

Priority communication

Synthesis and properties of the alkynyl-bridged heterobimetallics
 $[\text{Mo}(\text{C}\equiv\text{CFc})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\eta\text{-C}_7\text{H}_7)]^z$ (Fc = ferrocenyl, $z = 0$ or $+1$)Zafar I. Hussain^a, Mark W. Whiteley^{a,*}, Eric J.L. McInnes^b^a Department of Chemistry, University of Manchester, Manchester M13 9PL, UK^b EPSRC CW EPR Service Centre, Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

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Abstract

Cyclic voltammetric investigations reveal that $[\text{Mo}(\text{C}\equiv\text{CFc})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) **1a**, undergoes two reversible one-electron oxidations; chemical oxidation with $[\text{FeCp}_2][\text{PF}_6]$ results in the formation of $[\text{Mo}(\text{C}\equiv\text{CFc})(\text{dppe})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ **1b**, accompanied by a negative shift in the infrared active $\nu(\text{C}\equiv\text{C})$ of 50 cm^{-1} . The solution esr spectrum of **1b**, with resolved hyperfine coupling to dppe phosphorus atoms and C_7H_7 ring hydrogens, suggests that the odd electron in **1b** is resident principally at the cycloheptatrienylmolybdenum centre. © 1997 Elsevier Science S.A.

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1. Introduction

The synthesis and properties of mixed-valence organometallic complexes containing two redox active metal centres linked by an alkynyl bridge have been the focus of many recent investigations [1–5] and an important division of this work involves ferrocenylacetylide complexes of the type $\text{M}'\text{C}\equiv\text{CFc}$ (M' = redox active metal centre) [3–5]. In a series of studies we have developed the redox chemistry of monometallic alkynyl complexes of the cycloheptatrienylmolybdenum auxiliary, including the synthesis [6], structure [7] and reactivity [8,9] of the isolable alkynyl radical cations $[\text{Mo}(\text{C}\equiv\text{CR})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ ($\text{R} = \text{Ph}, \text{Bu}^n$ or Bu^t). The ability of the $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ system to support reversible redox behaviour when attached to an alkynyl group and the characteristic esr spectral properties associated with the d^5 Mo centre in the radicals $[\text{Mo}(\text{C}\equiv\text{CR})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ [6] suggested the $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ auxiliary as a novel, redox-active M' centre to advance investigations on intermetallic electronic communication in bimetallic alkynyl-bridged systems. A recent report of extensive electron delocali-

sation between Fe centres in the mixed-valence cations $[\text{Fe}(\text{C}\equiv\text{CFc})(\text{dppe})(\eta\text{-C}_5\text{R}'_5)]^+$ ($\text{R}' = \text{H}$ or Me) [5] now prompts us to communicate our comparative findings on the related complex $[\text{Mo}(\text{C}\equiv\text{CFc})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$.

2. Results and discussion

The alkynyl complexes $[\text{Mo}(\text{C}\equiv\text{CR})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ ($\text{R} = \text{Ph}, \text{Bu}^n$ or Bu^t) are readily prepared by reaction of $[\text{Mo}(\text{acetone})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ (generated in situ from $[\text{Mo}(\eta\text{-C}_6\text{H}_5\text{Me})(\eta\text{-C}_7\text{H}_7)]^+$ and dppe in refluxing acetone) with terminal alkynes $\text{HC}\equiv\text{CR}$ to give the vinylidenes $[\text{Mo}(\text{C}=\text{CHR})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ which are subsequently deprotonated [6]. In an analogous procedure, reaction of $\text{HC}\equiv\text{CFc}$ with $[\text{Mo}(\text{acetone})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ gave $[\text{Mo}(\text{C}=\text{C}(\text{H})\text{Fc})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ which was deprotonated with KOBU^t in acetone to yield $[\text{Mo}(\text{C}\equiv\text{CFc})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ **1a**.¹ Complex **1a** was isolated as a brown solid following purification by column chromatography. The CH_2Cl_2 solution infrared spectrum of **1a** revealed a characteristic $\nu(\text{C}\equiv\text{C})$ stretching vibration at 2052 cm^{-1} similar to that of $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ ($\nu(\text{C}\equiv\text{C}), \text{CH}_2\text{Cl}_2, 2045\text{ cm}^{-1}$ [6]).

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Table 1

Comparison of cyclic voltammetric data for $[M(C\equiv CFC)(dppe)(\eta-C_nR'_n)]^a$

Complex	M	n	R'	E_1°	E_2°	ΔE° ($E_2^\circ - E_1^\circ$)	$E_{([M'(C\equiv CPh)]^\circ)}$
1a	Mo	7	H	-0.23	0.63	0.86	-0.15
2a ^b	Fe	5	Me	-0.05	0.67	0.72	-0.04 ^c
3a ^b	Fe	5	H	0.09	0.68	0.59	0.20

^a All potentials vs. SCE, $E_{(HC\equiv CFC)}^\circ = 0.71$ V.^b Data from Ref. [5], potentials adjusted to SCE reference using data for $FeCp_2 \leftrightarrow FeCp_2^+$.^c Data from Ref. [10].

The redox behaviour of **1a** was probed by cyclic voltammetric investigations in CH_2Cl_2 .² Two reversible one-electron oxidations [E° (V) vs. SCE: E_1° , -0.23; E_2° , 0.63] were observed which, on the basis of comparison with reference compounds run under identical conditions [E° (V) $[Mo(C\equiv CPh)(dppe)(\eta-C_7H_7)]$, -0.15 [6]; $HC\equiv CFC$, 0.71] were assigned respectively to the $Mo(dppe)(\eta-C_7H_7)$ and Fc centres. This redox behaviour of $M'C\equiv CFC$, in which the M' centre is oxidised first, is also observed for $M' = Fe(dppe)(\eta-C_5R'_5)$ ($R' = Me$, **2a** or H , **3a** [5]) and some important points of comparison are summarised in Table 1. First, $\Delta E^\circ = (E_2^\circ - E_1^\circ)$ is largest for **1a** and decreases in the order **1a** > **2a** > **3a**; the principal factor in this change appears to be a decrease in electron density at the M' centre (as determined by independent measurements on the monometallic alkynyls $[M'(C\equiv CPh)]$ [5,6,10,11], see Table 1). Second, in all cases ΔE° is very similar to $[E_{(HC\equiv CFC)}^\circ - E_{(M'(C\equiv CPh))}^\circ]$ [for $M' = Mo(dppe)(\eta-C_7H_7)$, $0.71 - (-0.15) = 0.86$ V] and E_1° and E_2° are not shifted significantly from $E_{(M'(C\equiv CPh))}^\circ$ and $E_{(HC\equiv CFC)}^\circ$ respectively. These results contrast with those of $[Ru(C\equiv CFC)(PPh_3)_2(\eta-C_5H_5)]$ for which substantial shifts in E_1° and E_2° from the reference monometallic compounds are observed [3].

In search of alternative probes to determine the extent of communication between M' and Fc centres in the complexes **1**, the synthesis and properties of the radical monocation $[Mo(C\equiv CFC)(dppe)(\eta-C_7H_7)]^+$ **1b** were explored. Reaction of **1a** with one equivalent of $[FeCp_2][PF_6]$ in CH_2Cl_2 gave a purple solution from which **1b**¹ was isolated as a deep purple solid.

One parameter which has been employed as an indicator for the extent of interaction between M' and Fc

centres is the change in the infrared active $\nu(C\equiv C)$ stretch effected by one-electron oxidation of $M'C\equiv CFC$ to $[M'C\equiv CFC]^+$. In complexes of the $Fe(dppe)(\eta-C_5R'_5)$ auxiliary, one-electron oxidation is accompanied by a shift in $\nu(C\equiv C)$ to low wavenumber by [**2a**, -96; **3a**, -112 cm^{-1}] [5] and a similar $\Delta\nu(C\equiv C)$ (-86 cm^{-1}) is observed for $[Ru(C\equiv CFC)(PPh_3)_2(\eta-C_5H_5)]^z$ [3]. This shift in $\nu(C\equiv C)$ has been attributed to the contribution of an allenylidene resonance form $[M'=C=C=Fc]^+$ in the structure of the cationic mixed-valence species, arising from electron delocalisation between M' and Fc centres [3,5]. The CH_2Cl_2 solution infrared spectrum of **1b** exhibits a strong, sharp band at 2002 cm^{-1} and therefore $\Delta\nu(C\equiv C)$ resulting from one-electron oxidation of **1a** to **1b** is -50 cm^{-1} . The magnitude of this shift is significant by comparison with that observed for the monometallic redox pair $[Mo(C\equiv CPh)(dppe)(\eta-C_7H_7)]^z$ ($z = 0$ or $+1$; $\Delta\nu(C\equiv C)$, -13 cm^{-1} [6]) and also for $[Pt(C\equiv CFC)(C_6H_4OMe-4)(PPh_3)_2]^z$ ($z = 0$ or $+1$; $\Delta\nu(C\equiv C)$, -8 cm^{-1}) in which ($z = +1$) the odd electron is essentially localised on the ferrocenyl centre [4], but seems small by comparison with the $\Delta\nu(C\equiv C)$ parameter for **2** and **3**. Attempts to prepare the dioxidised species $[Mo(C\equiv CFC)(dppe)(\eta-C_7H_7)][PF_6]_2$ to provide further insight into changes in $\nu(C\equiv C)$ have, so far, been unsuccessful.

A further technique used to examine electron delocalisation in $[Fe(C\equiv CFC)(dppe)(\eta-C_5H_5)]^+$ was esr spectroscopy, but the broad nature of the spectra and the absence of resolved hyperfine couplings preclude a detailed interpretation. By contrast, esr spectra of the alkynyl radical cations $[Mo(C\equiv CR)(dppe)(\eta-C_7H_7)]^+$ are well resolved with characteristic hyperfine coupling to phosphorus and the cycloheptatrienyl ring hydrogens [6], and this suggested that in the case of **1b**, esr spectroscopy would provide an effective technique to examine electron distribution, not available to the cyclopentadienyliron analogues. As anticipated, the X-band (frequency 9.622 GHz), CH_2Cl_2 solution esr spectrum of **1b** (Fig. 1) is well resolved with spectral parameters [$\langle g \rangle$, 1.998; $a(^{31}P)$, 21; $a(H)$, 4.0; $a(^{95,97}Mo)$, 30.2 G]; the hyperfine coupling constants were determined with the aid of spectral simulation which also confirms that $a(H)$ originates from coupling to the seven hydrogens of the cycloheptatrienyl ring. Clearly, these results establish that the odd electron in **1b** is resident on the cycloheptatrienyl molybdenum centre, but furthermore the general appearance of the spectrum of **1b** and the spectral parameters bear a striking resemblance to data for monometallic $[Mo(C\equiv CPh)(dppe)(\eta-C_7H_7)]^+$ [$\langle g \rangle$, 1.996; $a(^{31}P)$, 22.5; $a(H)$ 4.3; $a(^{95,97}Mo)$, 32 G] [6]. Comparison of hyperfine couplings for $[Mo(C\equiv CPh)(dppe)(\eta-C_7H_7)]^+$ and **1b** reveals a small but consistent decrease in values for the bimetallic, compatible with a limited additional

¹ In addition to cyclic voltammetric, infrared and esr data detailed in the text, mass spectral (FAB, $M^+ = 796$) and satisfactory microanalytical (C and H) data were obtained for **1a** and **1b**. Complex **1b** exhibited complementary cyclic voltammetry to that of **1a**.

² Cyclic voltammetric studies at 20°C on CH_2Cl_2 solutions, 10^{-3} M in complex and 0.2 M in supporting electrolyte $[Bu_4N][BF_4]$ at a carbon working electrode. All potentials (V) vs. saturated calomel electrode (SCE); E° for the couple $FeCp_2 \leftrightarrow FeCp_2^+$ measured under identical conditions, 0.56 V.

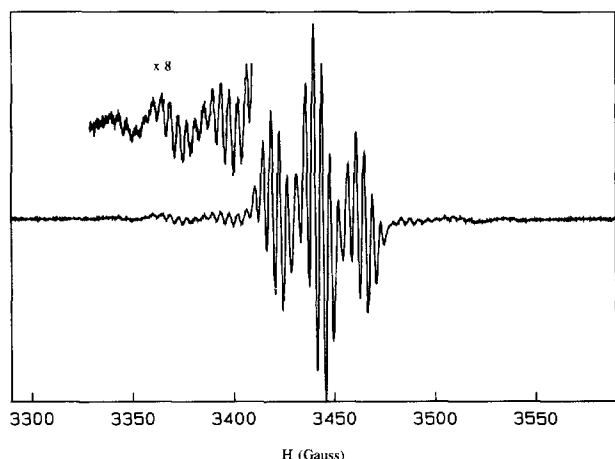


Fig. 1. The X-band CH_2Cl_2 solution esr spectrum of $[\text{Mo}(\text{C}\equiv\text{CFc})(\text{dppe})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ **1b**.

delocalisation onto the alkynyl bridge of **1b**, but the results do not support extensive delocalisation between Mo and Fc centres.

In summary, our preliminary findings, based on infrared and esr spectroscopy, suggest that the odd electron in the cycloheptatrienylmolybdenum complex **1b** is less fully delocalised than in $[\text{Fe}(\text{C}\equiv\text{CFc})(\text{dppe})(\eta\text{-C}_5\text{R}'_5)]^+$ and therefore it appears that the electronic properties of $\text{M}'\text{C}\equiv\text{CFc}$ are critically dependent upon the identity of M' , even in those systems where the first oxidation is based at the M' centre. We propose that the dissimilarity between the properties of complexes **1** and the cyclopentadienyliron analogues is related to the magnitude of ΔE° (Table 1), which is considerably larger for **1** than for **2** or **3**. Further studies are in

progress to elucidate the structure of **1b** and to quantify the extent of electron delocalisation between $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ and Fc centres.

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