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Synthesis, structure and properties of new iron–molybdenum and –tungsten fulvalene-bridged heterobimetallic complexes

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Reaction of Li[$C_5H_4Fe(C_5H_5)$] with 2,3,4,5-tetramethylcyclopent-2-enone followed by acid work-up afforded the ferrocenyl-substituted cyclopentadiene [$Fe(C_5H_5)(C_5H_4C_5Me_4H)$] **1**. Lithiation of **1** with LiBu^n in hexane gave Li[$C_5Me_4C_5H_4Fe(C_5H_5)$]. Reactions of this salt or the previously described lithium 3,4-dimethylcyclopentadienide or indenide homologues, Li[$C_5H_2Me_2C_5H_4Fe(C_5H_5)$] or Li[$C_9H_6C_5H_4Fe(C_5H_5)$], with the allyl complexes [$MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)$] or [$WCl(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)$] led to the corresponding fulvalene (and related)-bridged, Fe–Mo or Fe–W heterobimetallic derivatives [$(C_5H_5)Fe(C_5H_4C_5Me_4)Mo(CO)_2(\eta\text{-}C_3H_5)$] **2**, [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)M(CO)_2(\eta\text{-}C_3H_5)$] (M = Mo **3** or W **4**) and [$(C_5H_5)Fe(C_5H_4C_9H_6)M(CO)_2(\eta\text{-}C_3H_5)$] (M = Mo **5** or W **6**). The crystal structure of **5** has been determined. Reaction of the cinnamyl complex [$MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_4Ph)$] with Li[$C_5H_2Me_2C_5H_4Fe(C_5H_5)$] or Li[$C_9H_6C_5H_4Fe(C_5H_5)$] yielded [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(CO)_2(\eta\text{-}C_3H_4Ph)$] **7** or [$(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2(\eta\text{-}C_3H_4Ph)$] **8** respectively, both of which exist as a mixture of isomers. Treatment of **7** with [$Cr(CO)_6$] in Bu$^n_2$O–tetrahydrofuran gave the Fe–Mo–Cr heterotrimetallic complex [$(C_5H_5)Fe(CH_4C_5H_2Me_2)(OC)_2Mo(\mu\text{-}\eta^3:\eta^6\text{-}C_3H_4Ph)Cr(CO)_3$] **9**. The new monometallic analogue [$Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}CMe_5)$] **10** has also been prepared. Cyclic voltammetric studies of some of the new heterobimetallic complexes and of **10**, [$Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)$] and [$Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_9H_7)$] are described.

The study of the chemistry and physical properties of mixed-valence compounds is an area of continuing interest which brings together synthetic inorganic, molecular and solid state, physical and theoretical chemistry. Many inorganic and organometallic examples of homobimetallic molecular species of the general type [$L_nM(\text{bridge})ML_n$] have been described since the complexes [$(NH_3)_5Ru^{II}(\mu\text{-pyz})Ru^{III}(NH_3)_5$]$^{5+}$ (pyz = pyrazine; the Creutz–Taube ion),[1] biferrocene,[2] and its mixed-valence iron(II,III) monocation, were reported shortly after the first modern theoretical treatments of mixed valence.[3–5] The study of mixed-valence homobimetallic compounds has allowed a significant advance in the understanding of electron-transfer and charge-delocalisation effects. A detailed picture continues to emerge of how site delocalisation is affected by the nature of the organic linkage connecting the metal centres, ancillary ligands and local environment effects such as ion pairing, solvation and lattice structures.[6–16] A concise review of mixed-valence binuclear complexes has appeared recently and the reader should consult this for further leading references.[17]

Attendant on the successful investigations of homobimetallic molecular systems are studies of electronic co-operativity in heterobimetallic complexes.[18–21] Such complexes offer a unique opportunity to explore the dependence of electronic co-operativity on redox asymmetry, and of chemical reactivity upon the presence of a second redox centre. Many heterobimetallic complexes contain a ferrocenyl unit as one of the metal centres because of its well understood redox behaviour and chemical robustness. For homobimetallic complexes a fulvalene [1-(cyclopenta-2,4-dienylidene)cyclopenta-2,4-diene, $C_{10}H_8$] or biphenyl μ-hydrocarbyl bridge (or derivatised versions thereof) commonly links the two metal centres. In contrast, however, the significant majority of ferrocene-containing *hetero*bimetallic complexes feature non-fulvalenyl bridges.[22–25] Furthermore, the few examples of fulvalene-bridged, ferrocene-containing heterobimetallics are mostly of the bis(metallocene) type, namely [$(C_5H_5)FeC_5H_4C_nR_mM(C_5R'_5)L_x$].[26–33] This historically reflects a paucity of useful synthetic routes to such complexes.[26,34–38] The preparation of fulvalene (and related)-bridged heterobimetallics of the type [$(C_5H_5)FeC_5H_4C_nR_mML_n$] where ML_n is not metallocene-like in nature is therefore an attractive goal because of the huge variety of possible metal–ligand combinations ML_n and the proven ability of the fulvalene linkage to enable communication between metal centres.

Salt-elimination reactions between alkali-metal cyclopentadienides and transition-metal halides are ubiquitous methods for the preparation of transition-metal cyclopentadienyl complexes. Therefore ferrocenyl-substituted alkali-metal cyclopentadienides should be useful precursors to fulvalene-bridged Fe–M (M = transition metal) heterobimetallic complexes. Indeed the anion [$Fe\{\eta\text{-}C_5H_4C(O)Me\}(\eta\text{-}C_5H_4C_5H_4)$]$^-$ {electrochemically generated from the complex [$Fe_2\{\eta\text{-}C_5H_4C(O)Me\}_2(\mu\text{-}C_{10}H_8)$]} may be sequentially treated with [$W(CO)_3(PrCN)_3$] and then MeI to yield the fulvalene-bridged heterobimetallic [$Fe\{\eta\text{-}C_5H_4C(O)Me\}(\mu\text{-}C_{10}H_8)W(CO)_3Me$] in 26% yield.[31] This route, however, is not easily scaled up and the $\mu\text{-}C_{10}H_8$-containing precursor itself requires a multistage synthesis. The simple ferrocenyl cyclopentadienide Li[$C_5H_4C_5H_4Fe(C_5H_5)$] has also been described in a three-stage linear synthesis starting from Li[$C_5H_4Fe(C_5H_5)$] and norbornen-2-one, and was characterised by its conversion into the known [$Co\{C_5H_4C_5H_4\text{-}Fe(C_5H_5)\}_2$][$PF_6$].[32] Unfortunately no yields for the lithium compound were reported and the neutral, conjugate acid [$C_5H_5C_5H_4Fe(C_5H_5)$] dimerises rapidly even at 0 °C. Recently, however, Scott and co-workers[26] and also Plenio[39] have described efficient syntheses of some ferrocenyl-cyclopentadiene and -indene derivatives of the type [$Fe(C_5H_5)(C_5H_4C_nR_m)$] (C_nR_m = 1- or 2-indenyl and $C_5H_3Me_2$-3,4) and [$Fe(\eta\text{-}C_5H_4C_nR_m)_2$] ($C_nR_m$ = 1-indenyl, C_5Me_4H or $C_5H_3Me_2$-3,4), the lithiated derivatives of which are precursors to ferrocenyl-substituted homo- and hetero-, bi- and tri-metallic metallocenes.

We anticipated that ferrocenyl-substituted cyclopentadienides of the type Li[$C_nR_mC_5H_4Fe(C_5H_5)$] would allow us access to a range of new, non-metallocene, heterobimetallic complexes. Here we describe the synthesis and properties of [$Fe(C_5H_5)(C_5H_4C_5Me_4H)$], Li[$C_5Me_4C_5H_4Fe(C_5H_5)$], and a number of new ferrocenyl-based, fulvalene-bridged heterobimetallic complexes containing the $M(CO)_2(\eta\text{-}C_3H_4R)$ fragment (M = Mo or W, R = H or Ph), together with their electrochemical behaviour and the new heterotrimetallic complex $[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)(OC)_2Mo(\mu\text{-}\eta^3:\eta^6\text{-}C_3H_4Ph)Cr(CO)_3]$. A preliminary account of these studies has been communicated.[40]

Results

Synthesis of Fe–Mo and Fe–W fulvalene (and related)-bridged heterobimetallic complexes

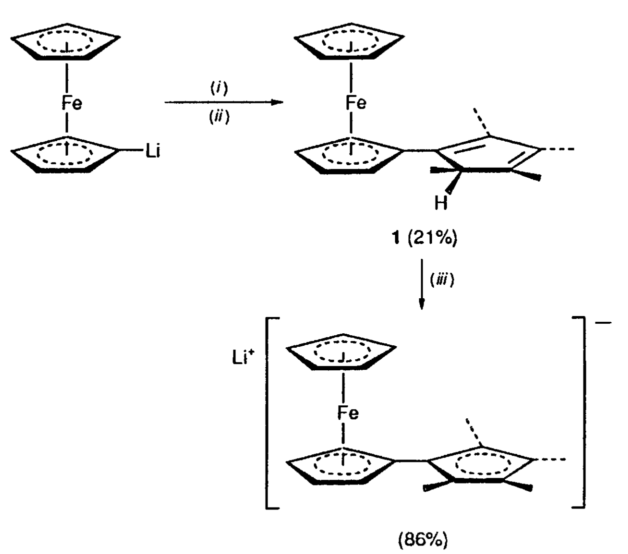
We elected to prepare fulvalene-bridged heterobimetallic complexes of the type $[(C_5H_5)Fe(C_5H_4C_nR_m)M(CO)_2(\eta\text{-}C_3H_4R')]$ (M = Mo or W, R′ = H or Ph) because: (*i*) monomeric complexes of the type $[M(CO)_2(\eta\text{-}C_3H_4R')(\eta\text{-}C_nR_m)]$ are readily prepared;[41,42] (*ii*) the redox potential of the non-Fe metal centre (M) in the complexes $[(C_5H_5)Fe(C_5H_4C_nR_m)M(CO)_2(\eta\text{-}C_3H_4R')]$ may, in principal, be tuned simply by selecting the appropriate C_nR_m fragment; (*iii*) the CO ligands act as convenient spectroscopic registers of the electron density at M; (*iv*) the η-allyl group may be further elaborated (*e.g.* R′ = Ph) with a view to the synthesis of trimetallic complexes, possibly by complexation of a third metal fragment to the pendant phenyl ring of an $\eta\text{-}C_3H_4Ph$ ligand. We also took the opportunity to extend the range of ferrocenyl cyclopentadienes $[Fe(C_5H_5)(C_5H_4C_5R_4H)]$ to include the fully ring-methylated analogue (*i.e.* R = Me).

Thus reaction of $Li[C_5H_4Fe(C_5H_5)]$[43] with 2,3,4,5-tetramethylcyclopent-2-enone[44] followed by standard work-up afforded $[Fe(C_5H_5)(C_5H_4C_5Me_4H)]$ **1** as a spectroscopically pure red oil in a modest yield of 21% which was characterised by ^1H NMR and mass spectrometry. Attempts further to purify **1** by column chromatography were unsuccessful and a satisfactory elemental analysis of the oil could not be obtained, possibly due to retention of small quantities of solvent. The ^1H NMR ($CDCl_3$) spectrum, together with selective homonuclear decoupling experiments, showed **1** to exist predominantly as the 1-ferrocenyl-2,3,4,5-tetramethylcyclopentadiene isomer as shown in Scheme 1.

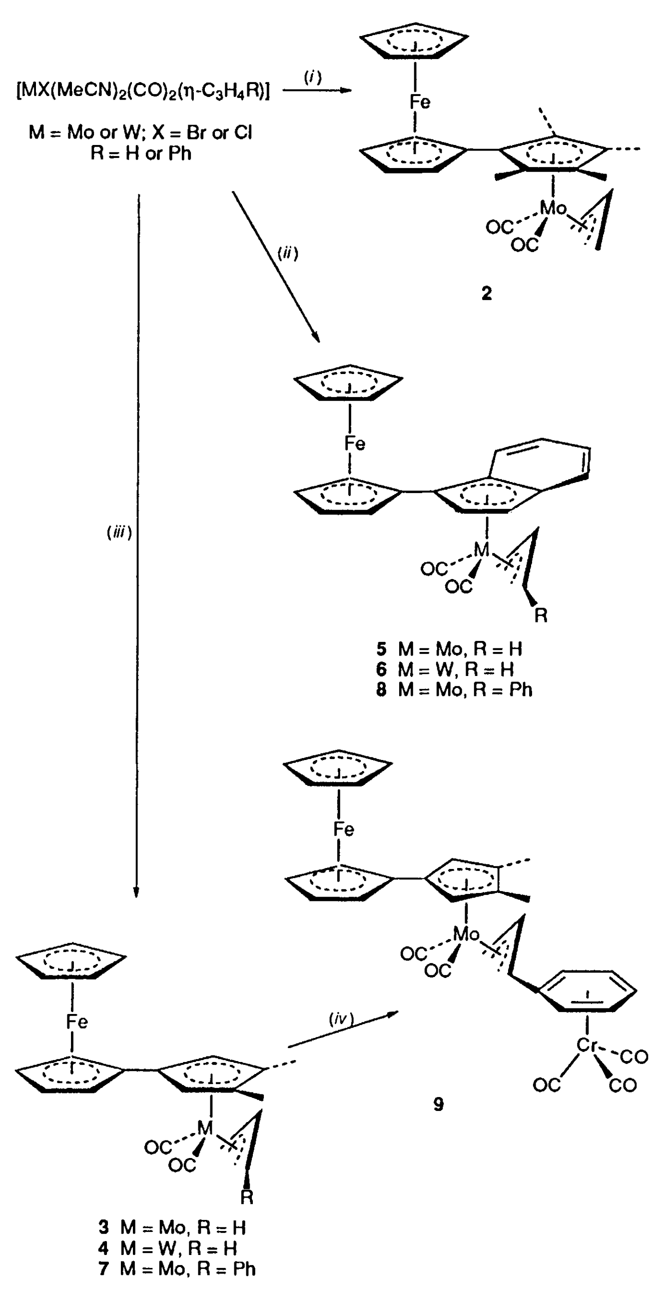
Subsequent treatment of a diethyl ether solution of compound **1** with $LiBu^n$ in hexane gave $Li[C_5Me_4C_5H_4Fe(C_5H_5)]$ as a highly air- and moisture-sensitive orange-brown solid in 86% yield based on **1**. Although the overall percentage yield from $Li[C_5H_4Fe(C_5H_5)]$ and tetramethylcyclopent-2-enone is modest (18%), the ready availability of ferrocene and the ketone nonetheless means that **1** and the lithium salt can quite reasonably be prepared in gram quantities.

The neutral complexes $[Fe(C_5H_5)(C_5H_4C_5H_3Me_2)]$ and $[Fe(C_5H_5)(C_5H_4C_9H_7)]$ were prepared according to the literature procedures[39] except that the final step of purification by column chromatography {to remove residual $[Fe(C_5H_5)_2]$} was not performed. We found that treatment of hexane solutions of the crude complexes with $LiBu^n$ in hexane readily gave $Li[C_5H_2Me_2C_5H_4Fe(C_5H_5)]$ and $Li[C_9H_6C_5H_4Fe(C_5H_5)]$ as orange-brown precipitates leaving $[Fe(C_5H_5)_2]$ (which is not lithiated under these conditions) in the solution phase.

Reaction of $Li[C_5Me_4C_5H_4Fe(C_5H_5)]$ with the molybdenum allyl precursor $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$[41] afforded the Fe–Mo heterobimetallic complex $[(C_5H_5)Fe(C_5H_4C_5Me_4)Mo(CO)_2(\eta\text{-}C_3H_5)]$ **2** which was purified by column chromatography on deactivated alumina and obtained in a poor yield of only 8% (Scheme 2). This poor yield prompted the investigation of an alternative synthetic approach that has



Scheme 1 (*i*) 2,3,4,5-Tetramethylcyclopent-2-enone; (*ii*) NH_4Cl, toluene-*p*-sulfonic acid; (*iii*) $LiBu^n$ hexanes



Scheme 2 Only one isomer is shown in each case (*i*) $Li[C_5Me_4C_5H_4Fe(C_5H_5)]$, thf, 15 h, 8%; (*ii*) $Li[C_9H_6C_5H_4Fe(C_5H_5)]$, thf, 15 h, 25 (**5**), 3 (**6**) 74% (**8**); (*iii*) $Li[C_5H_2Me_2C_5H_4Fe(C_5H_5)]$, thf, 15 h, 23 (**3**), 5 (**4**) 47% (**7**); (*iv*) $[Cr(CO)_6]$, $Bu^n{}_2O$–thf (10 : 1), 120 °C, 16 h, 16%

Table 1 Selected bond lengths (Å) and angles (°) for $[(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2(\eta\text{-}C_3H_5)]$ **5** with estimated standard deviations in parentheses*

Mo–C(1)	1.940(4)	C(3)–C(4)	1.366(6)
Mo–C(2)	1.929(3)	C(4)–C(5)	1.372(6)
Mo–C(3)	2.337(4)	C(14)–C(15)	1.482(5)
Mo–C(4)	2.196(4)	Mo–C_5	2.04
Mo–C(5)	2.329(4)	Fe–Cp1	1.64
C(1)–O(1)	1.153(4)	Fe–Cp2	1.64
C(2)–O(2)	1.154(4)		
C(1)–Mo–C(2)	78.5(1)	C(2)–Mo–C_5	121.9
Mo–C(1)–O(1)	175.8(3)	C(3)–C(4)–C(5)	123.3(4)
Mo–C(2)–O(2)	177.9(3)	Cp1–Fe–Cp2	179.2
C(1)–Mo–C_5	118.8		

* C_5, Cp1 and Cp2 refer to the computed ring centroids for the five-membered rings C(6)–C(8), C(13), C(14); C(15)–C(19) and C(20)–C(24) respectively.

been used in related systems.[45] Thus $Li[C_5Me_4C_5H_4Fe(C_5H_5)]$ and $[Mo(CO)_6]$ were heated together in diglyme (2,5,8-trioxanonane) at 140–150 °C until evolution of CO ceased. To the red mixture was added first allyl chloride and then freshly sublimed trimethylamine *N*-oxide to eliminate CO_2 from the expected intermediate $[(C_5H_5)Fe(C_5H_4C_5Me_4)Mo(CO)_3(\eta^1\text{-}C_3H_5)]$ (not isolated). However, after column chromatography the compound **2** was again isolated in only 8% yield. Reaction of $Li[C_5Me_4C_5H_4Fe(C_5H_5)]$ with the tungsten allyl precursor $[WCl(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$[42] gave a colour change to red-brown but no Fe–W bimetallic product could be isolated.

The reaction of $Li[C_5H_2Me_2C_5H_4Fe(C_5H_5)]$ with the molybdenum or tungsten precursors $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ or $[WCl(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ yielded the corresponding Fe–Mo and Fe–W complexes $[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)M(CO)_2(\eta\text{-}C_3H_5)]$ (M = Mo **3** or W **4**) in 23 and 5% isolated yield respectively. Similarly, the reaction of $Li[C_9H_6C_5H_4Fe(C_5H_5)]$ with the molybdenum or tungsten halide allyl precursors gave the analogous ferrocenyl-substituted indenyl complexes $[(C_5H_5)Fe(C_5H_4C_9H_6)M(CO)_2(\eta\text{-}C_3H_5)]$ (M = Mo **5** or W **6**) in 25 and 3% isolated yield (Scheme 2).

The four complexes **2**–**6** were characterised by elemental analysis, mass, IR (see below) and ^1H and ^{13}C [CPD (composite pulse proton decoupled), DEPT (distortionless enhancement by polarisation transfer) and two-dimensional] NMR spectroscopy. The NMR spectra showed the presence of two isomers (*exo*- and *endo*-allyl ligand orientations; ratio of between 6:1 and 4:1 respectively). It is assumed that the major species for all these complexes is the *exo* isomer (as illustrated in Scheme 2) as observed for most previously described monometallic complexes $[M(CO)_2(\eta\text{-}C_3R_5)(ring)]$ (M = Mo or W; ring = indenyl or cyclopentadienyl; R = alkyl or aryl).[46–49] The high-field shift of the allyl ligand methine resonance for $[(C_5H_5)Fe(C_5H_4C_9H_6)M(CO)_2(\eta\text{-}C_3H_5)]$ **5** and **6** is also consistent with the presence of *exo* isomers.[46,47]

Good-quality crystals of complex **5** were obtained by careful crystallisation from hexane and its structure was determined (Fig. 1). Important bond lengths and angles are given in Table 1. Details of the structure determination have appeared elsewhere.[40] Very weakly diffracting crystals of **2** gave a poor-quality data set that did, nevertheless, confirm the connectivity and *exo* orientation of the $\eta\text{-}C_3H_5$ ligand shown in Scheme 2.[50]

The solid-state molecular structure of complex **5** is consistent with the solution NMR data and reveals mutually *trans* $(C_5H_5)Fe$ and $Mo(CO)_2(\eta\text{-}C_3H_5)$ moieties linked by a $C_5H_4C_9H_6$ bridge. The allyl ligand has the anticipated *exo* configuration and the $C_5H_4C_9H_6$ bridging ligand is approximately planar with the angle between the normals to the computed C_5H_4 and C_9H_6 best-fit least-squares planes being approximately 3°. All other angles and distances about the Mo and Fe are in the ranges expected.[48,51,52] The six-membered ring of the C_9H_6 fragment lies above the allyl group which is in good agreement with the results obtained from semiquantitative models for $[Mo(CO)_2(\eta\text{-}C_3H_5)(C_9H_7)]$.[47] The bond length between the carbon atoms linking the C_5H_4 and C_9H_6 rings [C(14)–C(15) 1.482(5) Å] is comparable to the inter-ring C-C distances found for biferrocene (1.48 Å)[53] and $[Fe_2(C_{10}H_8)_2]$ [1.476(9) Å][54] and hence is consistent with a degree of double-bond character for this linkage. Since both biferrocene and $[Fe_2(C_{10}H_8)_2]$ show, to some extent, electronic co-operativity between the iron centres mediated through the planar fulvalene bridge there is the possibility of electronic communication between the Fe and Mo in **5** and its homologues.

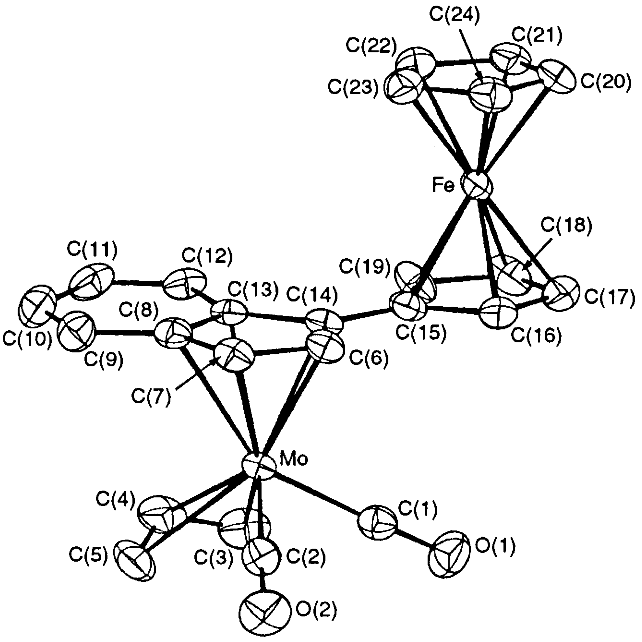


Fig. 1 Thermal ellipsoid plot (30% probability) of $[(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2(\eta\text{-}C_3H_5)]$ **5**. Hydrogen atoms omitted for clarity

We were also interested to prepare $\eta\text{-}C_3H_4Ph$ (cinnamyl) analogues of these new heterobimetallic complexes with a view to elaborating further the pendant phenyl group. Since the Fe–W systems and the Fe–Mo complex **2** were formed in very low yield we restricted our further synthetic studies to Fe–Mo complexes and the C_9H_6- and $C_5H_2Me_2\text{-}C_5H_4Fe(C_5H_5)$ ligands. Cinnamyl analogues of **3** and **5** are readily prepared. Thus reaction of a thf solution of $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_4Ph)]$[55] with 1 equivalent of $Li[C_5H_2Me_2C_5H_4Fe(C_5H_5)]$ or $Li[C_9H_6C_5H_4Fe(C_5H_5)]$ afforded the new Fe–Mo cinnamyl complexes $[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(CO)_2(\eta\text{-}C_3H_4Ph)]$ **7** and $[(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2(\eta\text{-}C_3H_4Ph)]$ **8** in 47 and 74% yield respectively after rapid column chromatography on deactivated alumina (Scheme 2). Elemental analyses, EI mass, IR and NMR spectra confirmed the identity of the new complexes.

The ^1H NMR spectrum of complex **7** showed that it exists as a mixture of *exo* and *endo* isomers (*ca.* 3:1 ratio) in solution and confirmed that the phenyl group of the cinnamyl ligand is oriented *syn* to the allylic 2-methine proton as illustrated in Scheme 2. A detailed chemical shift assignment for the major isomer was made possible from the one- and two-dimensional and selective homonuclear decoupled ^1H and ^{13}C NMR spectra. The NMR spectra of **8** were more complicated and showed the presence of four isomers in the approximate ratio 4:3:2:2 as indicated by integration of the individual singlets arising from the C_5H_5 rings of four different ferrocenyl groups. Thus a full assignment of the NMR spectra was not possible but sets of resonances clearly attributable to Ph, ferrocenyl, C_9H_6 and C_3H_4 moieties were apparent. The existence of four isomers presumably arises because neither the $(C_5H_5)Fe\text{-}C_5H_4C_9H_6$ nor the $Mo(CO)_2(\eta\text{-}C_3H_4Ph)$ fragment contains a mirror plane and the cinnamyl ligand may adopt either an *endo* or *exo* configuration.

Both complexes **7** and **8** are potential precursors to heterotrimetallic complexes, but because of the large number of isomers found for **8** further studies were confined to the more symmetrical **7**. Heating a $Bu^n{}_2O$–thf (10:1) solution of **7** with $[Cr(CO)_6]$ for 16 h gave a dark green solution from which the Fe–Mo–Cr heterotrimetallic complex $[(C_5H_5)Fe(C_5H_4\text{-}C_5H_2Me_2)(OC)_2Mo(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4Ph)Cr(CO)_3]$ **9** was obtained as an orange powder in 16% yield. The FAB mass spectrum showed a parent molecular ion envelope centred around *m/z* 684 (^{56}Fe, ^{96}Mo, ^{52}Cr) with a nuclear isotope pattern comparable to that calculated. Elemental analysis and IR and NMR spectra also confirmed the identity of **9**.

Once again the NMR spectra were complicated by the presence of isomers. There were two distinct C_5H_5 resonances (for the ferrocenyl group) at δ 4.04 and 3.96 in the ratio 4:3 (presumably for *exo* and *endo* isomers) and a full assignment of the spectra was not possible due to multiple overlaps for the two isomers of this unsymmetrical complex. Importantly, however, the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra showed clearly the expected shift of the phenyl group resonances to higher field (as compared to those of the precursor **7**) consistent with co-ordination of the $Cr(CO)_3$ group.

Solution IR spectra of the new complexes

The ν(CO) values for a series of homologous transition-metal carbonyl complexes can give an indication of the relative electron density at the metal centre. Solution (CH_2Cl_2) IR spectra of the new complexes have been recorded. We shall discuss here the molybdenum congeners and consider only those absorptions attributable to ν(CO) vibrations. In order to compare CH_2Cl_2 solution ν(CO) data for our heterobimetallic complexes with those for model monometallic molybdenum complexes we prepared $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ and $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_9H_7)]$ according to the literature methods.[47] Surprisingly the pentamethylcyclopentadienyl homologue has not previously been described so we therefore prepared this compound for the purposes of comparison.

Treatment of $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ with $Li[C_5Me_5]$ as in Scheme 3 afforded $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5Me_5)]$ **10** in only 5% isolated yield. An improved yield was achieved by treating a diglyme solution of $Li[Mo(CO)_3(\eta\text{-}C_5Me_5)]$[56] first with allyl chloride and then with Me_3NO {to remove CO, as CO_2, from the presumed intermediate $[Mo(CO)_3(\eta^1\text{-}C_3H_5)(\eta\text{-}C_5Me_5)]$ which was not isolated}. Rapid column chromatography of the product mixture afforded **10** as a yellow solid in an improved yield of 25% (Scheme 4). The ^1H NMR spectrum in $CDCl_3$ showed a mixture of *exo* and *endo* isomers {ratio *ca.* 4:1, comparable to that found for $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ and $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_9H_7)]$ in the same solvent[47]}. The crystal structure of the congener $[W(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5Me_5)]$ showed the allyl group in the *exo* conformation.[51]

$$[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)] \xrightarrow{(i)} [Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5Me_5)]$$

10 (5%)

Scheme 3 (*i*) $Li[C_5Me_5]$, thf, room temperature (r.t.)

Table 2 summarises CH_2Cl_2 solution ν(CO) values for the monometallic complexes $[Mo(CO)_2(\eta\text{-}C_3H_5)(C_nR_m)]$ (C_nR_m = C_9H_7, C_5H_5 or C_5Me_5 **10**), the Fe–Mo bimetallic complexes **2**, **3**, **5**, **7** and **8**, and for the $Mo(CO)_2$ fragment in the Fe–Mo–Cr trimetallic complex **9**. In CH_2Cl_2 (and also MeCN) solution separate pairs of ν(CO) bands for the minor *endo* isomer were not resolved and identical ν(CO) values were obtained in the two solvents. Each of the complexes is expected to give two ν(CO) bands for the $Mo(CO)_2$ fragment, as is observed. Since we are interested in variations in electron density at the Mo in these complexes we should strictly compare their *average* ν(CO) frequencies since (for equivalent or near-equivalent *cis*-CO groups) the unweighted mean ν value is directly related to the CO bond force constant.[57,58]

The average ν(CO) value for the the monometallic complexes $[Mo(CO)_2(\eta\text{-}C_3H_5)(ring)]$ decreases in the order ring = $C_9H_7 > C_5H_5 > C_5Me_5$. The ν(CO) values listed in Table 2 for the C_9H_7 and C_5H_5 derivatives are slightly different to those reported previously for cyclohexane solutions.[47] The average ν(CO) value for the the Fe–Mo heterobimetallic complexes $[(C_5H_5)Fe(C_5H_4C_nR_m)Mo(CO)_2(\eta\text{-}C_3H_5)]$ decreases in the order C_nR_m = C_9H_6 (**5**) > $C_5H_2Me_2$ (**3**) > C_5Me_4 (**2**), and for the cinnamyl homologues $[(C_5H_5)Fe(C_5H_4C_nR_m)Mo(CO)_2(\eta\text{-}C_3H_4Ph)]$ the average ν(CO) for C_nR_m = C_9H_6 (**8**) is greater than for C_nR_m = $C_5H_2Me_2$ (**7**). The average ν(CO) values for **10** and **2** and those for $[Mo(CO)_2(C_3H_5)(\eta\text{-}C_9H_7)]$, **5** and **8** are probably identical within intrumental resolution (2 cm^{-1}). The average ν(CO) values for **3** and **7** are also probably the same within error.

Finally we note that the average ν(CO) value for complex **7** is 5 cm^{-1} lower than that for the $Mo(CO)_2$ fragment in the $Cr(CO)_3$-substituted derivative **9**. Bands attributable to ν(CO) modes for the $Cr(CO)_3$ fragment in **9** occur at 1964 and 1881 cm^{-1} and are assigned by comparison with literature values for monometallic η-arylchromium tricarbonyl complexes.[59,60]

Electrochemical studies of mono- and heterobi-metallic complexes

For homobimetallic complexes of the general type $[L_nM(bridge)ML_n]$ cyclic voltammetry (CV) and associated techniques can provide important information about any metal–metal co-operative effects.[17] We were interested to examine the electrochemical behaviour of the Fe–Mo heterobimetallic derivatives **2**, **3** and **5** and the model monometallic cyclopentadienyl and indenyl molybdenum complexes. The results of the cyclic voltammetric experiments are summarised in Table 2.

Cyclic voltammograms of $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_9H_7)]$, $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ and **10** were recorded in CH_2Cl_2 and MeCN solutions at 0 °C. The cyclopentadienyl complexes showed almost fully reversible oxidation waves in CH_2Cl_2. The oxidation of $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_9H_7)]$ was only partially chemically reversible in CH_2Cl_2 ($i_c/i_a \approx 0.5$ at scan rates of 500 mV s^{-1}) and was completely irreversible in MeCN showing a negligible cathodic current and a new irreversible reduction wave with $E_p{}^c = 0.24$ V. This new peak presumably represents an EC (electrochemical–chemical) product. Cyclic voltammograms of the cyclopentadienyl complexes $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ and **10** recorded in MeCN showed small additional irreversible cathodic waves at $E_p{}^c = 0.04$ and -0.27 V respectively. This is consistent with the formation of a small quantity of EC product, although i_a/i_c for the main redox process appeared to be the same as in CH_2Cl_2

$$[Mo(CO)_6] \xrightarrow{(i)} Li[Mo(CO)_3(\eta\text{-}C_5Me_5)] \xrightarrow{(ii)} [Mo(CO)_3(\eta^1\text{-}C_3H_5)(\eta\text{-}C_5Me_5)] \xrightarrow{(iii)} [Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5Me_5)]$$

(not isolated) (not isolated) **10**

{25% based on $[Mo(CO)_6]$}

Scheme 4 (*i*) $Li[C_5Me_5]$, diglyme, 140 °C; (*ii*) $ClCH_2CH{=}CH_2$, thf, r.t.; (*iii*) Me_3NO, thf, r.t.

Table 2 Selected infrared and electrochemical data

	IR data[a]/cm^{-1}			Cyclic voltammetric data[b]			
Compound	ν_{sym}	ν_{asym}	Average ν	$E_{\frac{1}{2}}$ (CH_2Cl_2)	i_c/i_a	$E_{\frac{1}{2}}$ (MeCN)	i_c/i_a
$[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_9H_7)]$	1945	1862	1903.5	0.79	≈0.50	0.82[c]	Irreversible
$[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$	1942	1855	1898.5	0.70	>0.90	0.67	>0.90
10 $[Mo(CO)_2(\eta\text{-}C_3H_5)(\eta\text{-}C_5Me_5)]$	1931	1845	1888	0.55	>0.90	0.53	>0.90
5 $[(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2(\eta\text{-}C_3H_5)]$	1944	1861	1902.5	0.51	>0.90	0.53	>0.90
				0.80	≈0.35	Further waves complex	
3 $[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(CO)_2\text{-}(\eta\text{-}C_3H_5)]$	1936	1851	1893.5	0.47	>0.90	0.47	>0.90
				0.65	*d*	Further waves complex	
2 $[(C_5H_5)Fe(C_5H_4C_5Me_4)Mo(CO)_2(\eta\text{-}C_3H_5)]$	1930	1846	1888	0.50	≈0.70	0.53[c]	Irreversible
				0.66	*d*	Further waves complex	
8 $[(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2(\eta\text{-}C_3H_4Ph)]$	1942	1862	1902				
7 $[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(CO)_2\text{-}(\eta\text{-}C_3H_4Ph)]$	1935	1854	1894.5				
9 $[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)(OC)_2Mo\text{-}(\mu\text{-}C_3H_4Ph)Cr(CO)_3]$	1939	1860	1899.5				

[a] Assigned to $\nu(CO)$ vibrations for the $Mo(CO)_2$ fragment and measured as CH_2Cl_2 solutions. All bands are strong. [b] Recorded with a scan rate of 500 mV s^{-1} at 0 °C for 0.001 mol dm^{-3} complex in CH_2Cl_2 or MeCN solution and 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate or tetraethylammonium tetrafluoroborate as supporting electrolyte respectively. Under our conditions we take the ferrocene–ferrocenium couple as $E_{\frac{1}{2}} = 0.47$ V in both CH_2Cl_2 and MeCN solution and the $E_{\frac{1}{2}}$ values (V) are quoted relative to this. The ΔE_p values for all waves are comparable to that of the added $[Fe(\eta\text{-}C_5Me_5)_2]$ internal standard. [c] Irreversible wave; this value corresponds to E_p^a. [d] i_c/i_a cannot be reliably estimated for the second redox process due to the overlapping nature of the cathodic waves.

solution. Clearly even these cyclopentadienyl complexes exhibit some degree of chemical irreversibility on the CV time-scale.

In CH_2Cl_2 ΔE_p for the three monometallic complexes was comparable to that of the $[Fe(C_5Me_5)_2]$ internal standard; in addition, i_a for the molybdenum complexes corresponded to that of the standard (1 equivalent added). We therefore propose that all three monometallic complexes undergo a one-electron oxidation process. In CH_2Cl_2 the oxidation potentials ($E_{\frac{1}{2}}$) increase in the order: C_5Me_5 (0.55) < C_5H_5 (0.70) < C_9H_7 (0.79 V), consistent with ideas about the electron-donating ability of the three ligands and correlating with the average $\nu(CO)$ values listed in Table 2. In all these studies we take the ferrocene–ferrocenium couple as 0.47 V.

Table 2 summarises cyclic voltammetric data for the heterobimetallic complexes **2**, **3** and **5**. In CH_2Cl_2 solution all three show two successive oxidation waves of equal anodic peak height. For **2** the first wave ($E_{\frac{1}{2}} = 0.50$ V) is partially chemically reversible with $i_a/i_c \approx 0.70$ with an associated irreversible back reduction wave with $E_p^c = 0.04$ V. The second wave has $E_{\frac{1}{2}} =$ 0.66 V but we cannot estimate its degree of chemical reversibility due to overlap of the two cathodic peaks. For both **3** and **5** the first oxidation is apparently chemically reversible ($i_a/i_c > 0.90$) on the CV time-scale with $E_{\frac{1}{2}} = 0.47$ and 0.51 V respectively; however, the second wave for **5** is substantially more irreversible with $i_a/i_c = 0.35$ and $E_{\frac{1}{2}} = 0.80$ V. For **3** we cannot reliably estimate i_c/i_a for the second oxidation due to overlap of the two cathodic peaks. However, an irreversible back reduction with $E_p^c = 0.01$ V was associated with the second oxidation wave of **3** and was absent in cyclic voltammograms where the scan was stopped before the second wave E_p^a was reached. The irreversible back reductions associated with the second oxidation wave for **5** overlapped with the cathodic part of the first wave and could not be made out clearly. It is apparent that the first-wave oxidation process for **2** is only partly chemically reversible in CH_2Cl_2, whereas for **3** and **5** it appears that it is the second wave that is only partly chemically reversible while the first wave is fully chemically reversible.

Cyclic voltammograms for complexes **2**, **3** and **5** were also recorded in MeCN solution. The traces were considerably more complicated suggesting solvent participation coupling with the oxidation processes. For **2** the first wave was chemically completely irreversible with two associated irreversible cathodic reductions at $E_p^c = 0.01$ and -0.11 V. For **3** and **5** the first wave in MeCN appeared chemically reversible on the CV time-scale ($i_a/i_c > 0.90$) with $E_{\frac{1}{2}} = 0.47$ and 0.53 V respectively. However, the subsequent oxidation processes following the first waves for **3** and **5** were very complex and several anodic maxima could be distinguished. The electrochemical behaviour of **2**, **3** and **5** in MeCN was therefore not investigated further.

Discussion

Salt elimination routes are well established methods for the synthesis of cyclopentadienyl and related complexes.[61] Our use of the reagents $Li[C_nR_mC_5H_4Fe(C_5H_5)]$ is an extension of this general strategy and allows the synthesis of fulvalene-bridged, ferrocene-based heterobimetallics. The isolated yields of the ferrocenyl-substituted complexes are consistently lower than those for the monometallic analogues (*e.g.* yield of **2** is 8%, that of **10** is 25%). However, provided that the metal halide precursors are available in reasonable quantities this should not be prohibitive as the $Li[C_nR_mC_5H_4Fe(C_5H_5)]$ salts may be isolated in gram quantities. Note also that none of the yields we report here has been optimised. The yields of the molybdenum heterobimetallic complexes are higher than those of their tungsten congeners and an attempted synthesis of the tungsten analogue of $[(C_5H_5)Fe(C_5H_4C_5Me_4)Mo(CO)_2(\eta\text{-}C_3H_5)]$ **2** failed completely. Our strategy of using the η-cinnamyl Fe–Mo bimetallics **7** and **8** to prepare trimetallic complexes was successful and allows three different metals to be linked though π ligands.

The trends in average $\nu(CO)$ values (Table 2) for the monometallic complexes $[Mo(CO)_2(\eta\text{-}C_3H_5)(ring)]$ (ring = C_9H_7, C_5H_5 or C_5Me_5) follow that expected from these η-hydrocarbyl ligands.[62] The expected increase in electron density at the metal centre in these complexes is apparently reflected in the $E_{\frac{1}{2}}$ values measured in CH_2Cl_2 (Table 2) which show, as anticipated, that choice of the appropriate η-hydrocarbyl ligand allows the $E_{\frac{1}{2}}$ of the molybdenum centre to be brought closer to that of $[Fe(\eta\text{-}C_5H_5)_2]$ (0.47 V). Although the electrochemical oxidation of $[Mo(CO)_2$-

(η-C_3H_5)(η-C_9H_7)] is only partly chemically reversible (even on the CV time-scale) in CH_2Cl_2 ($i_c/i_a \approx 0.5$ at scan rates of 500 mV s^{-1}), its oxidation becomes completely irreversible in MeCN, presumably due to solvent attack on the cation generated. The cyclopentadienyl homologues do, however, show reversible electrochemical behaviour in MeCN and so the instability of the indenyl monocation may be a manifestation of the well known 'indenyl effect'[63] where 'ring slippage' giving a 15-electron cation featuring an η^3-indenyl ligand might be occurring. Such a 15-electron species would presumably react very rapidly with donor solvent molecules.

As noted above, the average ν(CO) for the ferrocenyl-indenyl and -cyclopentadienyl complexes decreases in the order [$(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2$($\eta$-$C_3H_5$)] **5** > [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(CO)_2$($\eta$-$C_3H_5$)] **3** > [$(C_5H_5)Fe(C_5H_4$-$C_5Me_4)$ $Mo(CO)_2$(η-C_3H_5)] **2**. We have thus achieved our aim of preparing fulvalene-bridged heterobimetallic systems where we can 'tune' the electron density at one of the metal centres. The ν(CO) values for **2** and **5** are so close to those of the model monometallic complexes [$Mo(CO)_2$(η-C_3H_5)(η-C_5Me_5)] **10** and [$Mo(CO)_2$(η-C_3H_5)(η-C_9H_7)] respectively that we conclude that there is negligible 'leakage' of electron density between the iron and molybdenum centres in these heterobimetallic complexes. The $E_{\frac{1}{2}}$ values for the individual centres in, for example, **2** and **5** are therefore probably similar to those in the respective monomeric model complexes {*i.e.* [Fe(η-$C_5H_5)_2$] and [$Mo(CO)_2$(η-C_3H_5)(η-C_5Me_5)] for **2**, and [Fe(η-$C_5H_5)_2$] and [$Mo(CO)_2$(η-C_3H_5)(η-C_9H_7)] for **5**}. This information helps us in our interpretation of the electrochemical characteristics of the heterobimetallic complexes for which, unlike *homo*bimetallic species, we cannot assume that the first oxidation has an equal probability of occurring at either metal centre.

On the basis of the $E_{\frac{1}{2}}$ values (see Table 2) for [$Mo(CO)_2$(η-C_3H_5)(ring)] (ring = C_9H_7, C_5H_5 or C_5Me_5) and [Fe(η-$C_5H_5)_2$] we might predict that the first oxidation in complexes **2**, **3** and **5** would occur at the Fe and the second at the Mo. For **3** and **5** this expectation is supported by the experimental observations, but for **2** it apparently is not. Let us consider the electrochemical behaviour of **5** first as it is the most straightforward.

The first oxidation ($E_{\frac{1}{2}} = 0.51$ V) for complex **5** is chemically reversible in CH_2Cl_2 whereas the second ($E_{\frac{1}{2}} = 0.80$ V) is only partially reversible. In MeCN solution the first wave is still reversible but further oxidation processes are complex and irreversible. Since the oxidation of the model complex [$Mo(CO)_2$(η-C_3H_5)(η-C_9H_7)] was only partly reversible in CH_2Cl_2 ($E_{\frac{1}{2}} = 0.79$ V) and completely irreversible in MeCN we assign the first oxidation in **5** to $Fe^{II} \longrightarrow Fe^{III}$ and the second to $Mo^{II} \longrightarrow Mo^{III}$. The Fe in **5** is thus slightly more difficult to oxidise than that in [Fe(η-$C_5H_5)_2$] ($E_{\frac{1}{2}} = 0.47$ V) whereas the Mo of the monocation $\mathbf{5}^+$ is oxidised at approximately the same potential as that of the model complex [$Mo(CO)_2$(η-C_3H_5)(η-C_9H_7)].

The first ($E_{\frac{1}{2}} = 0.47$ V) oxidation wave for complex **3** is chemically reversible in CH_2Cl_2, whereas the second ($E_{\frac{1}{2}} = 0.65$ V) is only partially reversible. In MeCN solution the first oxidation is chemically reversible whereas subsequent oxidation waves are complex and irreversible. These observations are again most consistent with the first oxidation being $Fe^{II} \longrightarrow Fe^{III}$ and the second $Mo^{II} \longrightarrow Mo^{III}$. In our opinion it is more likely that the molybdenum(III) will be the chemically least stable as we have already shown that some [$Mo(CO)_2$(η-C_3H_5)(ring)]$^+$ cations are unstable, especially in MeCN. Thus in **3** the Fe is oxidised at the same potential as that of [Fe(η-$C_5H_5)_2$]. We have not studied the electrochemistry of di- or tri-methylcyclopentadienyl model complexes of the type [$Mo(CO)_2$(η-C_3H_5)(η-$C_5H_{5-n}Me_n$)] (n = 2 or 3) but we can estimate that their $E_{\frac{1}{2}}$ values would lie around 0.61–0.64 V if the effect of ring methylation on redox potential is additive. Hence the second oxidation in **3** is approximately where we would place it based on model monometallic redox potentials.

The electrochemistry of [$(C_5H_5)Fe(C_5H_4C_5Me_4)Mo(CO)_2$($\eta$-$C_3H_5$)] **2** is more interesting. The potentials of the model monometallic complexes [Fe(η-$C_5H_5)_2$] and **10** are 0.47 and 0.55 V in CH_2Cl_2. The redox potentials of the individual iron and molybdenum centres in **2** may be slightly different from these values, but (based on the IR spectra of **2** and **10**) we would certainly not expect their order to be reversed. However, in **2** the first oxidation process ($E_{\frac{1}{2}} = 0.50$ V) is only partially chemically reversible. In MeCN solutions the first wave is completely irreversible (unlike the case of **3** and **5** above) and so we assign the *first* oxidation to $Mo^{II} \longrightarrow Mo^{III}$ and the *second* to $Fe^{II} \longrightarrow Fe^{III}$. Unfortunately, attempts to gain further information about the nature of the mono- and di-cations of **2**, **3** and **5** were unsuccessful because of the unstable nature of these species.

It is indeed possible that the first oxidation of complex **2** does, in fact, occur at Fe (giving an $Fe^{III}Mo^{II}$ species) but that there exists (as required by the Nernst equation) a significant equilibrium concentration of the corresponding $Fe^{II}Mo^{III}$ valence isomer, and that it is this valence isomer which then undergoes further coupled chemical processes giving rise to the observed electrochemical behaviour. This explanation would require rapid intramolecular electron transfer between Mo^{II} and Fe^{III} in the first-formed valence isomer of $\mathbf{2}^+$. A considerably more detailed study than is possible using our equipment would be required to address properly this question. Nonetheless, there remains the observation that the difference in $E_{\frac{1}{2}}$ for the two oxidation processes in **2** (160 mV) is twice as large as that anticipated from the $E_{\frac{1}{2}}$ values for model complexes. For **3** and **5** the difference is essentially the same as (or slightly less than) that expected from the superimposition of the electrochemical behaviour of monometallic model complexes.

For homobimetallic complexes of the type [L_nM(bridge)-ML_n] the separation of two redox waves is an indication of the extent of interaction between the two centres.[17] For **3** and **5** we suggest that there is no significant interaction between the Mo and Fe and their cations are best described as Class I in the Robin and Day scheme.[3] For **2** our results are a little more reminiscent of a Class II system in this scheme.

Based on the respective model complexes there is a larger anticipated difference between the *isolated* metal centres in **3** and **5** (*ca.* 320 and 170 mV) than in **2** (*ca.* 80 mV). The difference in electrochemical behaviour of **2** might therefore be attributable to a smaller degree of redox asymmetry than found in **3** and **5**. This is consistent with earlier studies of asymmetrically substituted, homobimetallic analogues of both biferrocene and the Creutz–Taube ion where it was found that the degree of interaction between the metal centres decreased with increased asymmetry.[18,19]

Conclusion

We have demonstrated a route to fulvalene-bridged, heterobimetallic complexes where the redox potential of the non-iron metal centre can be systematically tuned and have crystallographically characterised one of the derivatives. This route can be extended to heterotrimetallic complexes. Although our electrochemical studies were hampered by the instability of the cationic complexes, they appear to suggest that decreasing the difference in redox potential between two different metal centres might lead to a greater interaction between them in the electrochemically generated monocation.

Experimental

General methods and instrumentation

All manipulations were carried out under an atmosphere of dinitrogen using either standard Schlenk-line or dry-box techniques. Solvents were predried over molecular sieves and refluxed over sodium (di-n-butyl ether, diglyme, toluene), sodium–potassium alloy (1:3 w/w) [diethyl ether, pentane, light petroleum (b.p. 40–60 °C)] potassium (tetrahydrofuran, hexane), sodium–benzophenone (1,4-dioxane) or calcium hydride (dichloromethane, acetonitrile) under an atmosphere of dinitrogen and collected by distillation. The solvents $CDCl_3$ and CD_2Cl_2 were dried over calcium hydride, distilled under vacuum and stored under N_2 in Young's ampoules, C_3D_6O was used as received (Aldrich). The NMR samples were prepared in a dry-box in Teflon valve (Young's) tubes. Aluminium oxide (Aldrich Brockmann Grade 1, STD grade, *ca.* 150 mesh) for column chromatography was deactivated by addition of water (1:20 w/w). Column chromatography was performed under an atmosphere of dinitrogen and eluents were degassed prior to use. Electrolytes for cyclic voltammetry (tetrabutylammonium hexafluorophosphate and tetraethylammonium tetrafluoroborate) were recrystallised prior to use. Ferrocene and decamethylferrocene (Aldrich) were sublimed prior to use. Toluene-*p*-sulfonic acid (Aldrich) was used as received.

Proton and ^{13}C NMR spectra were recorded on either Brüker WM 250, JEOL EM 270 or Brüker AM 400 spectrometers. The spectra were referenced internally to the residual protiosolvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ 0). Infrared spectra were recorded on a Perkin-Elmer 983 or 2000 FTIR spectrometer as CH_2Cl_2 or MeCN solutions between sodium chloride windows, mass spectra on either a VG Micromass 7070E or an AEI MS902 spectrometer. Elemental analyses were carried out by the analysis department of this laboratory.

Cyclic voltammograms were recorded using an EG&G Princeton Applied Research model 362 scanning potentiostat and plotted on a J. J. Instruments LP2 X–Y recorder. The electrochemical cell comprised a Pyrex glass vessel with a nitrogen inlet, platinum-wire counter electrode, an outlet for nitrogen through a bubbler, a platinum-disc working electrode, and a silver-wire pseudo-reference electrode sealed in a capillary. The experiments were performed using dichloromethane or acetonitrile solutions with tetrabutylammonium hexafluorophosphate or tetraethylammonium tetrafluoroborate respectively as supporting electrolyte. The solutions were made up to 0.1 mol dm^{-3} electrolyte and 0.001 mol dm^{-3} of the organometallic species under investigation. Experiments were carried out at 0 °C and the solutions were purged with nitrogen for approximately 5 min before a voltammogram was recorded. Couples were referenced with respect to the standard calomel electrode using an internal decamethylferrocene–decamethylferrocenium couple ($E_{\frac{1}{2}}$ taken as −0.04 and −0.08 V for acetonitrile and dichloromethane solutions respectively) or ferrocene–ferrocenium couple ($E_{\frac{1}{2}}$ taken as 0.47 V).

Preparations

The compounds $Li[C_5H_4Fe(C_5H_5)]$, $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_4R)]$ (R = H or Ph), $[WCl(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ and 2,3,4,5-tetramethylcyclopent-2-enone were prepared according to literature procedures.[41–44,55] The neutral complexes $[Fe(C_5H_5)(C_5H_4C_5H_3Me_2)]$ and $[Fe(C_5H_5)(C_5H_4C_9H_7)]$ were prepared as previously described,[39] except that the final chromatographic step was not performed.

$[Fe(C_5H_5)(C_5H_4C_5Me_4H)]$ 1. The salt $Li[C_5H_4Fe(C_5H_5)]$ (3.67 g, 19.1 mmol) suspended in diethyl ether (50 cm^3) at 0 °C was slowly treated with 2,3,4,5-tetramethylcyclopent-2-enone (2.64 g, 19.1 mmol) in diethyl ether (3 cm^3). The resulting red-orange solution was left to stir (15 h) before being carefully hydrolysed with HCl (1.9 cm^3, 10 mol dm^{-3}). The mixture was stirred for 15 min then washed with water (3 × 50 cm^3). The ether layer was separated and stirred with $p\text{-}MeC_6H_4SO_3H$ for 2 h, then washed with saturated $NaHCO_3(aq)$ solution (3 × 25 cm^3) and water (3 × 25 cm^3). The organic phase was dried over $MgSO_4$, filtered and the volatiles were removed under reduced pressure leaving complex **1** as a red oil. Yield: 1.21 g, 21%. Attempts further to purify this spectroscopically (^1H NMR) pure oil by column chromatography were unsuccessful. ^1H NMR ($CDCl_3$, 250 MHz): δ 4.40–4.30 (2 H, overlapping 2 m, C_5H_4), 4.20–4.15 (2 H, overlapping 2 m, C_5H_4), 4.05 (5 H, s, C_5H_5), 2.85 [1 H, q of q (^3J = 7.6, ^4J = 1.3), $C_5Me_4\textit{H}$], 2.06 [3 H, d (^4J = 1.3), 4-$C_5\textit{Me}_4H$], 1.84 (3 H, s, 2- or 3-Me of C_5Me_4H), 1.81 (3 H, s, 3- or 2-Me of C_5Me_4H) and 1.08 [3 H, d (^3J = 7.6 Hz), 5-Me of C_5Me_4H]. EI mass spectrum (calculated for ^{56}Fe): *m/z* 306 (M^+), 121 [$(C_5H_5)Fe^+$] and 56 (Fe^+).

$Li[C_5Me_4C_5H_4Fe(C_5H_5)]$. A solution of complex **1** (1.21 g, 3.95 mmol) in diethyl ether (20 cm^3) at 0 °C was treated with $LiBu^n$ in hexane (2.7 cm^3 of a 1.67 mol dm^{-3} solution) and allowed to stir (15 h). The yellow-brown precipitate was filtered off, washed with small aliquots of hexane and dried *in vacuo.* This powder was not characterised further but was shown by subsequent reactions to be the required salt. Yield: 1.06 g, 86%. The compounds $[Fe(C_5H_5)(C_5H_4C_5H_3Me_2)]$ and $[Fe(C_5H_5)(C_5H_4C_9H_7)]$ were lithiated in the same manner.

$[(C_5H_5)Fe(C_5H_4C_5Me_4)Mo(CO)_2(\eta\text{-}C_3H_5)]$ 2. To a stirring solution of $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ (1.14 g, 3.2 mmol) in thf (25 cm^3) was added slowly a solution of $Li[C_5Me_4C_5H_4Fe(C_5H_5)]$ (1.0 g, 3.2 mmol) in thf (25 cm^3) and the reaction mixture was stirred for 15 h. The volatiles were removed under reduced pressure and the orange solid was rapidly chromatographed on deactivated alumina with hexane eluent to yield complex **2** as an orange powder. Yield: 0.12 g, 8%. NMR ($CDCl_3$, 250 MHz): ^1H, for dominant *exo* isomer, δ 4.26, 4.24 [2 × 2 H, 2 virtual t (apparent *J* = 2.6), C_5H_4], 4.11 (5 H, s, C_5H_5), 2.67 [1 H, t of t (^3J = 10.7, ^2J = 7.2), $C\textit{H}(CH_2)_2$], 2.15 [2 H, d of d (^3J = 7.2, ^2J = 1.1), *syn*-$CH(C\textit{H}_2)_2$], 2.11 (6 H, s, 2,5- or 3,4-Me_2 of C_5Me_4), 2.00 (6 H, s, 3,4- or 2,5-Me_2 of C_5Me_4) and 0.94 [2 H, d of d (^3J = 10.7, ^2J = 1.1 Hz), *anti*-$CH(C\textit{H}_2)_2$]; ^{13}C-{^1H} DEPT, only signals for *exo* isomer detected, δ 76.2 [$\textit{C}H(CH_2)_2$], 69.1 (C_5H_5), 68.2, 67.7 (2 CH of C_5H_4), 44.6 [$CH(\textit{C}H_2)_2$], 12.7, 11.2 (2 $C_5\textit{Me}_4$). Selected IR data (CH_2Cl_2 solution): ν(CO) 1930s and 1846s cm^{-1}. EI mass spectrum (calculated for ^{56}Fe and ^{96}Mo): *m/z* 499 (M^+), 433 (M^+ − 2 CO), 121 [$(C_5H_5)Fe^+$] and 56 (Fe^+) (Found: C, 58.4; H, 5.4. Calc. for $C_{24}H_{26}FeMoO_2$: C, 57.8; H, 5.3%).

The complex was also prepared as follows. A suspension of $[Mo(CO)_6]$ (1.32 g, 5 mmol) in diglyme (40 cm^3) and thf (5 cm^3) was added to a suspension of $Li[C_5Me_4C_5H_4Fe(C_5H_5)]$ (1.54 g, 5 mmol) in diglyme (40 cm^3) and the mixture was heated at 140–145 °C for 3 h until evolution of CO ceased. The resulting yellow solution was cooled to r.t. before the addition of an excess of allyl chloride (2.0 cm^3, 23 mmol). The mixture was stirred overnight and the volatiles were removed under reduced pressure leaving an orange-red solid which was dissolved in thf (25 cm^3). Freshly sublimed trimethylamine *N*-oxide (1.35 g, 18 mmol) was added and the mixture was stirred. After the reaction was complete (*ca.* 30 min as monitored by IR spectroscopy) the volatiles were removed under reduced pressure and the orange oil was rapidly chromatographed on deactivated alumina with hexane eluent to give orange crystals of complex **2**. Yield: 0.20 g, 8%.

$[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(CO)_2(\eta\text{-}C_3H_5)]$ 3. This compound was prepared as for **2** but using $Li[C_5H_2Me_2C_5H_4Fe(C_5H_5)]$ (1.20 g, 4.32 mmol) and $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ (1.53 g, 4.32 mmol). Hexane–diethyl ether (9:1) was used as the eluent for rapid column chromatography on deactivated alumina which gave the orange compound **3**.

Yield: 0.47 g, 23%. NMR: ^{1}H ($CDCl_3$, 400 MHz), for dominant *exo* isomer only, δ 5.17 (2 H, s, $C_5H_2Me_2$), 4.11 [4 H, overlapping 2 virtual t (apparent J = 2.6), C_5H_4], 3.96 (5 H, s, C_5H_5), 3.02 [1 H, t of t (^3J = 10.8, ^3J = 7.1), $CH(CH_2)_2$], 2.32 [2 H, d (^3J = 7.1), *syn*-$CH(CH_2)_2$], 2.00 (6 H, s, $C_5H_2Me_2$) and 0.86 [2 H, d (^3J = 10.8 Hz), *anti*-$CH(CH_2)_2$]; ^{13}C-{^{1}H} (100.6 MHz), for dominant *exo* isomer only, δ 230.9 (CO), 107.1, 105.6 [C bonded to ferrocenyl and *C*Me of $C_5H_2Me_2$], 89.4 (CH of $C_5H_2Me_2$), 79.0 (C of C_5H_4 bonded to $C_5H_2Me_2$), 74.1 [$CH(CH_2)_2$], 69.6 (C_5H_5), 68.5, 65.2 (2 CH of C_5H_4), 43.0 [$CH(CH_2)_2$] and 12.9 (Me). Selected IR data (CH_2Cl_2 solution): ν(CO) 1936s and 1851s cm^{-1}. EI mass spectrum (calculated for ^{56}Fe and ^{96}Mo): *m/z* 470 (M^+), 414 (M^+ − 2 CO), 373 [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo^+$], 278 [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)^+$], 186 [$(C_5H_5)_2Fe^+$] and 56 ($Fe^+$) (Found: C, 56.2; H, 5.1. Calc. for $C_{22}H_{22}FeMoO_2$: C, 56.3; H, 4.7%).

$[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)W(CO)_2(\eta\text{-}C_3H_5)]$ 4. This compound was prepared as for **2** but using $Li[C_5H_2Me_2C_5H_4Fe(C_5H_5)]$ (0.21 g, 0.52 mmol) and $[WCl(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ (0.14 g, 0.52 mmol). Hexane–diethyl ether (2:1) was used as the eluent for rapid column chromatography on deactivated alumina which gave the orange compound **4**. Yield: 15 mg, 5%. ^{1}H NMR ($CDCl_3$, 250 MHz): for the dominant *exo* isomer only, δ 5.28 (2 H, s, $C_5H_2Me_2$), 4.17, 4.15 [2 × 2 H, 2 virtual t (apparent J = 2.6), C_5H_4], 4.03 (5 H, s, C_5H_5), 2.63 [1 H, t of t (^3J = 6.9, 10.1), $CH(CH_2)_2$], 2.32 [2 H, d (^3J = 6.9), *syn*-$CH(CH_2)_2$], 2.17 [6 H, s, $C_5H_2Me_2$] and 1.12 [2 H, d (^3J = 10.1 Hz), *anti*-$CH(CH_2)_2$] (Found: C, 47.7; H, 4.2. Calc. for $C_{22}H_{22}FeO_2W$: C, 47.4; H, 4.0%).

$[(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2(\eta\text{-}C_3H_5)]$ 5. This compound was prepared as for **2** but using $Li[C_9H_6C_5H_4Fe(C_5H_5)]$ (0.41 g, 1.34 mmol) and $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ (0.48 g, 1.34 mmol). Hexane–diethyl ether (2:1) was used as the eluent for rapid column chromatography on deactivated alumina which gave the required orange compound **5**. Yield: 0.16 g, 25%. NMR (C_3D_6O): ^{1}H (400 MHz), for the dominant *exo* isomer only, δ 7.72, 7.33 [2 × 1 H, 2 d (^3J = 8.6), 4- and 7-H of C_9H_6], 7.25, 7.11 [2 × 1 H, 2 d of d (^3J = 8.6, ^2J = 7.7), 5- and 6-H of C_9H_6], 6.18, 6.06 [2 × 1 H, 2 d (^3J = 2.8), 2- and 3-H of C_9H_6], 4.79, 4.70, 4.37, 4.32 [4 × 1 H, 4 virtual q (apparent J = 2.6), C_5H_4], 4.04 (5 H, s, C_5H_5), 2.14, 1.98 [2 × 1 H, 2 d of d (^3J = 7.2, ^2J = 1.4), *syn*-$CH(CH_2)_2$], 0.96 [1 H, m, $CH(CH_2)_2$] and 0.79, 0.71 [2 × 1 H, 2 d of d (^3J = 10.9, ^2J = 1.4 Hz), *anti*-$CH(CH_2)_2$]; ^{13}C-{^{1}H} (100.6 MHz), for the dominant *exo* isomer only, δ 126.6 (5- or 8-C of C_9H_6), 125.3, 124.7 (5- and 6-C of C_9H_6), 123.7 (8- or 5-C of C_9H_6), 111.3, 111.0 (4- and 5-C of C_9H_6), 101.5 (1-C of C_9H_6), 90.7 (2- or 3-C of C_9H_6), 83.0 [$CH(CH_2)_2$], 80.5 (C of C_5H_4 bonded to C_9H_6), 78.2 (3- or 2-C of C_9H_6), 70.0 (C_5H_5), 69.5, 68.6, 67.9, 67.5 (CH of C_5H_4) and 49.3, 48.6 [2 $CH(CH_2)_2$] (quaternary carbons for CO ligands not observed). Selected IR data (CH_2Cl_2 solution): ν(CO) 1944s and 1861s cm^{-1}. EI mass spectrum (calculated for ^{56}Fe and ^{96}Mo): *m/z* 492 (M^+), 436 (M^+ − 2 CO), 395 [$(C_5H_5)Fe(C_5H_4C_9H_6)Mo^+$] and 299 [$(C_5H_5)Fe(C_5H_4C_9H_6)^+$] (Found: C, 58.7; H, 4.4. Calc. for $C_{24}H_{20}FeMoO_2$: C, 58.6; H, 4.1%).

$[(C_5H_5)Fe(C_5H_4C_9H_6)W(CO)_2(\eta\text{-}C_3H_5)]$ 6. A solution of $[WCl(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)]$ (1.30 g, 3.27 mmol) in thf (25 cm^3) was added slowly to a solution of $Li[C_9H_6C_5H_4Fe(C_5H_5)]$ (1.0 g, 3.27 mmol) in thf (50 cm^3). The solution became dark green and was left to stir overnight. The volatiles were removed under pressure and the green solid was rapidly chromatographed on deactivated alumina with hexane–diethyl ether (3:1) eluent to give complex **6** as an orange powder. Yield: 50 mg, 3%. ^{1}H NMR (C_3D_6O, 250 MHz): for the dominant *exo* isomer only, δ 7.70 [1 H, d (^3J = 2.7) 4- or 7-H of C_9H_6], 7.35–7.18 (3 H, overlapping 2 virtual t and d, 5- and 6-, 7- or 4-H of C_9H_6), 6.23, 6.18 [2 × 1 H, 2 d (^3J = 2.7), 2- and 3-H of C_9H_6], 4.78, 4.72, 4.37, 4.33 [4 × 1 H, 4 virtual t (apparent J = 2.6 Hz), C_5H_4], 4.07 (5 H, s, C_5H_5), 2.13–1.99 [2 H, 2 overlapping d of d, *syn*-$CH(CH_2)_2$], 0.94–1.05 [2 H, 2 overlapping d of d, *anti*-$CH(CH_2)_2$], and 0.32 [1 H, m, $CH(CH_2)_2$]. EI mass spectrum (calculated for ^{56}Fe and ^{184}W): *m/z* 580 (M^+), 482 [$(C_5H_5)Fe(C_5H_4C_9H_6)W^+$], 299 [$(C_5H_5)Fe(C_5H_4C_9H_6)^+$] and 56 ($Fe^+$) (Found: C, 49.5; H, 3.8. Calc. for $C_{24}H_{20}FeO_2W$: C, 49.7; H, 3.5%).

$[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(CO)_2(\eta^3\text{-}C_3H_4Ph)]$ 7. This compound was prepared as for **2** but using $Li[C_5H_2Me_2C_5H_4Fe(C_5H_5)]$ (0.52 g, 1.81 mmol) and $[MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_4Ph)]$ (0.78 g, 1.8 mmol). Hexane–diethyl ether (4:1) was used as the eluent for rapid column chromatography on deactivated alumina which gave the orange compound **7**. Yield: 0.47 g, 47%. NMR: ^{1}H ($CDCl_3$, 250 MHz), for the dominant *exo* isomer only, δ 7.26–6.95 (5 H, overlapping m, Ph), 5.27, 4.70 [2 × 1 H, 2 d (^4J = 2.0), 2- and 5-H of $C_5H_2Me_2$], 4.22 [2 H, 2 overlapping virtual q (apparent J = 2.6), C_5H_4], 4.02 (5 H, s, C_5H_5), 4.00–3.95 [3 H, 2 overlapping virtual q (apparent J = 2.6) and m, C_5H_4 and $CH(CH_2)(CHPh)$ respectively], 2.64 [1 H, d (^3J = 10.7), $CH(CH_2)(CHPh)$], 2.13 (3 H, s, 3- or 4-Me of $C_5H_2Me_2$), 1.97 [1 H, d of d (^3J = 7.3, ^2J = 1.9), *syn*-$CH(CH_2)(CHPh)$], 1.71 (3 H, s, 4- or 3-Me of $C_5H_2Me_2$) and 1.05 [1 H, d of d (^3J = 10.4, ^2J = 1.9 Hz), *anti*-$CH(CH_2)(CHPh)$]; ^{13}C-{^{1}H} (C_3D_6O, 68.9 MHz), for the dominant *exo* isomer only, δ 231.4, 227.7 (CO), 141.4 (C_q of Ph), 128.5, 128.1, 125.8, 125.5, 125.2 (5 CH of Ph), 109.8, 106.9, 103.4 [C bonded to ferrocenyl and 2 *C*Me of $C_5H_2Me_2$], 94.9, 89.1 (2 CH of $C_5Me_2H_2$), 78.4 (C of C_5H_4), 72.0 (CH of C_5H_4), 69.7, 69.7 (overlapping C_5H_5 and CH of C_5H_4), 68.5 (CH of C_5H_4), 65.3 [overlapping $CH(CH_2)(CHPh)$], 64.9 (CH of C_5H_4), 39.2 [$CH(CH_2)(CHPh)$], and 13.3, 12.3 (Me). Selected IR data (CH_2Cl_2 solution): ν(CO) 1935s and 1854s cm^{-1}. EI mass spectrum (calculated for ^{56}Fe and ^{96}Mo): *m/z* 546 (M^+), 518 (M^+ − CO), 373 [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo^+$] and 56 ($Fe^+$) (Found: C, 60.5; H, 4.8. Calc. for $C_{28}H_{26}FeMoO_2$: C, 60.6; H, 4.8%).

$[(C_5H_5)Fe(C_5H_4C_9H_6)Mo(CO)_2(\eta^3\text{-}C_3H_4Ph)]$ 8. This compound was prepared as for **2** but using $Li[C_9H_6C_5H_4Fe(C_5H_5)]$ (0.15 g, 4.73 × 10^{-4} mol) and $[MoBr(MeCN)_2(CO)_2(\eta^3\text{-}C_3H_4Ph)]$ (0.20 g, 0.47 mmol). Hexane–diethyl ether (2:1) was used as the eluent for rapid column chromatography on deactivated alumina which gave the orange compound **8**. Yield: 0.20 g, 74%. ^{1}H NMR ($CDCl_3$, 250 MHz): for all isomers, a complete assignment is not possible, δ 8.0–7.0 (overlapping m, Ph and 4-, 5-, 6-, 7-H of C_9H_6), 6.10–5.90 (overlapping d, 2- and 3-H of C_9H_6), 5.70–3.30 (overlapping virtual q, C_5H_4), 4.15–3.80 (4 s, C_5H_5), and 3.35–0.6 [overlapping m, $CH(CH_2)(CHPh)$]. Selected IR data (CH_2Cl_2 solution): ν(CO) 1942s and 1862s cm^{-1}. EI mass spectrum (calculated for ^{56}Fe and ^{96}Mo): *m/z* 512 (M^+ − 2 CO), 395 [$(C_5H_5)Fe(C_5H_4C_9H_6)Mo^+$] and 299 [$(C_5H_5)Fe(C_5H_4C_9H_6)^+$] (Found: C, 64.1; H, 4.7. Calc. for $C_{28}H_{26}FeMoO_2$: C, 63.4; H, 4.3%).

$[(C_5H_5)Fe(C_5H_4C_5H_2Me_2)(OC)_2Mo(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4Ph)Cr(CO)_3]$ 9. Complex **7** (0.47 g, 0.86 mmol) and $[Cr(CO)_6]$ (0.57 g, 2.6 mmol) were heated in $Bu^n{}_2O$–thf (10:1) at 120 °C for 16 h resulting in a dark green solution. The volatiles were removed under reduced pressure and the remaining solid was extracted with hexane to leave behind excess of $[Cr(CO)_6]$. The hexane washings were combined and the volatiles were removed to give **9** as an orange solid. Yield: 94 mg, 16%. NMR ($CDCl_3$): ^{1}H

(270 MHz), for both isomers, a complete assignment is not possible, major isomer, δ 3.96 (5 H, s, C_5H_5), 3.69 [1 H, m, $C\mathit{H}(CH_2)(CHPh)$], 2.81 [1 H, d of d ($^3J = 6.3$, $^2J = 1.7$), *syn*-$CH(C\mathit{H}_2)(CHPh)$], 1.37 [1 H, d ($^3J = 10.2$), $CH(CH_2)(C\mathit{H}Ph)$] and 1.10 [1 H, d of d ($^3J = 10.4$, $^2J = 1.7$), *anti*-$CH(C\mathit{H}_2)(CHPh)$]; minor isomer, δ 4.04 (5 H, s, C_5H_5); both isomers, 5.4–4.4 (overlapping Ph and $C_5\mathit{H}_2Me_2$), 4.83–4.52 [overlapping d ($^4J \approx 6$ Hz), $C_5\mathit{H}_2Me_2$], 4.3–3.8 (overlapping C_5H_4) and 2.2–1.8 (overlapping $C_5H_2\mathit{Me}_2$); $^{13}C-\{^1H\}$ DEPT (67.9 MHz), for both isomers, a complete assignment is not possible, δ 95–86 (Ph), 87.4, 86.1 (2- and 5-CH of $\mathit{C}_5Me_2H_2$), 72–60 [C_5H_5, C_5H_4, $\mathit{C}H(CH_2)(\mathit{C}HPh)$], 38.4 [$CH(\mathit{C}H_2)(CHPh)$] and 13.0, 12.9 (Me). Selected IR data (CH_2Cl_2 solution): ν(CO) 1964s, 1939s, 1881s and 1860s cm^{-1}. FAB mass spectrum (calculated for ^{56}Fe, ^{52}Cr and ^{96}Mo): *m/z* 684 (M^+), 626 ($M^+ - 2$ CO), 598 ($M^+ - 3$ CO), 518 [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(CO)(\eta\text{-}C_3H_4Ph)^+$], 490 [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo(\eta\text{-}C_3H_4Ph)^+$] and 373 [$(C_5H_5)Fe(C_5H_4C_5H_2Me_2)Mo^+$] (Found: C, 54.8; H, 4.1. Calc. for $C_{31}H_{26}CrFeMoO_2$: C, 54.6; H, 3.8%).

[Mo(CO)$_2$(η^3-C$_3$H$_5$)(η-C$_5$Me$_5$)] 10. To a solution of [$MoBr(MeCN)_2(CO)_2(\eta\text{-}C_3H_5)$] (0.99 g, 2.78 mmol) in thf (25 cm^3) was slowly added a suspension of Li[C_5Me_5] (0.4 g, 2.78 mmol) in thf (25 cm^3). The mixture was stirred overnight resulting in a dark red solution. The volatiles were removed under pressure and the remaining red solid was rapidly chromatographed on deactivated alumina with hexane eluent to give complex **10** as a yellow solid which was further purified by sublimation [80 °C, 10^{-2} mbar (1 Pa)]. Yield: 45 mg, 5%. ^1H NMR ($CDCl_3$, 250 MHz): for dominant *exo* isomer only, δ 2.82 [1 H, m, $C\mathit{H}(CH_2)_2$], 2.17 [2 H, d of d ($^3J = 6.2$, $^2J = 0.9$), *syn*-$CH(C\mathit{H}_2)_2$], 1.86 (15 H, s, C_5Me_5) and 0.98 [2 H, d of d ($^3J = 10.8$, $^2J = 0.9$ Hz), *anti*-$CH(C\mathit{H}_2)_2$]. Selected IR data (CH_2Cl_2 solution): ν(CO) 1931s and 1845s cm^{-1} (Found: C, 53.9; H, 6.5. Calc. for $C_{15}H_{20}MoO_2$: C, 54.5; H, 6.1%).

Alternatively, a suspension of [$Mo(CO)_6$] (1.83 g, 6.93 mmol) in diglyme (50 cm^3) and thf (10 cm^3) was added to a suspension of Li[C_5Me_5] (0.99 g, 6.93 mmol) in diglyme (50 cm^3) and the mixture heated at 140–145 °C for 3 h until evolution of CO ceased. The resulting yellow solution was cooled to r.t. before the addition of an excess of allyl chloride (2.1 cm^3, 24.3 mmol). The mixture was stirred overnight to give a green solution. The volatiles were removed under reduced pressure leaving an orange-red oil which was dissolved in thf (30 cm^3), freshly sublimed trimethylamine *N*-oxide (1.4 g, 18 mmol) added and the mixture was stirred. After the reaction was complete (30 min as monitored by IR spectroscopy) the volatiles were removed under reduced pressure and the orange oil was rapidly chromatographed on deactivated alumina with light petroleum eluent to give yellow crystals of complex **10**. Yield: 0.57 g, 25%.

Acknowledgements

We thank the University of Nottingham for a New Lecturer's Research Grant (to P. M.), the Royal Society for an equipment grant, EPSRC and Zeneca Specialties for a CASE award (to S. W.) and Drs. N. G. Connelly, S. B. L. Lyons and M. D. Ward for helpful comments.

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Received 31*st October* 1995; *Paper* 5/07178J