Synthesis, redox properties, EPR and ENDOR spectroscopy of the 17-electron cycloheptatrienylmolybdenum complexes [MoX(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(η-C$_7$H$_7$)]$^{z+}$ (z = 1, X = I, Br, Cl, F, NCO, NCS, CN, ^{13}CN, Me, C≡CPh; z = 2, X = NCMe, CNMe, ^{13}CNMe, oxacyclopentylidene)

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The synthesis of a series of new 18-electron cycloheptatrienylmolybdenum complexes [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; z = 0, X = NCO, NCS, CN, ^{13}CN; z = 1, X = CNMe, ^{13}CNMe, oxacyclopentylidene) and [Mo(triphos)(η-C$_7$H$_7$)]$^+$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) is reported. Cyclic voltammetric investigations reveal that each of these complexes undergoes a reversible one-electron oxidation to the corresponding 17-electron radicals which have been generated by chemical oxidation, isolated and characterised. Additional examples of 17-electron radicals [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ (z = 1, X = I, Br, Cl, F, Me, C≡CPh; z = 2, X = NCMe) were either isolated directly or reinvestigated in this work. Fluid solution, X-band EPR studies at 243 K on the 17-electron radicals [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ (z = 1 or 2) afford well resolved spectra characteristic of molybdenum species split by ligand hyperfine interactions with two equivalent phosphorus atoms, seven equivalent protons of the cycloheptatrienyl ring and an additional splitting from the ligand X (where this contains nuclei with non-zero spin). Calculations to determine contributions to the ground state molecular orbital from (i) the ns orbital of the ligand X (based on the EPR work) and (ii) the dppe phosphorus s and p orbitals (based on ENDOR work) suggest that the unpaired electron occupies an essentially metal-based molecular orbital.

The redox chemistry of complexes based on metal phosphine auxiliaries such as ML$_2$(η-C$_5$R$_5$) (M = Fe or Ru, L = PPh$_3$, PMe$_3$ etc., L$_2$ = dppm, dppe; R = H or Me) or Re(NO)(PPh$_3$)-(η-C$_5$R$_5$) has evolved from fundamental electrochemical studies on [MXL$_2$(η-C$_5$R$_5$)] (X = halide, pseudo-halide etc.)[1,2] to detailed electrochemical and spectroscopic investigations on ligand-bridged, mixed-valence systems.[3,4] Our interest in this area has focused upon the cycloheptatrienyl molybdenum auxiliary Mo(dppe)(η-C$_7$H$_7$) and, building upon the work of Green and co-workers,[5,6] we have developed the synthesis and redox chemistry of a range of derivatives [MoX(dppe)-(η-C$_7$H$_7$)], [X = C≡CPh,[7] C,[8] Me,[9] C≡CFc[10] (Fc = ferrocenyl)]. The distinctive features of the cycloheptatrienylmolybdenum system which have stimulated our investigations are (i) the ease of one-electron oxidation to the corresponding 17-electron radical cations [MoX(dppe)(η-C$_7$H$_7$)]$^+$, (ii) the stability of these 17-electron radicals and finally (iii) the well resolved solution EPR spectra obtainable for these complexes. This paper draws together our investigations on the synthesis and redox chemistry of an extended series of 18-electron complexes [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ (z = 0 or 1) and presents the results of EPR and ENDOR investigations on the 17-electron radicals [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ (z = 1 or 2). The EPR and ENDOR work furnish new data with which to explore the composition of the SOMO (singly occupied molecular orbital) in these systems.

Results and discussion

Synthetic studies

The complexes [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ under investigation in this paper fall into two groups. In type 1 systems the ligand X is formally a uninegatively charged species (halide, NCO, NCS, C≡N, Me, C≡CR) giving rise to neutral 18-electron complexes [MoX(dppe)(η-C$_7$H$_7$)]. In type 2 systems, X is a neutral ligand (NCMe, CNMe, oxacyclopentylidene) resulting in cationic 18-electron complexes [MoX(dppe)(η-C$_7$H$_7$)]$^+$. The majority of these complexes are accessible directly by reaction of a source of the ligand X$^-$/X with an acetone solution of [Mo(OCMe$_2$)-(dppe)(η-C$_7$H$_7$)][PF$_6$] (generated by reaction of the toluene sandwich complex [Mo(η-C$_6$H$_5$Me)(η-C$_7$H$_7$)][PF$_6$] with dppe in acetone).[5,6] The objective of the synthetic work was to obtain a series of complexes of the type [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ with a wide range of ligands X, both as 18-electron species and 17-electron radical cations, thus promoting investigations on the effect of X on electrochemical properties and EPR spectral data.

Type 1 complexes

Reaction of [Mo(OCMe$_2$)(dppe)(η-C$_7$H$_7$)][PF$_6$] with an excess of anhydrous LiX (X = I, Br, Cl) in acetone affords directly the known[6] 17-electron radical cations [MoX(dppe)(η-C$_7$H$_7$)][PF$_6$]
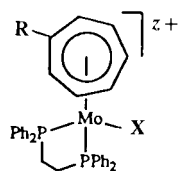
X (R = H unless stated otherwise)	z = 0	z = 1	z = 2
I		1b	
Br		2b	
Cl		3b	
F		4b	
Cl (R = Me)		5b	
NCO	6a	6b	
NCS	7a	7b	
CN	8a	8b	
^{13}CN	9a	9b	
CNMe		10a	10b
^{13}CNMe		11a	11b
CCH$_2$CH$_2$CH$_2$O		12a	12b

Scheme 1

(X = I, **1b**; Br, **2b**; Cl, **3b**; see Scheme 1). The direct formation of the 17-electron systems is unexpected and we cannot exclude the operation of adventitious oxidants in the reaction mixture. However the reactions are reproducible and we have consistently observed[8] this outcome in the reaction of LiCl with both [Mo(OCMe$_2$)(dppe)(η-C$_7$H$_7$)][PF$_6$] and [Mo(NCMe)(dppe)(η-C$_7$H$_7$)][PF$_6$] although in some other cases, mixtures of neutral 18-electron and cationic 17-electron complexes have been isolated as reaction products.[11] The neutral 18-electron complexes [MoX(dppe)(η-C$_7$H$_7$)] (X = I, **1a**; Br, **2a**; Cl, **3a**) have been reported previously[6] and, as we have demonstrated for the chloride derivative, can be conveniently prepared by cobaltocene reduction of the 17-electron radicals in toluene.[8] In addition to the known halide complexes (X = I, Br, Cl), two new systems were prepared. The novel fluoride derivative [MoF-(dppe)(η-C$_7$H$_7$)][PF$_6$] **4b** was isolated as a green solid from the reaction of [Mo(OCMe$_2$)(dppe)(η-C$_7$H$_7$)][PF$_6$] with anhydrous LiF and the ring-substituted complex [MoCl(dppe)(η-C$_7$H$_6$-Me)][PF$_6$] **5b** was prepared starting from [Mo(η-C$_6$H$_5$Me)-(η-C$_7$H$_6$Me)][PF$_6$].[12] Attempts to reduce **4b** to its neutral 18-electron counterpart were unsuccessful and reduction of ring-substituted **5b** was not pursued.

The pseudo-halide ligands X = NCO, NCS, C≡N were also introduced to the molybdenum centre by direct reaction of X$^-$ with [Mo(OCMe$_2$)(dppe)(η-C$_7$H$_7$)][PF$_6$]. Treatment of an acetone solution of [Mo(OCMe$_2$)(dppe)(η-C$_7$H$_7$)][PF$_6$] with excess KNCO resulted in the formation of the neutral 18-electron cyanate complex [Mo(NCO)(dppe)(η-C$_7$H$_7$)] **6a** which was isolated as a green solid. However an analogous reaction with excess KNCS gave a product mixture of [Mo(NCS)(dppe)-(η-C$_7$H$_7$)] **7a** and [Mo(NCS)(dppe)(η-C$_7$H$_7$)][PF$_6$] **7b** together with a further unidentified species. As described in the Experimental section, the 17-electron radical **7b** was successfully separated from the product mixture and subsequently reduced to neutral **7a** by reaction with cobaltocene in toluene. The 18-electron cyanide complex [Mo(CN)(dppe)(η-C$_7$H$_7$)] **8a** was isolated as a pink solid following purification by column chromatography from the reaction of KCN with [Mo(OCMe$_2$)-

(dppe)(η-C$_7$H$_7$)][PF$_6$] in acetone–methanol (1:10) and the carbon-13 labelled analogue [Mo(^{13}CN)(dppe)(η-C$_7$H$_7$)] **9a** was prepared by an identical procedure but employing K^{13}CN as a reagent. Cyclic voltammetric investigations (see below) revealed that each of **6a**, **8a** and **9a** undergo reversible one-electron oxidations to the corresponding 17-electron radical cations at potentials accessible to the ferrocenium ion as a chemical oxidant and accordingly the radicals [MoX(dppe)(η-C$_7$H$_7$)]-[PF$_6$] (X = NCO, **6b**; X = CN, **8b**) were isolated by respective one-electron oxidation with [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] in CH$_2$Cl$_2$. The synthesis and characterisation of the remaining type 1 complexes discussed in this paper, [MoMe(dppe)(η-C$_7$H$_7$)] and [Mo(C≡CPh)(dppe)(η-C$_7$H$_7$)] have been described previously.[7,9]

Type 2 complexes

In these systems, X is a neutral, 2-electron ligand resulting in 18-electron complexes of formulation [MoX(dppe)(η-C$_7$H$_7$)]$^+$ and 17-electron radical dications of formulation [MoX(dppe)-(η-C$_7$H$_7$)]$^{2+}$. The principal derivatives for which both members of the redox pair are isolable are: X = NCMe,[8] CNMe and CCH$_2$CH$_2$CH$_2$O (oxacyclopentylidene). Other derivatives (X = C=C(Me)Bu^t,[11] CO[6]) were investigated by cyclic voltammetry but their 17-electron radical dications were not isolable.

The red-pink isocyanide complex [Mo(CNMe)(dppe)-(η-C$_7$H$_7$)][BF$_4$] **10a** was prepared by methylation of the cyanide complex **8a** by reaction with [Me$_3$O][BF$_4$] in CH$_2$Cl$_2$ and the carbon-13 labelled analogue [Mo(^{13}CNMe)(dppe)(η-C$_7$H$_7$)]-[BF$_4$] **11a** was obtained from **9a** by an identical procedure. The radical dication [Mo(CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$]$_2$ **10b** was successfully isolated following oxidation with [NO][BF$_4$] or [Fe(η-C$_5$H$_5$){η-C$_5$H$_4$(C(O)CH$_3$)}][BF$_4$] in CH$_2$Cl$_2$ but proved to be sensitive in solution with respect to reduction back to 18-electron **10a**. The synthesis of the cyclic oxacarbene complex [Mo(CCH$_2$CH$_2$CH$_2$O)(dppe)(η-C$_7$H$_7$)][PF$_6$] **12a** by reaction of [Mo(OCMe$_2$)(dppe)(η-C$_7$H$_7$)][PF$_6$] with HC≡CCH$_2$CH$_2$OH in refluxing acetone has been described previously.[13] Cyclic voltammetric studies revealed that **12a** undergoes a reversible one-electron oxidation and chemical oxidation with [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] led to isolation of [Mo(CCH$_2$CH$_2$CH$_2$O)(dppe)-(η-C$_7$H$_7$)][PF$_6$]$_2$ **12b** as a yellow-orange solid. Our attempts to prepare stable, isolable phosphine complexes of the type [Mo(PR$_3$)(dppe)(η-C$_7$H$_7$)][PF$_6$] were unsuccessful, probably due to the restrictions of the relatively crowded metal centre of the Mo(dppe)(η-C$_7$H$_7$) auxiliary.[14] However a related tris-phosphine substituted system [Mo(triphos)(η-C$_7$H$_7$)][PF$_6$] **13a** was realised from the reaction of [Mo(η-C$_6$H$_5$Me)(η-C$_7$H$_7$)]-[PF$_6$] with 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) in refluxing acetone. Complex **13a** undergoes a reversible one-electron oxidation in CH$_2$Cl$_2$ and the radical dication [Mo-(triphos)(η-C$_7$H$_7$)][PF$_6$]$_2$ **13b** was successfully isolated from treatment of **13a** with [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] although the reaction was incomplete due to unfavourable redox potentials (see below).

Spectroscopic studies (excluding EPR work)

Details of the characterisation of the new complexes described in this work are presented in Table 1 (microanalytical, IR and mass spectroscopic data) and Table 2 (^{1}H and ^{13}C{^{1}H} NMR spectroscopic data). Several of the ligands X include a group with an infrared active v(C≡N) stretch and two points of interest arise from the infrared data. First, examination of the pairs of natural isotopic abundance carbon and carbon-13 labelled cyanide and isocyanide complexes (**8a**, **9a**) and (**10a**, **11a**) confirms the expected shift to lower wavenumber by incorporation of carbon-13. In the case of the cyanide complexes **8a** and **9a**, v(C≡N) for the carbon-13 labelled complex **9a** can be predicted to within one wavenumber based on v(C≡N) for **8a** and the application of a reduced mass calculation.

Table 1 Microanalytical, infrared and mass spectroscopic data

Complex	Analysis[a] (%)			Infrared[b] $\nu(C\equiv N)/cm^{-1}$	Mass spectral data[c]
	C	H	N		
4b [MoF(dppe)(η-C$_7$H$_7$)][PF$_6$]	53.0 (52.9)	4.1 (4.1)			606 (M^+), 587 ([M − F]$^+$)
5b [MoCl(dppe)(η-C$_7$H$_6$Me)][PF$_6$]	52.5 (52.3)	4.3 (4.2)			637 (M^+), 602 ([M − Cl]$^+$)
6a [Mo(NCO)(dppe)(η-C$_7$H$_7$)]	65.4 (65.1)	5.2 (4.9)	2.3 (2.2)	2225	629 (M^+), 587 ([M − NCO]$^+$)
6b [Mo(NCO)(dppe)(η-C$_7$H$_7$)][PF$_6$]	53.2 (52.9)	4.0 (4.0)	1.8 (1.8)	2217	629 (M^+), 587 ([M − NCO]$^+$)
7a [Mo(NCS)(dppe)(η-C$_7$H$_7$)]	63.4 (63.5)	4.8 (4.8)	2.1 (2.2)	2084	645 (M^+), 587 ([M − NCS]$^+$)
7b [Mo(NCS)(dppe)(η-C$_7$H$_7$)][PF$_6$]	52.1 (51.8)	4.2 (3.9)	1.5 (1.8)	2030	645 (M^+), 587 ([M − NCS]$^+$)
8a [Mo(CN)(dppe)(η-C$_7$H$_7$)]	66.6 (66.8)	5.3 (5.1)	2.0 (2.3)	2073	613 (M^+), 587 ([M − CN]$^+$)^d
8b [Mo(CN)(dppe)(η-C$_7$H$_7$)][PF$_6$]	53.4 (54.0)	4.0 (4.1)	1.7 (1.9)	2103	613 (M^+), 587 ([M − CN]$^+$)
9a [Mo(^{13}CN)(dppe)(η-C$_7$H$_7$)]	66.8 (66.8)	5.4 (5.1)	2.1 (2.3)	2027	614 (M^+), 587 ([M − ^{13}CN]$^+$)^d
10a [Mo(CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$]	59.1 (58.9)	4.8 (4.8)	1.9 (2.0)	2147	628 (M^+), 587 ([M − CNMe]$^+$)
10b [Mo(CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$]$_2$	52.5 (52.5)	4.3 (4.3)	1.7 (1.8)	2228	628 (M^+), 587 ([M − CNMe]$^+$)
11a [Mo(^{13}CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$]	58.6 (59.0)	4.7 (4.8)	1.9 (2.0)	2108	629(M^+)^d
12b [Mo($\overline{CCH_2CH_2CH_2O}$)(dppe)($\eta$-C$_7H_7$)][PF$_6$]$_2$	46.3 (47.0)	4.0 (3.9)			657 (M^+), 587 ([M − $\overline{CCH_2CH_2CH_2O}$]$^+$)
13a [Mo(triphos)(η-C$_7$H$_7$)][PF$_6$]	60.2 (60.3)	5.0 (4.8)			813 (M^+)^d
13b [Mo(triphos)(η-C$_7$H$_7$)][PF$_6$]$_2$	52.3 (52.3)	4.7 (4.2)			406 (M^{2+})^d

^{a} Calculated values in parentheses. ^{b} Solution spectra in CH$_2$Cl$_2$. ^{c} FAB mass spectra unless stated otherwise, m/z values based on ^{98}Mo. ^{d} Electrospray mass spectrum.

Table 2 ^{1}H and selected ^{13}C{^{1}H} NMR data for [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ ($z = 0$ or 1) and [Mo(triphos)(η-C$_7$H$_7$)]$^{+ a}$

Complex	^{1}H NMR data				^{13}C NMR data			
			dppe/triphos				dppe	
	X	C$_7$H$_7$	Ph	CH$_2$	X	C$_7$H$_7$	Ph	CH$_2$
6a^b		4.79, t, (1.8)	7.71, m, 7.43, m, 7.29, m	2.06 (br)		87.2	138.2–128.4	25.8, m
7a^b		4.82, t, (1.8)	7.69, m, 7.46, m, 7.29, m	2.01 (br)	143.3, NCS	87.3	138.2–128.5	25.9, m
8a^b		4.84, t, (2.1)	7.73, m, 7.39, m, 7.28, m	2.48, m, 2.06 m	157.6, t, {20}, CN	87.4	139.9–127.9	26.9, m
9a^b		4.82, dt, (2.1), [0.7]	7.70, m, 7.37, m, 7.27, m	2.44, m, 2.04 m	157.8, t, {20}, CN	87.4	139.9–128.1	26.9, m
10a	2.50, t, (1.9) CNCH_3	5.01, t, (2.2)	7.47, m, 7.27, m	2.42 (br)	163.7, (br) CNMe, 29.4, CNMe	89.1	137.6–127.7	27.1, m
11a^c	2.40, dt, [3.7], (1.9) CNCH_3	5.02	7.53, m, 7.28, m	2.49, m	164.9, {18} CNMe, 29.1, CNMe	89.0	137.1–129.0	27.0, m
13a^d		5.50, q, (2.2)	7.37, m, 7.29, m, 7.23, m	2.49, m, CH$_2$, 2.05, q (2.2) Me				

^{a} 300 MHz ^{1}H NMR spectra, 75 MHz ^{13}C NMR spectra; all signals singlets unless stated otherwise, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants in Hz indicated in parentheses: ( ) indicates J(P–H), [ ] indicates J(^{13}C–H), { } indicates J(P–C). Chemical shifts downfield from SiMe$_4$, spectra recorded in CDCl$_3$ unless stated otherwise. ^{b} Trace quantity of CoCp$_2$ added to NMR sample. ^{c} In CD$_2$Cl$_2$. ^{d} In acetone-d$_6$. ^{31}P{^{1}H} NMR (acetone-d$_6$), (122 MHz), δ 20.1.

Table 3 Shift in ν(CN) or ν(CC) ($\Delta\nu$) resulting from one-electron oxidation of 18-electron [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ ($z = 0$ or 1) to the corresponding 17-electron radicals^a

X	z	$\nu(C\equiv C)/(C\equiv N)$ (cm^{-1}) 18-electron complex	$\nu(C\equiv C)/(C\equiv N)$ (cm^{-1}) 17-electron complex	$\Delta\nu$ (cm^{-1})
CNMe	1	2147	2228	81
^{13}CNMe	1	2108	2188	80
CN	0	2073	2103	30
^{13}CN	0	2027	2058	31
NCMe^b	1	2261	2279	18
NCO	0	2225	2217	−8
C≡CPh^c	0	2045	2032	−13
C≡CFc^d	0	2052	2002	−50
NCS	0	2084	2030	−54

^{a} All spectra recorded in CH$_2$Cl$_2$. ^{b} Data from ref. 8. ^{c} Data from ref. 7. ^{d} Data from ref. 10.

The data in Table 3 present the effect of one-electron oxidation upon infrared active $\nu(C\equiv N)$ or $\nu(C\equiv C)$ stretches in a series of redox pairs based on the Mo(dppe)(η-C$_7$H$_7$) auxiliary

from this and previous work.[7,8,10] It is generally accepted that ligands (X≡Y) such as CO, which act as good π-acceptors exhibit an increase in stretching frequency resulting from metal-based one-electron oxidation processes.[15] This may be attributed to a reduced component of π-back donation to the ligand π^* orbitals resulting in strengthening of the (X≡Y) triple bond. Typically in the case of the CO ligand, ν(CO) increases by *ca.* 100 cm^{-1} ($\Delta\nu$) following a metal-based one-electron oxidation. Inspection of Table 3 reveals that both the isocyanide (CNMe) and cyanide ligands comply with the expectations of operation as good π-acceptor ligands. By contrast we,[7] and more recently, others,[16] have observed that alkynyl ligands exhibit a negative $\Delta\nu$ following a metal-based one-electron oxidation and, in the more extreme cases (generally involving an alkynyl bridge linking two metal centres) the decrease in ν(C≡C) has been attributed to an allenylidene resonance form[17] (M=C=C=Fc in the case of ferrocenyl systems). It is in this context that the results for X = NCO or NCS (complexes **6a**, **6b** and **7a**, **7b**) are of especial interest. In the case of the NCO ligand, ν(C≡N) is not significantly affected by the redox state of the metal centre but by contrast one-electron oxidation of the analogous NCS complex **7a** results in a large decrease in ν(C≡N) (-54 cm^{-1}). We attribute this to a significant contribution from the resonance

form M=N⁺=C=S in the oxidised species **7b**. Inspection of the literature reveals a similar large and negative Δv (-44 cm^{-1}) for the related redox pair [Fe(NCS)(dppe)(η-C$_5$H$_5$)]$^{z+}$ ($z = 0$, v(C≡N) (KBr) 2084 cm^{-1};[18] $z = 1$, v(C≡N) (KBr) 2040 cm^{-1}).

Hydrogen-1 and ^{13}C{^{1}H} NMR data are presented in Table 2; as we have discussed previously, well resolved NMR data for easily oxidised type 1 complexes (in the case of this work **6a**, **7a**, **8a** and **9a**) are best obtained by the addition of a trace quantity of the one-electron reductant [Co(η-C$_5$H$_5$)$_2$] to the NMR sample.[19,20] Inspection of Table 2 reveals a fairly standard data set for the Mo(dppe)(η-C$_7$H$_7$) auxiliary with the cyclohepta-trienyl ring resonance in the ^{1}H NMR spectra appearing as a triplet signal due to a coupling of *ca.* 2 Hz to the two equivalent phosphorus atoms of the dppe ligand. The triphos complex **13a** exhibited a quartet pattern for the C$_7$H$_7$ resonance and this, together with the observation of only a singlet resonance in the ^{31}P{^{1}H} NMR spectrum for the three phosphorus donor atoms of the triphos ligand supports the formulation of **13a** as a complex with a tridentate triphos ligand. The principal features of interest in the NMR spectra arise from the ligands (X = CN, CNMe) and the effects of carbon-13 labelling. In the ^{13}C{^{1}H} NMR spectrum of [Mo(CN)(dppe)(η-C$_7$H$_7$)], **8a**, the cyanide carbon is observed as a weak triplet signal with J(P–C) 20 Hz and this assignment is definitively confirmed in the ^{13}C{^{1}H} spectrum of [Mo(^{13}CN)(dppe)(η-C$_7$H$_7$)], **9a** for which the cyanide carbon was observed as a high intensity resonance. A further feature of **9a**, evident in the ^{1}H NMR spectrum and not observed for **8a**, is a small coupling (0.7 Hz) to the C$_7$H$_7$ protons superimposed upon the triplet pattern due to J(P–H) coupling. We believe that this additional feature may be attributed to the observation of J(^{13}C–H) coupling. The isocyanide carbon of [Mo(CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$], **10a** was observable only as a broad resonance in the ^{13}C{^{1}H} NMR spectrum but again the carbon-13 labelled sample **11a** provided well resolved and definitive data. In the ^{1}H NMR spectra the two samples **10a** and **11a** differed principally in the pattern of the isocyanide methyl resonance. In common with the isomeric acetonitrile derivative,[8] both present long range ^5J(P–H) coupling but in addition the carbon-13 labelled sample **11a** exhibits ^3J(^{13}C–H) coupling between the isocyanide carbon and the methyl protons.

Electrochemical investigations

Our previous synthetic and electrochemical investigations have established that the Mo(dppe)(η-C$_7$H$_7$) auxiliary supports reversible one-electron oxidation processes for a wide range of ligands X. The majority of the 17-electron radicals [MoX(dppe)-(η-C$_7$H$_7$)]$^{z+}$ ($z = 1$ or 2) are stable, not only on the electrochemical timescale, but also on a timescale long enough to allow chemical generation, isolation and subsequent characterisation as detailed in the synthetic studies above. We now present a compilation of cyclic voltammetric data for an extended series of complexes including the new systems described in this work and those reported previously.

The initial scans in the cyclic voltammograms of each of the 18-electron complexes [MoX(dppe)(η-C$_7$H$_7$)] (X = Me, C≡CPh, NCO, NCS, CN), [MoX(dppe)(η-C$_7$H$_7$)]$^+$ (X = NCMe, CNMe, $\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$, C=C(Me)Bu^t) and [Mo(triphos)(η-C$_7$H$_7$)]$^+$ in CH$_2$Cl$_2$ are all characterised by reversible one-electron oxidation processes. The electron-transfer processes are diffusion controlled ($i_p^{ox}/v^{\frac{1}{2}}$ is constant for scan rates v = 50–500 mV s^{-1}) and chemically reversible with the ratio of cathodic to anodic currents being unity over the same scan range. The observed separation between the cathodic and anodic peak potentials compared well with that measured for the ferrocene–ferrocenium couple measured under identical conditions. The 17-electron radical cations [MoX(dppe)(η-C$_7$H$_7$)]$^+$ (X = I, Br, Cl, F, NCO, NCS, CN), [MoCl(dppe)(η-C$_7$H$_6$Me)][PF$_6$], [MoX(dppe)(η-C$_7$H$_7$)]$^{2+}$ (X = CNMe, $\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$) and

Table 4 Cyclic voltammetric data for [MoX(dppe)(η-C$_7$H$_6$R)]$^{z+}$ and [Mo(triphos)(η-C$_7$H$_7$)]$^{z+}$

X	z	Complex	$E°$/V	Ref.
Me	0		−0.37	9
C≡CPh	0		−0.15	7
I	1	**1b**	0.04	This work
Br	1	**2b**	0.00	This work
Cl	1	**3b**	−0.05	7
F	1	**4b**	−0.28	This work
Cl (R = Me)	1	**5b**	−0.09	This work
NCO	0	**6a**	−0.04	This work
NCO	1	**6b**	−0.04	This work
NCS	0	**7a**	0.11	This work
NCS	1	**7b**	0.11	This work
CN	0	**8a**	0.21	This work
CN	1	**8b**	0.20	This work
^{13}CN	0	**9a**	0.21	This work
NCMe	1		0.51	8
CNMe	1	**10a**	0.70	This work
CNMe	2	**10b**	0.70	This work
^{13}CNMe	1	**11a**	0.70	This work
$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$	1	**12a**	0.57	This work
$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$	2	**12b**	0.56	This work
C=C(Me)Bu^t	1		1.05	This work
CO	1		1.23	This work
triphos	1	**13a**	0.64	This work
triphos	2	**13b**	0.64	This work

R = H unless stated otherwise. $E°$ values (in V) recorded in CH$_2$Cl$_2$ with 0.2 M [NBu$^n_4$][BF$_4$] as supporting electrolyte at a carbon working electrode relative to SCE and standardised with respect to the ferrocene–ferrocenium couple as internal calibrant for which $E°$ = 0.56 V under these conditions.

[Mo(triphos)(η-C$_7$H$_7$)][PF$_6$]$_2$ were investigated as one-electron reduction processes and again the criteria for diffusion control and chemical reversibility were fully satisfied. The designation of the electron-transfer processes observed in the cyclic voltammetry as one-electron changes is, in many cases, fully established by the synthetic studies and the isolation and characterisation of both members of the redox pair for each separate identity of X.

A compilation of data for the formal reduction potentials $E°$ (*vs.* SCE) for each of the complexes considered is presented in Table 4. The halide complexes [MoX(dppe)(η-C$_7$H$_7$)]$^+$ represent only the second example in which reversible electrode potentials are available for a complete organometallic L$_n$MX series (X = I, Br, Cl or F). Our results complement the work of Tilset and co-workers[21] on the complexes [FeX(dppe)(η-C$_5$-Me$_5$)]$^{z+}$ ($z = 0$, X = I, Br, Cl; $z = 1$, X = F). For both series [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ and [FeX(dppe)(η-C$_5$Me$_5$)]$^{z+}$ there is a small but consistent shift of $E°$ to more negative values from X = I to X = Cl, probably associated with the enhanced π-donor capacity of chloride with respect to iodide. This trend continues with the fluoride derivatives but here there is a much larger negative shift in $E°$ (*ca.* 0.2 V) than expected from the trend for the I, Br and Cl analogues. This discontinuity in the trend has been attributed to the ability of the fluoride ligand to act as an exceptionally good donor.[21] Comparison of $E°$ data for the chloride complexes **3b** and **5b** permits an estimation of the effect of methyl substitution at the cycloheptatrienyl ring and, in accord with related studies,[22] a shift in $E°$ to negative potential by approximately 40 mV for substitution of one hydrogen by a methyl substituent is observed.

Type 2 complexes for which the formulation of the 18-electron systems is [MoX(dppe)(η-C$_7$H$_7$)]$^+$ (X = NCMe, CNMe, $\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$, C=C(Me)Bu^t, CO) are clearly more difficult to oxidise to their 17-electron radicals than their type 1 counterparts as evidenced by the $E°$ values in Table 4. Nevertheless both [Mo(NCMe)(dppe)(η-C$_7$H$_7$)][PF$_6$]$_2$[8] and the carbene complex [Mo($\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$)(dppe)($\eta$-C$_7H_7$)][PF$_6$]$_2$ **12b**

Table 5 Isotropic EPR parameters obtained from the CH_2Cl_2 fluid solution X-band spectra of $[MoX(dppe)(\eta\text{-}C_7H_6R)]^{z+}$ at 243 K [a]

Complex							
No.	X	g_{iso}	$A_{iso}(Mo)$	$a_{iso}(^{31}P)$	$a_{iso}(^{1}H)$	$a_{iso}(X)$	% s-orbital character
	Me	2.002	38.0	24.6	4.7(7)	6.8 (3, ^{1}H)	1.34
	C≡CPh	1.995	34.8	22.7	4.3(7)	—	—
1b	I [b]	2.055					
2b	Br	2.014	39.0	23.2	4.2(7)	9.7 (^{79,81}Br)	0.08
3b	Cl	1.991	40.0	23.2	4.6(7)	2.1 (^{35,37}Cl)	0.10
4b	F	1.978	41.5	22.7	4.9(7)	28.0 (^{19}F)	0.15
5b	Cl (R = Me)	1.989	40.0	23.2	5.0(6) 5.3(3)		
6b	NCO	1.985	40.0	22.5	4.9(7)	1.5 (^{14}N)	0.23
7b	NCS	1.985	38.0	22.2	4.3(7)	2.2 (^{14}N)	0.34
8b	^{12}CN	1.996	34.0	23.2	4.7(7)	—	—
9b	^{13}CN	1.996	34.0	23.2	4.7(7)	9.4 (^{13}C)	0.70
	NCMe [c]	1.990	41.0	22.7	4.5(7)	3.5–3.1 (3, ^{1}H) 1.0–0.0 (^{14}N)	
10b	^{12}CNMe [c]	1.997	35.0	22.8	4.3(7)	—	—
11b	^{13}CNMe [c]	1.997	35.0	22.8	4.3(7)	6.0 (^{13}C)	0.45
12b	oxacarbene [c]	1.998	35.5	24.0	4.5(7)	—	—
13b	triphos [c]	1.998	38.0	23.5	4.5(7)	[d]	

[a] R = H, $z = 1$ unless stated otherwise. All hyperfine splitting constants are in G (1 G = 10^{-4} T), the numbers in parentheses for $a_{iso}(^{1}H)$ are the numbers of equivalent protons. Estimated errors: g values ±0.001, $A_{iso}(Mo)$, ±0.5 G, a_{iso}(other), ±0.1 G. Oxacarbene = $\overline{CCH_2CH_2CH_2O}$, triphos replaces (dppe + X). [b] Hyperfine splittings not resolved for X = I. [c] $z = 2$. [d] All phosphorus atoms in the ligand give the same a_{iso}.

could be obtained by ferrocenium oxidation of the 18-electron precursors. The $E°$ value for the isocyanide derivative [Mo(CNMe)(dppe)(η-C_7H_7)][PF$_6$] **10a** is too positive for the radical dication to be accessible by ferrocenium oxidation but use of either [NO][BF$_4$] or the acetylferrocenium ion [$E°$ (CH$_2$Cl$_2$) 0.81 V under the standard conditions used in this work] effected a synthesis of the 17-electron radical **10b**. Complexes **10a/10b** and **12a/12b** were confirmed as redox pairs by complementary cyclic voltammetric data. Finally the complexes [Mo{C=C(Me)-Bu^t}(dppe)(η-C_7H_7)][PF$_6$] and [Mo(CO)(dppe)(η-C_7H_7)][PF$_6$] incorporate very efficient π-acceptor vinylidene and carbonyl ligands and this is reflected in the large and positive $E°$ values (note that the disubstituted vinylidene ligand was selected to avoid complications arising from redox-induced C–H bond fission in complexes with mono-substituted vinylidene ligands of the type C=C(H)R).[23] The electrochemical data for the vinylidene complex [Mo{C=C(Me)Bu^t}(dppe)(η-C_7H_7)][PF$_6$] fully satisfy the criteria for chemical and electrochemical reversibility but data for the carbonyl complex [Mo(CO)(dppe)(η-C_7H_7)]-[PF$_6$] reveal a steady decline in the ratio i_p^c/i_p^a as the scan rate is decreased (i_p^c/i_p^a = 0.9 for a scan rate of 50 mV s^{-1}). Attempts to generate and observe the 17-electron radical derived from [Mo{C=C(Me)Bu^t}(dppe)(η-C_7H_7)][PF$_6$] were unsuccessful. However comparison of $E°$ data for the oxacarbene system **12a** and the vinylidene analogue [Mo{C=C(Me)Bu^t}(dppe)-(η-C_7H_7)][PF$_6$] suggests that the vinylidene ligand is a much more efficient π-acceptor ligand.

Although not strictly a member of the series [MoX(dppe)(η-C_7H_7)]$^+$, the triphos complex **13a** gives an indication of the position of complexes of the type [Mo(PR$_3$)(dppe)(η-C_7H_7)]$^+$ within the redox series. The measured $E°$ value for **13a** (0.64 V) is to positive potential of $E°$ for [Mo(NCMe)(dppe)(η-C_7H_7)]$^+$ and also of the FeCp$_2$–FeCp$_2^+$ couple but oxidation of **13a** with a small excess of the ferrocenium ion did afford low yields of the 17-electron radical **13b** in an incomplete reaction. We estimate that, taking $\Delta E°$ = −0.08 V and for equimolar quantities of reagents, the redox reaction might be expected[24] to generate **13b** in 20% yield.

EPR and ENDOR Investigations

EPR Spectroscopy. Fluid solution EPR investigations on selected complexes [MoX(dppe)(η-C_7H_7)]$^+$ (X = I, Br, Cl,[6] C≡CPh,[7] Me[9]) and [Mo(NCMe)(dppe)(η-C_7H_7)]$^{2+}$[8] have been reported previously. However in the current work, significant

advances were achieved both in the quality of the experimental data and in its interpretation through the use of variable temperature studies, second derivative spectra and the application of simulation techniques. Fluid solution spectra in CH$_2$Cl$_2$ were obtained at 243 K on the radicals **1b** to **13b**, [MoX(dppe)-(η-C_7H_7)]$^+$ (X = Me or C≡CPh) and [Mo(NCMe)(dppe)-(η-C_7H_7)]$^{2+}$ at X-band frequency as second derivative spectra. Optimum resolution was in all cases realised at around 243 K and this temperature was used as a standard for the spectral investigations. With the exception of the iodo derivative **1b** (for which no hyperfine splittings could be resolved), all the examples investigated gave well resolved spectra characteristic of a molybdenum species split by ligand hyperfine interactions. The spectra of the non ring-substituted dppe complexes were simulated satisfactorily by incorporating hyperfine splitting with two equivalent phosphorus atoms, seven equivalent protons plus an additional hyperfine splitting from the ligand X, where this contains nuclei with non-zero nuclear spin. The parameters obtained from spectral simulation are presented in Table 5 and the experimental and simulated spectra for each of three examples (X = CN, NCS, F) which illustrate the effect of increasing the magnitude of $a_{iso}(X)$ on the spectral pattern are shown in Fig. 1 to 3. The molybdenum hyperfine splittings given in Table 5 were derived from the wings of the first derivative spectra and a typical example (X = NCS) together with the simulation is shown in Fig. 4.

In complexes other than ring-substituted **5b**, the proton splitting required to simulate the fluid solution X-band spectra is attributed to seven equivalent protons on the cycloheptatrienyl ligand. The magnitude of this splitting is in the range 4.2 to 4.9 G and is comparable to that (4.6 G) previously reported[19] for [Mo(CNBu^t)(bipy)(η-C_7H_7)][PF$_6$]$_2$. There seems to be no obvious relationship between the magnitude of $a(^{1}H)$ and the identity of X. To establish further the assignment of hyperfine coupling to the protons of the cycloheptatrienyl ring, the ring-substituted derivative **5b** was investigated. The only parameters which would reproduce the experimental spectrum required six equivalent ring protons plus a separate set of three equivalent protons. The three equivalent protons are attributed to the ring methyl substituent and spectral simulation reveals that the a_{iso} for these is larger than that for the six ring protons. Further observations of note are the trend in g values along the series X = I, Br, Cl, F (**1b** to **4b**) and the observation of coupling to ^{14}N for X = NCO (**6b**), NCS (**7b**) supporting the view that these ligands are N-bonded. However the hyperfine coupling to ^{14}N
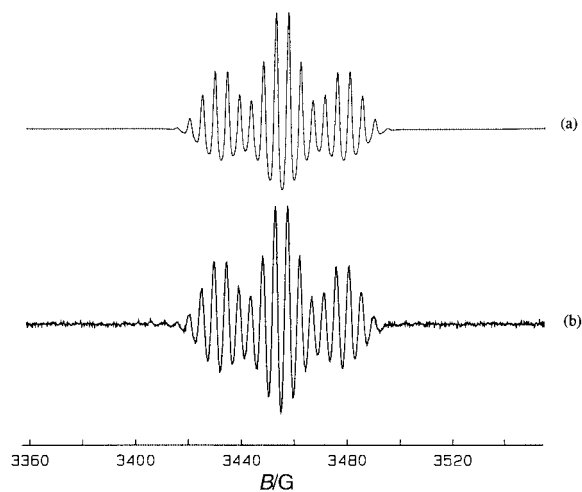
Fig. 1 Fluid solution (CH$_2$Cl$_2$), second derivative X-band spectrum of [Mo(CN)(dppe)(η-C$_7$H$_7$)][PF$_6$], **8b**, $v = 9.633$ GHz. (a) Simulated spectrum using the parameters in Table 5 with Lorentzian lineshape and peak to peak width 4.0 G; (b) experimental spectrum.
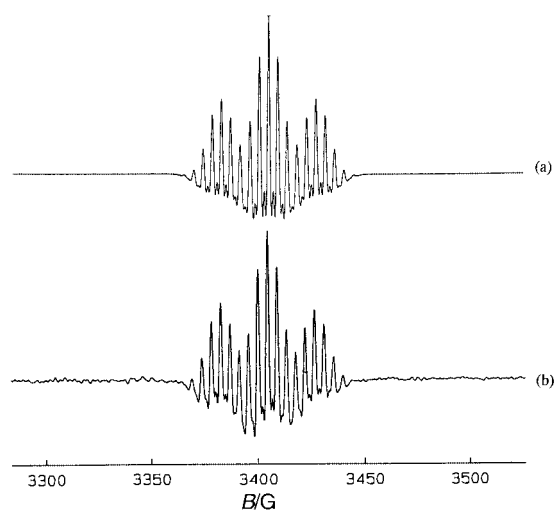

Fig. 2 Fluid solution (CH$_2$Cl$_2$), second derivative X-band spectrum of [Mo(NCS)(dppe)(η-C$_7$H$_7$)][PF$_6$], **7b**, $v = 9.452$ GHz. (a) Simulated spectrum using the parameters in Table 5 with Lorentzian lineshape and peak to peak width 4.3 G; (b) experimental spectrum.

Fig. 3 Fluid solution (CH$_2$Cl$_2$), second derivative X-band spectrum of [MoF(dppe)(η-C$_7$H$_7$)][PF$_6$], **4b**, $v = 9.450$ GHz. (a) Simulated spectrum using the parameters in Table 5 with Lorentzian lineshape and peak to peak width 5.0 G; (b) experimental spectrum.

Fig. 4 Fluid solution (CH$_2$Cl$_2$), first derivative X-band spectrum of [Mo(NCS)(dppe)(η-C$_7$H$_7$)][PF$_6$], **7b**, $v = 9.399$ GHz. (a) Experimental spectrum; (b) simulated spectrum with the parameters in Table 5 plus peak to peak Lorentzian linewidth of 3.5 G.

in the acetonitrile derivative [Mo(NCMe)(dppe)(η-C$_7$H$_7$)]$^{2+}$ was less clearly defined with satisfactory simulations obtained for a range of values of a_{iso}(^{14}N) and a_{iso}(^{1}H) (from the acetonitrile methyl group) as detailed in Table 5. In the case of ligands X with a carbon donor atom possessing zero nuclear spin [complexes **8b**, **10b**, **12b** and [MoX(dppe)(η-C$_7$H$_7$)]$^+$ (X = Me, C≡CPh)], information derived from hyperfine coupling to X is not available (although coupling to the methyl protons of [MoMe(dppe)(η-C$_7$H$_7$)][PF$_6$] was observed). However our previous synthetic and spectroscopic studies on alkynyl derivatives of the Mo(dppe)(η-C$_7$H$_7$) auxiliary suggest some delocalisation of the unpaired electron onto the ligand X as evidenced by the ligand-centred dimerisation of the radical [Mo(C≡CPh)-(dppe)(η-C$_7$H$_7$)]$^+$ and spectroscopic studies on the alkynyl-bridged bimetallic [Mo(C≡CFc)(dppe)(η-C$_7$H$_7$)]$^+$. To provide a more effective spectroscopic probe for study of these observations with carbon-bonded X ligands, we synthesised and investigated the EPR spectra of the carbon-13 labelled complexes [Mo(^{13}CN)(dppe)(η-C$_7$H$_7$)]$^+$ and [Mo(^{13}CNMe)(dppe)-(η-C$_7$H$_7$)]$^{2+}$. The results in Table 5 reveal a marked difference in a_{iso}(X) between the cyanide and isocyanide derivatives but even so the magnitudes of the hyperfine couplings do not support significant delocalisation of the unpaired electron onto CN or CNMe ligands.
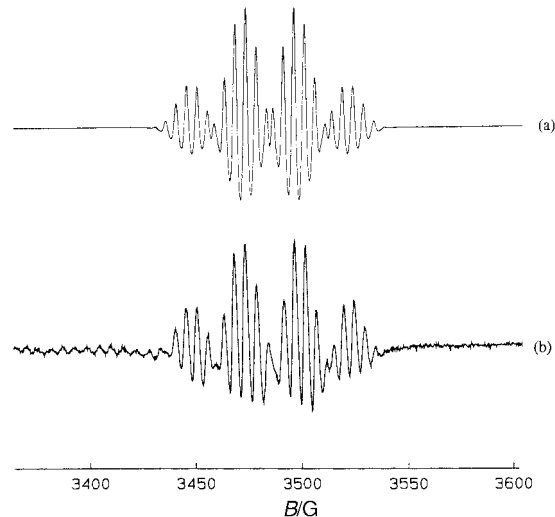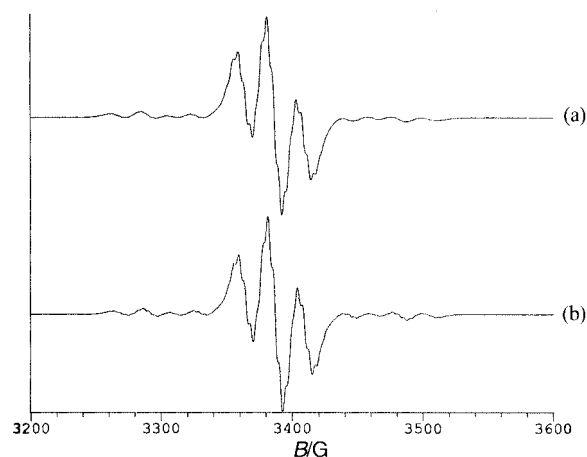
The X-band solution spectra of the radicals **1b**, **2b**, and **3b** may be compared with the related molybdenum systems [MoX$_2$(dppe)(η-C$_5$H$_5$)] (X = I, Br or Cl).[25] In the case of [MoX$_2$(dppe)(η-C$_5$H$_5$)] there is a corresponding trend in g values with variation in X and the magnitudes of a_{iso}(^{31}P) are also similar but typical A_{iso}(Mo) values are rather smaller than in the [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ system. Moreover coupling to the protons of the cyclopentadienyl ring was not observed and, only in one case (X = Br), was hyperfine coupling to the ligand X resolved.

In an attempt to obtain anisotropic parameters, frozen solution (CH$_2$Cl$_2$–toluene) spectra of the radical complexes [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ ($z = 1$ or 2) were obtained at both X- and Q-band frequencies. All of the X-band spectra were broad and poorly resolved, mainly due to small g-anisotropy and unresolved ligand hyperfine splittings and no attempt was made to interpret these spectra. The Q-band spectra were also broad but here there was evidence for g-value anisotropy. In a few cases numerical differentiation to give second derivative spectra, followed by Fourier transformation to remove the high frequency noise, afforded useable spectra which, although not fully resolved, were amenable to spectrum simulation; Fig. 5 illustrates a representative example. In these cases (**4b** to **8b**) the g values and anisotropic ^{31}P hyperfine split-

Table 6 Anisotropic EPR parameters for [MoX(dppe)(η-C$_7$H$_6$R)]$^+$ from frozen Q-band spectra[a]

Complex	g_1	g_2	g_3	$a_1(^{31}P)$	$a_2(^{31}P)$	$a_3(^{31}P)$	$\langle g \rangle$	$\langle a(^{31}P) \rangle$
4b[b]	2.008	1.988	1.955	22.0 (61.9)	22.0 (61.9)	25.0 (68.4)	1.984	23.0
5b (R = Me)	2.010	1.995	1.986	22.0 (61.9)	26.5 (73.9)	24.5 (68.1)	1.997	26.3
6b	2.006	1.992	1.966	21.5 (60.4)	23.5 (65.5)	24.2 (66.6)	1.988	23.1
7b	2.011	1.995	1.968	21.2 (59.7)	22.5 (62.8)	24.2 (66.6)	1.991	22.6
8b	2.004	1.999	1.993	25.0 (70.1)	25.0 (69.9)	25.0 (69.7)	1.999	25.0

[a] In CH$_2$Cl$_2$–toluene (10:1). Values of $a(^{31}P)$ are in G with values in parentheses in MHz. Estimated errors: g values ±0.001, $a(^{31}P)$ ±1.0 G.
[b] In addition $a_1(^{19}F)$ = 25.0 G, $a_2(^{19}F)$ = 84.0 G, $a_3(^{19}F)$ = 10.0 G.

Table 7 The ^{31}P hyperfine splitting parameters from the frozen solution (10 K) ENDOR spectra and the calculated percentage of ^{31}P s- and p-orbital character[a]

Complex	$a_1(^{31}P)$	$a_2(^{31}P)$	$a_3(^{31}P)$	$a_{iso}(^{31}P)$[b]	b	% s	% p	s:p
3b	62.4	62.4	71.6	65.5 (64.6)	3.10	0.54	0.85	1.6
4b	59.8	62.5	69.7	64.0 (62.8)	2.85	0.48	0.76	1.6
7b	59.3	59.3	67.8	62.1 (61.7)	2.80	0.47	0.76	1.6
8b	59.5	63.4	72.0	65.0 (64.8)	3.52	0.49	0.96	2.0

[a] In CH$_2$Cl$_2$–toluene (10:1). All values of $a(^{31}P)$ are in MHz. [b] Values in parentheses are from the X-band fluid solution spectra.
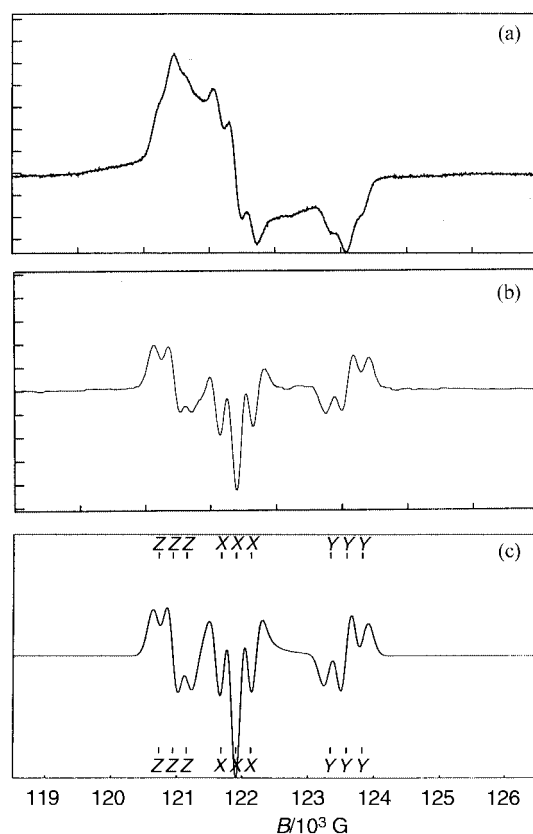

Fig. 5 Frozen solution (CH$_2$Cl$_2$–toluene) Q-band spectra of [Mo-(NCS)(dppe)(η-C$_7$H$_7$)][PF$_6$] **7b** at 120 K, ν = 34.040 GHz. (a) First derivative spectrum; (b) second derivative of (a) obtained by numerical differentiation followed by Fourier filtering; (c) simulation of (b) using the parameters in Table 6 plus a Gaussian lineshape function with peak to peak linewidths w_x = 18.0 G, $w_y = w_z$ = 20.0 G.

ting constants were obtained. In addition, for **4b** it was necessary to include anisotropic ^{19}F hyperfine splitting. Because of the incomplete resolution, the ligand hyperfine splitting parameters are subject to relatively large errors of approximately ±1 G. A summary of the observed g values and typical hyperfine parameters is given in Table 6. Despite the possible large errors, the derived ^{31}P hyperfine parameters are comparable with those obtained from ENDOR spectroscopy (see later and Table 7).

ENDOR Spectroscopy. In an attempt to obtain more precise ligand hyperfine parameters from the frozen solutions, ENDOR spectra at X-band frequencies were obtained on selected compounds (**3b**, **4b**, **7b** and **8b**). The low g-value anisotropy makes it impossible to perform orientation selection experiments[26,27] and therefore the field positions for the ENDOR experiments were chosen at the centre of each frozen solution spectrum. This means that the vast majority of molecular orientations were selected by the magnetic field. This in turn resulted in ENDOR spectra in which the observed features correspond to all principal values of the local hyperfine splitting tensors.

The main features in the experimental ENDOR spectra were attributed to ^1H and ^{31}P coupling to the unpaired electron. No signals assignable to $^{35,37}Cl$, ^{19}F or ^{14}N, where these elements were the donor atom of ligand X, were identified. The large number of protons in each complex, together with the use of protic solvents, made the interpretation of the proton ENDOR extremely difficult and this has not been attempted. The results therefore focus on the ^{31}P hyperfine splitting. A typical ^{31}P ENDOR spectrum is shown in Fig. 6 and the ^{31}P hyperfine parameters, obtained directly from the ENDOR spectra, are presented in Table 7. These anisotropic parameters are similar to the less accurate values obtained above from simulation of the frozen solution Q-band EPR spectra (see Table 6). In addition the average values calculated from the ENDOR results are comparable to those derived from the fluid solution X-band EPR spectra (Table 5).

The average values and the anisotropies in g, where they have been measured, taken together with the values of $A_{iso}(Mo)$ are compatible with a metal-based molecular orbital for the unpaired electron and this is reinforced by the small ligand hyperfine couplings observed. The anisotropies in g, and the values, are indicative of an orbital singlet state, with excited electronic states well separated from the ground state. An orbital singlet ground state is compatible with the formulations of the complexes which at best indicate C_s point symmetry. In this point symmetry all of the degeneracy of the metal d-orbitals will be removed.

Where they have been measured, there is good agreement between the values of $\langle a(^{31}P) \rangle$ from the frozen solution Q-band EPR spectra and from the ENDOR spectra and $a_{iso}(^{31}P)$ obtained from the fluid solution X-band EPR spectra. This indicates that there are no significant structural changes on cooling to 10 K. The ENDOR results reveal a small degree of anisotropy in $a(^{31}P)$, see Table 7. These results enable an
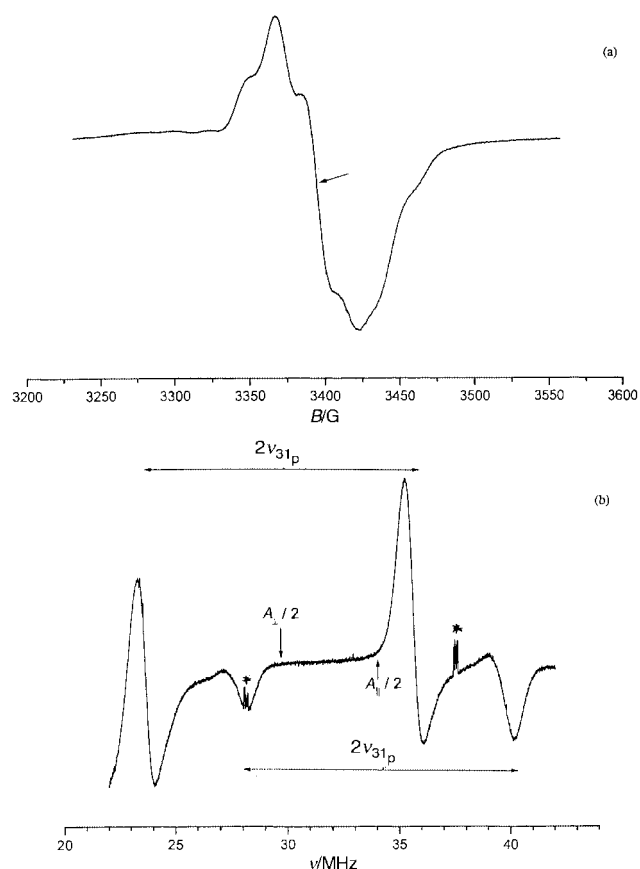
Fig. 6 ENDOR spectrum of [Mo(NCS)(dppe)(η-C$_7$H$_7$)][PF$_6$], **7b**, in CH$_2$Cl$_2$–toluene at 10 K and v = 9.465 GHz (a) CW EPR spectrum indicating the field position for the ENDOR experiment. (b) ^{31}P ENDOR spectrum (* indicates instrumental artifacts).

estimate of the s- and p-orbital character of phosphorus in the ground state molecular orbital to be made using the following equations:

$$a_{iso} = \tfrac{1}{3}[a_1 + a_2 + a_3]$$

$$b = \tfrac{1}{3}[a_1 - \tfrac{1}{2}(a_2 + a_3)]$$

(where a_1 is the a value with the largest magnitude).

$$\% \text{ s-orbital character} = a_{iso} \times 100/a_0$$

$$\% \text{ p-orbital character} = b \times 100/b_0$$

(where a_0 = 13306 MHz and b_0 = 366.8 MHz, the intrinsic splittings for an unpaired electron in a ^{31}P s- and p-orbital respectively[28]).

The results, which make no allowance for any dipolar contribution to the ligand hyperfine splitting from the unpaired electron on the metal, are given in Table 7. Within the approximations used, the s- and p-orbital character and the ratio of s:p orbital character from the phosphorus ligand are essentially independent of the nature of X. Using tabulated values[28,29] of a_0(X) and the experimental a_{iso}(X) in Table 5, the ns-orbital contribution from the ligand X to the ground state molecular orbital has also been calculated (see Table 5). As for the phosphorus ligand, these s-orbital contributions are small, further supporting the view that the unpaired electron in radical complexes of general formulation [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ (z = 1 or 2) occupies an essentially metal-based molecular orbital.

Conclusions

Syntheses of an extensive class of 17-electron radicals [MoX-

(dppe)(η-C$_7$H$_7$)]$^{z+}$ (z = 1 or 2) have been developed starting from the sandwich complex [Mo(η-C$_6$H$_5$Me)(η-C$_7$H$_7$)][PF$_6$]. The electrochemical, EPR and ENDOR spectroscopic properties of these complexes have been investigated. Cyclic voltammetric studies at a carbon electrode reveal reversible one-electron processes for the 18/17-electron couples with $E°$ values ranging from -0.37 (X = Me) to 1.23 V (X = CO) dependent on the identity of X. The X-band, CH$_2$Cl$_2$ solution EPR spectra of the 17-electron radicals [MoX(dppe)(η-C$_7$-H$_7$)]$^{z+}$ (z = 1 or 2) at 243 K are exceptionally well resolved and permit determination of hyperfine couplings to the two equivalent phosphorus atoms of the dppe ligand, the seven protons of the cycloheptatrienyl ring and exceptionally an additional hyperfine splitting from the ligand X where this contains nuclei with non-zero nuclear spin. X-Band and Q-band EPR investigations, supplemented by ENDOR studies lead to the conclusion that the unpaired electron in radical complexes of general formulation [MoX(dppe)(η-C$_7$H$_7$)]$^{z+}$ (z = 1 or 2) occupies an essentially metal-based molecular orbital.

Experimental

General procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complexes [Mo(η-C$_6$H$_5$Me)(η-C$_7$H$_7$)][PF$_6$],[30] [Mo-(η-C$_6$H$_5$Me)(η-C$_7$H$_6$Me)][PF$_6$],[12] [MoX(dppe)(η-C$_7$H$_7$)][PF$_6$] (X = Me,[9] C≡CPh,[7] $\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$,[13] C=C(Me)Bu^t,[11] CO[6]), [Mo(NCMe)(dppe)(η-C$_7$H$_7$)][PF$_6$]$_2$[8] and [Fe(η-C$_5$H$_5$){η-C$_5$H$_4$-(C(O)Me)}][BF$_4$][24] were prepared by published procedures. The chemicals dppe, 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos), K^{13}CN, [Me$_3$O][BF$_4$] and [NO][BF$_4$] were supplied by Aldrich Chemical Co. and alumina (Brockmann activity II) for column chromatography was purchased from Merck. 300 MHz ^{1}H and 75 MHz ^{13}C{^{1}H} NMR spectra were recorded on Bruker AC 300 E, Varian Associates XL 300 or Varian Unity Inova 300 spectrometers. Infrared spectra were obtained on a Perkin-Elmer FT 1710 spectrometer and mass spectra using Kratos Concept 1S (FAB spectra) or Micromass Platform II (electrospray spectra) instruments. X- (*ca.* 9.6 GHz) and Q-band (*ca.* 34 GHz) spectra on fluid and frozen solutions were recorded on a Bruker ESP 300E spectrometer. Spectrum manipulations were performed using the Bruker software supplied with the spectrometer. Spectral simulations were performed using in-house software which has been described elsewhere.[31] ENDOR spectra were recorded on frozen solutions at 10 K using a Bruker ESP 300E ESR/ENDOR spectrometer fitted with an ESP 360 DICE ENDOR unit and an ENI A300 RF amplifier operating at 8 dB and 12.5 kHz modulation frequency. Cyclic voltammetric studies were carried out, as described previously,[7] at a carbon working electrode (area 0.28 cm^2) using 0.2 M [NBu$^n_4$][BF$_4$] as supporting electrolyte in solutions purged with nitrogen gas. All potentials are referenced to an aqueous calomel electrode and, under these conditions, $E°$ for the couple [Fe(η-C$_5$H$_5$)$_2$]–[Fe(η-C$_5$H$_5$)$_2$]$^+$ is 0.56 V in CH$_2$Cl$_2$. Microanalyses were conducted by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparations

[MoCl(dppe)(η-C$_7$H$_7$)][PF$_6$] 3b. An acetone solution of [Mo(OCMe$_2$)(dppe)(η-C$_7$H$_7$)][PF$_6$] [prepared by overnight reflux of [Mo(η-C$_6$H$_5$Me)(η-C$_7$H$_7$)][PF$_6$] (0.917 g, 2.16 mmol) with dppe (0.864 g, 2.17 mmol) in acetone (40 cm^3)] was treated with anhydrous LiCl (0.457 g, 10.75 mmol). The resulting green solution was refluxed for a further 4 h then the solution was filtered, and the filtrate reduced to dryness *in vacuo*. Two successive recrystallisations of the residue from CH$_2$Cl$_2$–diethyl

ether gave **3b** as a bright yellow solid; yield 0.517 g (31%) (Found: C, 52.1; H, 5.4. Calc. for $C_{33}H_{31}ClMoP_3F_6$: C, 51.8; H, 4.1%). The yellow bromide derivative **2b** was similarly prepared in 10% yield using LiBr in place of LiCl (Found: C, 49.4; H, 3.9. Calc. for $C_{33}H_{31}BrMoP_3F_6$: C, 48.9; H, 3.8%) and the purple-red iodide derivative **1b** in 35% yield using LiI as the reagent (Found: C, 47.3; H, 4.0. Calc. for $C_{33}H_{31}IMoP_3F_6$: C, 46.2; H, 3.6%).

[MoF(dppe)(η-C₇H₇)][PF₆] 4b. An acetone solution of [Mo(OCMe₂)(dppe)(η-C₇H₇)][PF₆] [prepared by overnight reflux of [Mo(η-C₆H₅Me)(η-C₇H₇)][PF₆] (0.772 g, 1.82 mmol) with dppe (0.729 g, 1.83 mmol) in acetone (40 cm³)] was treated with anhydrous LiF (0.241 g, 9.27 mmol). The resulting green solution was refluxed for 1 h then the volume was reduced and the crude product precipitated by addition of diethyl ether. The crude product was dissolved in thf (20 cm³), the resulting solution filtered and the product again precipitated by addition of diethyl ether. Finally the product was dissolved in acetone (5 cm³) and precipitated as three fractions by slow addition of diethyl ether. A pure sample of green [MoF(dppe)(η-C₇H₇)]-[PF₆] was isolated from the final fraction; yield 0.235 g (17%).

[MoCl(dppe)(η-C₇H₆Me)][PF₆] 5b. An acetone solution of [Mo(OCMe₂)(dppe)(η-C₇H₆Me)][PF₆] [prepared by overnight reflux of [Mo(η-C₆H₅Me)(η-C₇H₆Me)][PF₆] (0.500 g, 1.14 mmol) with dppe (0.457 g, 1.15 mmol) in acetone (40 cm³)] was treated with anhydrous LiCl (0.247 g, 5.81 mmol). The resulting yellow solution was refluxed for a further 1 h then reduced to dryness *in vacuo*. The residue was dissolved in CH₂Cl₂ (50 cm³), the resulting solution filtered, reduced in volume and diethyl ether added to precipitate the product as a yellow solid. Further recrystallisation from acetone–diethyl ether gave a pure sample of yellow [MoCl(dppe)(η-C₇H₆Me)][PF₆]; yield 0.130 g (15%).

[Mo(NCO)(dppe)(η-C₇H₇)] 6a. An acetone solution of [Mo(OCMe₂)(dppe)(η-C₇H₇)][PF₆] [prepared by overnight reflux of [Mo(η-C₆H₅Me)(η-C₇H₇)][PF₆] (0.641 g, 1.51 mmol) with dppe (0.602 g, 1.51 mmol) in acetone (40 cm³)] was treated with KNCO (1.008 g, 12.44 mmol). The resulting brown-green solution was refluxed for a further 5 h then reduced to dryness *in vacuo*. The residue was dissolved in CH₂Cl₂ (50 cm³), the resulting solution filtered, reduced in volume and n-hexane added to precipitate the product as a green solid. Further recrystallisation from toluene–n-hexane gave a pure sample of green [Mo(NCO)(dppe)(η-C₇H₇)]; yield 0.340 g (36%).

[Mo(NCO)(dppe)(η-C₇H₇)][PF₆] 6b. A mixture of [Mo-(NCO)(dppe)(η-C₇H₇)] (0.200 g, 0.319 mmol) and [Fe(η-C₅H₅)₂][PF₆] (0.107 g, 0.323 mmol) was stirred for 10 min in CH₂Cl₂ (20 cm³) to give a green solution. The volume of the reaction mixture was then reduced *in vacuo* and diethyl ether added to precipitate the crude product which was washed with toluene and dried. Two subsequent recrystallisations from acetone–diethyl ether gave pure [Mo(NCO)(dppe)(η-C₇H₇)]-[PF₆] as a bright yellow solid; yield 0.054 g (22%).

[Mo(NCS)(dppe)(η-C₇H₇)][PF₆] 7b. An acetone solution of [Mo(OCMe₂)(dppe)(η-C₇H₇)][PF₆] [prepared by overnight reflux of [Mo(η-C₆H₅Me)(η-C₇H₇)][PF₆] (1.01 g, 2.38 mmol) with dppe (0.945 g, 2.37 mmol) in acetone (40 cm³)] was treated with KNCS (1.92 g, 19.78 mmol). The resulting brown solution was refluxed for a further 1 h then reduced to dryness *in vacuo*. The residue was dissolved in CH₂Cl₂ (40 cm³) and the resulting solution filtered and toluene (40 cm³) added. Slow reduction in volume *in vacuo* resulted in the precipitation of a red-purple solid, identified as **7b**, which was isolated by filtration and further recrystallised from CH₂Cl₂–diethyl ether; yield 0.224 g (12%). IR spectroscopy on samples from the brown, CH₂Cl₂–toluene mother liquors from which **7b** was isolated revealed the

presence of two further components of the reaction mixture: [Mo(NCS)(dppe)(η-C₇H₇)] **7a** (v(CO) (CH₂Cl₂) 2084 cm⁻¹) and an unidentified species (v(CO) (CH₂Cl₂) 2064 cm⁻¹). However all attempts to isolate pure **7a** from the mother-liquors of the reaction mixture were unsuccessful.

[Mo(NCS)(dppe)(η-C₇H₇)] 7a. A mixture of [Mo(NCS)-(dppe)(η-C₇H₇)][PF₆] (0.140 g, 0.18 mmol) and [Co(η-C₅H₅)₂] (0.038 g, 0.20 mmol) in toluene (40 cm³) was stirred for 25 min to give a green solution. The reaction mixture was filtered, reduced to 2 cm³ volume *in vacuo* and treated with n-hexane to precipitate **7a** as a yellow-brown solid; yield 0.012 g (10%).

[Mo(CN)(dppe)(η-C₇H₇)] 8a. An acetone solution of [Mo-(OCMe₂)(dppe)(η-C₇H₇)][PF₆] [prepared by overnight reflux of [Mo(η-C₆H₅Me)(η-C₇H₇)][PF₆] (1.134 g, 2.67 mmol) with dppe (1.065 g, 2.68 mmol) in acetone (80 cm³)] was reduced in volume to *ca.* 10 cm³ and then AnalaR methanol (80 cm³) added. The resulting solution was immediately treated with KCN (0.83g, 12.77 mmol) then stirred at room temperature for 20 min and finally gently refluxed for 20 min to give a purple-red reaction mixture which was reduced to dryness *in vacuo*. The residue was extracted with CH₂Cl₂ (60 cm³), filtered to remove the majority of KCN, and again evaporated to dryness. The resulting crude purple-red product was dissolved in CH₂Cl₂ and transferred to an alumina–n-hexane chromatography column. Elution with acetone–n-hexane (1:1) increasing to neat acetone gave a red-pink band which was collected and evaporated to dryness. Recrystallisation of the crude product from CH₂Cl₂–hexane gave pure [Mo(CN)(dppe)(η-C₇H₇)] as a pink solid, yield 0.540 g (33%). A second, minor product of this reaction, eluted from the column with neat acetone after [Mo(CN)(dppe)-(η-C₇H₇)] as an orange-red band, was the cyanide bridged bimetallic [{Mo(dppe)(η-C₇H₇)}₂(μ-CN)][PF₆]. Further details on the synthesis and properties of this system will be reported in a subsequent paper. The carbon-13 labelled complex [Mo(¹³CN)(dppe)(η-C₇H₇)] **9a** was prepared as a pink solid (yield 0.165 g, 23%) by an identical procedure to that described for **8a** starting from [Mo(η-C₆H₅Me)(η-C₇H₇)][PF₆] (0.498 g, 1.17 mmol) and dppe (0.467 g, 1.17 mmol) in acetone (40 cm³) followed by treatment with K¹³CN (0.223 g, 3.38 mmol) in acetone–methanol (1:3).

[Mo(CN)(dppe)(η-C₇H₇)][PF₆] 8b. A mixture of [Mo(CN)-(dppe)(η-C₇H₇)] (0.207 g, 0.34 mmol) and [Fe(η-C₅H₅)₂][PF₆] (0.110 g, 0.33 mmol) was stirred for 20 min in CH₂Cl₂ (20 cm³) to give a yellow solution. The volume of the reaction mixture was then reduced *in vacuo* and diethyl ether added to precipitate the product as a yellow solid which was washed with diethyl ether and dried; yield 0.113 g (44%). Dichloromethane solutions of the carbon-13 labelled analogue [Mo(¹³CN)(dppe)-(η-C₇H₇)][PF₆] **9b** for EPR investigations were prepared similarly starting from **9a** and [Fe(η-C₅H₅)₂][PF₆]. Owing to the small scale, complex **9b** was not isolated but the observed shift (Δv) in the v(C≡N) stretching frequency following one-electron oxidation, identical to that observed in the formation of **8b** from **8a** (see Table 3), points to the successful generation of **9b**.

[Mo(CNMe)(dppe)(η-C₇H₇)][BF₄] 10a. Addition of [Me₃O][BF₄] (0.081 g, 0.55 mmol) to a stirred solution of [Mo(CN)(dppe)(η-C₇H₇)] **8a** (0.216 g, 0.35 mmol) in CH₂Cl₂ resulted in a colour change from purple-red to a paler red-pink solution over the course of 1 h. After this time the reaction mixture was evaporated to dryness and the residue recrystallised from CH₂Cl₂–diethyl ether to give **10a** as a red-pink solid; yield 0.055 g (22%). The carbon-13 labelled analogue [Mo-(¹³CNMe)(dppe)(η-C₇H₇)][BF₄] **11a** was prepared by an identical procedure (yield, 0.035 g, 60%) starting from **9a** (0.050 g 0.082 mmol) and [Me₃O][BF₄] (0.018 g, 0.12 mmol).

[Mo(CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$]$_2$ 10b. A solution of [Mo-(CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$] (0.242 g, 0.34 mmol) in CH$_2$Cl$_2$ (20 cm^3) was treated with [NO][BF$_4$] (0.060 g, 0.51 mmol). After stirring for 5 min the resulting deep red solution was filtered, reduced in volume and diethyl ether added to precipitate the crude product. Recrystallisation from CH$_2$Cl$_2$–diethyl ether gave [Mo(CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$]$_2$ as a red solid; yield 0.107 g (39%). Dichloromethane solutions of the carbon-13 labelled analogue [Mo(^{13}CNMe)(dppe)(η-C$_7$H$_7$)][BF$_4$]$_2$ **11b** for EPR investigations were prepared similarly starting from **11a** and [Fe(η-C$_5$H$_5$){η-C$_5$H$_4$(C(O)CH$_3$)}][BF$_4$]. Owing to the small scale, **11b** was not isolated but the observed shift (Δν) in the ν(C≡N) stretching frequency following one-electron oxidation, identical to that observed in the formation of **10b** from **10a** (see Table 3), points to the successful generation of **11b**.

[Mo($\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$)(dppe)(η-C$_7H_7$)][PF$_6$]$_2$ 12b. An orange solution of [Mo($\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$)(dppe)(η-C$_7H_7$)][PF$_6$] **12a** (0.310 g, 0.387 mmol) in CH$_2$Cl$_2$ (30 cm^3) was treated with [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] (0.128 g, 0.387 mmol) resulting in an immediate colour change to yellow-green. After 1 h the solvent was removed *in vacuo* and the residue washed with toluene and dried. Recrystallisation from CH$_2$Cl$_2$–diethyl ether gave **12b** as a yellow-orange solid; yield 0.084 g (23%).

[Mo(triphos)(η-C$_7$H$_7$)][PF$_6$] 13a. The sandwich complex [Mo(η-C$_6$H$_5$Me)(η-C$_7$H$_7$)][PF$_6$] (0.500 g, 1.179 mmol) was refluxed in acetone (40 cm^3) for 10 min to give a red solution which was then cooled and treated with triphos (0.737 g, 1.181 mmol). The reaction mixture was refluxed overnight then reduced to low volume *in vacuo* and the crude product precipitated by addition of diethyl ether. Subsequent recrystallisation from CH$_2$Cl$_2$–diethyl ether gave **13a** as a lilac solid; yield 0.889 g (79%).

[Mo(triphos)(η-C$_7$H$_7$)][PF$_6$]$_2$ 13b. A mixture of [Mo(triphos)-(η-C$_7$H$_7$)][PF$_6$] (0.147 g, 0.15 mmol) and [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] (0.061 g, 0.18 mmol) was stirred for 30 min in CH$_2$Cl$_2$ (15 cm^3) to give a green-blue solution. The volume of the reaction mixture was then reduced *in vacuo* resulting in the precipitation of unreacted [Fe(η-C$_5$H$_5$)$_2$][PF$_6$]. Filtration through Celite gave an orange solution which was treated with small aliquots of diethyl ether to the onset of precipitation of **13b** as a bright orange solid. The product was recrystallised from acetone–diethyl ether; yield 0.043 g (25%).

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