the $[M(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ system. However it is reasonable to conclude that in the complexes (η-arene)(η-cycloheptatrienyl)metal(1+) electron density at the C_6 ring decreases from Cr to Mo. The observation of corresponding trends in ^1H NMR spectra may be complicated by the effects of local magnetic anisotropies and shieldings but the ^1H NMR spectra for **2a** and **4a** do exhibit a clear trend consistent with the $^{13}C\text{-}\{^1H\}$ data. For the chromium derivative **2a** the three arene ring protons are located to high field but for the molybdenum derivative **4a** the chemical shift ordering is reversed and it is the C_7 ring protons which are found at higher field.

Electrochemical investigations and synthetic redox chemistry

Cyclic voltammetric investigations on the mixed-sandwich cycloheptatrienyl systems (η-cycloheptatrienyl)(η-cyclopentadienyl)metal (M = Cr,[6] Mo[10] or W[12]) and (η-cycloheptadienyl)(η-cycloheptatrienyl)molybdenum[25] reveal reversible one-electron oxidations to the corresponding 17-electron radical cations which in selected cases have been isolated and fully characterised. By contrast, investigations on the redox chemistry of $(\eta\text{-arene})(\eta\text{-}C_7H_7)$metal(1+) are limited to $[Mo(\eta\text{-}C_6H_5BPh_3)(\eta\text{-}C_7H_7)]$ which is reported to exhibit three reversible redox processes.[26] We therefore set out to investigate the cyclic voltammetry of an extended range of complexes (η-arene)(η-cycloheptatrienyl)metal(1+).

The initial scans in the room temperature cyclic voltammograms of the 18-electron chromium complexes (η-arene)(η-cycloheptatrienyl)chromium(1+) **1a** to **3a** in the region −1.0 to +1.0 V in CH_3CN are all characterised by reversible one-electron oxidation processes. The electron-transfer processes are diffusion controlled ($i_p^{ox}/v^{\frac{1}{2}}$ is constant for scan rates v = 50–500 mV s^{-1}) and chemically reversible with the ratio of cathodic to anodic currents unity over the same scan range. The observed separation between the cathodic and anodic peak potentials compared well with that measured for the ferrocene–ferrocenium couple measured under identical conditions. Extension of the scan range to −2.0 to +1.0 V led to the observation of an irreversible reduction process around −1.6 V but there was no evidence for the multiple stable oxidation states reported for $[Mo(\eta\text{-}C_6H_5BPh_3)(\eta\text{-}C_7H_7)]$. A compilation of the cyclic voltammetric data for each of the complexes **1a** to **3a** in NCMe is presented in Table 4. The values of $E°$ for the reversible one-electron oxidation process and E_p^c for the reduction process follow the trend expected for variation in the degree of alkyl substitution at the arene ring; thus $E°$ decreases in steps of 30 mV along the series **3a**, **1a** and **2a** but correspondingly the complexes become more difficult to reduce. Attempts were also made to carry out the electrochemistry in CH_2Cl_2 but the cyclic voltammograms so obtained were severely distorted with depressed i_p^c values; this problem may arise from the insolubility of the radical dications (η-arene)(η-cycloheptatrienyl)chromium(2+) in CH_2Cl_2 (see below).

Table 4 Cyclic voltammetric data for (η-arene)(η-cycloheptatrienyl)metal(z+) (z = 1 or 2)[a]

Complex	$E°$ $(^{+2/+1})$/V	$E_p^{c\,b}$/V
1a	0.46	−1.55
2a	0.43	−1.63
3a	0.49	−1.45
4a	0.41	−1.69
$[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]^+$	0.41[c]	−1.62
5a	0.55	−1.68
1b	0.47	
2b	0.44	
3b	0.49	
5b	0.55	

[a] $E°$ values (in V) recorded in CH_3CN with 0.2 M $[NBu^n_4][BF_4]$ as supporting electrolyte at a carbon working electrode relative to SCE and standardised with respect to the $FeCp^*_2\text{–}FeCp^*_2{}^+$ couple as internal calibrant for which $E° = -0.07$ V under these conditions ($FeCp_2\text{–}FeCp_2{}^+$ 0.43 V). [b] Determined at a scan rate of 100 mV s^{-1}. [c] Estimated $E°$ determined at −30 °C.

The room temperature, single scan, cyclic voltammogram of the molybdenum complex $[Mo(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta\text{-}C_7H_7)][PF_6]$ **4a** in CH_3CN in the region −2.0 to +1.0 V revealed two primary redox processes similar to those of the chromium analogues but with the distinction that the one-electron oxidation was chemically irreversible even at a scan rate of 500 mV s^{-1} (v = 500 mV s^{-1}, $i_p^c/i_p^a = 0.9$; v = 50 mV s^{-1}, $i_p^c/i_p^a = 0.6$). However, cooling the test solution to −20 °C resulted in a fully reversible process on the electrochemical timescale over the full scan rate range and this permitted determination of the $E°$ value for **4a** given in Table 4. In addition to the two primary processes detailed in Table 4, the multiple scan, room temperature cyclic voltammogram of **4a** over the scan range −0.2 to +0.8 V exhibits a new reversible couple ($E° = 0.08$ V) assigned to a secondary product resulting from irreversible oxidation of **4a**; the couple was observed only when the scan range was extended positive of 0.4 V. Very similar results, including an identical secondary product couple, were obtained for the cyclic voltammetry of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ (Table 4) except that in this case the primary oxidation process was totally irreversible at room temperature and, even on cooling to −30 °C, only an estimate of $E°$ could be made (v = 200 mV s^{-1}, $i_p^c/i_p^a = 0.6$, $E° = 0.41$ V).

The outcome of the irreversible oxidation of complexes **4a** and $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ in CH_3CN was further probed by synthetic and electrochemical investigations. It is well established that these complexes are labile towards arene displacement in refluxing CH_3CN to give $[Mo(NCMe)_3(\eta\text{-}C_7H_7)]^+$ which is a precursor to a range of substituted half-sandwich systems. We reasoned that the arene displacement process might also be redox-induced and offer the following evidence to support this hypothesis. When a mixture of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ and dppe ($Ph_2PCH_2CH_2PPh_2$) was stirred at room temperature in CH_3CN there was no reaction. However, addition of an equimolar quantity of the chemical oxidant $[FeCp_2][PF_6]$ resulted in a rapid change from green to red and formation of the arene-displaced products $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)]^{z+}$ ($z = 1$ or 2).[27] We suggest that this reaction proceeds *via* the intermediacy of the 17-electron radical $[Mo(NCMe)_3(\eta\text{-}C_7H_7)]^{2+}$ which is generated by one-electron oxidation of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$. Evidence for the existence of this radical and its generation from $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ or **4a** is derived from cyclic voltammetry of an authentic sample of $[Mo(NCMe)_3(\eta\text{-}C_7H_7)]^+$ in CH_3CN. This revealed a reversible one-electron oxidation process with $E° = 0.10$ V, essentially identical to that of the secondary product observed in the cyclic voltammograms of **4a** and $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$.

By contrast with complex **4a** and $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$, the cyclic voltammetry of $[Mo(\eta\text{-}C_6H_3Bu^t{}_3\text{-}1,3,5)(\eta\text{-}C_7H_7)]^+$ **5a** in the scan range −2.0 to +1.0 V in CH_3CN much more closely resembles the behaviour of the chromium analogues **1a** to **3a**. Thus the one-electron oxidation process fully meets the criteria for chemical and electrochemical reversibility with no evidence for formation of the secondary product provisionally assigned as $[Mo(NCMe)_3(\eta\text{-}C_7H_7)]^+$. The magnitude of E_p^c for reduction of **5a** is consistent with other data in Table 4 but $E°$ for one-electron oxidation is to anomalously positive potential; we have no clear explanation for this but note that the properties of **5a** are atypical for the molybdenum system.

The magnitudes of $E°$ and the reversibility of the redox processes suggested that, with appropriate chemical redox reagents, synthesis and isolation of the radical dications derived from complexes **1a**, **2a**, **3a** and **5a** might be achieved but the selection of suitable chemical redox reagents to effect one-electron oxidation presented some initial difficulty. Inspection of Table 4 reveals that all the $E°$ values for **1a** to **5a** measured in CH_3CN are equal to, or to positive potential of, that determined for the ferrocene–ferrocenium couple under identical conditions ($E° = 0.43$ V). Moreover, the PF_6 counter ion present in **1a** to **5a** further restricted the choice of oxidant to a hexafluorophosphate salt for the generation of samples suitable for microanalysis. Possible alternative redox reagents to $[FeCp_2][PF_6]$ which act as stronger oxidants include $Ag[PF_6]$ and the acetylferrocenium ion $[FeCp\{\eta\text{-}C_5H_4(C(O)Me)\}]^+$. We wished to avoid the use of silver reagents in very small scale preparations and therefore turned to the potentially much more easily handled acetylferrocenium ion. The standard literature preparation of $[FeCp\{\eta\text{-}C_5H_4(C(O)Me)\}]^+$ involves oxidation of $[FeCp\{\eta\text{-}C_5H_4(C(O)Me)\}]$ with $Ag[BF_4]$ and isolation of the product as a BF_4 salt.[28] We modified this procedure to the use of $Ag[PF_6]$ and succeeded in isolating $[FeCp\{\eta\text{-}C_5H_4\text{-}(C(O)Me)\}][PF_6]$ albeit in rather lower yield than the BF_4 salt (the PF_6 counter ion appears to result in reduced solubility in CH_2Cl_2). In the event however the acetylferrocenium ion was employed only in oxidation of the molybdenum complexes **4a** and **5a**. The very similar $E°$ values for the ferrocene–ferrocenium couple and those of the chromium derivatives **1a**, **2a** and **3a**, together with the very low solubility of the 17-electron radical products in CH_2Cl_2, were sufficient to drive the reactions of **1a**, **2a** and **3a** with $[FeCp_2][PF_6]$ in CH_2Cl_2.

Treatment of green, CH_2Cl_2 solutions of the chromium complexes **1a**, **2a** and **3a** with $[FeCp_2][PF_6]$ resulted in the respective precipitation of the 17-electron, radical dications $[Cr(\eta\text{-arene})(\eta\text{-}C_7H_6R')][PF_6]_2$ ($R' = H$, arene $= C_6H_4Me_2$-1,4, **1b**, or $C_6H_3Me_3$-1,3,5, **2b**; $R' = C_6H_4Me$-4, arene $= C_6H_5Me$, **3b**) as buff coloured (**1b**, **2b**) or orange-yellow (**3b**) solids. Complexes **1b**, **2b** and **3b** were soluble in acetone but almost totally insoluble in CH_2Cl_2. In view of the rather more positive $E°$ value for the molybdenum derivative **5a**, the dication $[Mo(\eta\text{-}C_6H_3Bu^t{}_3\text{-}1,3,5)(\eta\text{-}C_7H_7)][PF_6]_2$ **5b** was prepared by reaction of **5a** with the more powerful one-electron oxidant $[FeCp\{\eta\text{-}C_5H_4(C(O)Me)\}][PF_6]$ in acetone. Finally, the cyclic voltammetric studies on $[Mo(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta\text{-}C_7H_7)][PF_6]$ **4a** suggested that the corresponding radical dication might be obtained by a low temperature synthesis. The reaction of **4a** with $[FeCp\{\eta\text{-}C_5H_4(C(O)Me)\}][PF_6]$ in acetone at −20 °C proceeded rapidly and treatment of the reaction mixture with diethyl ether led to precipitation of a white solid which gave an FAB mass spectrum ($m/z = 309$) consistent with formation of $[Mo(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta\text{-}C_7H_7)][PF_6]_2$ **4b**. However the complex was unstable in solution (even at low temperature) and therefore difficult to purify such that satisfactory characterisation data were not obtained. Characterisation data for the isolable 17-electron complexes **1b**, **2b**, **3b** and **5b** are presented in Table 1 (microanalytical and mass spectroscopic data) and Table 4 (cyclic voltammetric data). The cyclic voltammetry of the 17-electron radicals was investigated as reductions in CH_3CN and again the criteria for diffusion control and chemical reversibility were fully satisfied. Moreover the identity of **1a**/**1b**, **2a**/**2b**, **3a**/**3b** and **5a**/**5b** as redox pairs was established by the complementary cyclic voltammetric data.

EPR Spectroscopy

Fluid solution spectra of complexes **1b**, **2b**, **3b**, and **5b** in acetone were recorded as both first and second derivatives, at X-band frequencies and 243 K (this temperature gave optimum resolution in all cases). The spectra were those expected for the metals in natural abundance with additional ligand hyperfine splittings. Simulation of these spectra gave the isotropic parameters presented in Table 5 and the second derivative experimental and simulated spectra for **5b** are illustrated in Fig. 1. The additional hyperfine splitting is attributed to the protons attached directly to the arene and cycloheptatrienyl

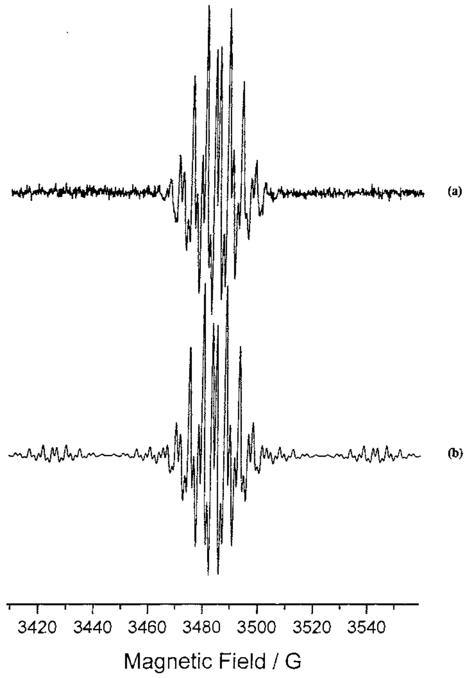

Fig. 1 Fluid solution (acetone, 243 K), second derivative X-band spectrum of $[Mo(\eta\text{-}C_6H_3Bu^t{}_3\text{-}1,3,5)(\eta\text{-}C_7H_7)][PF_6]_2$ **5b**, $\nu = 9.6298$ GHz: (a) experimental; (b) simulated with parameters from Table 5 plus peak to peak Lorentzian linewidth of 3.0 G.

Table 5 EPR data[a]

Complex	$g_{\parallel}$[a]	$g_{\perp}$[b]	$A_{\parallel}$[b]	$A_{\perp}$[b]	g_{iso}[c]	A_{iso}[c]	$a_{iso}(^1H)$[c,d]
1b	2.0030	1.9774	(10.6)	29.5	1.984	23.2	3.0 (11H)
2b	2.0035	1.9775	(10.9)	29.5	1.984	23.3	3.1 (7H) 2.9 (3H)
3b	2.0030	1.9768	(8.6)	30.5	1.984	23.2	2.8 (6H) 3.0 (5H)
5b	2.0024	1.9710	10.0	55.0	1.979	39.0	4.9 (7H) 3.4 (3H)

[a] Values of $A_{\parallel}$, $A_{\perp}$, A_{iso} and $a(^1H)$ are in Gauss (1 Gauss = 10^{-4} Tesla). Estimated errors are $g_{\parallel}$ and $g_{\perp}$ ± 0.0005, g_{iso} ± 0.001, $A_{\parallel}$, $A_{\perp}$ and A_{iso} ± 0.5 G and $a(^1H)$ ± 0.1 G. [b] Q-Band measurements; values of $A_{\parallel}$ in parentheses are calculated from $A_{\perp}$ and A_{iso}. [c] X-Band measurements. [d] The numbers in parentheses for $a_{iso}(^1H)$ are the numbers of equivalent protons.

Table 6 Metal to ring distances (Å) in mixed sandwich cycloheptatrienyl complexes $[M(\eta\text{-}L)(\eta\text{-}C_7H_7)]$

	M–C(average)		M–ring plane	
Complex	L	C_7H_7	L	C_7H_7
$[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_7H_7)]$[10]	2.31	2.25	1.982	1.583
$[Mo(\eta^5\text{-}C_7H_9)(\eta\text{-}C_7H_7)]$[25]	2.32	2.26	1.783	1.591
$[Mo(\eta\text{-}C_6H_5BPh_3)(\eta\text{-}C_7H_7)]$[26]	2.34	2.275(5)	1.887	1.596
$[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$[8]	2.18	2.16		
3a	2.182(3)	2.145(3)	1.688	1.429
3b	2.206(2)	2.166(2)	1.709	1.446

rings; there was no evidence for interaction with protons from the substituents (Me, Bu^t or C_6H_4Me-4) on either ring. The differences in $a_{iso}(^1H)$ for the arene and cycloheptatrienyl ligands in **2b** and **3b**, although small, led to much improved simulations compared with those in which all the proton splittings were assumed to be the same. However no such differences were required for satisfactory simulation of the spectrum of **1b**. In the case of the molybdenum complex **5b** there is a greater difference in the splittings for the protons on the two ring systems compared with those found for the chromium complexes. Furthermore, the magnitudes of the hyperfine splittings, even after allowing for the differences in g_{iso} values, indicate a greater degree of unpaired electron density on both the arene and cycloheptatrienyl rings in **5b** by comparison with the chromium derivatives. In addition **5b**, in contrast with the chromium derivatives, exhibits significantly more unpaired electron density on the cycloheptatrienyl ring than on the $C_6H_3Bu^t_3$ ring, an observation consistent with the conclusions drawn from NMR data for the 18-electron monocations.

The anisotropy in g and the metal hyperfine splitting constants (A) were determined from the simulation of frozen solution (acetone–toluene, 10 : 1) spectra at Q-band frequencies. The g and A values for each complex display axial EPR symmetry. We found no evidence for proton hyperfine splitting in these spectra. The g and A values are consistent with a HOMO that is essentially metal based and in addition the pattern of the g anisotropy ($g_{\parallel} \approx 2$, $g_{\perp} < 2$) is that expected from the $(d_{xy}, d_{x^2-y^2})^4 (d_{z^2})^1$ configuration proposed by Green *et al.*[29]

X-Ray crystallographic studies

The principal objectives of the structural studies were (i) to determine the effect of the identity of the metal (Cr *vs.* Mo) on the metal-to-ring bond distances and (ii) to establish the structural changes effected by one-electron oxidation through comparison of the molecular geometries of a redox pair of complexes.

Structural studies have been reported for each of the main classes of mixed sandwich cycloheptatrienyl systems, (η-cycloheptatrienyl)(η-cyclopentadienyl)metal,[10] (η-cycloheptadienyl)(η-cycloheptatrienyl)metal[25] and $[M(\eta\text{-arene})(\eta\text{-}C_7H_7)]^+$,[26] but in all three cases the complex selected for investigation was one of molybdenum; although limited structural data are also available for $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$[8] these are not substantiated by a full report. A summary of the principal aspects of the structural data available for the representative cycloheptatrienyl sandwich systems is presented in Table 6 and three points of interest arise. First, considering the three molybdenum complexes $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_7H_7)]$, $[Mo(\eta\text{-}C_7H_9)(\eta\text{-}C_7H_7)]$ and $[Mo(\eta\text{-}C_6H_5BPh_3)(\eta\text{-}C_7H_7)]$, there is a very close similarity between the mean Mo–C_7 bond lengths in the three complexes and also in the Mo to cycloheptatrienyl ring plane distances. Secondly, although the Mo to ring plane distances vary for the cyclopentadienyl, arene and cycloheptadienyl ligands, the mean molybdenum to ring carbon bond lengths do not alter significantly with the ligand and in each case are approximately 0.06 Å longer than the corresponding molybdenum to cycloheptatrienyl carbon bond length. Finally, comparison of mean metal-to-ring bond distances in $[Cr(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ and $[Mo(\eta\text{-}C_5H_4Me)(\eta\text{-}C_7H_7)]$ suggests a metal dependent structural effect. Both M–C_7 and M–C_5 bond distances are shorter for the chromium derivative but most importantly, in the chromium system, the mean metal-to-ring carbon distances are nearly equal for the C_5 and C_7 rings. A similar metal dependent effect in $[M(\eta\text{-arene})(\eta\text{-}C_7H_7)]^+$ would be consistent with the observed differences in reactivity and spectroscopic properties of the chromium and molybdenum systems and we therefore set out to determine the molecular structure of one example of a chromium complex of the type (η-arene)(η-cycloheptatrienyl)chromium(1+).

Attempts to obtain crystals of the mesitylene complex $[Cr(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta\text{-}C_7H_7)][PF_6]$ **2a** suitable for X-ray crystallographic analysis met with no success but the cycloheptatrienyl ring-substituted derivative **3a** proved to be more suitable for crystallisation. The molecular configuration of **3a**, annotated with the crystallographic numbering scheme, is presented in Fig. 2 and important bond lengths and angles for **3a** are summarised in Table 7. The principal structural dimensions of interest are the chromium-to-ring carbon distances. The chromium to arene ring carbon distances lie in the range 2.161(7) to 2.217(7) Å with the carbon bearing the methyl substituent [C(6)] exhibiting the longest bond. Similarly for the cycloheptatrienyl ring, it is C(12) bearing the tolyl substituent

Table 7 Selected bond lengths (Å) and angles (°) for complexes **3a** and **3b**

	3a	**3b**		**3a**	**3b**
Cr(1)–C(1)	2.181(7)	2.191(4)	C(1)–C(6)	1.379(9)	1.405(6)
Cr(1)–C(2)	2.161(7)	2.195(4)	C(2)–C(3)	1.38(1)	1.383(6)
Cr(1)–C(3)	2.179(8)	2.194(4)	C(3)–C(4)	1.360(10)	1.384(6)
Cr(1)–C(4)	2.183(7)	2.192(4)	C(4)–C(5)	1.408(9)	1.395(6)
Cr(1)–C(5)	2.174(7)	2.211(4)	C(5)–C(6)	1.392(9)	1.398(6)
Cr(1)–C(6)	2.217(7)	2.252(4)	C(6)–C(7)	1.494(10)	1.488(6)
Cr(1)–C(8)	2.132(8)	2.164(4)	C(8)–C(9)	1.38(1)	1.401(6)
Cr(1)–C(9)	2.133(7)	2.156(4)	C(8)–C(14)	1.38(1)	1.395(6)
Cr(1)–C(10)	2.114(7)	2.148(4)	C(9)–C(10)	1.366(10)	1.385(6)
Cr(1)–C(11)	2.143(7)	2.164(4)	C(10)–C(11)	1.370(9)	1.398(5)
Cr(1)–C(12)	2.201(7)	2.225(4)	C(11)–C(12)	1.414(9)	1.412(5)
Cr(1)–C(13)	2.149(7)	2.159(4)	C(12)–C(13)	1.401(9)	1.406(5)
Cr(1)–C(14)	2.142(8)	2.144(4)	C(13)–C(14)	1.401(10)	1.397(6)
C(1)–C(2)	1.379(10)	1.399(6)	C(12)–C(15)	1.489(9)	1.491(5)
C(2)–C(1)–C(6)	120.3(7)	121.6(4)	C(8)–C(9)–C(10)	127.8(7)	128.3(4)
C(1)–C(2)–C(3)	121.6(7)	119.5(4)	C(9)–C(10)–C(11)	130.1(8)	129.3(4)
C(2)–C(3)–C(4)	119.2(8)	120.1(4)	C(10)–C(11)–C(12)	130.2(7)	130.2(4)
C(3)–C(4)–C(5)	119.8(7)	120.3(4)	C(11)–C(12)–C(13)	124.3(7)	124.8(4)
C(4)–C(5)–C(6)	120.9(7)	121.1(4)	C(12)–C(13)–C(14)	130.5(8)	130.4(4)
C(1)–C(6)–C(5)	118.2(7)	117.4(4)	C(8)–C(14)–C(13)	128.0(8)	129.4(4)
C(9)–C(8)–C(14)	129.0(8)	127.6(4)			

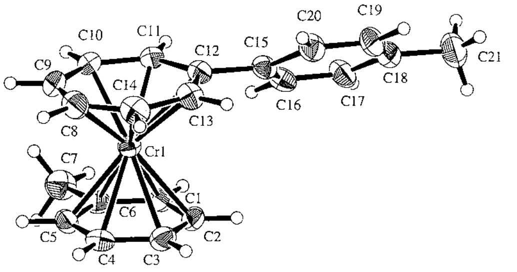

Fig. 2 Molecular structure of complex **3a**; PF_6 counter anion omitted.

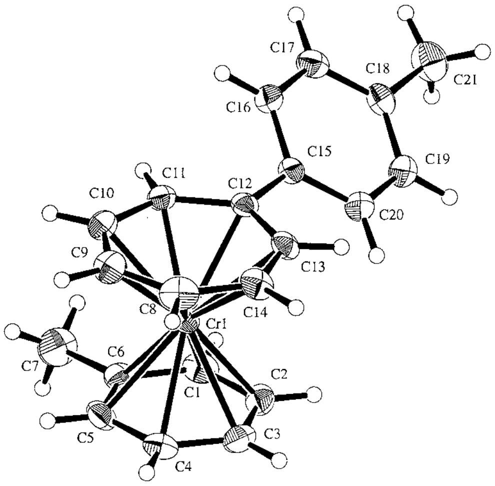

Fig. 3 Molecular structure of complex **3b**; PF_6 counter anions omitted.

which displays the longest Cr–C bond and chromium to C_7 bond lengths lie in the range 2.114(7) to 2.201(7) Å. The calculated mean Cr to ring carbon distance and metal-to-ring plane distances are summarised in Table 6 for direct comparison with related cycloheptatrienyl mixed sandwich systems. Comparison of the data for **3a** and [Mo(η-$C_6H_5BPh_3$)(η-C_7H_7)] leads to very similar conclusions to those drawn from comparison of [Cr(η-C_5H_5)(η-C_7H_7)] and [Mo(η-C_5H_4Me)(η-C_7H_7)], *i.e.* the chromium derivative possesses shorter bond distances to both rings and a reduced asymmetry in metal-to-ring carbon distances between C_6 and C_7 rings. These results, together with the differences in NMR chemical shift data for analogous chromium and molybdenum systems **2a** and **4a**, clearly suggest that the arene ring in the chromium complexes is attached more strongly to the metal centre than in the analogous molybdenum system.

There are no reports of a direct structural comparison of a redox pair of mixed sandwich complexes containing a cycloheptatrienyl ligand. However where redox pairs of sandwich complexes have been investigated the structural changes resulting from one-electron oxidation from an 18- to a 17-electron configuration are generally rather limited. This has been attributed to removal of an electron from a molecular orbital which is essentially non-bonding or very weakly bonding with respect to the metal–ring bonding interaction. A generalised MO scheme for sandwich systems with C_5, C_6 or C_7 rings, including mixed sandwich complexes (η-arene)(η-cycloheptatrienyl)metal(1+), has been developed previously,[29] and isolation of the stable radical **3b** now provides the opportunity to test the validity of this MO description.

The crystal structure of the 17-electron radical dication [Cr(η-C_6H_5Me)(η-$C_7H_6C_6H_4$Me-4)][PF_6]$_2$ **3b** is shown in Fig. 3 and important bond lengths and angles are given in Table 7. For ease of comparison the same crystallographic numbering scheme is employed for both **3a** and **3b**. In **3b**, as for **3a**, the chromium to carbon bond lengths to each discrete ring lie within a fairly narrow range but the carbon bearing the ring substituent displays a slightly elongated chromium–carbon bond length. The mean chromium-to-ring carbon bond distances and the chromium to ring plane distances are presented in Table 6 and again the chromium to C_6 and to C_7 distances are similar with the bonds to the cycloheptatrienyl ring slightly shorter. The principal structural effect resulting from one-electron oxidation of **3a** to **3b** is a small increase (*ca.* 0.02 Å) in each of the mean Cr–C_6 and Cr–C_7 distances consistent with a highest molecular orbital (HOMO) which is non-bonding or only very weakly bonding with respect to the metal ring interaction and in accord with the simple MO scheme developed for these mixed-sandwich systems.

Conclusion

Reaction of [M(CO)$_3$(η-C_7H_7)]$^+$ (M = Cr or Mo) with arene solvents provides a general synthesis of the mixed sandwich complexes (η-arene)(η-cycloheptatrienyl)metal(1+) but the tungsten analogues remain elusive. The 17-electron radical dications (η-arene)(η-cycloheptatrienyl)chromium(2+) are isolable and stable for a range of arene ligands. By contrast, in the molybdenum system the radical dications are generally unstable (probably with respect to arene displacement) although the $C_6H_3Bu^t_3$-1,3,5 complex (**5b**) provides a notable exception. The results of reactivity studies, NMR spectroscopic and X-ray crystallographic investigations all suggest that the metal to arene bonding interaction in the chromium complexes is enhanced by comparison with the analogous molybdenum system. The X-ray crystallographic comparison of the redox pair $[Cr(\eta-C_6H_5Me)(\eta-C_7H_6C_6H_4Me-4)][PF_6]_n$ ($n = 1$ or 2) taken together with the EPR data (*g* and *A* values) for the 17-electron radical dications are consistent with a HOMO in these systems that is essentially metal based.

Experimental

General procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complex $[Mo(\eta-C_6H_5Me)(\eta-C_7H_7)][PF_6]$ was prepared by a published procedure[19] and $HC{\equiv}CBu^t$ was supplied by Lancaster Synthesis. 300 MHz ^1H and 75 MHz ^{13}C-{^1H} NMR spectra were recorded on Bruker AC 300 E, Varian Associates XL 300 or Varian Unity Inova 300 spectrometers, infrared spectra on a Perkin-Elmer FT 1710 spectrometer and mass spectra using a Kratos Concept 1S instrument. X-Band (*ca.* 9.5 GHz) fluid solution and Q-band (*ca.* 34 GHz) frozen solution spectra were recorded on a Bruker ESP 300E spectrometer. Magnetic fields were calibrated with a Bruker ER035M Gaussmeter and the microwave frequencies measured with an EIP 588C microwave counter. Spectrum manipulations were performed using the Bruker software supplied with the spectrometer. Spectral simulations were performed using in-house software which has been described elsewhere.[30] Cyclic voltammetric studies were carried out, as described previously,[31] at a carbon working electrode (area 0.28 cm^2) using 0.2 M $[NBu^n_4][BF_4]$ as supporting electrolyte in solutions purged with nitrogen gas. All potentials are referenced to an aqueous calomel electrode and, under these conditions, $E°$ for the couple $[Fe(\eta-C_5H_5)_2]$–$[Fe(\eta-C_5H_5)_2]^+$ is 0.43 V in CH_3CN. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparations

$[Cr(\eta-C_6H_4Me_2-1,4)(\eta-C_7H_7)][PF_6]$ 1a. A red suspension of $[Cr(CO)_3(\eta-C_7H_7)][PF_6]$ (1.000 g, 2.69 mmol) in *p*-xylene (40 cm^3) was refluxed for 3.5 h to give a green precipitate in a green solution. The mother liquors were removed by syringe and the remaining solid dried *in vacuo*. The product was dissolved in CH_2Cl_2 and the solution filtered then treated with diethyl ether to give complex **1a** as a pale green solid; yield 0.51 g (48%). The mesitylene derivative $[Cr(\eta-C_6H_3Me_3-1,3,5)(\eta-C_7H_7)][PF_6]$ **2a** was similarly prepared in 39% yield from $[Cr(CO)_3(\eta-C_7H_7)][PF_6]$ (1.000 g, 2.69 mmol) and mesitylene (40 cm^3) except that the reaction time was 1.5 h.

$[Cr(CO)_3(\eta-C_7H_6C_6H_4Me-4)][PF_6]$. Reflux of $Cr(CO)_6$ (2.042 g, 9.28 mmol) in NCMe (50 cm^3) for 20 h gave a bright yellow solution from which $[Cr(CO)_3(NCMe)_3]$ was isolated by removal of the solvent *in vacuo*. The solid residue of $[Cr(CO)_3(NCMe)_3]$ was then treated with a solution of 7-(4-MeC_6H_4)C_7H_7 [3.142 g, 17.3 mmol in thf (40 cm^3)]. The resulting red solution was warmed to 40 °C for $\frac{1}{2}$ h and gently refluxed for $1\frac{1}{2}$ h. Solvent was then removed to give a red oil which was dissolved in diethyl ether (10 cm^3) and transferred to an n-hexane–alumina chromatography column. Elution with n-hexane–diethyl ether (1:1) gave a deep red band which was collected, reduced in volume and further n-hexane added. The solution was cooled to −20 °C overnight and the product $[Cr(CO)_3\{\eta^6-7-(4-MeC_6H_4)C_7H_7\}]$ as an *exo–endo* mixture at C-7 was separated from the mother liquors and isolated as a red solid; yield 1.65 g (56%). The $[Cr(CO)_3\{\eta^6-7-(4-MeC_6H_4)C_7H_7\}]$ (1.65 g, 5.19 mmol) so obtained was dissolved in methylcyclohexane (30 cm^3) and refluxed for 20 minutes to effect H migration at the C_7 ring thus facilitating subsequent hydride abstraction.[22,32] The methylcyclohexane solvent was removed *in vacuo* and the residue, dissolved in CH_2Cl_2 (40 cm^3), was treated with $[Ph_3C][PF_6]$ (1.89 g, 4.87 mmol). After stirring for 1 h the orange precipitate of the product $[Cr(CO)_3(\eta-C_7H_6C_6H_4Me-4)][PF_6]$ was collected by filtration, washed with diethyl ether and dried; yield 1.83 g (76%) (Found: C, 44.4, H, 2.6. Calc. for $C_{17}H_{13}CrF_6O_3P$: C, 44.2, H, 2.8%). FAB mass spectrum (*m/z*): 317 (M^+), 289 ($[M - CO]^+$), 261 ($[M - 2CO]^+$) and 233 ($[M - 3CO]^+$). Infrared spectrum: ν(CO) (CH_2Cl_2) 2066 and 2028 cm^{-1}. ^1H NMR in acetone-d_6: δ 7.96 {d, 2H, *J*(H–H) 8, C_6H_4Me}; 7.49 {d, 2H, *J*(H–H) 8 Hz, C_6H_4Me}; 7.13 {br, 4H} and 6.93 {br, 2H}, $C_7H_6C_6H_4Me$; and 2.47 {s, 3H, C_6H_4Me}. ^{13}C NMR in acetone-d_6; δ 222.3 [CO]; 143.0, 134.5, [C(11) and C(8)], 131.0, 129.7 [C(9), C(10), C(12), C(13)]; 126.2 [C(7)], 105.8, 105.7, 104.3 [C(1)–C(6)]; and 21.1 [C_6H_4Me].

$[Cr(\eta-C_6H_5Me)(\eta-C_7H_6C_6H_4Me-4)][PF_6]$ 3a. A suspension of $[Cr(CO)_3(\eta-C_7H_6C_6H_4Me-4)][PF_6]$ (0.81 g, 1.74 mmol) in toluene (35 cm^3) was refluxed for 2 h to give a green precipitate which was separated from the mother liquors and then dried *in vacuo*. The product was dissolved in CH_2Cl_2 and the solution filtered then treated with diethyl ether to give complex **3a** as a pale green solid; yield 0.43 g (53%).

$[Mo(\eta-C_6H_3Me_3-1,3,5)(\eta-C_7H_7)][PF_6]$ 4a. A suspension of $[Mo(CO)_3(\eta-C_7H_7)][PF_6]$ (1.01 g, 2.43 mmol) in mesitylene (30 cm^3) was refluxed for 3 h to give a green precipitate which was separated from the mother liquors and then dried *in vacuo*. The precipitate was dissolved in CH_2Cl_2 (100 cm^3) and the solution filtered then reduced in volume and treated with diethyl ether to give complex **4a** as a green solid; yield 0.638 g (58%).

$[Mo(\eta-C_6H_3Bu^t_3-1,3,5)(\eta-C_7H_7)][PF_6]$ 5a. A solution of $[Mo(\eta-C_6H_5Me)(\eta-C_7H_7)][PF_6]$ (0.992 g, 2.34 mmol) in AnalaR acetone (40 cm^3) was treated with $HC{\equiv}CBu^t$ (1.012 g, 12.34 mmol) and the reaction mixture then refluxed with stirring for 6 h to give a white precipitate in a green solution. The reaction mixture was filtered to remove $HC{\equiv}CBu^t$ polymer and the resulting green solution evaporated to dryness. The residue was recrystallised from CH_2Cl_2–diethyl ether and subsequently acetone–diethyl ether to give complex **5a** as a green solid; yield 0.061 g (5%).

$[Cr(\eta-C_6H_4Me_2-1,4)(\eta-C_7H_7)][PF_6]_2$ 1b. A pale green solution of $[Cr(\eta-C_6H_4Me_2-1,4)(\eta-C_7H_7)][PF_6]$ (0.026 g, 0.066 mmol) in CH_2Cl_2 (5 cm^3) was treated with $[FeCp_2][PF_6]$ (0.022 g, 0.066 mmol) and then stirred for 1.5 h resulting in precipitation of the crude product which was then separated from the mother liquors. Subsequent recrystallisation from acetone–diethyl ether gave complex **1b** as a buff coloured solid; yield 0.020 g (56%). The mesitylene derivative $[Cr(\eta-C_6H_3Me_3-1,3,5)(\eta-C_7H_7)][PF_6]_2$ **2b** was similarly prepared in 81% yield from $[Cr(\eta-C_6H_3Me_3-1,3,5)(\eta-C_7H_7)][PF_6]$ (0.102 g, 0.25 mmol) and $[FeCp_2][PF_6]$ (0.083 g, 0.25 mmol).

$[Cr(\eta-C_6H_5Me)(\eta-C_7H_6C_6H_4Me-4)][PF_6]_2$ 3b. Treatment of a stirred, green solution of $[Cr(\eta-C_6H_5Me)(\eta-C_7H_6C_6H_4Me-4)][PF_6]$ (0.05 g, 0.11 mmol) with $[FeCp_2][PF_6]$ (0.04 g, 0.12 mmol) in CH_2Cl_2 (10 cm^3) led to gradual formation of a yellow-brown precipitate. After 2 h the crude product was

Table 8 Crystal and data collection parameters for complexes **3a** and **3b**

	3a	**3b**
Formula	$C_{21}H_{21}CrF_6P$	$C_{21}H_{21}CrF_{12}P_2$
Mass	470.36	615.32
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	$P2_1/n$ (no. 14)
T/°C	22	23
a/Å	13.019(3)	12.747(5)
b/Å	27.297(8)	12.697(4)
c/Å	11.095(3)	14.317(5)
β/°		93.22(3)
V/Å^3	3943(1)	2313(1)
Z	8	4
μ(Mo-Kα)/cm^{-1}	7.21	7.39
Total data	3893	4509
'Observed' data [$I > 3\sigma(I)$], N_o	2173	3115
R	0.062	0.045
R_w	0.045	0.043

separated from the mother liquors then washed with toluene, diethyl ether and dried *in vacuo*. Subsequent recrystallisation from acetone–diethyl ether gave complex **3b** as a bright orange-yellow solid; yield 0.018 g (26%).

[Mo(η-$C_6H_3Bu^t_3$-1,3,5)(η-C_7H_7)][PF_6]$_2$ 5b. Treatment of a stirred, green-yellow solution of [Mo(η-$C_6H_3Bu^t_3$-1,3,5)(η-C_7H_7)][PF_6] (0.024 g, 0.042 mmol) with [FeCp{η-C_5H_4-(C(O)Me)}][PF_6] (0.016 g, 0.043 mmol) in AnalaR acetone (5 cm^3) resulted in a rapid change to orange. After 10 min the volume was reduced and diethyl ether added to give the product as a white solid which was washed with diethyl ether and dried; yield 0.021 g (69%).

Crystallography

The majority of the details of the structure analyses carried out on complexes **3a** and **3b** are given in Table 8. Both structures were solved on a Rigaku AFC5R diffractometer which utilised a Mo-Kα source ($\lambda = 0.71069$ Å). Neutral atom scattering factors were taken from ref. 33 and all calculations performed using the TEXSAN crystallographic software package.[34]

[Cr(η-C_6H_5Me)(η-$C_7H_6C_6H_4$Me-4)][PF_6] 3a. Green tabular crystals were grown by vapour diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. The intensities of three representative reflections were measured after every 150. Over the course of data collection the standards increased by 0.1% and a linear correction factor was applied to account for this. An empirical absorption correction based on azimuthal scans was applied and the data were corrected for Lorentz and polarisation effects. The structure was solved by and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included but not refined.

[Cr(η-C_6H_5Me)(η-$C_7H_6C_6H_4$Me-4)][PF_6]$_2$ 3b. Orange, prismatic crystals were grown by vapour diffusion of diethyl ether into an acetonitrile solution of the complex. The intensities of three representative reflections were measured after every 150. Over the course of data collection the standards increased by 0.9% and a linear correction factor was applied to account for this. Subsequent data treatment was as for **3a**. One of the PF_6 counter ions has fluorines disordered over 2 sets of positions with 0.6 : 0.4 occupancies [F(7)–F(12)] : [F(13)–F(18)].

CCDC reference number 186/2259.

See http://www.rsc.org/suppdata/dt/b0/b007830l/ for crystallographic files in .cif format.

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