Redox Reactions of Metallocenes with Tungsten and Molybdenum Hexafluoride

Klaus H. Moock*,[a] **and Michael H. Rock**[b]
[a] *Department of Chemistry, University of Lethbridge, Lethbridge, Alberta T1K 3M4, Canada*
[b] *Department of Chemistry, Keele University, Keele ST5 5BG, UK*

Tungsten and molybdenum hexafluoride react in acetonitrile with a series of metallocenes to give coloured salts. Oxidation of iodo-, bromo- and 1,1′-dibromo-ferrocene with both hexafluorides resulted in the formation of 1 : 1 halogenoferrocenium hexafluoro-tungstate(V) and -molybdate(V) compounds, $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Br)][MF_6]$, $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4I)][MF_6]$ and $[Fe(\eta\text{-}C_5H_4Br)_2][MF_6]$ (M = W or Mo). Cobaltocene reduced MoF_6 in a two-electron step to give a 2 : 1 adduct, $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[MoF_6]$, while with WF_6 the 1 : 1 product $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN][WF_6]$ was formed. The redox reactions involving metallocenes and the hexafluorides are in agreement with the thermodynamic stabilities of their oxidation states found by electrochemical methods. The electrode potentials obtained for the metallocene hexafluorometalates consist of the two one-electron reduction steps for $[MF_6]^{0/-/2-}$ (M = W or Mo) and the reversible one-electron steps for the metallocene–metallocenium couples.

Quantitative knowledge of the relative stabilities of various oxidation states of $[WF_6]^{q-}$ and $[MoF_6]^{q-}$ ($q = 0$, 1 or 2) in acetonitrile has been obtained by detailed electrochemical studies.[1] It has been found that WF_6 is a weaker oxidizing agent than MoF_6, but the anions $[WF_6]^-$ and $[MoF_6]^-$ also differ in their redox strength. While the monoanions $[MoF_6]^-$ and $[WF_6]^-$ are known to exist for a wide range of metal and non-metal cations,[2] only the dianion of molybdenum, $[MoF_6]^{2-}$, is well established.[3] In a recent theoretical study the instability of $[WF_6]^{2-}$ was discussed.[4] A vast number of metallocenes, such as substituted ferrocenes and cobaltocene, are stable in at least two different oxidation states[5] and should undergo redox reactions with WF_6 and MoF_6. Recently we were successful in the synthesis of a novel class of salts by treating ferrocene with MF_6 to form $[Fe(\eta\text{-}C_5H_5)_2][MF_6]$ (M = W, Mo or U).[6] This paper describes the extension of this class of compounds by the use of substituted ferrocenes and cobaltocene, employing investigative electrochemistry as an important analytical tool.

Results and Discussion

Reaction of Hexafluorides with Substituted Ferrocenes.—The addition of a slight excess of WF_6 or MoF_6 to a frozen solution of substituted ferrocenes $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4X)]$ (X = Br or I) or $[Fe(\eta\text{-}C_5H_4Br)_2]$ in MeCN results, upon subsequent warming to room temperature, in the immediate formation of dark brown solutions. After the removal of all of the volatile material at ambient temperature dark brown and black microcrystalline solids are isolated. They have been identified as 1 : 1 compounds of iodo-, bromo- and 1,1′-dibromo-ferrocenium hexafluoro-tungstate(v) and -molybdate(v) [equations (1) and (2)]. The air- and moisture-sensitive compounds can be stored in sealed ampoules at room temperature.

$$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4X)] + MF_6 \xrightarrow{MeCN} [Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4X)][MF_6] \quad (1)$$

$$[Fe(\eta\text{-}C_5H_4Br)_2] + MF_6 \xrightarrow{MeCN} [Fe(\eta\text{-}C_5H_4Br)_2][MF_6] \quad (2)$$

Reaction of Hexafluorides with Cobaltocene.—The reaction of $[Co(\eta\text{-}C_5H_5)_2]$ with WF_6 or MoF_6 in MeCN results in a change of colour from intensely dark brown through red to dark yellow, as the mixture warms slowly from 77 K to room temperature. The reaction with an excess of WF_6 leads to a 1 : 1 salt, cobaltocenium hexafluorotungstate(v)–acetonitrile(1/2), $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN][WF_6]$ [equation (3)]. With an excess of MoF_6 a 2 : 1 salt, dicobaltocenium hexafluoromolybdate(IV)–acetonitrile (1/4), $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[MoF_6]$, forms [equation (4)]. Both are involatile solids and are air- and moisture-sensitive. They decompose even *in vacuo* at room temperature, but can be stored for several weeks in sealed ampoules at 233 K. Prolonged pumping leads to loss of MeCN and eventual decomposition.

$$[Co(\eta\text{-}C_5H_5)_2] + WF_6 \xrightarrow{MeCN} [Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN][WF_6] \quad (3)$$

$$2[Co(\eta\text{-}C_5H_5)_2] + MoF_6 \xrightarrow{MeCN} [Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[MoF_6] \quad (4)$$

Spectroscopic Characterization.—The infrared spectra of the solid substituted-ferrocene salts are consistent with the presence of halogenoferrocenium cations and octahedral $[MF_6]^-$. The characteristic ν_3 bands of $[WF_6]^-$ and $[MoF_6]^-$ are observed at 595, 602, 604 and 612, 620 cm^{-1} respectively. The band positions in the substituted ferrocene/ferrocenium moieties are little influenced by the oxidation state of the iron.[7] Band assignments are made by comparison with the IR spectra of bromo-,[8] 1,1′-dibromo-ferrocene,[9] the ferrocenium cation[6,10] and various salts of hexafluoro-tungstate(v)[2e,2g,6] and -molybdate(v)[2e,2h,11] previously reported. The IR spectra of bromo- and iodo-ferrocene were also recorded and are given in the Experimental section. From these spectra there is no evidence for associated MeCN in the substituted ferrocenium compounds.

The IR spectrum of $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN][WF_6]$ (Table 1) contains bands of the cobaltocenium cation[7,12] and a band at 601 cm^{-1} assigned to ν_3 of $[WF_6]^-$.[2e,2g,6] For $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[MoF_6]$ the spectrum shows bands for

Table 1 IR spectra (cm^{-1}) of cobaltocenium hexafluorometalates*

$[Co(\eta-C_5H_5)_2\cdot 2MeCN]_2[MoF_6]$	$[Co(\eta-C_5H_5)\cdot 2MeCN][WF_6]$	Assignment
3100s	3095m	CH str. (cp)
2312s	2310s	CH_3 def. + CC str.
2298m	2295m	(A_1), CN str. (MeCN)
2248w	2250w	2 × CC str. (MeCN) +
2050w	2045vw	CCN def. (A_1, MeCN)
1610m	1610m	
1420vs	1414s	Antisym. CC str. (cp)
1354m	1356m	CH_3 def. (a_1, MeCN)
1165m	1167w	CH def. (cp)
1115m	1118w	CH def. (cp)
1061m	1060m	
1028m	1030m	CH_3 rock (E, MeCN)
1010s	1015s	CH def ($\parallel$) (cp)
975m (br)	985m (br)	
930m	931m	CC str. (A_1, MeCN)
855w	853w	CH def. ($\perp$) (cp)
807w	810vw	CH def. ($\perp$) (cp)
786m	790m	2 × CCN def. (MeCN)
660w	660w	
	601vs (br)	ν_3 $[WF_6]^-$ (F_{1u})
590m	590m	
545s (br)		ν_3 $[MoF_6]^{2-}$ (F_{1u})
500m	503m	Asym. ring tilt
461s	459s	Asym. metal–ring str.
405m	406m	CCN def. (E, MeCN)

* At room temperature, Nujol mull between KSR-5 or CsI, v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder; cp = η-C_5H_5.

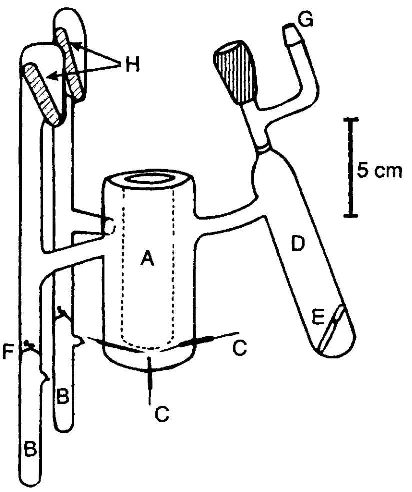

Fig. 1 Electrochemical cell comprising the main body (A) with cooling finger and platinum wire electrodes (C), sidearms (B) with the compound and electrolyte under break seal (F), and a rotaflo compartment (D) containing frangible ampoule (E) with the reference compound. There is a connection to vacuum line (G) and the break seals (F) are opened by poly(tetrafluoroethylene)-shielded metal bars (H)

the cobaltocenium cation[7,12] and strong band at 545 cm^{-1} assigned to ν_3 of $[MoF_6]^{2-}$ by analogy with the spectra of $Cs_2[MoF_6]$,[3b] and $[N_2H_4][MoF_6]$.[13] Band assignments of MeCN in both cobaltocenium salts, Table 1, are made by comparison with the vibrational spectra of metal cations and adducts containing associated MeCN.[14] Raman spectra of the metallocenium compounds could not be obtained due to decomposition of the samples by the laser beam even at 77 K.

Mass spectra for all six substituted ferrocenium salts show the ions of $[Fe(\eta-C_5H_5)(\eta-C_5H_4X)]^+$ (X = Br or I), $[Fe(\eta-C_5H_4Br)_2]^+$, $[WF_5]^+$ and $[MoF_5]^+$. This pattern of break-up has been observed previously in the study of ferrocenium hexafluorometalates(V).[6] The spectra for both cobaltocenium compounds show the $[Co(\eta-C_5H_5)_2]^+$ ion as the strongest signal and peaks for CH_3CN^+ and CH_2CN^+ were also observed. The $[WF_5]^+$ and the $[MoF_5]^+$ fragments give weak signals. Overall the mass spectra are consistent with the ionic formulation of the compounds.

Electrochemistry.—Voltammetric studies of all the hexafluorometalate salts in acetonitrile/NEt_4PF_6 solutions on a platinum three-electrode system were performed in an evacuable electrochemical cell, Fig. 1, as described in the Experimental section. The main advantage of this cell, which has been used in several studies of air- and moisture-sensitive compounds,[6,15] lies in the minimization of hydrolysis. The all-glass design, by avoiding the use of cone and socket joints,[16] the 'Swagelock' technique[17] for electrode fitting, or greaseless 'O'-ring connections[2a] for solvent manipulations, allows for vigorous flame drying of all parts. Solvents and gases are vacuum distilled into the cell and all solid materials can be added by using break-seal techniques.

The electrode potentials for accessible oxidations and reductions of the hexafluoro-tungstate and -molybdate salts are given in Table 2, together with the conditions chosen to achieve electrochemical reversibility or quasi-reversibility. The $E_{\frac{1}{2}}$ values in Table 2 were obtained from cyclic (c.v.) and alternating current (a.c.) voltammetry and were internally referenced to the ferrocene–ferrocenium couple of added ferrocene, reported *versus* the saturated calomel electrode (SCE). The criteria for assessing reversibility were the separation of the anodic (E_a) and cathodic (E_c) peaks of the c.v. and the width of the half height of the a.c. peak.

All electrode processes involving the redox couples of the hexafluorometalates, $[MF_6]$–$[MF_6]^-$ and $[MF_6]^-$–$[MF_6]^{2-}$ (M = W or Mo), were found to be quasi-reversible. For the oxidation process MF_6–$[MF_6]^-$ this can be explained in terms of the change of an involatile hexafluorometalate(V) salt to a volatile hexafluoride, while the reduction of $[MF_6]^-$ results in the relatively unstable $[MF_6]^{2-}$ anion.[4] Assignments of the couples MF_6–$[MF_6]^-$ and $[MF_6]^-$–$[MF_6]^{2-}$ were made by comparison with previous studies of ferrocenium,[6] alkali metal, silver and copper salts.[1,2a] Reversible $E_{\frac{1}{2}}$ potentials for the halogenoferrocenes and cobaltocene were measured in MeCN

Table 2 Electrochemical data for metallocenium hexafluorometalates[a]

	Hexafluorometalates				Metallocene [M′][b]	
	$[WF_6]^{0/-}$	$[WF_6]^{-/2-}$	$[MoF_6]^{0/-}$	$[MoF_6]^{-/2-}$	$[M']^{0/+}$	$[M']^{0/-}$
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Br)][MoF_6]$			+2.08	+0.04[d]	+0.68	
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Br)][WF_6]$	+1.07[c]	−0.91[f]			+0.68	
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4I)][MoF_6]$			+1.99[g]	+0.01[h]	+0.65	
$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4I)][WF_6]$	+1.08[e]	−0.93[f]			+0.64	
$[Fe(\eta\text{-}C_5H_4Br)_2][MoF_6]$			+2.04[c]	+0.07[d]	+0.62	
$[Fe(\eta\text{-}C_5H_4Br)_2][WF_6]$	+1.03[e]	−0.98[f]			+0.62	
$[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[MoF_6]$			+2.07[c]	+0.15[i]	−0.83	−1.8
$[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[WF_6]$	+1.08[j]	−0.9[k]			−0.8[l]	−1.8

[a] At a platinum electrode in MeCN, 0.1 mol dm^{-3} in NEt_4PF_6; half-wave potentials, $E_{\frac{1}{2}}$, are referenced to the SCE such that $E_{\frac{1}{2}} = +0.38$ V for $[Fe(\eta\text{-}C_5H_5)_2]^{+/0}$. [b] Reversible conditions also confirmed by a.c. voltammetry at scan rate $\nu = 10$ mV s^{-1}. [c] Separation of anodic (E_a) and cathodic (E_c) peak = 100 mV at $\nu = 100$ mV s^{-1} and 0 °C. [d] $E_a - E_c = 160$ mV at $\nu = 100$ mV s^{-1} and 0 °C. [e] $E_a - E_c = 150$ mV at $\nu = 200$ mV s^{-1} and 20 °C. [f] $E_a - E_c = 200$ mV at $\nu = 200$ mV s^{-1} and 20 °C. [g] $E_a - E_c = 130$ mV at $\nu = 200$ mV s^{-1} and −10 °C. [h] $E_a - E_c = 180$ mV at $\nu = 200$ mV s^{-1} and −10 °C. [i] $E_a - E_c = 200$ mV at $\nu = 100$ mV s^{-1} and 0 °C. [j] $E_a - E_c = 120$ mV at $\nu = 100$ mV s^{-1} and 0 °C. [k] Obscured by $[Co(\eta\text{-}C_5H_5)_2]^{0/+}$ couple. [l] Obscured by $[MoF_6]^{-/2-}$ couple.

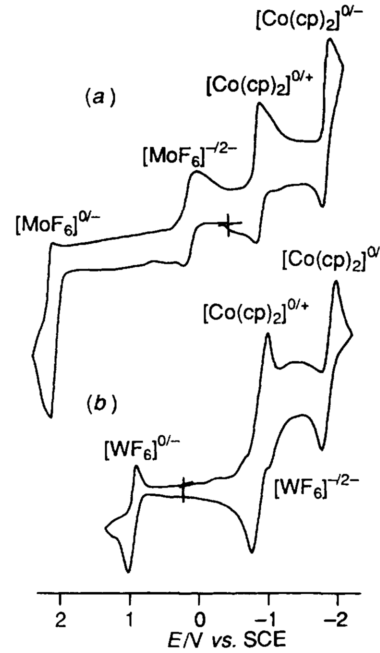

Fig. 2 Cyclic voltammograms for $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[MoF_6]$ (*a*) and $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN][WF_6]$ (*b*) in MeCN, 0.1 mol dm^{-3} in NEt_4PF_6 and *ca.* 5 × 10^{-4} mol dm^{-3} in sample, run at 100 mV s^{-1} and 0 °C; cp = $\eta\text{-}C_5H_5$

at +0.68 V for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Br)]^{0/+}$, at +0.65 V for $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4I)]^{0/+}$ and at +0.62 V for $[Fe(\eta\text{-}C_5H_4Br)_2]^{0/+}$. The two electrode processes for cobaltocene in MeCN are observed at −0.80 V for $[Co(\eta\text{-}C_5H_5)_2]^{0/+}$ and at −1.8 V for $[Co(\eta\text{-}C_5H_5)_2]^{0/-}$. The obtained electrode potentials of the metallocenium hexafluorometalates are analysed as a combination of the two one-electron steps for $[MF_6]^{0/-/2-}$ (M = W or Mo) and the reversible one-electron steps of the metallocenes. Fig. 2 shows the cyclic voltammograms of $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[MoF_6]$ and $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN][WF_6]$ in MeCN.

The fluorides WF_6 and MoF_6 are oxidizing agents of differing strength, MoF_6 being the stronger oxidant with a difference of *ca.* 1 V.[1] The electrode potentials of the halogenoferrocenes show that oxidation of the halogenoferrocenium compounds with WF_6 and MoF_6 proceeds according to equations (1) and (2). Further reduction of $[MoF_6]^-$ and $[WF_6]^-$ by the halogenoferrocenium ions is thermodynamically not feasible. However, the oxidation strength of $[MoF_6]^-$ (+0.1 V) is sufficient for the oxidation of cobaltocene leading to the 2:1 compound $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN]_2[MoF_6]$ [equation (4)]. The compound is stable in solution for several hours, then decomposition starts with the formation of $MoOF_4$, $E_{\frac{1}{2}} = +0.96$ V. The value of using $E_{\frac{1}{2}}$ potentials as thermodynamic parameters is also seen in the formation of $[Co(\eta\text{-}C_5H_5)_2{\cdot}2MeCN][WF_6]$; the oxidation strength of $[WF_6]^-$ (−0.9 V) is not sufficient to oxidize cobaltocene (−0.80 V) and the reaction therefore proceeds according to equation (3).

Experimental

Cyclic voltammetry (ν = 20–500 mV s^{-1}) and phase-sensitive a.c. experiments (ω = 350 Hz, ν = 10 mV s^{-1}) were carried out with a PAR 173 potentiostat, PAR 5208 lock-in analyser, 175 Universal Programmer and recorded on a Linseis LY 18100 X-Y-Y plotter. The electrolyte, NEt_4PF_6, was prepared by neutralizing 40% aqueous NEt_4OH with HPF_6 (pH-meter). The precipitate was filtered off, washed with distilled water, recrystallized twice from boiling ethanol and vacuum dried for 24 h at +80 °C. Ferrocene was sublimed prior to use.

Fig. 1 shows the all-Pyrex electrochemical cell. It consists of the main body (A) with the electrode arrangement and cooling finger, the two sidearms (B) with the storage compartment for electrolyte and compound and the Rotaflo limb (D) for the necessary vacuum manipulation and solvent transfer. The Rotaflo stopcock can be sealed off if required. The electrodes are all platinum wires. The auxiliary- and quasi-reference electrodes (diameter 0.4 mm) are vacuum sealed by spot welding to tungsten wire. This allows for similar expansion coefficients for the glass and the metals, since the platinum wire is thus not directly attached to the glass wall of the main body. The micro platinum working electrode (diameter 0.1 mm) is prepared by sawing through a platinum-glass capillary with a diamond saw.

The cell is set up for an experiment by glass-blowing the electrolyte and compound compartments onto the sidearms, followed by degassing the cell and flame drying. After the solvent is vacuum distilled into the Rotaflo compartment, the break seal of the electrolyte compartment is opened and the working potential range of the solvent/electrolyte system determined. Solute manipulation from one compartment to another is achieved by tipping the cell. The parts A, B and D are arranged with suitable angles to facilitate this operation. The compound compartment is opened and the solute tipped into the main body for the electrochemical study. If cooling is required this can be achieved by inserting a cooling system (*e.g.* methanol–solid CO_2 or liquid nitrogen) into the cooling finger. The reference compound is normally stored in a frangible ampoule (E) in the Rotaflo compartment and added to the solution at a later stage of the experiment. The ferrocene–

ferrocenium couple was determined in MeCN at +0.38 V *vs.* SCE.

Where necessary operations were carried out in a Pyrex vacuum line or an argon filled glove-box (Braun). Reaction vessels, fitted with Rotaflo stopcocks, had two limbs for distillation and decanting of solutions under vacuum. Glass systems were flamed out prior to use.

Bromoferrocene [ν_{max} 3094m, 1408s, 1198m, 1150s, 1124m, 1105s, 1017s, 1002s, 971m (br), 898w, 872vs, 835w, 817vs, 807m, 491vs cm^{-1}], iodoferrocene [ν_{max} 3096m, 1404m, 1195vs, 1145s, 1125m, 1105s, 1018s, 1009w, 1000m, 968s (br), 898w, 863vs, 833w, 819vs, 808m, 488vs cm^{-1}], and 1,1'-dibromoferrocene were prepared using a published procedure.[18] Cobaltocene was prepared by treating water-free $CoCl_2$ with NaC_5H_5 in tetrahydrofuran.[19] The volatile fluorides, WF_6 and MoF_6 (Ozark Mahoning) were purified by low-temperature trap-to-trap distillation over dried NaF. Acetonitrile (Merck, analytical grade) was purified and dried as previously described,[20] stored and degassed over 3 Å molecular sieves. IR spectra were obtained on a Perkin Elmer 883 spectrometer as Nujol mulls between CsI or KSR-5 plates. Raman spectra at low temperature were attempted on a Cary Instrument model 82 spectrometer. Mass spectra were recorded on a Varian MAT 711, 80 eV (*ca.* 1.28 × 10^{-17} J) spectrometer; observed intensities include all isotopes on the basis of ^{56}Fe. Microanalyses were by Beller, Göttingen, FRG.

Preparation of Substituted Ferrocenium Hexafluorometalates.—*Monoiodoferrocenium hexafluorotungstate*(V). A solution of iodoferrocene (6.2 mmol) in MeCN (15 cm^3) was prepared *in vacuo* and WF_6 (*ca.* 7 mmol) condensed onto the frozen solution. On warming to room temperature a dark brown colour was observed and the mixture stirred for about 30 min. Removal of all volatile material left a dark brown, almost black solid in quantitative yield (Found: C, 20.2; H, 1.6; F, 18.1; Fe, 9.3; I, 21.1; W, 29.2. $C_{10}H_9F_9FeIW$ requires C, 19.7; H, 1.5; F, 18.7; Fe, 9.2; I, 20.75; W, 30.15%); IR 3114s, 1410s, 1197vs, 1149m, 1125m, 1105w, 1018vs, 970s (br), 896m, 852s, 835w, 820w, 810w, 699s, 643s, 604vs (ν_3 of $[WF_6]^-$), 490m, 465m cm^{-1}; electron impact (EI) mass spectrum *m/z* 312 ($FeC_{10}H_9I$, 100), 279 (WF_5, 7), 260 (WF_4, 5), 247 (FeC_5H_4I, 16), 241 (WF_3, 1), 185 ($FeC_{10}H_9$, 4), 184 ($FeC_{10}H_8$, 9), 127 (I, 18) and 121 (FeC_5H_5, 31%).

Monoiodoferrocenium hexafluoromolybdate(V). This compound was prepared in a similar fashion while avoiding a large excess of $[MoF_6]$. The mixture was stirred for 10 min at room temperature and all volatile material was removed rapidly to give an intense dark, almost black solid in 95% yield (Found: C, 23.25; H, 1.9; F, 21.0; Fe, 10.6; I, 23.2; Mo, 18.0. $C_{10}H_9F_6FeIMo$ requires C, 23.0; H, 1.7; F, 21.8; Fe, 10.7; I, 24.4; Mo, 18.4%); IR 3100m, 1408s, 1197vs, 1150m, 1125m, 1100w, 1015m, 970s (br), 900m, 851s, 820w, 805vw, 620s (ν_3 of $[MoF_6]^-$), 520s (br), 465 m cm^{-1}; EI mass spectrum *m/z* 312 ($FeC_{10}H_9I$, 100), 247 (FeC_5H_4I, 9), 193 (MoF_5, 4), 185 ($FeC_{10}H_9$, 2), 184 ($FeC_{10}H_8$, 8), 127 (I, 13) and 121 (FeC_5H_5, 17%). Using a two- to three-fold excess of MoF_6 resulted in a partial oxidative break-up of the ferrocenium salt and in the formation of I^+-containing products.[2h]

Monobromoferrocenium hexafluorotungstate(V). The compound was prepared similarly as a brown solid in quantitative yield (Found: C, 21.2; H, 1.6; Br, 14.05; F, 20.4; Fe, 9.8; W, 32.4. $C_{10}H_9BrF_6FeW$ requires C, 21.3; H, 1.6; Br, 14.2; F, 20.25; Fe, 9.9; W, 32.7%); IR 3115m, 1410s, 1200m (br), 1150m, 1123m, 1104w, 1018vs, 969m (br), 897w, 871m, 853s, 835(sh), 820w, 810w, 699m, 641s, 620vs (br) (ν_3 of $[WF_6]^-$), 492m, 462m cm^{-1}; EI mass spectrum *m/z* 279 (WF_5, 5), 265 ($FeC_{10}H_9Br$, 100), 260 (WF_4, 2), 199 (FeC_5H_4Br, 10), 185 ($FeC_{10}H_9$, 6), 121 (FeC_5H_5, 14) and 79 (Br, 7%).

Monobromoferrocenium hexafluoromolybdate(V). The preparation of this compound was similar with the reaction mixture stirred for 5 min. Rapid removal of all volatiles gave a medium brown solid in quantitative yield (Found: C, 25.6; H, 2.0; Br, 16.4; F, 23.8; Fe, 11.9; Mo, 20.5. $C_{10}H_9BrF_6FeMo$ requires C, 25.3; H, 1.9; Br, 16.8; F, 24.0; Fe, 8.7; Mo, 20.2%); IR 3110m, 1411s, 1200m (br), 1153w, 1125m, 1098w, 1013vs, 970vs, 898w, 872m, 853m, 820vw, 807vw, 770w, 620vs (ν_3 of $[MoF_6]^-$), 525s (br) cm^{-1}; EI mass spectrum *m/z* 265 ($FeC_{10}H_9Br$, 100), 199 (FeC_5H_4Br, 15), 193 (MoF_5, 5), 185 ($FeC_{10}H_9$, 3), 121 (FeC_5H_5, 20) and 79 (Br, 10%). Using a large excess of MoF_6 did not lead to a break-up of the bromoferrocenium salt.

1,1'-Dibromoferrocenium hexafluorotungstate(V). The preparation of this compound was analogous. A microcrystalline dark brown solid was isolated in quantitative yield (Found: C, 18.5; H, 1.2; Br, 25.1; F, 17.9; Fe, 8.9; W, 29.0. $C_{10}H_8Br_2F_6FeW$ requires C, 18.7; H, 1.3; Br, 24.9; F, 17.8; Fe, 8.7; W, 28.65%); IR 3110m, 1414s, 1198m, 1158m, 1125w, 1105w, 1017vs, 971vs, 900(sh), 871s, 852s, 835w, 825w, 810vw, 769w, 699s, 641s, 595vs (br) (ν_3 of $[WF_6]^-$), 490m, 463m; EI mass spectrum *m/z* 343 ($FeC_{10}H_8Br_2$, 100), 279 (WF_5, 9), 264 ($FeC_{10}H_8Br$, 2), 260 (WF_4, 3), 241 (WF_3, 1), 199 (FeC_5H_4Br, 20) and 79 (Br, 12%).

1,1'-Dibromoferrocenium hexafluoromolybdate(V). The preparation of this compound was analogous, with the reaction mixture stirred for 10 min. A microcrystalline brown solid was obtained, in quantitative yield (Found: C, 21.5; H, 1.4; Br, 28.6; F, 20.7; Fe, 9.8; W, 32.9. $C_{10}H_8Br_2F_6FeW$ requires C, 21.7; H, 1.45; Br, 28.9; F, 20.6; Fe, 10.1; W, 33.2%); IR 3107m, 1414s, 1197s, 1150m, 1125s, 1100w, 1007s, 971s, 899m, 870m, 853m, 835(sh), 820w, 770w, 612vs (ν_3 of $[MoF_6]^-$), 535m (br) cm^{-1}; EI mass spectrum *m/z* 343 ($FeC_{10}H_8Br_2$, 100), 264 ($FeC_{10}H_8Br$, 1), 199 (FeC_5H_4Br, 24), 193 (MoF_5, 4) and 79 (Br, 7%).

Cobaltocenium hexafluorotungstate(V)*-acetonitrile* (1/2). Cobaltocene (5.4 mmol) was dissolved in MeCN (10 cm^3) and WF_6 (*ca.* 7 mmol) added to the frozen solution. After warming to room temperature the mixture was stirred for 15 min and a colour change from dark brown, through red, to orange was observed. A further amount of WF_6 (*ca.* 5 mmol) was condensed onto the mixture and after 20 min stirring at room temperature all volatiles were removed under vacuum. Pumping for 1 h left a dark yellow solid (Found: C, 29.3; H, 2.7; Co, 10.5; F, 20.3; N, 4.5; W, 32.7. $C_{14}H_{16}CoF_6N_2W$ requires C, 29.55; H, 2.8; Co, 10.35; F, 20.0; N, 4.9; W, 32.3%). EI mass spectrum: *m/z* 279 (WF_5, 7), 260 (WF_4, 1), 189 ($CoC_{10}H_{10}$, 100), 188 ($CoC_{10}H_9$, 3), 187 ($CoC_{10}H_8$, 6), 124 (CoC_5H_5, 35), 59 (Co, 8), 41 (CH_3CN, 2) and 40 (CH_2CN, 14%).

Dicobaltocenium hexafluoromolybdate(IV)*-acetonitrile* (1/4). Cobaltocene (9.7 mmol) was dissolved in MeCN (15 cm^3) and MoF_6 (*ca.* 10 mmol) condensed onto the frozen solution. On warming to room temperature a rapid colour change from dark brown, through red to dark yellow was observed and the mixture was stirred for 10 min. After removal of all volatile material *in vacuo* fresh MeCN (10 cm^3) and MoF_6 (*ca.* 5 mmol) were added to the reaction mixture and the pale yellow solution stirred for 15 min at room temperature. The solvent and excess of MoF_6 were removed *in vacuo* for 1 h and a yellow microcrystalline solid was isolated (Found: C, 44.3; H, 4.1; Co, 15.9; F, 15.3; Mo, 12.7; N, 7.3. $C_{28}H_{32}Co_2F_6MoN_4$ requires C, 44.7; H, 4.3; Co, 15.7; F, 15.15; Mo, 12.75; N, 7.45%). EI mass spectrum: *m/z* 193 (MoF_5, 2), 189 ($CoC_{10}H_{10}$, 100), 188 ($CoC_{10}H_9$, 2), 187 ($CoC_{10}H_8$, 12), 124 (CoC_5H_5, 40), 59 (Co, 10), 41 (CH_3CN, 3), 40 (CH_2CN, 19%). Pumping for longer than 2 h at room temperature led to a loss of MeCN and decomposition.

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