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The chemistry of cycloheptatrienyl complexes of molybdenum and tungsten: synthesis and redox chemistry of some phosphine- and phosphite-substituted halide and acetonitrile derivatives

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Abstract

Reaction of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ (C_6H_5Me = toluene) with two equivalents of $P(OMe)_3$ in refluxing acetonitrile affords $[Mo(NCMe)\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$, which is a precursor for the neutral complex $[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ (**2**) and the radical cation $[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ (**3**). Treatment of $[WI(CO)_2(\eta\text{-}C_7H_7)]$ with PPh_3 gives $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (**6**), which is a starting material for the synthesis of $[W(CO)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and hence $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**9**). Reaction of **9** with LiCl gives a mixture of $[WCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**14**) and $[WCl(dppe)(\eta\text{-}C_7H_7)]$. Cyclic voltammetric studies on **2**, **3**, **6**, **9**, $[Mo(NMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**10**), and **14** reveal reversible one-electron transfer processes, and $[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][BF_4]$ (**4**), $[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ (**5**) and $[M(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$ (**11**, M = W; **12**, M = Mo) have been isolated by use of chemical redox reagents. The radicals **3**, **4**, **11**, **12** and **14** have been studied by ESR spectroscopy.

Although the chemistry of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and related bis-phosphine substituted derivatives is extensive [1], reports of analogous cycloheptatrienyl complexes of the group 6 transition metals are restricted to those of $[MoX(dppe)(\eta\text{-}C_7H_7)]^{n+}$ (X = halide; $n = 0$ or 1; dppe = 1,2-bis(diphenylphosphino)ethane) [2,3]. Our interest in complexes of the type $[MX(P)_2(\eta\text{-}C_7H_7)]^{n+}$ (M = Mo or W; X = halide; P = phosphorus-donor ligand; $n = 0$ or 1) arises from their synthetic applications (especially in the formation of alkynyl derivatives [4]) and from their redox chemistry. Previous investigations concerned with the redox properties of these complexes [2–4] have indicated two general conclusions which are examined further in the current study. Firstly, cyclic voltammetric studies on the reversible one-electron oxidation of $[MoCl(dppe)(\eta\text{-}C_7H_7)]$ and $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]$ (R = Ph or Bu^t) afford values for formal reduction potentials $E^{\ominus}$ [4] which are to

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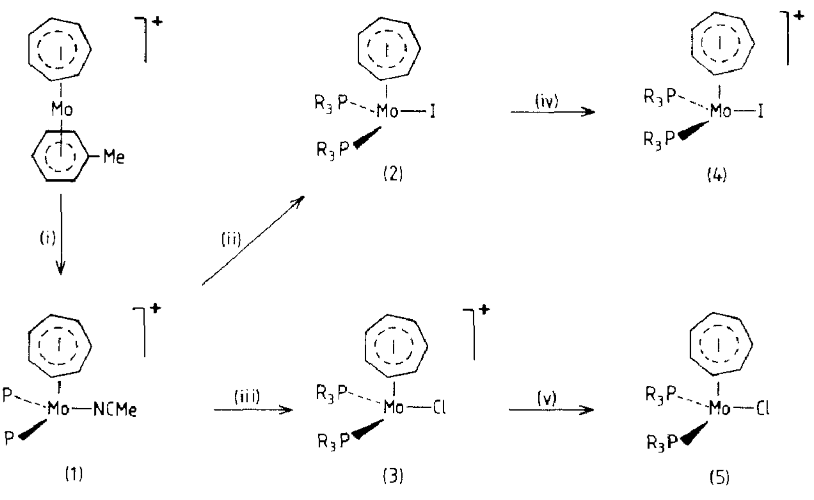
negative potential of those observed for the corresponding one-electron oxidation of analogous cyclopentadienyl-iron or -ruthenium derivatives [5,6]. Secondly, the sharp, well resolved ESR spectra obtained for the radicals $[MoCl(dppe)(\eta\text{-}C_7H_7)]^+$ [3] and $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)]^+$ [4] may be taken as evidence for a d^1 Mo^V metal centre with the implication that the cycloheptatrienyl ligand in these complexes has a formal trinegative charge [3].

This paper relates the synthesis and redox properties of a series of halide complexes $[MX(P)_2(\eta\text{-}C_7H_7)]^{n+}$ ($n = 0$ or 1) including the first examples of tungsten derivatives. The formation of precursor acetonitrile complexes $[M(NCMe)(P)_2(\eta\text{-}C_7H_7)]^+$ is also described.

Results and discussion

To extend the chemistry of complexes $[MoX(P)_2(\eta\text{-}C_7H_7)]$ we investigated the synthesis of derivatives incorporating two mono-dentate phosphorus-donor ligands. In view of the large steric requirements of the cycloheptatrienyl ring [7], $P(OMe)_3$ (cone angle 107° [8]) was chosen as a suitable ligand to give potentially stable complexes, and furthermore we previously synthesised bis(trimethylphosphite) substituted $[Cr(CO)\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ [9]. By use of an analogous synthetic route to that reported [10] for $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$, a red solution of $[Mo(NCMe)_3(\eta\text{-}C_7H_7)][PF_6]$ (generated in situ from $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ in refluxing acetonitrile) was treated with two equivalents of $P(OMe)_3$ to give a brown-red solution, which after work up afforded good yields of brown air sensitive, $[Mo(NCMe)\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ (1) (Scheme 1). Details of the characterisation of **1** by elemental analysis and infrared spectroscopy (Table 1) and by ^1H and ^{31}P NMR spectroscopy (Table 2) are given in the appropriate table.

The facile replacement of the acetonitrile ligand of $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ on treatment with LiI [3] suggested an investigation of the corresponding chemistry of **1** as a route to $[MoX\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]^{n+}$ (X = halide, $n = 0$



Scheme 1. R = OMe. (i) $P(OMe)_3$ in refluxing MeCN; (ii) NaI in refluxing acetone; (iii) LiCl in refluxing acetone; (iv) $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ in CH_2Cl_2; (v) $[Co(\eta\text{-}C_5H_5)_2]$ in toluene.

Table 1

Infrared, microanalytical and electrochemical data

Complex	Yield (%)	Infrared (cm^{-1}) [a]	Analysis [b] (%)			$E^{\ominus}$ [c] (V)
			C	H	N	
$[Mo(NCMe)\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$	73	2265	29.0	4.6	2.6	
(1)			(29.0)	(4.5)	(2.3)	
$[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ [d]	44		27.3	4.3		
(2)			(27.8)	(4.5)		0.10
$[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$	53		25.5	4.0	[e]	
(3)			(25.4)	(4.1)		0.01
$[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][BF_4]$	19		24.0	4.0		
(4)			(24.0)	(3.9)		0.09
$[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$	30		33.6	5.4	[f]	
(5)			(33.2)	(5.3)		0.00
$[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ [g]	70	1913 [h]	44.9	3.1	[j]	
(6)			(45.1)	(3.2)		0.49
$[MoI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$	[k]					0.58
(7)						
$[W(CO)(dppe)(\eta\text{-}C_7H_7)][PF_6]$	71	1942 [h]	48.0	3.7		
(8)			(48.2)	(3.7)		
$[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$	57	2251	48.7	3.8	1.5	
(9)			(48.9)	(4.0)	(1.6)	0.23 [l]
$[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$	[m]	2261				0.37 [l]
(10)						
$[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$	65	2274	42.3	3.4	1.3	
(11)			(41.8)	(3.4)	(1.4)	0.22 [l]
$[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$ [n]	86	2279	46.8	4.0	1.4	
(12)			(46.8)	(4.1)	(1.5)	0.36 [l]
$[WCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$	82		46.9	3.9	[p]	
(14)			(46.4)	(3.6)		−0.22
$[WCl(dppe)(\eta\text{-}C_7H_7)]$ [q]	14		56.9	4.9	[r]	
(15)			(55.9)	(4.4)		−0.21

[a] In CH_2Cl_2 $\nu(C\equiv N)$ unless stated otherwise. [b] Calculated values are given in parentheses. [c] In CH_2Cl_2 unless stated otherwise. vs. SCE at a carbon working electrode, $0.2\,M$ $[Bu^n_4N][BF_4]$ supporting electrolyte. Under these conditions $E^{\ominus}$ for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+/[Fe(\eta\text{-}C_5H_5)_2]$ is 0.56 V in CH_2Cl_2 and 0.43 V in CH_3CN. [d] m/e by electron impact mass spectroscopy 316 ($M^+ - 2P(OMe)_3$). [e] Cl Found 6.6%, calcd. 5.8%; P Found 15.4%, calcd. 15.1%. [f] Cl Found 7.5%, calcd. 7.6%. [g] m/e by electron impact mass spectroscopy 430 ($M^+ - PPh_3$). [h] $\nu(CO)$. [j] I Found 18.3%, calcd. 18.3%. [k] Other characterisation data given in ref. 14. [l] In CH_3CN. [m] Other characterisation data given in ref. 10. [n] Analytical data consistent with 1 acetone solvent of crystallisation, Mo Found 9.8%, calcd. 10.1%, P Found 12.7%, calcd. 12.6%, infrared $\nu(CO)(CH_2Cl_2)$ 1712 cm^{-1}. [p] Cl Found 4.7%, calcd. 4.1%. [q] m/e by FAB mass spectroscopy 708 (M^+). [r] Cl Found 4.9%, calcd. 5.0%.

or +1). Accordingly treatment of **1** with NaI in refluxing acetone was found to afford moderate yields of the green neutral iodide derivative $[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ **(2)** characterised as detailed in Table 1. By contrast, the radical cation $[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ **(3)** is formed in the reaction of **1** with LiCl in acetone. The paramagnetic character of **3** was confirmed by its ESR spectrum in dichloromethane, which reveals fine structure due to $^{95,97}Mo$, and ^{31}P nuclei and a further small coupling A(ii) (Fig. 1). ESR parameters for **3** are given in Table 3, and are comparable with data obtained for the related radicals $[MoCl(dppe)(\eta\text{-}C_7H_7)]^+$ and $[Mo(C\equiv CPh)(dppe)(\eta\text{-}C_7H_7)]^+$ [3,4].

Table 2

Proton and ^{31}P NMR spectral data [a]

Complex	^{1}H(δ) [b]	^{31}P(ppm) [c]
1	5.20(br,7H,C_7H_7), 3.45[t,J(P–H)5,18H,P(OMe)$_3$]	160.2
6 [d]	7.51, 7.39(br,15H,Ph), 4.98[d, J(P–H)2,7H,C_7H_7]	3.9 $\lvert J(^{183}W-P)\rvert$323
8	7.58, 7.44, 7.20(br,20H,Ph), 5.10[t,J(P–H)2, 7H,C_7H_7], 2.74, 2.42(br,4H,CH_2)	38.4 $\lvert J(^{183}W-P)\rvert$331
9	7.59, 7.41, 7.24(br,20H,Ph), 4.92[t,J(P–H)2, 7H, C_7H_7], 2.50, 2.28(br,4H,CH_2), 1.36[t,J(P–H)1.5, 3H, CH_3CN]	43.3 $\lvert J(^{183}W-P)\rvert$360

[a] In CD_3CN unless stated otherwise; d, doublet; t, triplet; br, broad; J values in Hz. [b] Chemical shifts downfield from $SiMe_4$. [c] Positive chemical shifts downfield from H_3PO_4. [d] In $CDCl_3$.

The reversible one-electron oxidation processes exhibited by [MoX(dppe)(η-C_7H_7)] (X = halide) and [Mo(C≡CR)(dppe)(η-C_7H_7)] (R = Ph or Bu^t) and the isolation of the corresponding radical cations encouraged us to investigate the electrochemistry of **2** and **3**. Cyclic voltammetric studies at a glassy carbon electrode in dichloromethane reveal that **2** and **3** undergo reversible one-electron transfer processes (**2** is oxidised, **3** is reduced). In each case electron transfer is diffusion controlled ($i_p/\nu^{\frac{1}{2}}$ = constant) for scan rates ν 50–500 mVs^{-1} and chemically reversible, with the ratio of peak currents of unity over the same scan range. Moreover the observed separation between cathodic and anodic peak potentials agreed well with that measured for ferrocene under identical conditions. Values obtained for the formal reduction potentials $E^{\ominus}$ of **2** and **3** are given in Table 1; note that $E^{\ominus}$ for the iodide derivative **2** is to positive potential of that for the chloride complex **3** (the same trend is observed for [FeX(dppe)(η-C_5H_5)] (X = I or Cl) [5]) and that, as expected, $E^{\ominus}$ for **3** is to positive potential of that for [MoCl(dppe)(η-C_7H_7)] ($E^{\ominus}$ −0.05 V recorded under identical conditions [4]).

The magnitudes of $E^{\ominus}$ for **2** and **3** and the reversibility of the redox processes as determined by cyclic voltammetric studies suggested that chemical syntheses of

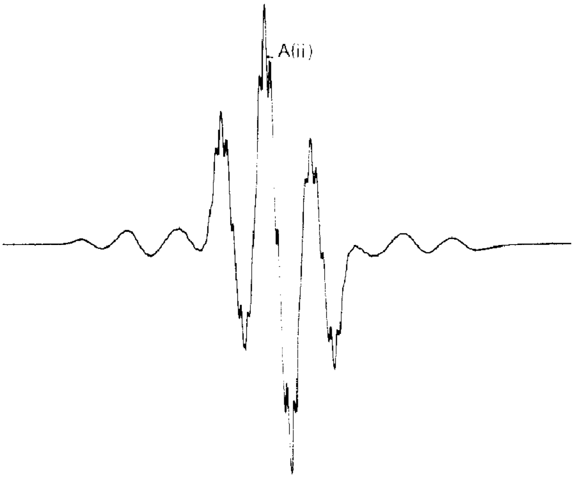
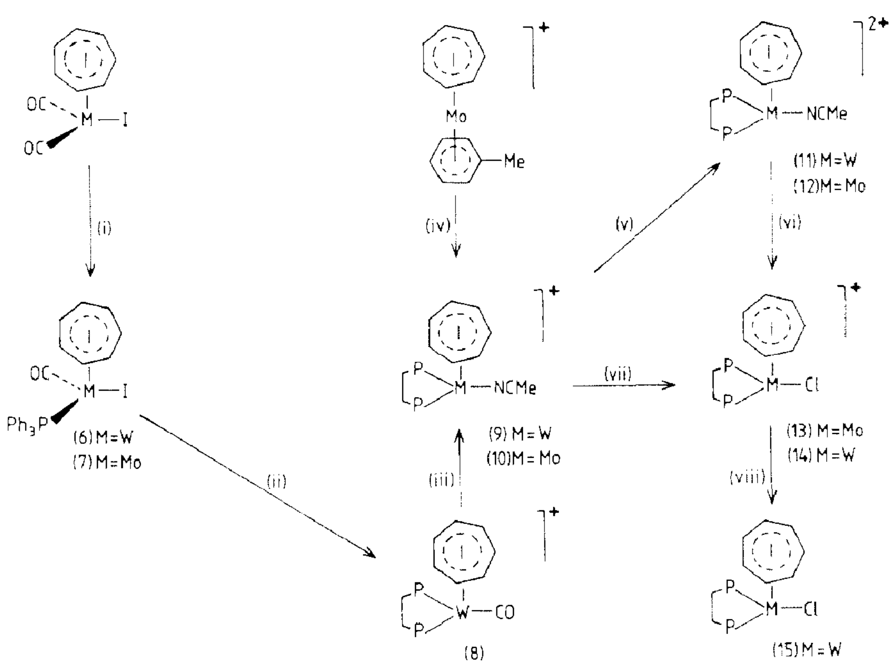


Fig. 1. The ESR spectrum of [MoCl{P(OMe)$_3$}$_2$(η-C_7H_7)][PF$_6$] (**3**) in CH_2Cl_2.

$[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]^+$ (**4**) and $[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ (**5**) might be achieved with appropriate chemical redox reagents such as $[Fe(\eta\text{-}C_5H_5)_2]^+$ and $[Co(\eta\text{-}C_5H_5)_2]$. Thus addition of $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ to a green solution of neutral **2** in dichloromethane immediately produced a violet solution which afforded low yields of the radical cation **4**. The radical **4** is also formed (32% yield) on treatment of **2** with $[NO][BF_4]$, indicating that one-electron oxidation is preferred to formation of the substituted product $[MoI\{P(OMe)_3\}(NO)(\eta\text{-}C_7H_7)][BF_4]$. Complex **4** was characterised by elemental analysis, cyclic voltammetry (the results of which are complimentary to the data obtained for **2**), and ESR spectroscopy in dichloromethane. In contrast to the result for **3**, the ESR spectrum of **4** was very broad (linewidth ca. 96 G) with no resolved fine structure. The synthesis of $[MoCl(dppe)(\eta\text{-}C_7H_7)]$ from the radical $[MoCl(dppe)(\eta\text{-}C_7H_7)]^+$ has been achieved by use of sodium-mercury amalgam as reducing agent [3] but this method was found to be unsatisfactory for the formation of $[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ (**5**) from **3**. However treatment of **3** with $[Co(\eta\text{-}C_5H_5)_2]$ in toluene affords moderate yields of green **5**, which was characterised as detailed in Table 1; $[Co(\eta\text{-}C_5H_5)_2]$ also brings about the one-electron reduction of $[MoCl(dppe)(\eta\text{-}C_7H_7)]^+$ in moderate yield. As with **2** and **4**, complimentary cyclic voltammetry is observed for the two complexes **3** and **5**, which constitute a redox pair. Attempts to obtain informative ^1H NMR spectra of either of the neutral halide derivatives **2** and **5** were unsuccessful, as was the case for $[MoX(dppe)(\eta\text{-}C_7H_7)]$ (X = I or Cl) and $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)]$ [3,4].

We also examined the synthesis of the tungsten analogues of the known complexes $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)]^+$ and $[MoCl(dppe)(\eta\text{-}C_7H_7)]^{n+}$ ($n = 0$ or $+1$). Entry to the chemistry of bisphosphine-substituted cycloheptatrienyltungsten complexes is not a trivial problem, since the synthetic routes available in cycloheptatrienylmolybdenum chemistry are either inaccessible or unproductive. Thus the sandwich complex $[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ appears to be unobtainable, and furthermore, whilst $[RuI(CO)_2(\eta\text{-}C_5H_5)]$ and $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ react with dppe to give respectively $[Ru(CO)(dppe)(\eta\text{-}C_5H_5)]I$ [11] and $[Mo(CO)(dppe)(\eta\text{-}C_7H_7)]I$ [12] (formation of the latter proceeds via the thermally unstable $[MoI(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$), treatment of $[WI(CO)_2(\eta\text{-}C_7H_7)]$ with dppe gives $[WI(CO)_2(dppe)(\eta^3\text{-}C_7H_7)]$, from which the carbonyl ligands are exceedingly difficult to displace [13]. We have previously reported the first example of a bisphosphine substituted cycloheptatrienyltungsten complex $[W(CO)(dppm)(\eta\text{-}C_7H_7)][PF_6]$ (dppm = 1,2-bis(diphenylphosphino)methane), synthesised [13] in two steps from $[WI(CO)_2(dppm)(\eta^3\text{-}C_7H_7)]$, but this route cannot be extended to the dppe derivative. However the synthesis of $[W(CO)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**8**) (Scheme 2) leading to $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ and $[WCl(dppe)(\eta\text{-}C_7H_7)]^{n+}$ ($n = 0$ or 1) has been achieved through reaction of dppe with $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$.

Although the formation of a series of phosphine and phosphite substituted complexes of molybdenum $[MoI(CO)(PR_3)(\eta\text{-}C_7H_7)]$ (R = Ph, Bu^n, OPh, OMe etc.) was reported some time ago [14], and the chemistry of $[MoI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ has been investigated in detail [15], the corresponding chemistry of tungsten has been limited to phosphite derivatives $[WI(CO)\{P(OR')_3\}(\eta\text{-}C_7H_7)]$ (R′ = Et or Pr^i), which were obtained in very low yield. We have now succeeded in synthesising the triphenylphosphine derivative $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (**6**) (Scheme 2) in good yield using a modification of the thermal method employed by Houk and Beall [14].



Scheme 2. P⌒P = dppe. (i) PPh_3 in refluxing toluene; (ii) M = W, dppe in refluxing toluene then $[NH_4][PF_6]$ in acetone; (iii) $Me_3NO.2H_2O$ in refluxing MeCN; (iv) dppe in refluxing acetonitrile; (v) $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in MeCN; (vi) LiCl in acetone; (vii) LiCl in acetone, M = Mo room temperature, M = W reflux; (viii) $[Co(\eta\text{-}C_5H_5)_2]$ in toluene.

Dropwise addition of a toluene solution of PPh_3 to a solution of $[WI(CO)_2(\eta\text{-}C_7H_7)]$ in refluxing toluene gives a brown mixture which, after column chromatography on silica to remove $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)]^+$ [16] and a further unidentified side product ($\nu(CO)(CH_2Cl_2)$ 1889 cm^{-1}), affords **6** as a yellow brown solid which has been characterised by elemental analysis, infrared spectroscopy, and cyclic voltammetry (Table 1), and by ^1H and ^{31}P NMR spectroscopy (Table 2).

Previous cyclic voltammetric and synthetic studies on the molybdenum complex $[MoI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (**7**) in acetonitrile [15] suggest that one-electron oxidation affords the unstable 17-electron radical $[MoI(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$ which undergoes a facile reduction to reform **7**, or alternatively reacts with acetonitrile to yield secondary products. To probe further the existence of radicals $[MI(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$ (M = Mo or W) the redox chemistry of both **6** and **7** was investigated, but initial studies were conducted in dichloromethane in an attempt to prevent solvent-connected reactions. At a glassy carbon electrode in dichloromethane, **6** undergoes a reversible one-electron oxidation that is diffusion controlled ($i_p^A/\nu^{\frac{1}{2}}$ constant) for scan rates ν 50–500 mVs^{-1} and chemically reversible with the ratio of peak currents i_p^C/i_p^A unity over the same scan range. Under identical conditions the molybdenum analogue **7** also undergoes a one-electron oxidation with a coupled reduction, but the ratio of peak currents i_p^C/i_p^A decreases from unity at a scan rate of 500 mVs^{-1} to 0.6 at a scan rate of 50 mVs^{-1}. Values of $E^{\ominus}$ (Table 1) are metal dependent, and, as might have been expected, are more negative for the tungsten derivative.

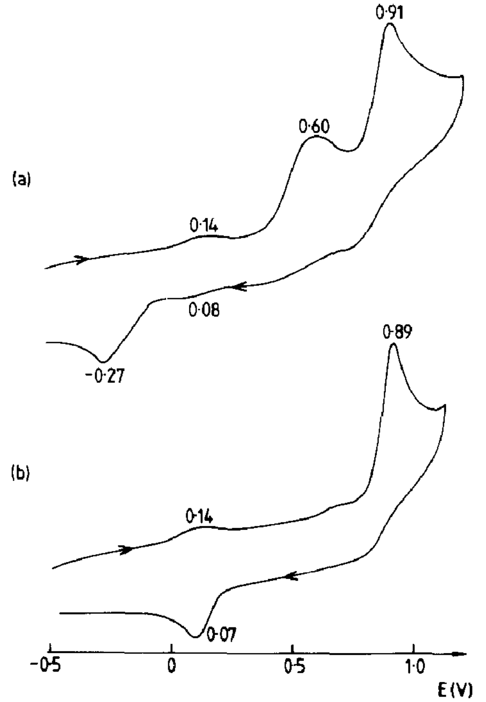


Fig. 2. Single scan cyclic voltammograms of (a) $[MoI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ ($-0.5 \rightarrow 1.2$ V) and (b) $[Mo(CO)(NCMe)(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$ ($-0.5 \rightarrow 1.1$ V), in acetonitrile. Scan rate 200 mVs^{-1}, potentials (V) vs. saturated calomel electrode.

The stability of the primary product resulting from one-electron oxidation of **6**, at least on the electrochemical time scale, and the favourable value of $E^{\ominus}$ prompted synthetic studies with a chemical redox reagent. Treatment of a yellow solution of **6** with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ produced an immediate colour change to violet. Spectroscopic data for the product recorded in situ ($\nu(CO)(CH_2Cl_2)$ 2056 cm^{-1}, ESR in CH_2Cl_2 $g_{av.} = 2.062$ (broad signal, linewidth 45 G)) were consistent with formation of the radical $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$, but instability with respect to reformation of **6** prevented its isolation and further characterisation.

The solvent dependence of the redox chemistry of complexes $[MI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ is highlighted by a reinvestigation of the cyclic voltammetry of **7** in acetonitrile. At a glassy carbon electrode the single scan cyclic voltammogram of **7** (Fig. 2a) appears to be more complex than reported previously. Two major current peaks at 0.60 V and 0.91 V (scan rate 200 mVs^{-1}) are observed in the oxidative half cycle; comparison with data obtained in dichloromethane suggests that the wave at 0.60 V should be assigned to oxidation of **7**. A probable secondary product resulting from the oxidation of **7** in acetonitrile is the previously reported $[Mo(CO)(NCMe)(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$ [15] (the single scan cyclic voltammogram of which is shown in Fig. 2b), and this complex is tentatively assigned to the wave at 0.91V in Fig. 2a. A marked increase in the peak current of a third oxidation wave at 0.14 V occurs for subsequent scans on **7** and identical behaviour is observed for a precisely corresponding feature in the cyclic voltammogram of $[Mo(CO)(NCMe)(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$.

In contrast to the analogous reaction with $[WI(CO)_2(\eta\text{-}C_7H_7)]$ [13], dppe reacts with **6** only upon heating, to give cationic $[W(CO)(dppe)(\eta\text{-}C_7H_7)]I$ via displacement of iodide and PPh_3 ligands. Treatment of $[W(CO)(dppe)(\eta\text{-}C_7H_7)]I$ with $[NH_4][PF_6]$ in acetone resulted in anion exchange and formation of $[W(CO)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**8**), characterised as detailed in Tables 1 and 2. The carbonyl ligand of **8** proved difficult to displace, but reaction with an excess of $Me_3NO \cdot 2H_2O$ in refluxing acetonitrile gave a red solution, which, after work up and column chromatography on Florisil, afforded moderate yields of pink $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**9**), which was characterised as indicated in Tables 1 and 2. Comparison of infrared data for **9** and $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**10**) establishes a small metal dependence of the nitrile stretching frquency $\nu(C{\equiv}N)$.

The iron complexes $[Fe(NCMe)(dppe)(\eta\text{-}C_5R_5)][PF_6]$, analogues of **9** and **10**, are reported [17] to undergo reversible one-electron oxidations in acetonitrile (R = H, $E^\ominus$ 0.66 V; R = Me, $E^\ominus$ 0.47 V, measured under closely comparable conditions to those used in this paper). The relatively low values of $E^\ominus$ are attributed to a high electron density at iron, which is thought to result from a very limited back-bonding ability of the nitrile ligand [18]. To investigate further our premise concerning the relative values of $E^\ominus$ for corresponding one-electron oxidation processes in cycloheptatrienyl-molybdenum and -tungsten vs. cyclopentadienyl-iron and -ruthenium analogues, we carried out cyclic voltammetric studies on **9** and **10**. At a glassy carbon electrode in acetonitrile both **9** and **10** undergo reversible one-electron oxidations with conditions for $i_p^A/\nu^{\frac{1}{2}}$, the peak current ratio and peak potential separations, satisfied as described for **2** and **3**. The magnitudes of $E^\ominus$ for **9** and **10** (Table 1) were, as expected, found to be to negative potential of those reported for $[Fe(NCMe)(dppe)(\eta\text{-}C_5R_5)]^+$, and suggested that chemical oxidation with the ferrocenium ion might be achieved. Accordingly addition of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ to a red, acetonitrile solution of the tungsten derivative **9** produced a yellow solution, which gave good yields of the radical dication $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$ (**11**), the first isolated example of a paramagnetic cycloheptatrienyltungsten complex. Similarly $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$ (**12**) was formed in the reaction of **10** with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ and isolated, after work up, as a pink mono acetone solvate. The radical dications **11** and **12** are readily characterised by elemental analysis, infrared spectroscopy, cyclic voltammetry (Table 1) and by ESR spectroscopy (Table 3). In acetonitrile the cyclic voltammetry of **11** and **12** is complementary to that of the monocation precursors **9** and **10** and $E^\ominus$ values within each redox pair

Table 3

ESR spectral data [a]

Complex	$g_{av.}$	$A(^{31}P)$ (G) [b]	A(other) (G)
3 [c]	1.990	32	A(ii) 4 $A(^{95}Mo, ^{97}Mo)$ 36 [d]
4	2.060		
11 [e]	1.964		
12 [e,f]	1.990	23	$A(^{95}Mo, ^{97}Mo)$ 23 [d]
14	1.959		

[a] Fluid solution spectra in CH_2Cl_2 unless stated otherwise. [b] 1 G = 10^{-4} T. [c] See Fig. 1. [d] Estimated value. [e] In CH_3CN. [f] See Fig. 3.

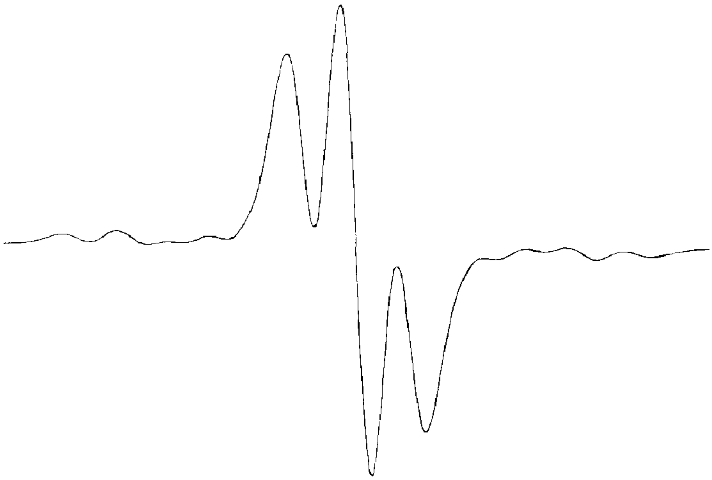


Fig. 3. The ESR spectrum of $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$ (**12**) in CH_3CN.

(**9** and **11**, **10** and **12**) are virtually identical. The solution ESR spectrum of the tungsten complex **11** in acetonitrile is broad (linewidth ca. 70 G) with no resolved fine structure; that of the molybdenum derivative **12** (Fig. 3) exhibits coupling assigned to $^{95,97}Mo$ and ^{31}P.

Infrared data reveal that one-electron oxidation of **9** to **11** and **10** to **12** results in a small but consistent (ca. 20 cm^{-1}) increase in the nitrile stretching frequency $\nu(C{\equiv}N)$ compatible with a description of metal–acetonitrile bonding involving a limited degree of metal to ligand π-back donation. This view, which would imply weakening of the metal-acetonitrile bond via one-electron oxidation of **9** and **10**, is also consistent with the greater ease of substitution of acetonitrile by chloride in the dications **11** and **12** than in the monocations **9** and **10** (see later).

The ultimate aim in synthesis of $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)]^{n+}$ ($n = 1$ or 2) was to employ these complexes in the formation of new halide derivatives $[WX(dppe)(\eta\text{-}C_7H_7)]^{n+}$ ($n = 0$ or 1) via displacement of acetonitrile with halide. Before proceeding we examined the reactions of the more readily available molybdenum derivatives **10** and **12** with LiCl in acetone. Previous investigations [2,3] reported rapid reactions between **10** and LiI and between $[Mo(acetone)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ and LiCl, to give neutral $[MoX(dppe)(\eta\text{-}C_7H_7)]$ (X = I or Cl, respectively). However we have consistently found that reaction of **10** with LiCl in acetone proceeds slowly to give high yields of the radical $[MoCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**13**); this result also accords with our findings for the reaction of **1** with LiCl. Treatment of the radical dication **12** with LiCl in acetone also gives **13**, but its formation is much faster than that from **10**, an observation which might be explained by relative metal–nitrile bond strengths, as discussed previously. Samples of **13** prepared from **10** and **12** were identified by elemental analysis, cyclic voltammetry ($E^{\ominus}$ −0.05 V in CH_2Cl_2) and by solution ESR spectroscopy in CH_2Cl_2.

The reactions of LiCl with the tungsten acetonitrile complexes **9** and **11** indicate a less facile substitution of acetonitrile than for the corresponding molybdenum derivatives **10** and **12**. Thus reaction of the radical dication **11** with LiCl in acetone proceeds slowly at room temperature affording good yields of the radical monocation $[WCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (**14**), whilst **9** reacts with LiCl only after prolonged reflux in acetone to give a separable mixture of **14** and [WCl(dppe)(η-C_7H_7)] (**15**). The neutral chloride derivative **15** was also prepared independently by the one-electron reduction of **14** with [Co(η-C_5H_5)$_2$]. Assignment of **14** and **15** as a redox pair is confirmed by cyclic voltammetric studies in dichloromethane which reveal complimentary one-electron transfer processes with the diagnostic tests for chemical and electrochemical reversibility described previously fully satisfied; full characterisation details for **14** and **15** are given in Tables 1 and 3. The ESR spectrum of **14** in dichloromethane is poorly resolved by comparison with that of [MoCl(dppe)(η-C_7H_7)]$^+$ although some unassigned fine structure was observed as shoulders superimposed upon a broad signal of linewidth 70 G. Infact, of the five isolated 17-electron radical complexes investigated in this work, only [MoCl{P(OMe)$_3$}$_2$(η-C_7H_7)][PF_6] (**3**) exhibited a well resolved ESR solution spectrum. We suggest therefore that assignment of a trinegative charge to the cycloheptatrienyl ligand in its complexes with the group 6 transition metals should be made with caution; indeed the ability of [Mo(NCMe)(dppe)(η-C_7H_7)]$^+$ and [MoCl(dppe)(η-C_7H_7)] to promote the rearrangement of a l-alkyne to a vinylidene [4] would seem to be at least as consitent with a Mo d^6 centre and a cycloheptatrienyl ligand with a formal unipositive charge.

Experimental

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_6H_5Me)(η-C_7H_7)][PF_6] [19], [MoI(CO)(PPh_3)(η-C_7H_7)] [14], [Mo(CO)(NCMe)(PPh_3)(η-C_7H_7)][BF_4] [15], [Mo(NCMe)(dppe)(η-C_7H_7)][PF_6] [10], and [WI(CO)$_2$(η-C_7H_7)] [20] were prepared by published procedures. Aldrich Chemical Co. supplied P(OMe)$_3$ (Gold Label), PPh_3, dppe, NaI, LiCl and [NH_4][PF_6], [Co(η-C_5H_5)$_2$] was purchased from Strem Chemicals Inc., Florisil (60–100 mesh) and silica for column chromatography were obtained from F.S.A. Laboratory Supplies, Loughborough, and Merck, respectively.

The ^1H NMR spectra were recorded on a Varian Associates SC 300 instrument, and ^{31}P NMR spectra at 32.4 MHz on a Brucker WP 80 spectrometer. Infrared spectra were recorded on a Perkin–Elmer FT 1710 spectrometer. Electron impact mass spectra were obtained with an AEI MS 30 instrument and FAB mass spectra (with 3-nitrobenzyl alcohol as matrix) with the VG ZAB-E instrument of the SERC Mass Spectrometry Centre, Swansea. The X-band ESR spectra were recorded on Varian Associates E112 or E4 spectrometers, and cyclic voltammetric studies were carried out as described previously [6]. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparation of [Mo(NCMe){P(OMe)$_3$}$_2$(η-C_7H_7)][PF_6] (1)

A stirred solution of [Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6] (2.54 g, 5.99 mmol) in acetonitrile (100 cm^3) was refluxed for 1 h then treated with P(OMe)$_3$ (1.49 g, 12.02 mmol). The mixture was refluxed for a further 4 h, filtered, then evaporated to dryness, to give a dark brown oily residue, which solidified after being washed several times with diethyl ether, and was then dried in vacuo. A solution of the crude product in a minimum volume of acetonitrile was added dropwise to a large volume of vigorously stirred diethyl ether to give a precipitate of $[Mo(NCMe)\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ as a brown solid, yield 2.72 g (73%).

Preparation of $[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ (2)

Addition of NaI (1.21 g, 8.07 mmol) to a brown solution of $[Mo(NCMe)\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ (2.50 g, 4.03 mmol) in stirred refluxing acetone (120 cm^3) caused a rapid colour change to dark green. The refluxing was continued for 1 h, then the solvent was removed in vacuo to leave a green oily residue, which was crystallised from dichloromethane/n-hexane to give pure $[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ as a green solid, yield 1.00 g (44%).

$[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ (**3**) was prepared in 53% yield from $[Mo(NCMe)\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ (1.26 g, 2.03 mmol) and LiCl (0.17 g, 4.0 mmol) by an identical procedure to that described for **2** except that the final recrystallisation was carried out from CH_2Cl_2/diethyl ether.

Preparation of $[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][BF_4]$ (4)

Treatment of a stirred solution of $[MoI\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ (0.24 g, 0.43 mmol) with $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ (0.12 g, 0.44 mmol) in CH_2Cl_2 (20 cm^3) caused a rapid colour change from green to violet. After 30 min the solution was filtered and reduced in volume, and diethyl ether added to precipitate **4** as a violet solid, which was washed successively with toluene and diethyl ether then dried in vacuo, yield 0.053 g (19%).

Preparation of $[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)]$ (5)

A suspension of $[MoCl\{P(OMe)_3\}_2(\eta\text{-}C_7H_7)][PF_6]$ (0.408 g, 0.66 mmol) in toluene (30 cm^3) was treated with $[Co(\eta\text{-}C_5H_5)_2]$ (0.149 g, 0.79 mmol) and stirred for 2 h. The solution was filtered to remove precipitated $[Co(\eta\text{-}C_5H_5)_2][PF_6]$, and the green filtrate evaporated to dryness. Recrystallisation of the residue from toluene/n-hexane gave **5** as a green solid, yield 0.094 g (30%).

$[MoCl(dppe)(\eta\text{-}C_7H_7)]$ was prepared in 46% yield from $[MoCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (0.765 g, 1.0 mmol) and $[Co(\eta\text{-}C_5H_5)_2]$ (0.224 g, 1.2 mmol) and an identical procedure to that described for **5** except that the final recrystallisation was carried out from diethyl ether/n-hexane. (Found: C, 63.6; H, 5.5; Cl, 5.7. $C_{33}H_{31}MoP_2Cl$ calcd.: C, 63.8; H, 5.0; Cl, 5.7%)

Preparation of $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (6)

A solution of PPh_3 (1.26 g, 4.80 mmol) in toluene (30 cm^3) was added dropwise over a $1\frac{1}{2}$ h period to a stirred solution of $[WI(CO)_2(\eta\text{-}C_7H_7)]$ (1.99 g, 4.35 mmol) in refluxing toluene (60 cm^3). After completion of the addition the mixture was refluxed for a further 3 h then evaporated to dryness. A solution of the red-brown residue in CH_2Cl_2 (80 cm^3) was filtered, and reduced in volume to 10 cm^3, then transferred to a silica/CH_2Cl_2 chromatography column. Elution with CH_2Cl_2 produced a yellow-brown band, which was collected and evaporated to dryness. Recrystallisation from CH_2Cl_2/n-hexane gave pure $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ as a yellow-brown solid, yield 2.11 g (70%).

Preparation of $[W(CO)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (8)

A mixture of $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (2.11 g, 3.05 mmol) and dppe (1.28 g, 3.20 mmol) in toluene (70 cm^3) was refluxed with stirring for 30 min. The purple-grey precipitate formed was isolated from the yellow mother liquors, washed with toluene then with n-hexane, and dried in vacuo. The resulting product, crude $[W(CO)(dppe)(\eta\text{-}C_7H_7)]I$, was dissolved in acetone (50 cm^3) and treated with $[NH_4][PF_6]$ (2.16 g, 13.25 mmol). After 1.5 h stirring the solution was evaporated to dryness, and the residue extracted with CH_2Cl_2. The extract was filtered then reduced in volume and transferred to a Florisil/CH_2Cl_2 chromatography column. Elution with CH_2Cl_2/acetonitrile (4/1) gave a grey-brown band which was collected as a red solution which was evaporated to dryness. The residue was recrystallised from CH_2Cl_2/diethyl ether to give $[W(CO)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ as a pink-brown solid, yield 1.82 g (71%).

Preparation of $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (9)

A mixture of $[W(CO)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (0.46 g, 0.54 mmol) and $Me_3NO \cdot 2H_2O$ (0.30 g, 2.70 mmol) in acetonitrile (60 cm^3) was refluxed with stirring for $2\frac{1}{2}$ h. The resulting red solution was evaporated to dryness to give a pink residue, which was extracted with CH_2Cl_2. The solution was filtered then reduced in volume and transferred to a Florisil/CH_2Cl_2 chromatography column. Elution with CH_2Cl_2/acetonitrile (3/1) gave a purple-pink band, which was collected as a red solution and evaporated to dryness. Recrystallisation of the residue from CH_2Cl_2/diethyl ether gave $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)[PF_6]$ as a pink solid, yield 0.266 g (57%).

Preparation of $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$ (11)

Treatment of a stirred solution of $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (0.26 g 0.30 mmol) with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.10 g, 0.30 mmol) in acetonitrile (30 cm^3) produced an immediate colour change from red to yellow. After 45 min the solution was reduced in volume and diethyl ether added to give the crude product as an orange oil, which was dried in vacuo. A solution of the solid in acetonitrile (5 cm^3) was added dropwise to a large volume of vigorously stirred diethyl ether to give a precipitate of the pale orange $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$, yield 0.195 g (65%).

$[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2 \cdot (CH_3)_2C{=}O$ (**12**) was prepared in 86% yield from $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (0.51 g, 0.66 mmol) and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.22 g, 0.66 mmol) by an identical procedure to that described for **11** except that the final purification was carried out by use of acetone/diethyl ether.

*Formation of $[MoCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ from **10** and **12***

A red solution of $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (0.27 g, 0.35 mmol) in acetone (40 cm^3) was treated with LiCl (0.15 g, 3.5 mmol) then stirred for 20 h to give a yellow-green solution. Evaporation to dryness and recrystallisation of the residue from CH_2Cl_2/diethyl ether gave $[MoCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ as a yellow solid, yield 0.186 g (70%) (Found: C, 51.8; H, 4.2; Cl, 5.7; P, 12.2 $C_{33}H_{31}MoP_3ClF_6$ calcd.: C, 51.7; H, 4.1; Cl, 4.6; P, 12.1%). An identical procedure was employed for the synthesis of $[MoCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ in 66% yield from $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$ (0.15 g, 0.16 mmol) and LiCl (0.08 g, 1.9 mmol) in acetone (30 cm^3) except that reaction was complete within 30 min (Found: C, 51.2; H, 4.0; Cl, 5.2%).

Preparation of $[WCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (14)

A mixture of $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]_2$ (0.365 g, 0.364 mmol) and LiCl (0.154 g, 3.62 mmol) was stirred in acetone for 24 h to give a pale lemon yellow solution. Removal of acetone in vacuo and recrystallisation of the residue from CH_2Cl_2/diethyl ether gave [WCl(dppe)(η-C_7H_7)][PF_6] as a pale yellow solid, yield 0.256 g (82%).

Preparation of [WCl(dppe)(η-C_7H_7)] (15)

A suspension of [WCl(dppe)(η-C_7H_7)][PF_6] (0.234 g, 0.275 mmol) and [Co(η-C_5H_5)$_2$] (0.062 g, 0.330 mmol) in toluene (20 cm^3) was stirred for 2 h to give an olive-green solution. Filtration, evaporation to low volume, and addition of n-hexane gave a green precipitate of **15**, which was purified by recrystallisation from diethyl ether/n-hexane, yield 0.027 g (14%).

Reaction of [W(NCMe)(dppe)(η-C_7H_7)][PF_6] (9) with LiCl

A mixture of [W(NCMe)(dppe)(η-C_7H_7)][PF_6] (0.206 g, 0.24 mmol) and LiCl (0.106 g, 2.49 mmol) in acetone (60 cm^3) was refluxed with stirring for 24 h. The yellow-green solution was evaporated to dryness and the residue extracted with CH_2Cl_2. Filtration of the extract, reduction of its volume and addition of diethyl ether afforded [WCl(dppe)(η-C_7H_7)][PF_6], yield 0.043 g (21%) (Found C, 46.7; H, 3.8; Cl 4.3%). The remaining yellow-green mother liquors were evaporated to dryness, and the residue recrystallised from diethyl ether/n-hexane to give olive-green [WCl(dppe)(η-C_7H_7)], yield 0.049 g (29%) (Found: C, 54.7; H, 5.3; Cl, 4.3%).

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