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The synthesis of ring-substituted cycloheptatrienyl complexes $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ ($M = Cr$, Mo or W; $R = Me$, ^{t}Bu, C_6H_4–F-*p* or $C{\equiv}CPh$)

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Abstract

The relative merits of various routes to ring-substituted cycloheptatrienyl complexes $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ ($M = Cr$, Mo or W) have been explored. Substitution at a metal coordinated C_7H_7 ring is effected via addition, thermal rearrangement and subsequent H^- abstraction. Thus reaction of $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$ with NaOMe gives $[Mo(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}OMe)C_7H_7\}]$, which affords substituted cycloheptatriene complexes $[Mo(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}R)C_7H_7\}]$ [R = Me (**1**); ^{t}Bu (**2**); C_6H_4–F-*p* (**3**)] by reaction with RMgX; direct addition of $C{\equiv}CPh$ to $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$ to give $[M(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}C{\equiv}CPh)C_7H_7\}]$ [M = Cr (**4**); M = Mo (**5**)] is brought about by reaction with alkynyl cuprate reagents. Thermolysis of **1–4** gives isomeric mixtures of rearranged cycloheptatriene complexes $[M(CO)_3\{\eta^6\text{-}(n\text{-}R)C_7H_7\}]$ ($n = 1$, 2 or 3), which contain a CH_2 ring carbon with an *exo* hydrogen accessible to H^- abstraction by Ph_3C^+ to yield the ring-substituted cycloheptatrienyl complexes $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ [M = Mo; R = Me (**7**); ^{t}Bu (**8**); C_6H_4–F-*p* (**9**); M = Cr, R = $C{\equiv}CPh$ (**10**)]. Alternatively, substituted cycloheptatrienes C_7H_7R and cycloheptatrienyl ions $C_7H_6R^+$ may be coordinated directly to $[M(CO)_3(NCMe)_3]$. Reaction of 7-Me-C_7H_7 with $[M(CO)_3(NCMe)_3]$ ($M = Cr$, Mo or W) in THF affords $[M(CO)_3\{\eta^6\text{-}(7\text{-}Me)C_7H_7\}]$ as a (metal dependent) *exo/endo* isomeric mixture at C(7). The reaction of the cycloheptatrienyl ions $C_7H_6R^+$ (R = Me, ^{t}Bu, C_6H_4–F-*p*, $C{\equiv}CPh$) with $[M(CO)_3(NCR')_3]$ (M = Mo, R′ = Me; M = W, R′ = ^{n}Pr) proceeds at room temperature in THF or CH_2Cl_2 and provides convenient syntheses of **7**, **8**, **9**, $[Mo(CO)_3\{\eta^7\text{-}C_7H_6(C{\equiv}CPh)\}]^+$ (**11**) and $[W(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ [R = Me (**12**); C_6H_4–F-*p* (**13**)]. Complexes **7**, **8**, **9**, **12** and **13** are useful starting materials for investigation of the chemistry of ring-substituted cycloheptatrienyl complexes, as exemplified by the syntheses of $[MI(CO)_2(\eta^7\text{-}C_7H_6Me)]$ [M = Mo (**14**); M = W (**15**)] and the sandwich complex $[Mo(\eta^6\text{-toluene})(\eta^7\text{-}C_7H_6Me)]^+$ (**16**).

1. Introduction

In the extensive organometallic chemistry of ring-substituted cyclopentadienyl transition metal complexes there is much evidence that ring substitution can considerably influence the properties of such complexes [1,2] but, by contrast, there are few reports of the behaviour of the corresponding ring-substituted complexes of the cycloheptatrienyl ligand [3–5]. The neglect of this area may be due in part to the unavailability of good routes to the relevant cycloheptatrienyl complexes, and this paper presents the results of our efforts to develop and assess methods for the synthesis of mono-substituted derivatives of the cations $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ ($M = Cr$, Mo or W). The substituents R have been selected to provide a range of steric and electronic effects and the work has been directed chiefly towards the synthesis of complexes of Mo and W since these provide an entry into an extensive chemistry via $[MX(CO)_2(\eta^7\text{-}C_7H_6R)]$ (X = halide) and $[Mo(\eta^6\text{-toluene})(\eta^7\text{-}C_7H_6R)]^+$. Some of the new complexes $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ (M = Mo or W) reported here are analogues of known chromium species, but our findings suggest that existing routes to $[Cr(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ are generally unsuitable for extension to the chemistry of Mo and W. Therefore we describe an alternative, efficient synthesis of $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ (M = Mo or W) that provides the basis for investigation of ring substituent effects in cycloheptatrienyl complexes of Mo and W; ring substituent effects are known to influence the stability of transient η^3-cyclopentadienyl rhodium complexes [6], and may also permit an interesting extension to our own studies

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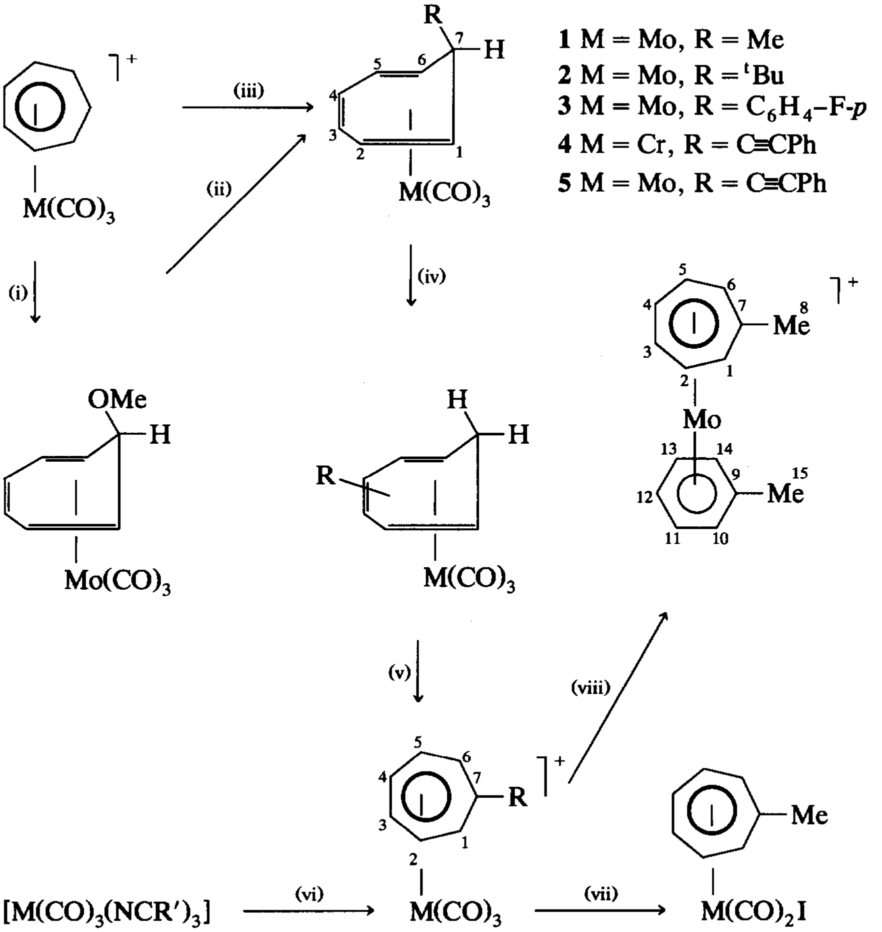
on $\eta^7 \leftrightarrow \eta^3$ hapticity interconversions in the cycloheptatrienyl ligand [7,8].

2. Results and discussion

The first strategy for the synthesis of $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ involves substitution at a metal-coordinated C_7H_7 ligand via the sequence of reactions illustrated in Scheme 1. There are three key steps. The first entails reaction of $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$ (M = Cr, Mo or W) with a nucleophilic source of the required substituent R to give the coordinated, substituted cycloheptatriene adduct $[M(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}R)C_7H_7\}]$. In this work the position of the ring substituent R is indicated by the established numbering system [9] that is shown in Scheme 1; the stereospecificity of these reactions, leading to addition of R exclusively *exo* to the metal, is also well established [10]. Conversion of

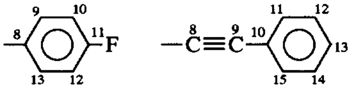


1 M = Mo, R = Me
2 M = Mo, R = ^{t}Bu
3 M = Mo, R = C_6H_4-F-*p*
4 M = Cr, R = C≡CPh
5 M = Mo, R = C≡CPh

7 M = Mo, R = Me; **8** M = Mo, R = ^{t}Bu
9 M = Mo, R = C_6H_4-F-*p*; **10** M = Cr, R = C≡CPh
11 M = Mo, R = C≡CPh; **12** M = W, R = Me
13 M = W, R = C_6H_4-F-*p*

14 M = Mo
15 M = W

Scheme 1. Reagents and conditions: (i) M = Mo, NaOMe in methanol 10 min.; (ii) M = Mo, RMgX (R = Me, ^{t}Bu or C_6H_4-F-*p*) in diethyl ether, 1.5 h −78°C then 1 h −30°C; (iii) M = Cr or Mo, "$(PhC{\equiv}C)_3CuLi_2$" in diethyl ether, 2 h −65°C then 1 h −20°C; (iv) **1** reflux in methylcyclohexane 18 h, **2** reflux in n-octane 6 h, **3** reflux in methylcyclohexane 2 h, **4** methylcyclohexane, 80°C, 20 min; (v) M = Mo, R = Me, ^{t}Bu or C_6H_4-F-*p*; M = Cr, R = C≡CPh; $[Ph_3C][PF_6]$ in CH_2Cl_2; (vi) $C_7H_6R^+/FeCp_2^+$ in CH_2Cl_2 or THF; M = Mo, R = Me, ^{t}Bu, C_6H_4-F-*p* or C≡CPh, R' = Me; M = W, R = H, Me or C_6H_4-F-*p*, R' = ^{n}Pr; (vii) M = Mo or W, R = Me, NaI in acetone, 1.5 h; (viii) M = Mo, R = Me, toluene reflux 27 h. Numbering scheme for R substituents:



$[M(CO)_3\{\eta^6\text{-(7-}exo\text{-R)}C_7H_7\}]$ into $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ requires abstraction of the 7-*endo* hydrogen of the coordinated cycloheptatriene ligand as H^- but this process is blocked sterically by the metal group. However, thermolysis of $[M(CO)_3\{\eta^6\text{-(7-}exo\text{-R)}C_7H_7\}]$ results in the formation of an isomeric mixture of $[M(CO)_3\{\eta^6\text{-(}n\text{-R)}C_7H_7\}]$ ($n = 1$, 2 or 3) [9] and these complexes contain a CH_2 ring carbon with an *exo* hydrogen that is accessible to H^- abstraction by Ph_3C^+ in the final step of the synthesis to yield $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$.

Direct addition of organolithium reagents, LiR, to $[Cr(CO)_3(\eta^7\text{-}C_7H_7)]^+$ and $[Mo(CO)_2(PPh_3)(\eta^7\text{-}C_7H_7)]^+$ has been reported [10,11], but corresponding reactions with $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$ result in extensive decomposition. Therefore the synthesis of the cycloheptatriene complexes $[Mo(CO)_3\{\eta^6\text{-(7-}exo\text{-R)-}C_7H_7\}]$ [R = Me, (**1**); ${}^tBu$, (**2**); $C_6H_4\text{–F-}p$ (**3**)] was approached by initial reaction of $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$ with NaOMe to give $[Mo(CO)_3\{\eta^6\text{-(7-}exo\text{-OMe)}C_7H_7\}]$ [12] followed by a subsequent reaction with the appropriate Grignard reagent RMgX (X = Cl or Br) in diethyl ether. Transfer of the product mixture to an alumina chromatography column maintained at −40°C followed by elution with CH_2Cl_2/diethyl ether afforded red bands which gave **1**, **2** and **3** as orange solids in good yield. Details of the characterization of **1**, **2** and **3** and of subsequently described complexes are given in Table 1 (microanalytical, infrared and mass spectral data) and Table 2 (${}^1H$ and ${}^{13}C$ NMR data). Complexes **1** and **2** have been described previously [13,14] but the spectroscopic data given here are more comprehensive and the current synthesis of **2** gives a much better yield.

Two further examples of cycloheptatriene complexes $[M(CO)_3\{\eta^6\text{-(7-}exo\text{-R)}C_7H_7\}]$ [R = C≡CPh; M = Cr (**4**), M = Mo (**5**)] have been obtained by direct addition to $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$, thus avoiding $[M(CO)_3\{\eta^6\text{-(7-}exo\text{-OMe)}C_7H_7\}]$ as an intermediate. The chromium derivative **4** has been synthesized previously [10] by reaction of $[Cr(CO)_3(\eta^7\text{-}C_7H_7)]^+$ with LiC≡CPh, but in our experience the reaction of the alkynyl cuprate reagent "$(PhC{\equiv}C)_3CuLi_2$" [15] with $[M(CO)_3(\eta^7\text{-}C_7H_7)]^+$ provides a better synthetic route. Complexes **4** and **5** were obtained as orange-yellow solids following purification by column chromatography.

The thermal rearrangement of the Me and ${}^tBu$ complexes **1** and **2** was investigated in refluxing n-octane and the progress of the reaction was monitored by periodically withdrawing samples and recording ${}^1H$ NMR spectra in $CDCl_3$. The NMR spectra of the isomeric mixtures $[M(CO)_3\{\eta^6\text{-(}n\text{-R)}C_7H_7\}]$ ($n = 1$, 2, 3 or 7) were exceedingly complex, but, nevertheless, the isomers could be distinguished on the basis of the Me and ${}^tBu$ signals. Thus the sequential formation of 3-, 1- and finally, 2-substituted isomers is clear from the respective appearance of singlets at $\delta(CDCl_3)$ 2.55 (3-Me), 1.92 (1-Me) and 2.04 (2-Me) starting from **1**, and at $\delta(CDCl_3)$ 1.44 (3-${}^tBu$), 1.01 (1-${}^tBu$) and 1.17 (2-${}^tBu$) starting from **2**. After 5 h in refluxing n-octane no $[Mo(CO)_3\{\eta^6\text{-(7-}exo\text{-Me)}C_7H_7\}]$ remained, but the conversion of the 7-*exo*-${}^tBu$ derivative was only approximately 65% complete as determined from ${}^1H$ NMR integrals. Nevertheless the thermal isomerization of

TABLE 1. Microanalytical, infrared and mass spectroscopic data

Complex	Analysis (%) [a]		Infrared [b] ν(CO) (cm^{-1})	Mass spectral data [c]
	C	H		
1	46.8 (46.2)	3.5 (3.5)	1996, 1932, 1908	288 M^+, 260 $[M-CO]^+$, 232 $[M-2CO]^+$, 204 $[M-3CO]^+$ [d]
2	51.2 (51.2)	5.1 (4.9)	1996, 1932, 1907	330 M^+, 273 $[M-2CO]^+$, 245 $[M-3CO]^+$ [d]
3	52.3 (52.4)	3.2 (3.0)	1999, 1936, 1912	368 M^+, 340 $[M-CO]^+$, 312 $[M-2CO]^+$, 284 $[M-3CO]^+$ [d]
4	65.8 (65.9)	3.7 (3.7)	1991, 1932, 1911	327 M^+, 191 $[M-Cr(CO)_3]^+$
5	57.7 (58.1)	3.0 (3.3)	1999, 1937, 1914	374 M^+, 318 $[M-2CO]^+$, 290 $[M-3CO]^+$ [d]
6	65.5 (65.9)	3.7 (3.7)	1990, 1933, 1911	328 M^+, 300 $[M-CO]^+$, 272 $[M-2CO]^+$, 244 $[M-3CO]^+$, 192 $[M-Cr(CO)_3]^+$ [d]
7	30.7 (30.7)	2.0 (2.1)	2078, 2029 [e]	287 M^+, 259 $[M-CO]^+$, 231 $[M-2CO]^+$, 203 $[M-3CO]^+$, 105 $[M-Mo(CO)_3]^+$
8	35.0 (35.6)	3.4 (3.2)	2075, 2030 [e]	329 M^+, 301 $[M-CO]^+$, 273 $[M-2CO]^+$, 245 $[M-3CO]^+$, 147 $[M-Mo(CO)_3]^+$
9	37.9 (37.7)	2.1 (2.0)	2078, 2031 [e]	367 M^+, 339 $[M-CO]^+$, 311 $[M-2CO]^+$, 283 $[M-3CO]^+$, 185 $[M-Mo(CO)_3]^+$
10	45.9 (45.8)	2.4 (2.3)	2070, 2037 [e,f]	327 M^+, 299 $[M-CO]^+$, 271 $[M-2CO]^+$, 243 $[M-3CO]^+$, 191 $[M-Cr(CO)_3]^+$
11	41.3 (42.0)	2.3 (2.2)	2080, 2037 [e,g]	373 M^+, 345 $[M-CO]^+$, 317 $[M-2CO]^+$, 191 $[M-Mo(CO)_3]^+$
12	25.9 (25.5)	1.5 (1.8)	2072, 2014 [e]	373 M^+, 345 $[M-CO]^+$, 317 $[M-2CO]^+$, 289 $[M-3CO]^+$, 105 $[M-W(CO)_3]^+$
13	32.5 (32.1)	1.6 (1.7)	2072, 2016 [e]	453 M^+, 425 $[M-CO]^+$, 397 $[M-2CO]^+$, 369 $[M-3CO]^+$, 185 $[M-W(CO)_3]^+$
14	31.2 (31.3)	2.3 (2.4)	2020, 1980	386 M^+, 358 $[M-CO]^+$, 330 $[M-2CO]^+$, 259 $[M-I]^+$
15	25.3 (25.5)	2.2 (1.9)	2009, 1959	472 M^+, 444 $[M-CO]^+$, 416 $[M-2CO]^+$
16	41.3 (41.1)	4.0 (3.9)		295 M^+, 203 $[M-C_6H_5Me]^+$

[a] Calculated values in parentheses. [b] Solution spectra in hexane unless stated otherwise. [c] By FAB mass spectroscopy unless stated otherwise, m/z values based on ${}^{98}Mo$ and ${}^{184}W$. [d] By electron impact mass spectroscopy. [e] In CH_2Cl_2. [f] ν(C≡C) 2211 cm^{-1}. [g] ν(C≡C) 2216 cm^{-1}.

the 7-^{t}Bu-C_7H_7 ligand in **2** proceeds much more readily than the corresponding thermal isomerization of the uncoordinated molecule [16]. For the purposes of the synthetic work, the methyl complex **1** was refluxed overnight in methylcyclohexane but **2** was refluxed for 6 h in n-octane; after this time some

TABLE 2. ^{1}H and ^{13}C NMR spectral data

Complex	^{1}H NMR data (δ) [a]	^{13}C NMR data (ppm) [a]
1	6.01 (m, 2H, H(3), H(4)); 4.89 (m, 2H, H(2), H(5)); 4.00 (m, 2H, H(1), H(6)); 3.07 (m, 1H, H(7)); 0.30 (d, 3H, Me, *J*(H(7)–Me) = 7)	220.0 (br, CO); 100.5 (C(3), C(4)); 97.1 (C(2), C(5)); 71.7 (C(1), C(6)); 34.2 (C(7)); 26.9 (Me)
2 [b]	5.89 (m, 2H, H(3), H(4)); 5.01 (m, 2H, H(2), H(5)); 3.91 (m, 2H, H(1), H(6)); 3.03 (t, 1H, H(7), *J*(H(7)–H(1)/H(6)) 8); 0.54 (s, 9H, ^{t}Bu)	219.5 (br, CO); 103.0 (C(3), C(4)); 95.9 (C(2), C(5)); 73.0 (C(1), C(6)); 52.4 (C(7)); 41.0 (CMe$_3$); 25.5 (CMe_3)
3	6.84 (m, 4H, C_6H_4–F-*p*); 6.02 (m, 2H, H(3), H(4)); 5.07 (m, 2H, H(2), H(5)); 4.40 (t, 1H, H(7), *J*(H(7)–H(1)/H(6)) = 8); 4.17 (m, 2H, H(1), H(6))	161.7 (d, C(11), *J*(C(11)–F) = 245); 143.0 (d, C(8), *J*(C(8)–F) = 3); 127.5 (d, C(9), C(13), *J*(C(9)/C(13)–F) = 8); 115.3 (d, C(10), C(12), *J*(C(10)/C(12)–F) = 22); 101.6 (C(3), C(4)); 96.6 (C(2), C(5)); 71.0 (C(1), C(6)); 44.6 (C(7))
4	7.23 (br, 5H, Ph); 6.10 (m, 2H, H(3), H(4)); 4.95 (m, 2H, H(2), H(5)); 4.04 (t, 1H, H(7), *J*(H(7)–H(1)/H(6)) = 8); 3.81 (m, 2H, H(1), H(6))	231.3 (CO); 131.3, 128.1 (C(11)–C(15)); 122.7 (C(10)); 99.0, 98.3 (C(2)–C(5)); 89.5, 83.6 (C(8), C(9)); 61.6 (C(1), C(6)); 27.3 (C(7))
5	7.26 (s, 5H, Ph); 6.16 (m, 2H, H(3), H(4)); 5.04 (m, 2H, H(2), H(5)); 4.10 (t, 1H, H(7), *J*(H(7)–H(1)/H(6)) = 8); 4.03 (m, 2H, H(1), H(6))	218.8 (br, CO); 131.4, 128.2 (C(11)–C(15)); 122.8 (C(10)); 100.2, 97.3 (C(2)–C(5)); 91.3, 83.1 (C(8), C(9)); 63.8 (C(1), C(6)); 30.2 (C(7))
6 [c]	7.56, 7.38 (m, 5H, Ph); 6.40 (d, 1H, H(4), *J*(H(4)–H(5)) 6); 5.12 (d, 1H, H(2), *J*(H(2)–H(1)) 9); 4.88 (dd, 1H, H(5), *J*(H(5)–H(6)) = 8); 3.43 (m, 2H, H(1), H(6)); 2.97 (m, 1H, H(7-*endo*)); 1.87 (d, 1H, H(7-*exo*), *J*(H(7-*exo*)–H(7-*endo*))-14)	231.7 (CO); 132.1, 129.0, 128.5 (C(11)–C(15)); 122.5 (C(10)); 104.2, 102.9, 99.5 (C(2), C(4), C(5)); 96.6 (C(3)); 90.2, 86.4 (C(8), C(9)); 57.5, 56.6 (C(1), C(6)); 24.2 (C(7))
7 [d]	6.72 (m, 2H, H(2), H(5)); 6.59 (m, 2H, H(3), H(4)); 6.41 (d, 2H, H(1), H(6), *J*(H(1)/H(6)–H(2)/H(5)) = 9); 2.93 (s, 3H, Me)	208.8 (CO); 121.1 (C(7)); 102.2, 101.7, 101.5 (C(1)–C(6)); 26.1 (Me)
8 [d]	6.96 (d, 2H, H(1), H(6), *J*(H(1)/H(6)–H(2)/H(5)) = 9); 6.66 (m, 2H, H(3), H(4)); 6.38 (m, 2H, H(2), H(5)); 1.53 (s, 9H, ^{t}Bu)	208.6 (CO); 133.4 (C(7)); 102.1, 100.6, 99.6 (C(1)–C(6)); 38.5 (CMe$_3$); 32.1 (CMe_3)
9 [d]	8.12 (m, 2H, H(9), H(13)); 7.48 (m, 2H, H(10), H(12)); 6.90 (m, 4H) and 6.73 (m, 2H), (H(1)–H(6))	208.5 (CO); 165.5 (d, C(11), *J*(C(11)–F) = 249); 134.6 (d, C(8), *J*(C(8)–F) = 3); 132.7 (d, C(9), C(13), *J*(C(9)/C(13)–F) = 8); 121.6 (C(7)); 117.5 (d, C(10), C(12), *J*(C(10)/C(12)–F) = 22); 101.9, 101.5, 101.2 (C(1)–C(6))
10 [e]	7.74 (m, 2H) and 7.60 (m, 3H), (Ph); 6.80 (m, 2H) and 6.60 (m, 2H), (H(2)–H(5)); 6.65 (d, 2H, H(1), H(6), *J*(H(1)/H(6)–H(2), H(5)) = 9)	220.0 (CO); 132.1, 130.6, 128.7 (C(11)–C(15)); 119.8 (C(10)); 106.7 (C(7)); 105.2, 104.2, 103.7 (C(1)–C(6)); 95.3, 86.0 (C(8), C(9))
11 [d]	7.76 (m, 2H) and 7.61 (m, 3H), (Ph); 6.88 (m, 2H) and 6.70 (m, 2H), (H(2)–H(5)); 6.79 (d, 2H, H(1), H(6), *J*(H(1)/H(6)–H(2)/H(5)) = 9)	207.5 (CO); 133.1, 131.4, 129.7 (C(11)–C(15)); 121.0 (C(10)); 103.1 (C(7)); 102.5, 101.3, 100.5 (C(1)–C(6)); 94.5, 86.8 (C(8), C(9))
12 [d]	6.66 (m, H(2), H(5)); 6.56 (m, H(3), H(4)); 6.38 (d, H(1), H(6), *J*(H(1)/H(6)–H(2)/H(5) = 9); 3.15 (s, 3H, Me)	197.4 (CO); 117.0 (C(7)); 98.4, 98.0, 97.5 (C(1)–C(6)); 25.1 (Me)
13 [d]	8.08 (m, 2H, H(9), H(13)); 7.49 (m, 2H, H(10), H(12)); 6.86 (m, 4H) and 6.69 (m, 2H), (C(1)–C(6))	197.1 (CO); 165.1 (d, C(11), *J*(C(11)–F) = 248); 133.4 (d, C(8), *J*(C(8)–F) = 3); 132.4 (d, C(9), C(13), *J*(C(9)/C(13)–F) = 9); 118.0 (C(7)); 116.9 (d, C(10), C(12), *J*(C(10)/C(12)–F) = 22); 98.2, 97.6, 97.0 (C(1)–C(6))
14	5.43 (m, 2H, H(2), H(5)); 5.36 (m, 2H, H(3), H(4)); 5.26 (d, 2H, (H(1), H(6), *J*(H(1)/H(6)–H(2)/H(5)) = 8); 2.61 (s, 3H, Me)	213.8 (CO); 109.4 (C(7)); 96.0, 93.0, 92.5 (C(1)–C(6)); 26.0 (Me)
15	5.32 (br, 4H, H(2)–H(5)); 5.18 (d, 2H, H(1), H(6), *J*(H(1)/H(6)–H(2)/H(5)) = 7); 2.74 (s, 3H, Me)	206.1 (CO); 105.2 (C(7)); 92.2, 89.1, 88.7 (C(1)–C(6)); 25.7 (Me)
16 [f]	6.19 (m, 2H); 6.11 (m, 2H) and 6.01 (m, 1H), (H(10)–H(14)); 5.64 (9br, 2H) and 5.56 (br, 4H), (H(1)–H(6)); 2.47 (s, 3H, Me); 2.25 (s, 3H, Me)	115.0, 102.0 (C(9), C(7)); 99.4, 97.1, 96.1 (C(10)–C(14)); 88.3, 86.1, 85.3 (C(1)–C(6)); 25.0 (C(8)); 20.7 (C(15))

[a] 300 MHz ^{1}H NMR spectra, 75 MHz ^{13}C NMR spectra, s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, chemical shifts downfield from $SiMe_4$, coupling constants in Hz, $CDCl_3$ solution spectra unless stated otherwise, numbering as in Scheme 1. [b] ^{13}C NMR assignments made with the aid of a DEPT experiment. [c] ^{1}H NMR spectrum assigned with the aid of a ^{1}H–^{1}H double irradiation experiment. [d] In acetone-d_6. [e] In CD_3CN. [f] In CD_2Cl_2.

[Mo(CO)$_3${η^6-(7-*exo*-^{t}Bu)C$_7$H$_7$}] remained unchanged but use of prolonged reaction times resulted in extensive decomposition. In general, the conversion of [M(CO)$_3${η^6-(7-*exo*-R)C$_7$H$_7$} into the rearranged forms [M(CO)$_3${η^6-(*n*-R)C$_7$H$_7$}] ($n = 1$, 2 or 3) is accompanied by a colour change from orange to deep red and a small shift to lower wavenumber of the infrared active carbonyl stretching frequencies; thus the deep red products resulting from thermolysis of **1** and **2** give ν(CO) (hexane) bands at 1993, 1929, 1905 and 1990, 1922, 1904 cm^{-1}, respectively.

The corresponding isomerizations of **3**, and the chromium complex **4**, were carried out in methylcyclohexane (**3**, 2 h, reflux; **4**, 20 min, 80°C). The reaction mixture from thermolysis of **3** exhibited ν(CO) (hexane) 1995, 1934 and 1909 cm^{-1} and a complex ^{1}H NMR spectrum indicative of an isomer mixture, but under the same conditions thermolysis of **4** gave almost exclusively a single isomer, [Cr(CO)$_3${η^6-(3-C≡CPh)C$_7$H$_7$}] (**6**), which was purified by column chromatography, isolated as a purple-red solid, and separately characterized. The initial formation of specific isomers of chromium complexes, *viz.* [Cr(CO)$_3${η^6-(3-R)C$_7$H$_7$}] (R = Me or C$_6$H$_4$-Me-p), by thermolysis of [Cr(CO)$_3${η^6-(7-*exo*-R)C$_7$H$_7$}], has been described previously [9], but our attempts to extend this procedure to the molybdenum derivatives **1**, **2** and **3** were unsuccessful; conditions sufficiently vigorous to initiate isomerization invariably gave isomeric mixtures of rearranged complexes before the conversion of [Mo(CO)$_3${η^6-(7-*exo*-R)C$_7$H$_7$}] had proceeded to a significant extent. Attempts to effect isomerization of the molybdenum complex [Mo(CO)$_3${η^6-(7-*exo*-C≡CPh)C$_7$H$_7$}] **5** were also unsuccessful; thermolysis in n-octane resulted in extensive decomposition.

The final stage of the synthesis of [M(CO)$_3$(η^7-C$_7$H$_6$R)]$^+$ involved reaction of [Ph$_3$C][PF$_6$] with [Mo(CO)$_3${η^6-(n-R)C$_7$H$_7$}] ($n = 1$, 2 or 3; R = Me, ^{t}Bu or C$_6$H$_4$–F-*p*} or the chromium complex **6** in CH$_2$Cl$_2$. To avoid losses during work-up the crude samples of [Mo(CO)$_3${η^6-(n-R)C$_7$H$_7$}] obtained as the residues from the thermolysis solutions were used for reaction with [Ph$_3$C][PF$_6$]. The required products, ring-substituted cycloheptatrienyl complexes [M(CO)$_3$(η^7-C$_7$H$_6$R)][PF$_6$] [M = Mo; R = Me, (**7**), R = ^{t}Bu (**8**), R = C$_6$H$_4$–F-*p* (**9**); M = Cr; R = C≡CPh (**10**)], separated from the reaction mixture directly (**7** and **8**) or on addition of diethyl ether (**9** and **10**), and were obtained as yellow or orange solids after purification.

The ^{1}H and ^{13}C NMR spectra of complexes **7**–**10** show characteristic signals for coordinated, monosubstituted cycloheptatrienyl ligands. In most examples, the ^{1}H NMR spectra exhibit three well-defined resonances for the three sets of ring protons [H(1)/H(6); H(2)/H(5); H(3)/H(4)] with a simple doublet for the protons H(1) and H(6) that are adjacent to the ring substituent. Considering the series of complexes, the chemical shift of the resonance for H(1)/H(6) varies relative to those for H(2)/H(5) and H(3)/H(4) in a way that is not easily rationalized, but in the ^{13}C NMR spectra, the chemical shift of the substituted carbon C(7) follows the expected trend, with electron-donating substituents causing a low field shift of the C(7) resonance.

The overall yields of the synthesis (based on [Mo(CO)$_3${η^6-(7-*exo*-R)C$_7$H$_7$}] as starting material) were: **7**, 76%; **8**, 4%; and **9**, 41%, and **10** was obtained in 65% yield from **6**. Thus except in the case of **8**, quantities sufficient for further work were obtained. However, an additional problem with this synthesis is that although samples of **7**, **8**, **9** and **10** obtained by this route gave satisfactory microanalytical data, the NMR data revealed minor contamination of the molybdenum derivatives **7**, **8** and **9** with [Mo(CO)$_3$(η^7-C$_7$H$_7$)]$^+$; the corresponding impurity in the case of the chromium derivative **10** was not observed.

In view of the difficulties encountered in syntheses involving substitution at a metal-coordinated cycloheptatrienyl ring, the alternative strategy, involving coordination of substituted cycloheptatrienes C$_7$H$_7$R and cycloheptatrienyl ions C$_7$H$_6$R$^+$, was investigated. The classical approach to [M(CO)$_3$(η^7-C$_7$H$_6$R)]$^+$ involves reaction of 7-R–C$_7$H$_7$ with a source of the M(CO)$_3$ fragment (generally M(CO)$_6$, [M(CO)$_3$(NCMe)$_3$] or [M(CO)$_3$(pyridine)$_3$]/BF$_3\cdot$Et$_2$O) to give [M(CO)$_3${η^6-(7-*endo*-R)C$_7$H$_7$}] followed by abstraction of the 7-*exo* hydrogen as H$^-$. However the application of this method appears to be quite restricted and further investigation has suggested an explanation. Reaction of 7-R–C$_7$H$_7$ with M(CO)$_6$, etc. may result in two isomeric products in which the 7-R substituent can be oriented *exo* or *endo* with respect to the M(CO)$_3$ group. If M = Cr, substituents such as Me which have a saturated carbon attached at C(7) of the cycloheptatriene ring, support formation of the *endo*-R isomer but other substituents (such as Ph) produce *exo*/*endo* mixtures [17]. Clearly the preferential formation of [M(CO)$_3${η^6-(7-*endo*-R)C$_7$H$_7$}] is desirable since abstraction of the 7-*exo* hydrogen as H$^-$ can proceed readily. The complete conversion of *endo*/*exo*-7-R isomer mixtures of [M(CO)$_3${η^6-(7-R)C$_7$H$_7$}] into [M(CO)$_3$(η^7-C$_7$H$_6$R)]$^+$ is, of course, possible but, as described above, an initial thermolysis, with attendant losses due to decomposition, must be carried out.

To examine the general applicability of synthesis via reaction of [M(CO)$_3$(NCMe)$_3$] with 7-R–C$_7$H$_7$, the reaction of [M(CO)$_3$(NCMe)$_3$] (M = Cr, Mo or W) with 7-Me–C$_7$H$_7$ in refluxing THF was investigated. The reasoning behind the choice of the substituent R and solvent was that the Me substituent should result in the optimum formation of the desired 7-*endo*-R isomer and also provide a clear spectroscopic marker for distinguishing between *exo* and *endo* isomers; the relatively low boiling point of THF averts complications arising from thermal isomerization. On completion of the reaction, THF was removed and the product, $[M(CO)_3\{\eta^6\text{-(7-Me)}C_7H_7\}]$ purified by recrystallization or column chromatography. The data in Table 3 present the characteristic ^1H NMR signals for *exo* and *endo* isomers, which can be distinguished on the basis of resonances for the 7-Me substituent and for H(1)/H(6); a summary of the *exo/endo* isomer ratios obtained on the basis of ^1H NMR integrals is also presented. For each of the metals investigated, two independent experiments were carried out, and the data for *exo/endo* ratios, shown in Table 3, are the average of two closely similar results; for each individual experiment, sample preparation and data collection were carried out on the same day. Where M = Cr or W, the *exo/endo* isomer ratios obtained were independent of the method of purification, but for M = Mo purification by column chromatography resulted in very significant losses of $[Mo(CO)_3\{\eta^6\text{-(7-}endo\text{-Me)}C_7H_7\}]$ and therefore the data shown are derived from samples purified by recrystallization only. It can be seen from Table 3 that, in terms of the isolated products, when M = Mo, a higher proportion of *exo*-Me isomer is observed; whether this effect is a genuine metal dependence or the result of the relative instability of $[Mo(CO)_3\{\eta^6\text{-(7-}endo\text{-Me)}C_7H_7\}]$ is not clear. Whichever the explanation, it is clear that the unfavourable isomer ratio observed when M = Mo suggests that the synthesis of $[Mo(CO)_3(\eta^7\text{-}C_7H_6Me)]^+$ via H^- abstraction from the product of the reaction of $7\text{-Me-}C_7H_7$ with $[Mo(CO)_3(NCMe)_3]$ has severe limitations. We recognize that our observation of the formation of $[Cr(CO)_3\{\eta^6\text{-(7-Me)}C_7H_7\}]$ as an *exo/endo* mixture at C(7) is at variance with previous reports [17] and that the discrepancy may originate from the choice of starting material and reaction solvent. However, reaction of $7\text{-Me-}C_7H_7$ with $Mo(CO)_6$ in refluxing n-heptane or with $[Mo(CO)_3(pyridine)_3]/BF_3 \cdot Et_2O$ in diethyl ether also resulted in the preferential formation of $[Mo(CO)_3\{\eta^6\text{-(7-}exo\text{-Me)}C_7H_7\}]$.

It is possible to avoid the problems that result from *exo/endo* isomerism at C(7) if thermal isomerization of $7\text{-R-}C_7H_7$ is carried out prior to coordination and a successful application of this strategy has been reported [4], but the isomerization of $7\text{-R-}C_7H_7$ must be carried out in a sealed tube. Finally, whilst the reaction of $Cr(CO)_6$ or $[Cr(CO)_3(pyridine)_3]/BF_3 \cdot Et_2O$ with substituted cycloheptatrienes has been reported to proceed in high yield [17], in our experience it is very difficult to obtain consistently good yields of $[Mo(CO)_3\{\eta^6\text{-(7-R)}C_7H_7\}]$ starting from $7\text{-R-}C_7H_7$ and $Mo(CO)_6$ or $[Mo(CO)_3(NCMe)_3]$, especially if the substituted cycloheptatriene ligand is not used in a large and wasteful excess.

The possibility of a direct reaction of cycloheptatrienyl cations with $[M(CO)_3(NCR')_3]$ (R' = alkyl) has only very recently been explored [18]. Thus reaction of $[W(CO)_3(NCEt)_3]$ with $[(1,2,4,6\text{-Me}_4)\text{-}C_7H_3][PF_6]$ in THF in the presence of small quantities of $[FeCp_2]^+$ proceeds to give high yields of the ring-substituted cycloheptatrienyl complex $[W(CO)_3\{\eta^7\text{-(1,2,4,6-Me}_4)\text{-}C_7H_3\}][PF_6]$, and we now report that this reaction has a wide application in the synthesis of a range of ring-substituted cycloheptatrienyl complexes of molybdenum and tungsten.

Treatment of $[Mo(CO)_3(NCMe)_3]$ with $[C_7H_6R][PF_6]$ (R = Me, ^tBu, $C_6H_4\text{-F-}p$ or C≡CPh) in THF or CH_2Cl_2 (generally in the presence of small quantities of ferricenium ion) gave respectively **7**, **8**, **9** and $[Mo(CO)_3\{\eta^7\text{-}C_7H_6(C{\equiv}CPh)\}]^+$ (**11**) in good (**7** and **9**) or moderate (**8** and **11**) yield after purification by recrystallization; yields are based on $C_7H_6R^+$, since $[Mo(CO)_3(NCMe)_3]$ was generated from $Mo(CO)_6$ and used without purification and moreover, an excess of

TABLE 3. Data for *exo/endo* $[M(CO)_3\{\eta^6\text{-(7-Me)}C_7H_7\}]$

	M = Cr		M = Mo		M = W	
	exo	*endo*	*exo*	*endo*	*exo*	*endo*
$\delta(CH_3)$ [a]	0.09, d, $J(H(7)\text{-}CH_3) = 7$	1.39, d, $J(H(7)\text{-}CH_3) = 7$	0.30, d, $J(H(7)\text{-}CH_3) = 7$	1.44, d, $J(H(7)\text{-}CH_3) = 7$	0.25, d, $J(H(7)\text{-}CH_3) = 7$	1.42, d, $J(H(7)\text{-}CH_3) = 7$
$\delta(H(1)/H(6))$ [a]	3.78, m	3.00, m	4.00, m	3.27, m	3.95, m	3.18, m
exo/endo (% isolated product) [b]	29	71	56	44	28	72

[a] ^1H NMR spectra in $CDCl_3$, d = doublet, m = multiplet, coupling constants in Hz. [b] *exo/endo* ratios as a % of the isolated product from the reaction of $[M(CO)_3(NCMe)_3]$ and $7\text{-Me-}C_7H_7$ as determined by ^1H NMR integrals.

$Mo(CO)_6$ was used to ensure efficient conversion of $C_7H_6R^+$ into the required cycloheptatrienyl complex. The successful synthesis of **11** by this method contrasts with our unsuccessful attempt to obtain **11** via a reaction sequence involving thermolysis of $[Mo(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}C{\equiv}CPh)C_7H_7\}]$. Similarly reaction of $[C_7H_6R][PF_6]$ (R = H, Me or C_6H_4–F-*p*) with equimolar $[W(CO)_3(NC^nPr)_3]$ affords $[W(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ [R = H Me (**12**) or C_6H_4–F-*p* (**13**)] in good yield. The direct synthesis of the unsubstituted derivative $[W(CO)_3(\eta^7\text{-}C_7H_7)]^+$ in 62% yield represents a considerable improvement on previously reported methods involving the cycloheptatriene complex $[W(CO)_3(\eta^7\text{-}C_7H_8)]$ as an intermediate [19,20]. However attempts to extend the reaction to the synthesis of chromium derivatives $[Cr(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ were wholly unproductive; infrared monitoring suggests that treatment of a THF solution of $[Cr(CO)_3(NCMe)_3]$ with $C_7H_6R^+$ leads to immediate formation of $[Cr(CO)_4(NCMe)_2]$.

TABLE 4. Cyclic voltammetric data for $C_7H_6R^+$ and $[M(CO)_3(NCR')_3]$

$E_p{}^c$ ($[C_7H_6R]^+$)		E^0 $[M(CO)_3(NCR')_3]$		
R =	$E_p{}^c$ (V) [a]	M =	R′ =	E^0 (V) [b]
H	−0.14 [c]	Cr	Me	−0.02
${}^tBu$	−0.27	Mo	Me	+0.33
Me	−0.26	W	Me	+0.24
C_6H_4–F-*p*	−0.14	W	${}^nPr$	+0.31 [d]
C≡CPh	+0.02			

[a] At a carbon electrode in CH_3CN, solutions 10^{-3} M in complex and 0.2 M in supporting electrolyte $[^nBu_4N][BF_4]$, potentials relative to SCE for scan rates of 100 mV s^{-1} and standardized with respect to the couple $FeCp_2$–$FeCp_2{}^+$ for which $E^0 = 0.43$ V in CH_3CN and 0.56 V in CH_2Cl_2. [b] Unless stated otherwise E^0 values taken from ref. 21 but adjusted via E^0 values for $FeCp_2$–$FeCp_2{}^+$. [c] $E_p{}^c$ (CH_2Cl_2) −0.01 V, other conditions as in [a]. [d] Current work, E^0 in CH_2Cl_2, other conditions as in [a].

Whilst the synthesis of $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ from $[M(CO)_3(NCR')_3]$ and $C_7H_6R^+$ has some limitations, our findings demonstrate that it provides a convenient and high yield route in most cases where M = Mo or W and R = alkyl or aryl. The importance of the reaction justifies some additional comments on our detailed findings. In all cases, reaction proceeded at room temperature at a rate dependent on the R substituent of $C_7H_6R^+$; with electron-withdrawing substituents (R = C≡CPh or C_6H_4–F-*p*) the reaction was complete within 10 min, whereas alkyl substituted systems required at least 1 h for completion. By contrast, addition of the corresponding cycloheptatrienes 7-R–C_7H_7 to $[M(CO)_3(NCR')_3]$ in THF proceeds at a significant rate only above 40°C. In most cases, addition of small quantities of ferricenium ion (up to 0.2 mole equivalents) to the reaction mixture of $[M(CO)_3(NCR')_3]$ and $C_7H_6R^+$ gave higher yields of $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$, but in all the examples reported in this paper, the reaction did occur in the absence of added $[FeCp_2]^+$.

A possible explanation for the unexpectedly facile reaction between $[M(CO)_3(NCR')_3]$ and $C_7H_6R^+$ is the operation of an electron transfer chain (ETC) process; such catalytic redox processes have been shown to occur in some substitution reactions of $[M(CO)_3(NCMe)_3]$ [21,22]. The complexes $[M(CO)_3(NCMe)_3]$ undergo a reversible one-electron oxidation in CH_3CN, with E^0 values as shown in Table 4; the E^0 values given in the literature [21] are not directly comparable with those in the current work, but an approximate conversion is possible by using known E^0 values for the redox couple $FeCp_2 \leftrightarrow FeCp_2^+$ from both investigations, and the validity of the conversion has been demonstrated by an independent measurement of E^0 for $[Mo(CO)_3(NCMe)_3]$. In most of the synthetic work, catalytic quantities of the ferricenium ion [$E^0(CH_3CN)$ $FeCp_2 \leftrightarrow FeCp_2^+ = 0.43$ V] could initiate an ETC process by formation of the substitution labile 17-electron species $[M(CO)_3(NCR')_3]^+$ but it should be noted that all the reactions of $C_7H_6R^+$ with $[M(CO)_3(NCR')_3]$ reported in this paper still proceed in the absence of $FeCp_2^+$. We cannot totally exclude the possibility that, in the absence of $FeCp_2^+$, the reaction may be initiated by trace quantities of O_2, but the consistent dependence of the reaction rate upon the nature of R in $C_7H_6R^+$ requires that $C_7H_6R^+$ must also be considered as the reaction initiator. The tropylium ion $C_7H_7^+$ has been employed previously as a one-electron oxidant [23] and the redox potentials for the one-electron reduction $C_7H_6R^+ \rightarrow C_7H_6R^{\cdot}$ (R = H or ${}^tBu$) have been determined by cyclic voltammetry [24]. To assess the ability of the ions $C_7H_6R^+$ (R = ${}^tBu$, Me, H, C_6H_4–F-*p* or C≡CPh) to act as one-electron oxidants, the cyclic voltammetry of each derivative was investigated in CH_3CN; in all cases, a well-defined, irreversible reduction process was observed, with E_p^c values as summarized in Table 4. On initial inspection, comparison of E^0 values for the one-electron oxidation of $[M(CO)_3(NCMe)_3]$ with E_p^0 values for reduction of $C_7H_6R^+$ suggests that when M = Mo or W none of the derivatives of $C_7H_6R^+$ investigated can oxidize $[M(CO)_3(NCMe)_3]$. However, in some cases $\Delta[E^0([M(CO)_3(NCMe)_3]) - E_p^c\ (C_7H_6R^+)]$ is quite small (approximately 0.2 V), and the operation of an ETC process initiated solely by $C_7H_6R^+$ may still be feasible in view of the irreversible character of both the reduction of $C_7H_6R^+$ and the coordination of $C_7H_6R^+$ to the $M(CO)_3$ fragment.

The principal aim of this work was to develop a convenient and good yield synthesis of $[M(CO)_3(\eta^7\text{-}$

$C_7H_6R)]^+$, where M = Mo or W, and this has been achieved via reaction of $C_7H_6R^+$ with [M(CO)$_3$(NC-R')$_3$]. The primary entries into the organometallic chemistry of half-sandwich complexes of Mo and W starting from [M(CO)$_3$(η^7-C_7H_7)]$^+$ involve reaction with NaX (X = halide) to give [MX(CO)$_2$(η^7-C_7H_7)] [19,25] or, where M = Mo, reaction of [Mo(CO)$_3$(η^7-C_7H_7)]$^+$ with toluene to give the sandwich complex [Mo(η^6-toluene)(η^7-C_7H_7)]$^+$, which is precursor of a wide range of complexes by displacement of the labile toluene ligand [26]. We have demonstrated that these basic syntheses are also applicable starting from [M(CO)$_3$(η^7-C_7H_6R)]$^+$, and a representative sample of the results obtained is given below.

Treatment of [M(CO)$_3$(η^7-C_7H_6Me)]$^+$ (M = Mo or W) with NaI in acetone gave after work-up, [MI(CO)$_2$(η^7-C_7H_6Me)] [M = Mo (**14**); M = W (**15**)] as deep green solids. A suspension of [Mo(CO)$_3$(η^7-C_7H_6Me)]$^+$ (**7**), refluxed in toluene for 27 h yielded [Mo(η^6-toluene)(η^7-C_7H_6Me)]$^+$ (**16**), and similarly [Mo(η^6-toluene){η^7-C_7H_6(C_6H_4–F-*p*)}]$^+$ was obtained from **9**, but after only 4 h reflux in toluene. The apparent R-dependent substitution lability of the CO ligands in [Mo(CO)$_3$(η^7-C_7H_6R)]$^+$ suggested that [W(CO)$_3${η^7-C_7H_6(C_6H_4-F-*p*)}]$^+$ (**13**) might act as a precursor of one of a class of previously unobtainable tungsten sandwich species [W(η^6-toluene)(η^7-C_7H_6R)]$^+$, but attempts to synthesize [W(η^6-toluene){η^7-C_7H_6(C_6H_4–F-*p*)}]$^+$ from **13** were unproductive.

3. Experimental details

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 [M(CO)$_3$(η^7-C_7H_7)]$^+$ (M = Cr [27], M = Mo [25]); [Mo(CO)$_3${η^6-(7-*exo*-OMe)C_7H_7}] [12]; [W(CO)$_3$(NC-$_n$Pr)$_3$] [20]; [FeCp$_2$][PF$_6$] [28] and 7-R-C_7H_7 (R = Me [29]; ^{t}Bu [16]; C_6H_4–F-*p* [30]; C≡CPh [31]) were prepared by published procedures. Column chromatography was carried out on alumina (Brockmann activity II) supplied by Merck Ltd. 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were recorded on Brucker AC 300 E or Varian Associates XL 300 spectrometers, infrared spectra were obtained on a Perkin-Elmer FT 1710 spectrometer and mass spectra using a Kratos Concept 1S instrument. Cyclic voltammetric studies were carried out as described previously [32]; all potentials are referenced to an aqueous calomel electrode and, under these conditions, E^0 for the couple FeCp$_2$-FeCp$_2{}^+$ is 0.43 V in CH_3CN. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

*3.1. Preparation of [Mo(CO)$_3${η^6-(7-*exo-*C_6H_4–F-*p*)C_7H_7}] (3)*

A stirred suspension of [Mo(CO)$_3${η^6-(7-*exo*-OMe)C_7H_7}] (1.03 g, 3.41 mmol) in diethyl ether (50 cm^3) was cooled to −78°C then treated with (C_6H_4–F-*p*)MgBr (1.65 cm^3 of a 2 M solution in diethyl ether). The reaction was continued for 1.5 h at −78°C then at −30°C for a further 1 h, and then the cold solution was transferred to an alumina/diethyl ether chromatography column maintained at −40°C. Elution with CH_2Cl_2/diethyl ether (1:3) gave a red band which was collected and the solution reduced in volume. Addition of n-hexane followed by cooling in dry ice gave the product **3** as an orange-red solid; yield 0.71 g (57%). Complexes **1** and **2** were prepared similarly; **1** was obtained in 60% yield from [Mo(CO)$_3${η^6-(7-*exo*-OMe)C_7H_7}] (1.00 g, 3.31 mmol) and MeMgBr (1.1 cm^3 of a 3 M solution) and **2** was obtained in 65% yield from the reaction of [Mo(CO)$_3${η^6-(7-*exo*-OMe)C_7H_7}] (2.25 g, 7.45 mmol) with ^{t}BuMgCl (9.3 cm^3 of a 2 M solution). In all cases, yields were lower if column chromatography was carried out at room temperature.

*3.2. Preparation of [Mo(CO)$_3${η^6-(7-*exo-*C≡CPh)-C_7H_7}] (5)*

A stirred suspension of CuBr · Me$_2$S (0.62 g, 3.01 mmol) in diethyl ether (20 cm^3) maintained at −65°C was treated with a solution of LiC≡CPh [prepared from HC≡CPh (0.80 g, 7.84 mmol) and ^{n}BuLi (4.5 cm^3 of a 1.6 M solution in hexane) in diethyl ether (20 cm^3)]. The resulting yellow suspension of "(PhC≡C)$_3$CuLi$_2$" was stirred for 0.5 h at −65°C then [Mo(CO)$_3$(η^7-C_7H_7)][PF$_6$] (1.01 g, 2.43 mmol) was added as a solid. The resulting orange suspension was stirred at −65°C for 2 h and at −20°C for a further 1 h then the cold suspension was transferred to an alumina/diethyl ether chromatography column (3 × 30 cm) which was maintained at −40°C. Elution with CH_2Cl_2 gave an orange band, which was collected. The solution was reduced in volume and addition of n-hexane followed by cooling with dry ice gave the product **5** as an orange-yellow solid; yield 0.65 g (72%). The chromium analogue **4** was prepared in 35% yield by an identical procedure starting from HC≡CPh (0.40 g, 3.92 mmol), ^{n}BuLi (2.5 cm^3 of a 1.6 M solution), CuBr · Me$_2$S (0.28 g, 1.36 mmol) and [Cr(CO)$_3$(η^7-C_7H_7)][PF$_6$] (0.48 g, 1.29 mmol).

3.3. Preparation of [Cr(CO)$_3${η^6-(3-C≡CPh)C_7H_7)}] (6)

A stirred suspension of **4** (0.57 g, 1.74 mmol) in methylcyclohexane (60 cm^3) was maintained at 80°C for 20 min during which the complex dissolved and the colour of the solution changed from red to deep purple-red. The solution was then evaporated to dryness and a CH_2Cl_2 extract of the residue was transferred to an alumina/n-hexane chromatography column. Elution with n-hexane/CH_2Cl_2(9 : 1) gave a brown-purple band and the eluate from this was reduced in volume. Addition of n-hexane and cooling with dry ice gave the product **6** as a deep red solid; yield 0.27 g (47%).

3.4. Preparation of $[Mo(CO)_3\{\eta^7\text{-}C_7H_6(C_6H_4F\text{-}p)\}][PF_6]$ (9) from 3

A stirred suspension of $[Mo(CO)_3\{\eta^6\text{-}(7\text{-}exo\text{-}C_6H_4\text{-}F\text{-}p)C_7H_7\}]$ (**3**) (0.23 g, 0.63 mmol) was refluxed in methylcyclohexane (30 cm^3) for 2 h during which the complex dissolved and the colour of the solution changed from orange-red to deep red. The solution was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (15 cm^3) and treated with $[Ph_3C][PF_6]$ (0.30 g, 0.77 mmol). After 1 h, diethyl ether was added to precipitate the crude product, which was recrystallized from CH_2Cl_2/diethyl ether to give **9** as an orange solid; yield 0.13 g (41%). Complexes **7** and **8** were prepared similarly; **7** was obtained as an orange solid in 76% yield by thermolysis of **1** (1.92 g, 6.72 mmol) in methylcyclohexane (40 cm^3) overnight followed by reaction with $[Ph_3C][PF_6]$ (3.13 g, 8.06 mmol) in CH_2Cl_2 (40 cm^3), and **8** was isolated in 4% yield as a yellow solid following thermolysis of **2** (0.40 g, 1.23 mmol) in refluxing n-octane for 6 h and subsequent treatment of the residue with $[Ph_3C][PF_6]$ (0.33 g, 0.85 mmol) in CH_2Cl_2 (10 cm^3) for a period of 3 h.

3.5. Preparation of $[Cr(CO)_3\{\eta^7\text{-}C_7H_6(C{\equiv}CPh)\}][PF_6]$ (10)

A mixture of **6** (0.52 g, 1.58 mmol) and $[Ph_3C][PF_6]$ (0.47 g, 1.21 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 1.5 h then the solution was reduced in volume and diethyl ether added to precipitate the crude product. Recrystallization from CH_2Cl_2/toluene followed by washing with diethyl ether gave pure **10** as a golden-yellow solid; yield 0.37 g (65% based on the limiting reagent $[Ph_3C][PF_6]$ which was used in a small deficiency to avoid purification problems associated with the use of equimolar $[Ph_3C][PF_6]$).

3.6. Reaction of $[W(CO)_3(NCMe)_3]$ with 7-Me-C_7H_7

A solution of $W(CO)_6$ (1.00 g, 2.84 mmol) in CH_3CN (50 cm^3) was refluxed for 6 days then evaporated to dryness, and the residue was treated with a solution of 7-Me-C_7H_7 (0.90 g, 8.49 mmol) in THF (20 cm^3). The mixture was stirred for 1 h at 45°C and for a further 1 h, under gentle reflux, and then evaporated to dryness. A CH_2Cl_2 extract of the residue was transferred to an alumina/n-hexane chromatography column and elution with n-hexane/diethyl ether gave an orange band. The eluate was reduced in volume and cooled to -78°C to give orange $[W(CO)_3\{\eta^6\text{-}(7\text{-}Me)C_7H_7\}]$ as an *exo–endo* mixture at C(7); yield 0.47 g (44% based on $W(CO)_6$). The chromium analogue $[Cr(CO)_3\{\eta^6\text{-}(7\text{-}Me)C_7H_7\}]$, again as an *exo–endo* mixture at C(7), was obtained in 34% yield by an identical procedure starting from $Cr(CO)_6$ (0.858 g, 3.90 mmol) with refluxing in CH_3CN for 20 h and 7-Me-C_7H_7 (0.853 g, 8.05 mmol). Application of the above method to the synthesis of $[Mo(CO)_3\{\eta^6\text{-}(7\text{-}Me)C_7H_7\}]$ from $Mo(CO)_6$, CH_3CN, and 7-Me-C_7H_7 gave a 21% yield of product which was almost exclusively *exo* at C(7); however, when chromatographic purification was replaced by solvent extraction of the reaction residue with diethyl ether, the complex was isolated as an *exo–endo* mixture.

3.7. Preparation of $[Mo(CO)_3(\eta^7\text{-}C_7H_6Me)][PF_6]$ (7) from $[Mo(CO)_3(NCMe)_3]$ and $[C_7H_6Me][PF_6]$

A solution of $Mo(CO)_6$ (2.96 g, 11.21 mmol) in CH_3CN (45 cm^3) was refluxed for 5 h then evaporated to dryness. The resulting residue of $[Mo(CO)_3(NCMe)_3]$ was suspended in CH_2Cl_2 (60 cm^3) and treated with $[C_7H_6Me][PF_6]$ (1.40 g, 5.60 mmol) followed by $[FeCp_2][PF_6]$ (0.38 g, 1.15 mmol). After 5 min, the

TABLE 5. Experimental details for the preparation of $[M(CO)_3(\eta^7\text{-}C_7H_6R)]^+$ from $C_7H_6R^+$ and $[M(CO)_3(NCR')_3]$ (R′ = Me or ^{n}Pr)

Complex	M = R =	A or B [a] (mmol)	$[C_7H_6R][PF_6]$ (mmol)	Solvent	Added $[FeCp_2][PF_6]$ (mmol)	Reaction time	Purification method [b]	Yield (%) [c]
8	Mo ^{t}Bu	**A** 3.14	1.57	THF (20 cm^3)	0.30	50 min	1	11
9	Mo C_6H_4–F-*p*	**A** 11.10	5.58	CH_2Cl_2 (40 cm^3)	0.82	15 min	1	61
11	Mo C≡CPh	**A** 3.89	2.98	CH_2Cl_2 (30 cm^3)	–	0.25 min	2	12
12	W Me	**B** 0.97	0.97	THF (10 cm^3)	0.09	1.5 h	1	64
13	W C_6H_4–F-*p*	**B** 1.95	1.95	THF (15 cm^3)	0.20	1 h	1	61
	W H	**B** 0.96	0.96	THF (10 cm^3)	–	1.5 h	1	62

[a] **A** ≡ $Mo(CO)_6$ converted to $[Mo(CO)_3(NCMe)_3]$ via reflux in CH_3CN for 5 h. **B** ≡ $[W(CO)_3(NC^nPr)_3]$. [b] 1 ≡ product precipitated directly from reaction mixture, mother liquors removed, 2 ≡ product precipitated from the reaction mixture after addition of diethylether, all products purified by recrystallisation from acetone/diethyl ether. [c] Yields based on $C_7H_6R^+$.

product **7** began to separate as a bright orange solid and after 1 h the mother liquor was removed and the product isolated as an orange solid by recrystallization from acetone/diethyl ether; yield 1.45 g (60% based on $[C_7H_6Me][PF_6]$). The essential details of the analogous preparation of **8, 9, 11, 12, 13** and $[W(CO)_3(\eta^7\text{-}C_7H_7)][PF_6]$ are summarized in Table 5.

3.8. *Preparation of* $[MoI(CO)_2(\eta^7\text{-}C_7H_6Me)]$ *(14)*

Addition of NaI (2.60 g, 17.33 mmol) to a stirred solution of $[Mo(CO)_3(\eta^7\text{-}C_7H_6Me)][PF_6]$ (**7**) (1.58 g, 3.67 mmol) in acetone (40 cm^3) caused a rapid colour change from red to green. After 1.5 h the solution was evaporated to dryness and the residue was recrystallized from CH_2Cl_2/n-hexane. Further recrystallization from diethyl ether/n-hexane gave the product **14** as a green solid; yield 0.59 g (42%). The tungsten analogue **15** was prepared in 64% yield by an identical procedure starting from $[W(CO)_3(\eta^7\text{-}C_7H_6Me)][PF_6]$ (**12**) (0.74 g, 1.43 mmol) and NaI (0.54 g, 3.61 mmol).

3.9. *Preparation of* $[Mo(\eta^6\text{-toluene})(\eta^7\text{-}C_7H_6Me)][PF_6]$ *(16)*

An orange suspension of **7** (0.52 g, 1.21 mmol) in toluene (200 cm^3) was refluxed for 27 h and a green precipitate was separated from the mother liquor. Subsequent recrystallization from CH_2Cl_2/diethyl ether gave the product **16** as a pale green solid; yield 0.35 g (66%).

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