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The chemistry of cycloheptatrienyl complexes of molybdenum and tungsten: synthesis and substitution chemistry of some new carbonylacetonitrile derivatives

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Abstract

Reaction of $[WI(CO)_2(\eta\text{-}C_7H_7)$ with $Ag[BF_4]$ in acetonitrile yields the trihaptocycloheptatrienyl complex $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)][BF_4]$ (**2**), which in CH_2Cl_2 is converted into $[W(CO)_2(NCMe)(\eta\text{-}C_7H_7)][BF_4]$ (**1**). A similar reaction sequence is observed starting from $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ and $Ag[BF_4]$, but a mixture of $[Mo(CO)_2(NCMe)(\eta\text{-}C_7H_7)][BF_4]$ (**3**) and a species formulated as $[Mo(CO)_2\text{-}(NCMe)_3(\eta^3\text{-}C_7H_7)][BF_4]$ (**4**) is obtained in acetonitrile. Treatment of CH_2Cl_2 solutions of **1** or **3** with phosphorus-donor ligands PR'_3 ($R' = OMe$ or Bu^n) or $Ph_2PCH_2PPh_2$ gives, respectively, $[M(CO)_2(PR'_3)(\eta\text{-}C_7H_7)][BF_4]$ and the pendent phosphine complexes $[M(CO)_2(Ph_2PCH_2PPh_2)(\eta\text{-}C_7H_7)][BF_4]$ (**11**, M = W; **12**, M = Mo). Dissolution of **11** in MeCN affords the chelated phosphine-trihaptocycloheptatrienyl derivative $[M(CO)_2(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^3\text{-}C_7H_7)][BF_4]$ (M = W, $n = 1$); analogous complexes (M = Mo or W, $n = 2$) result from reaction of **2** or **3** with $Ph_2P(CH_2)_2PPh_2$ in MeCN. Ultraviolet irradiation of **3** in MeCN yields $[Mo(CO)(NCMe)_2(\eta\text{-}C_7H_7)][BF_4]$.

The syntheses and synthetic applications of carbonylacetonitrile complexes such as $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)]^+$ (C_9H_7 = indenyl) and $[M(CO)_{3-n}(NCMe)_n(\eta\text{-}C_5R_5)]^+$ (M = Fe, R = Me, $n = 1$ or 2; M = Ru, R = H, $n = 1$ or 2) are well documented [1–3]. However examples of acetonitrile derivatives of related cycloheptatrienyl (C_7H_7) complexes of the group 6 transition metals have been confined to $[Mo(NCMe)_3(\eta\text{-}C_7H_7)]^+$ and phosphine substituted species [4] such as $[Mo(NCMe)(dppe)(\eta\text{-}C_7H_7)]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) and $[Mo(NCMe)_2(PPh_3)(\eta\text{-}C_7H_7)]^+$. Although these latter cycloheptatrienylmolybdenum complexes exhibit a wide range of reactions [4,5], the reactivity of the parent carbonylacetonitrile derivatives of both molybdenum and tungsten is clearly of interest. In this paper we report [6] the synthesis of $[M(CO)_2(NCMe)(\eta\text{-}C_7H_7)]^+$

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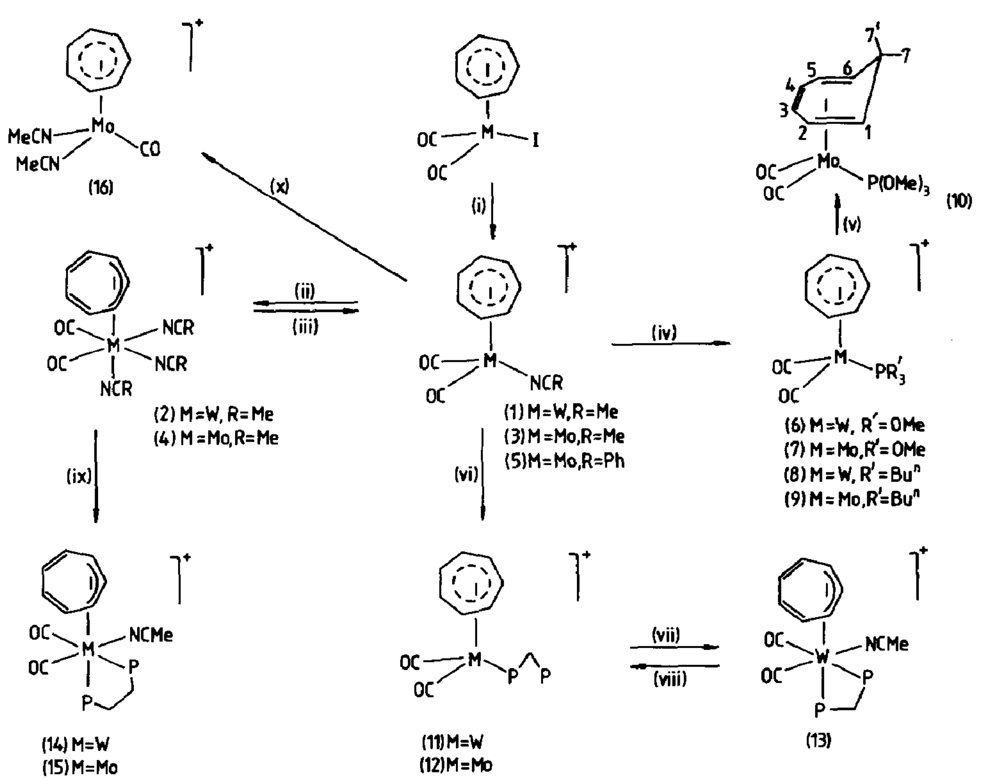

Scheme 1. (i) Ag[BF_4] in RCN (R = Me or Ph); (ii) stir in RCN; (iii) stir in CH_2Cl_2; (iv) R = Me, PR'_3 in CH_2Cl_2; (v) M = Mo, R' = OMe, Na[BH_4] in thf; (vi) R = Me, dppm in CH_2Cl_2; (vii) M = W, stir in MeCN; (viii) stir in CH_2Cl_2; (ix) R = Me, dppe in MeCN; (x) M = Mo, R = Me, UV irradiation in MeCN. P⌒P = dppm, P⌒P = dppe.

(**1**, M = W; **3**, M = Mo) (Scheme 1), $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)]^+$ (**2**) and $[Mo(CO)(NCMe)_2(\eta\text{-}C_7H_7)]^+$ (**16**) and present the results of exploration of one aspect of their synthetic application namely the formation of cationic phosphine derivatives of both tri- and hepta-hapto bonded cycloheptatrienyl complexes. The 'ring slip' process $\eta^7\text{-}C_7H_7 \rightarrow \eta^3\text{-}C_7H_7$ is an important feature of this work, and the finely balanced relative stabilities of the two bonding modes is revealed by observation on several complexes.

Results and discussion

Treatment of a green, acetonitrile solution of $[WI(CO)_2(\eta\text{-}C_7H_7)]$ with Ag[BF_4] rapidly affords a precipitate of silver iodide and an orange-yellow solution which upon work up yields the tris(acetonitrile) complex $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)][BF_4]$ (**2**), which was characterised by elemental analysis and infrared spectroscopy (Table 1) and by ^1H and ^{13}C NMR spectroscopy (Table 2). Formation of a tris(nitrile) complex takes place by the 'ring slip' process $\eta^7\text{-}C_7H_7 \rightarrow \eta^3\text{-}C_7H_7$ which is a well established feature [7,8] in cycloheptatrienyl chemistry of the group 6 transition metals. However complex **2**, an analogue [9] of the allyl complex $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_3H_5)]^+$, is of special significance as the first confirmed example of a cationic $\eta^3\text{-}C_7H_7$ species, and its isolation lends support to the

Table 1

Infrared and microanalytical data

Complex	Yield (%)	Infrared [a] ν(CO) [b] (cm^{-1})	Analysis [c] (%) C	H	N
$[W(CO)_2(NCMe)(\eta\text{-}C_7H_7)][BF_4]$	69	2022 1969	28.8	2.2	3.0
(1)			(28.8)	(2.2)	(3.1)
$[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)][BF_4]$	75	1956 1880 [d]	33.1	3.0	7.6
(2)			(33.3)	(3.0)	(7.8)
$[Mo(CO)_2(NCMe)(\eta\text{-}C_7H_7)][BF_4]$	61 [e]	2036 1993	35.2	2.7	3.6
(3)			(35.6)	(2.7)	(3.8)
$[Mo(CO)_2(NCPh)(\eta\text{-}C_7H_7)][BF_4]$	32 [e]	2040 1998	43.9	2.8	3.4
(5)			(44.3)	(2.8)	(3.2)
$[W(CO)_2\{P(OMe)_3\}(\eta\text{-}C_7H_7)][BF_4]$	82	2022 1972	26.6	2.9	
(6)			(26.6)	(3.0)	
$[Mo(CO)_2\{P(OMe)_3\}(\eta\text{-}C_7H_7)][BF_4]$	64	2033 1990	31.6	3.5	
(7)			(31.7)	(3.6)	
$[W(CO)_2(PBu^n{}_3)(\eta\text{-}C_7H_7)][BF_4]$	77	2004 1952	40.0	5.5	
(8)			(40.6)	(5.5)	
$[Mo(CO)_2(PBu^n{}_3)(\eta\text{-}C_7H_7)][BF_4]$	68	2015 1971	47.1	6.4	
(9)			(47.4)	(6.4)	
$[Mo(CO)_2\{P(OMe)_3\}(\eta^6\text{-}C_7H_8)]$ [f]	46	1933 1860 [g]	38.7	4.7	
(10)			(39.1)	(4.7)	
$[W(CO)_2(NCMe)(dppm)(\eta^3\text{-}C_7H_7)][BF_4]$	75 [h]	1953 1879 [d]	51.9	4.2	1.9
(13)			(51.2)	(3.8)	(1.7)
$[W(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_7)][BF_4]$	43	1944 1873 [d]	51.4	4.1	1.3
(14)			(51.8)	(4.0)	(1.6)
$[Mo(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_7)][BF_4]$	77	1948 1878 [d]	57.3	4.9	1.4
(15)			(57.7)	(4.4)	(1.8)
$[Mo(CO)(NCMe)_2(\eta\text{-}C_7H_7)][BF_4]$	25	1984	37.3	3.4	6.7
(16)			(37.5)	(3.4)	(7.2)

[a] Nujol mull data for absorptions between 2400-2100 cm^{-1}; relative intensities, s = strong, m = medium, w = weak (all absorptions weak by comparison with ν(CO)). (1) 2327(ms), 2294(s), (2) 2319(s), 2290(ms), (3) 2349(w), 2325(m), 2295(s), (5) 2252(s), (16) 2315(m), 2282(m). [b] In CH_2Cl_2 unless stated otherwise. [c] Calculated values are given in parentheses. [d] In CH_3CN. [e] Yield based on $[MoI(CO)_2(\eta\text{-}C_7H_7)]$. [f] $m/e = 370$ (^{98}Mo) by mass spectroscopy. [g] In hexane. [h] Yield based on **11**.

formulation of $[M(CO)_3(NCMe)_2(\eta^3\text{-}C_7H_7)]^+$ (M = Mo or W) as an intermediate in the formation of $[M(CO)_3(NCMe)_3]$ from $[M(CO)_3(\eta\text{-}C_7H_7)]^+$ at elevated temperature in acetonitrile [10]. The pseudo-octahedral molecular geometry assigned to **2**, incorporating *cis* carbonyl groups and a facial arrangement of acetonitrile ligands, (as established crystallographically for related $[Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_3H_5)]^+$ [11]) is based upon the relative intensities of the two infrared active carbonyl stretching frequencies [12] and, in the ^{13}C NMR spectrum, the observation of a single signal in the carbonyl carbon region. In common with spectroscopic studies on the related complexes $[MCl(CO)_2(en)(\eta^3\text{-}C_7H_7)]$ (M = Mo or W; en = 1,2-diaminoethane) [13] the room temperature ^{1}H and ^{13}C NMR spectra of **2** exhibit only a broad resonance for the cycloheptatrienyl ring; this may be explained by a relatively slow 1,2 shift of the metal group around the ring [14]. In the case of $[MCl(CO)_2(en)(\eta^3\text{-}C_7H_7)]$ low temperature studies were successful in 'freezing out' the 1,2 shift process, and the individual environments of the $\eta^3\text{-}C_7H_7$ ring were resolved [13], but this was not possible for **2** owing to its instability in solvents other

Table 2

Proton, ^{31}P and ^{13}C NMR spectral data [a]

Complex	$\delta(^1H)$ (ppm) [b]	^{31}P (ppm) [c]
1 [d]	5.68(s,7H,C_7H_7), 2.50(s,3H,NCMe)	
2 [e]	5.08(br,C_7H_7), 2.30(s,NCMe), 2.26(s,NCMe)	
3 [d]	5.75(s,7H,C_7H_7), 2.36(s,3H,NCMe)	
5 [d]	7.83(m,2H,Ph), 7.75(m,1H,Ph), 7.58(m,2H,Ph), 5.82(s,7H,C_7H_7)	
6 [f]	5.91[d,J(P–H)2.5,7H,C_7H_7], 3.70[d,J(P–H)12,9H,$P(OMe)_3$]	121.4[s,$J(^{183}W$–P)542]
7 [f]	5.99[d,J(P–H)3,7H,C_7H_7], 3.70[d,J(P–H)12,9H,$P(OMe)_3$]	153.4,s
8 [f]	5.78[d,J(P–H)2,7H,C_7H_7], 1.91(m,2H,CH_2), 1.42(m,2H,CH_2), 1.24(m,2H,CH_2), 0.91[t,J(H–H)7,3H,CH_3]	−9.4[s,$J(^{183}W$–P)381]
9 [f]	5.87[d,J(P–H)2,7H,C_7H_7], 1.83(m,2H,CH_2), 1.43(m,2H,CH_2), 1.27(m,2H,CH_2), 0.92[t,J(H–H)7,3H,CH_3]	18.6,s
10 [f,g]	5.85(m,2H,H(3),H(4), 4.80(m,2H,H(2),H(5), 3.65[d,J(P–H)11, 9H,$P(OMe)_3$], 3.45(m,2H,H(1),H(6), 2.88(m,1H,H(7), 2.51(m,1H,H(7′)	188.8,s
13 [h]	7.61(br,20H,Ph), 5.23(m,1H,CH_2), 5.23[t,J(P–H)1, 7H,C_7H_7], 4.77(m,1H,CH_2), 1.60[t,J(P–H)1.5,3H,NCMe]	−15.7[d,J(P–P)6, $J(^{183}W$–P)202] −31.1[d,J(P–P)6, $J(^{183}W$–P)189]
14	7.48(br,20H,Ph), 5.02(s,7H,C_7H_7), 2.80,2,60(br,4H,CH_2), 1.54[t,J(P–H)1,3H,NCMe]	42.5[d,J(P–P)7, $J(^{183}W$–P)229] 35.9[d,J(P–P)7, $J(^{183}W$–P)213]
15 [j]	7.48(br,20H,Ph), 5.29(s,7H,C_7H_7), 2.68(br,4H,CH_2) [k]	56.8[d,J(P–P)21] 50.7[d,J(P–P)21]
16 [d]	5.36(s,7H,C_7H_7), 2.39(s,6H,NCMe)	

[a] In CD_3CN unless stated otherwise. [b] Chemical shifts downfield from $SiMe_4$; s, singlet; d, doublet, t, triplet; m, multiplet; br, broad; J values in Hz. [c] Positive chemical shifts downfield from H_3PO_4. [d] In CD_2Cl_2. [e] ^{13}C NMR data (ppm); 214.3(s,CO), 124.2(s,N*C*Me), 100.9(br,C_7H_7). [f] In $CDCl_3$. [g] Numbering as in Scheme 1. [h] ^{13}C NMR data (ppm); 219.4[t,J(P–C)18], 209.7[t,J(P–C)6](CO), 133.5–126.7(Ph), 103.8(C_7H_7), 40.3(CH_2). [j] ^{13}C NMR data (ppm); 226.7[t,J(P–C)21], 220.0[t,J(P–C)8] (CO), 132.5–128.9(Ph), 106.8(C_7H_7), 26.9, 25.5(CH_2). [k] Coordinated NCMe not observed (see text).

than acetonitrile, which precluded investigations below − 40 °C. The ^1H NMR spectrum of **2** in CD_3CN also exhibits two sharp singlets, with chemical shifts characteristic of coordinated CH_3CN, and a third singlet at δ 1.86 ppm assigned to free CH_3CN. The implied lability of coordinated CH_3CN to exchange was confirmed by monitoring the ^1H NMR spectrum of **2** at intervals in CD_3CN; a steady increase in the concentration of free CH_3CN coincided with a decrease in the intensity of signals assigned to the two coordinated CH_3CN environments, and complete exchange of CH_3CN for CD_3CN was complete within 1 h at 25 °C.

In solvents such as tetrahydrofuran (thf) or CH_2Cl_2, which are very weakly- or non-coordinating to the tungsten centre, displacement of two acetonitrile ligands from **2** is accompanied by reversion to a heptahapto bonded cycloheptatrienyl ring and formation of green $[W(CO)_2(NCMe)(\eta\text{-}C_7H_7)][BF_4]$ (**1**), which was characterised from the data listed in Tables 1 and 2. Conversely, dissolution of **1** in acetonitrile leads to rapid reformation of **2**, indicating that the reaction of $[WI(CO)_2(\eta\text{-}C_7H_7)]$ with $Ag[BF_4]$ in acetonitrile proceeds via the intermediacy of **1** and subsequent reaction with the solvent to yield **2**.

The reaction of $[\mathrm{MoI(CO)_2(\eta\text{-}C_7H_7)}]$ with $\mathrm{Ag[BF_4]}$ in acetonitrile differs slightly from that of the tungsten analogue in that an equilibrium mixture of $[\mathrm{Mo(CO)_2(NCMe)(\eta\text{-}C_7H_7)}][\mathrm{BF_4}]$ (**3**) and a second complex formulated as $[\mathrm{Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)}][\mathrm{BF_4}]$ (**4**) is produced; thus four infrared active carbonyl stretching frequencies (2034, 1989, 1960 and 1887 $\mathrm{cm^{-1}}$) are observed in a green-brown solution of the reaction mixture. Removal of acetonitrile and dissolution of the residue in $\mathrm{CH_2Cl_2}$ affords, as the sole product, monoacetonitrile complex **3** (data are shown in Tables 1 and 2) which was shown to be the component of the equilibrium mixture giving carbonyl stretching frequencies at 2034 and 1989 $\mathrm{cm^{-1}}$ in acetonitrile. The formulation of the second component of the mixture as $[\mathrm{Mo(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)}][\mathrm{BF_4}]$ is prompted by the isolation of tungsten analogue **2**, which in acetonitrile exhibits closely similar carbonyl stretching frequencies, at 1956 and 1880 $\mathrm{cm^{-1}}$. The results of ^{1}H NMR studies on solutions of isolated **3** dissolved in $\mathrm{CD_3CN}$ are also consistent with the formation of an equilibrium mixture involving two cycloheptatrienyl complexes. Two singlets (δ 5.82 and 5.49 ppm) are observed in the region characteristic of cycloheptatrienyl protons, with integrals in the approximate ratio 2.5/1 (δ5.82/δ5.49), for initial concentrations of **3** in the range 0.02 *M* to 0.1 *M* at 20 °C. It is probable that the low field singlet comes from **3** but we could not make a definitive assignment. The benzonitrile complex $[\mathrm{Mo(CO)_2(NCPh)(\eta\text{-}C_7H_7)}][\mathrm{BF_4}]$ (**5**) was also prepared from the reaction of $[\mathrm{MoI(CO)_2(\eta\text{-}C_7H_7)}]$ with $\mathrm{Ag[BF_4]}$ in benzonitrile followed by stirring of a solution of the product in $\mathrm{CH_2Cl_2}$; in this case infrared monitoring of the crude reaction mixture in benzonitrile revealed only very weak carbonyl bands in the region attributable to a trisnitrile trihaptocycloheptatrienyl component. Characterisation data for complex **5** are shown in Tables 1 and 2.

Infrared spectra of complexes **1**, **2** and **3** in the region between 2400 and 2100 $\mathrm{cm^{-1}}$ each exhibit two absorptions of similar intensity which could arise from $\nu(\mathrm{C{\equiv}N})$ stretching of coordinated acetonitrile. Assignment of these absorptions is not simple, however, since a combination band, resulting from symmetrical $\mathrm{CH_3}$ deformation and C–C stretching, is a common feature in the $\nu(\mathrm{C{\equiv}N})$ region of acetonitrile complexes [15]. Moreover evidence that such a combination band must be considered, at least for **1** and **3**, is provided by comparison of data for the deuterated derivative $[\mathrm{Mo(CO)_2(NCCD_3)(\eta\text{-}C_7H_7)}][\mathrm{BF_4}]$ which exhibits only one significant absorption in this region at 2306 $\mathrm{cm^{-1}}$ (Nujol) together with a weak absorption at 2257 $\mathrm{cm^{-1}}$.

The wide range of examples of substitution of acetonitrile by tertiary phosphines and tertiary phosphites at a group 6 transition metal centre [1,16], together with the demonstrated lability towards exchange of the acetonitrile ligands of **2**, prompted us to investigate appropriate substitution reactions of **1**, **2** and **3**. In $\mathrm{CH_2Cl_2}$ the acetonitrile ligand of $[\mathrm{M(CO)_2(NCMe)(\eta\text{-}C_7H_7)}]^+$ (M = Mo or W) is readily replaced by tertiary phosphines and phosphites to give the known complexes $[\mathrm{M(CO)_2(PR'_3)(\eta\text{-}C_7H_7)}]^+$ (M = Mo, $\mathrm{PR'_3 = PPh_3}$, $\mathrm{P(OPh)_3}$ etc. [17]; M = W, $\mathrm{PR'_3 = PPh_3}$ [18]). Furthermore, derivatives of $[\mathrm{M(CO)_2(PR'_3)(\eta\text{-}C_7H_7)}]^+$, unattainable by established routes [17,19] owing to competitive displacement of the cycloheptatrienyl ring, have now been conveniently synthesised in high yield. Thus reaction of trimethylphosphite with either **1** or **3** proceeds rapidly and smoothly at room temperature in $\mathrm{CH_2Cl_2}$ to afford the previously inaccessible complexes $[\mathrm{M(CO)_2\{P(OMe)_3\}(\eta\text{-}C_7H_7)}][\mathrm{BF_4}]$ (**6**, M = W; **7**, M = Mo), data for which are given in Tables 1 and 2. Similarly reaction of PBu^n_3 with **1** or **3** in CH_2Cl_2 gives orange red $[M(CO)_2(PBu^n_3)(\eta\text{-}C_7H_7)][BF_4]$ (**8**, M = W; **9**, M = Mo) characterised by elemental analysis and infrared spectroscopy (Table 1) and by ^1H and ^{31}P NMR spectroscopy (Table 2). An additional advantage of the intermediacy of the relatively stable acetonitrile complexes **1** and **3** is that products are not contaminated with $[M(CO)_3(\eta\text{-}C_7H_7)]^+$ (M = Mo or W) (which may be formed in reactions involving treatment of $[MI(CO)_2(\eta\text{-}C_7H_7)]$ with $Ag[BF_4]$ in non-coordinating solvents such as CH_2Cl_2).

The trimethylphosphite derivative **7** did not undergo Michaelis Arbusov elimination on reaction with NaI in acetone, but treatment with $Na[BH_4]$ in thf and purification of the product by column chromatography gave the orange cycloheptatriene complex $[Mo(CO)_2\{P(OMe)_3\}(\eta^6\text{-}C_7H_8)]$ (**10**). Spectroscopic data for **10** reveal two features of note. The solution infrared spectrum in hexane displays two sharp carbonyl absorptions devoid of shoulders; this is in contrast to the behaviour of the triphenylphosphite analogue $[Mo(CO)_2\{P(OPh)_3\}(\eta^6\text{-}C_7H_8)]$, for which conformational isomers may exist [17]. In the ^1H NMR spectrum of **10** the *exo* and *endo* protons (H(7′) and H(7), respectively (Scheme 1)) exhibit discrete signals with distinctly different chemical shifts; the high field signal is tentatively assigned to the *exo* proton H(7′) on the basis of previous work on the ring substituted complexes [20] $[Cr(CO)_3(\eta^6\text{-}C_7H_7X)]$ (X = CN, Me, Ph etc.).

Reaction of **1** or **3** with the potentially bidentate phosphine 1,2-bis(diphenylphosphino)methane (dppm) in CH_2Cl_2 provides improved syntheses of the known pendent phosphine complexes $[M(CO)_2(dppm)(\eta\text{-}C_7H_7)][BF_4]$ (**11**, M = W [8]; **12**, M = Mo [21]), which were identified by comparison of infrared and ^{31}P NMR spectra with those of authentic samples. The molybdenum complex **12** is also formed when **3** is treated with dppm in acetonitrile, but the corresponding treatment of **1** in acetonitrile proceeds slowly to give the chelated phosphine-trihaptocycloheptatrienyl complex $[W(CO)_2(NCMe)(dppm)(\eta^3\text{-}C_7H_7)][BF_4]$ (**13**). Complex **13** was also formed when isolated samples of **11** were stirred in acetonitrile, and this latter method of preparation was found to be superior for the synthesis of analytically pure samples of **13**. The analogous dppe complexes $[M(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_7)][BF_4]$ (**14**, M = W; **15**, M = Mo) have been obtained by reaction of dppe with **2** and **3**, respectively, in acetonitrile; direct formation of the tungsten derivative **14** proceeds very slowly at ambient temperatures and so reflux conditions were employed, but by contrast the molybdenum analogue **15** is rapidly formed at room temperature from **3** (in acetonitrile **3** exists as a mixture with **4**). Complexes **13**, **14** and **15** were characterised by elemental analysis and infrared spectroscopy (Table 1) and ^1H, ^{31}P and (except **14**) ^{13}C NMR spectroscopy (Table 2). The IR spectra of **13**, **14** and **15** as Nujol mulls each appear to exhibit three absorptions around 2300 cm^{-1} typical of $\nu(C{\equiv}N)$ stretching but their intensities are so weak that we cannot confidently distinguish them from background noise. The ^1H NMR spectra of the tungsten derivatives **13** and **14** seem to exhibit a small and unusual long range coupling $^5J(P\text{-}H)$ to the methyl protons of the acetonitrile ligand; we are unaware of any related examples in the literature, but our own investigations on the ^1H NMR spectrum of $[W(NCMe)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ [22] accord with the observations described here. The ^1H NMR spectrum of the molybdenum complex **15** shows no signal attributable to coordinated acetonitrile, but a resonance corresponding to free CH_3CN is observed; this may be accounted for in terms of the higher lability to exchange of molybdenum coordinated acetonitrile, which is a consistent feature of this work.

Complexes **13**, **14** and **15** may also be synthesised by reaction of the appropriate iodide complex $[MI(CO)_2(P{-}P)(\eta^3\text{-}C_7H_7)]$ (M = W, P–P = dppm or dppe; M = Mo, P–P = dppe [8,23]) with $Ag[BF_4]$ in acetonitrile. However samples of **13**, **14** and **15** prepared by this method, whilst exhibiting identical infrared and ^{31}P NMR spectra to those of the authentic complexes, were found to contain small quantities of silver and iodine even after many recrystallisations.

On the basis of ^{31}P and ^{13}C NMR studies we have previously assigned a pseudo-octahedral molecular geometry to the neutral trihaptocycloheptatrienyl complexes $[MX(CO)_2(P{-}P)(\eta^3\text{-}C_7H_7)]$ (M = Mo or W; X = halide; P–P = dppm or dppe) in which inequivalent phosphorus-donor atoms are arranged *cis–cis* and *cis–trans* to two mutually *cis* carbonyl ligands [13]. An analogous structure for cationic **13**, **14** and **15**, illustrated in Scheme 1, would be consistent with infrared and ^{31}P NMR data for these complexes. However the carbonyl carbon regions of the ^{13}C NMR spectra of **13** and **15** each exhibit two apparent triplets, in marked contrast to the corresponding signals in the ^{13}C NMR spectra of the neutral halide analogues $[MX(CO)_2(P{-}P)(\eta^3\text{-}C_7H_7)]$ [13]. The low field triplet exhibits phosphorus-carbon coupling typical of a *trans* arrangement whilst the magnitude of $|^2J(^{31}P{-}^{13}C)|$ for the high field signal is more typical of *cis* coupling [24]; values for apparent couplings $|^2J(^{31}P{-}^{13}C)|$ are given in Table 2. The virtual equivalence of the phosphorus-donor atoms, as experienced by the carbonyl ligands of **13** and **15**, is unlikely to be attributable to a fluxional process resulting in averaging of the two phosphorus environments since the ^{13}C and ^{31}P NMR data reported for **13** and **15** were recorded at very similar temperatures. An alternative explanation, currently under investigation, involves an electronically favoured structural distortion from the pseudo-octahedral geometry of the neutral halide complexes $[MX(CO)_2(P{-}P)(\eta^3\text{-}C_7H_7)]$ to a new polytopal form (possibly related to the pentagonal-bipyramidal structure of $[MoCl(CO)_2\{P(OMe)_3\}_2(\eta^3\text{-}C_3H_5)]$ [25]) for the cationic acetonitrile derivatives $[M(CO)_2(NCMe)(P{-}P)(\eta^3\text{-}C_7H_7)][BF_4]$. However, any structural distortion that does occur must have very little effect on the inter-carbonyl angle as determined from a comparison of the relative intensities of carbonyl stretching frequencies for pairs of complexes $[MX(CO)_2(P{-}P)(\eta^3\text{-}C_7H_7)]$ and $[M(CO)_2(NCMe)(P{-}P)(\eta^3\text{-}C_7H_7)]^+$. A referee has pointed out that a side-on bonded η^2-acetonitrile ligand [15] should also be considered as a possible structural feature of complexes **13**, **14** and **15**.

The characterisation or purification of **13**, **14** and **15** in solvents other than acetonitrile was inhibited by the lack of stability of these complexes in non-coordinating solvents. Infrared monitoring of CH_2Cl_2 solutions of **13**, **14** and **15** revealed that whilst changes in **14** were minimal, **15** underwent incomplete conversion into a product tentatively assigned as $[Mo(CO)_2(dppe)(\eta\text{-}C_7H_7)][BF_4]$ [23] (ν(CO)(CH_2Cl_2) 2021, 1977 cm^{-1}), and **13** rapidly reformed **11**, as confirmed in an independent preparative experiment from which **11** was isolated and characterised. The reversible interconversion of **11** and **13** provides a further example of solvent-dependent selectivity between η^3- and $\eta^7\text{-}C_7H_7$ derivatives whilst the relative stability of **14** contrasted with our failure to isolate $[Mo(CO)_2(NCMe)(dppm)(\eta^3\text{-}C_7H_7)][BF_4]$ illustrates the extreme effects of chelate ring size and the identity of the metal upon such selectivity. Thus the pendent phosphine complex $[W(CO)_2(dppe)(\eta\text{-}C_7H_7)]$-

$[BF_4]$ (which has not yet been synthesised) could not be obtained from reaction of **1** with dppe even in CH_2Cl_2.

The nitrile substitution chemistry of cycloheptatrienylmolybdenum complexes has been further extended by the synthesis of the bis(acetonitrile) derivative $[Mo(CO)(NCMe)_2(\eta\text{-}C_7H_7)][BF_4]$ (**16**). Ultraviolet irradiation of a solution of **3** in acetonitrile or warming of the solution to 65 °C affords **16** (see Tables 1 and 2) which may be separated from traces of unchanged **3** by recrystallisation from CH_2Cl_2-thf. The synthetic potential of **16** is limited by the relatively low yields obtained, but again replacement of acetonitrile ligands proceeds readily; for example in situ treatment of a preformed acetonitrile solution of **16** with dppe affords moderate yields of known $[Mo(CO)(dppe)(\eta\text{-}C_7H_7)]^+$ [23].

Experimental

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, and distilled and deoxygenated before use. The complexes $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ [26] and $[WI(CO)_2(\eta\text{-}C_7H_7)]$ [7] were prepared by published procedures. Aldrich Chemical Co. supplied dppe, dppm, $P(OMe)_3$, PBu^n_3 and $Ag[BF_4]$; Florisil for column chromatography and $Na[BH_4]$ were purchased from BDH Chemicals. Ultraviolet irradiations were carried out by use of a water-cooled 500 W mercury lamp with solutions contained in quartz glassware.

Hydrogen-1 NMR spectra were recorded on a Varian Associates SC 300 instrument, ^{13}C NMR spectra at 75 MHz on a Varian Associates XL 300 spectrometer and ^{31}P NMR spectra at 32.4 MHz on a Bruker WP 80 spectrometer. Infrared spectra were obtained on a Perkin–Elmer FT 1710 spectrometer and electron impact mass spectra using an AEI MS 30 instrument. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparation of $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)][BF_4]$ (2)

A green, stirred solution of $[WI(CO)_2(\eta\text{-}C_7H_7)]$ (1.64 g, 3.58 mmol) in acetonitrile (50 cm^3) was treated with $Ag[BF_4]$ (0.70 g, 3.59 mmol) to form a precipitate of AgI and an orange-yellow solution. After 30 min the solution mixture was filtered and reduced in volume, and diethyl ether was added to precipitate the crude product. Recrystallisation from acetonitrile-diethyl ether afforded **2** as an orange-yellow solid; yield 1.45 g (75%).

Preparation of $[W(CO)_2(NCMe)(\eta\text{-}C_7H_7)][BF_4]$ (1)

A solution of $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)][BF_4]$ (**2**) (0.24 g, 0.44 mmol) in CH_2Cl_2 (50 cm^3) was stirred at room temperature for 2 h to give a deep green solution which was filtered and reduced in volume, and the product precipitated by addition of diethyl ether. Recrystallisation from CH_2Cl_2-diethyl ether gave the analytical sample of **1** as a green solid; yield 0.14 g (69%).

Preparation of $[Mo(CO)_2(NCMe)(\eta\text{-}C_7H_7)][BF_4]$ (3)

A stirred solution of $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ (0.77g, 2.08 mmol) in acetonitrile (50 cm^3) was treated with $Ag[BF_4]$ (0.40 g, 2.05 mmol). After 20 min the resulting brown solution was filtered and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (40 cm^3), stirred for 30 min, then filtered and reduced in volume. Diethyl ether was added to precipitate the crude product. Recrystallisation from CH_2Cl_2-diethyl ether gave **3** as a green solid; yield 0.47 g (61%). Green-brown $[Mo(CO)_2(NCPh)(\eta\text{-}C_7H_7)][BF_4]$ (**5**) was prepared similarly from $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ (0.51 g, 1.38 mmol) and $Ag[BF_4]$ (0.27 g, 1.38 mmol) in benzonitrile.

Preparation of $[W(CO)_2\{P(OMe)_3\}(\eta\text{-}C_7H_7)][BF_4]$ *(6)*

Addition of $P(OMe)_3$ (0.14 g, 1.13 mmol) to a stirred solution of $[W(CO)_2(NCMe)(\eta\text{-}C_7H_7)][BF_4]$ (0.52 g, 1.13 mmol) in CH_2Cl_2 (40 cm^3) caused a rapid colour change from green to red. After 1 h solvent was removed in vacuo and the residue recrystallised from CH_2Cl_2-diethyl ether to give (**6**) as an orange solid; yield 0.50 g (82%). The PBu^n_3 derivative (**8**) and the orange-red molybdenum complexes **7** and **9** were prepared by an identical procedure.

Preparation of $[Mo(CO)_2\{P(OMe)_3\}(\eta^6\text{-}C_7H_8)]$ *(10)*

To a stirred, cooled (0 °C) suspension of $[Mo(CO)_2\{P(OMe)_3\}(\eta\text{-}C_7H_7)][BF_4]$ (0.85 g, 1.87 mmol) in thf (60 cm^3), $Na[BH_4]$ (0.43 g, 11.32 m mol) was added in small portions during 1 h. The solution was stirred for a further 1 h then evaporated to dryness and the residue was dissolved in CH_2Cl_2 and transferred to a Florisil-n-hexane chromatography column. Elution with CH_2Cl_2 gave an orange band, which was collected and the solvent removed. Dissolution of the residue in n-hexane and cooling to −20 °C gave **10** as an orange-yellow solid; yield 0.32 g (46%).

Preparation of $[W(CO)_2(dppm)(\eta\text{-}C_7H_7)][BF_4]$ *(11) from 1*

A solution of **1** (0.26 g, 0.57 mmol) in CH_2Cl_2 (40 cm^3) was treated with dppm (0.22 g, 0.57 mmol) and the mixture was refluxed with stirring for 20 min. The resulting red solution was reduced in volume and diethyl ether was added to precipitate the crude product. Recrystallisation from acetone-diethyl ether gave **11** as a brick-red solid; yield 0.16 g (35%) (Found C, 50.3; H, 3.7. $C_{34}H_{29}BF_4WP_2O_2$ calcd.: C, 50.9; H, 3.6%). A similar procedure was employed for the preparation of $[Mo(CO)_2(dppm)(\eta\text{-}C_7H_7)][BF_4]$ (12) in 78% yield from **3** (0.205 g, 0.55 mmol) and dppm (0.21 g, 0.55 mmol) except that reaction occurred at room temperature.

Preparation of $[W(CO)_2(NCMe)(dppm)(\eta^3\text{-}C_7H_7)][BF_4]$ *(13) from 11 and the reversible formation of 11*

A solution of $[W(CO)_2(dppm)(\eta\text{-}C_7H_7)][BF_4]$ (**11**) (1.09 g, 1.36 mmol) was stirred at room temperature in acetonitrile (60 cm^3) for 20 min. Solvent was removed in vacuo and the residue recrystallised from acetonitrile-diethyl ether to give **13** as an orange-brown solid; yield 0.86 g (75%).

The pendent phosphine complex **11** was regenerated in 39% yield when **13** (0.16 g, 0.19 mmol) was stirred in CH_2Cl_2 (30 cm^3) at room temperature for 1 h; **11** was isolated by recrystallisation from CH_2Cl_2-diethyl ether and identified by microanalysis, IR and ^1H NMR spectroscopy.

Preparation of $[W(CO)_2(NCMe)(dppe)(\eta^3\text{-}C_7H_7)][BF_4]$ *(14) from 2*

A mixture of $[W(CO)_2(NCMe)_3(\eta^3\text{-}C_7H_7)][BF_4]$ (0.50 g, 0.92 mmol) and dppe (0.37 g, 0.93 mmol) in acetonitrile (80 cm^3) was refluxed with stirring for 15 min to give a dark orange solution. Filtration, reduction in volume, and addition of diethyl ether gave the product as a brown oil, which solidified when dried in vacuo and then washed with diethyl ether. Recrystallisation from acetonitrile-diethyl ether gave **14** as an orange-brown solid; yield 0.34 g (43%).

Preparation of [Mo(CO)$_2$(NCMe)(dppe)(η^3-C_7H_7)][BF$_4$] (15) from 3

A solution of [Mo(CO)$_2$(NCMe)(η-C_7H_7)][BF$_4$] (0.62 g, 1.67 mmol) in acetonitrile (40 cm^3) was stirred for 5 min then treated with dppe (0.66 g, 1.67 mmol). The resulting brown solution was stirred for a further 10 min then reduced in volume, and diethyl ether was added to precipitate the crude product as a brown oil, which solidified when treated as described for **14**. Recrystallisation from acetonitrile-diethyl ether gave **15** as an orange-red solid; yield 0.99 g (77%).

Preparation of [Mo(CO)$_2$(NCMe)(dppe)(η^3-C_7H_7)][BF$_4$] (15) from [MoI(CO)$_2$(dppe)(η^3-C_7H_7)]

A stirred mixture of [MoI(CO)$_2$(dppe)(η^3-C_7H_7)] (0.84 g, 1.10 mmol) and Ag[BF$_4$] (0.21 g, 1.08 m mol) in acetonitrile (40 cm^3) afforded an orange solution and a precipitate of silver iodide. After 50 min stirring the solution was filtered and reduced in volume, and diethyl ether was added to precipitate a red-brown oil which was dried in vacuo. Recrystallisation from acetonitrile-diethyl ether gave **15** as a red solid contaminated with small quantities of silver and iodine; yield 0.31 g. (Found C, 57.4; H, 4.7; N, 2.1; I, 1.0; Ag, 1.3%). Instability of **15** in solvents other than acetonitrile precluded alternative recrystallisation procedures.

Preparation of [Mo(CO)(NCMe)$_2$(η-C_7H_7)][BF$_4$] (16)

Ultraviolet irradiation of a stirred solution of [Mo(CO)$_2$(NCMe)(η-C_7H_7)][BF$_4$] (0.46g, 1.24 mmol) in acetonitrile (50 cm^3) for 6 h produced a green solution. Removal of solvent in vacuo and recrystallisation of the residue from CH_2Cl_2-thf to remove traces of unchanged **3** afforded **16** as a light green solid; yield 0.12 g (25%).

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