Alkyl, Aryl, Vinyl, Alkynyl and Carbene Derivatives of Cycloheptatrienylmolybdenum Complexes*

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A series of cycloheptatrienylmolybdenum complexes of general formulation $[MoR(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R = Me, Ph, vinyl or alkynyl; R' = Me or Ph) have been synthesised *via* reaction of $[MoBr(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R' = Me **1** or Ph **2**) with appropriate organolithium or Grignard reagents. Specific complexes reported are $[MoMe(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R' = Me or Ph), $[MoPh(CO)(PMe_3)(\eta\text{-}C_7H_7)]$, $[Mo(C_6F_5)(CO)(PPh_3)(\eta\text{-}C_7H_7)]$, $[Mo(CH{=}CH_2)(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R' = Me or Ph) and $[Mo(C{\equiv}CR'')(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R' = Me, R'' = Ph or Bu^t; R' = R'' = Ph). A new synthesis of $[MoMe(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_7H_7)]$ is also reported. Cyclic voltammetric studies reveal that some of the complexes undergo reversible, one-electron oxidation processes, and the radical cation $[MoMe(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_7H_7)]^+$ has been generated chemically and isolated. Protonation by $HBF_4{\cdot}Et_2O$ of the vinyl complex $[Mo(CH{=}CH_2)(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ followed by treatment with PR''_3 affords the 'trapped' carbene adducts $[Mo\{CH(PR''_3)Me\}(CO)(PMe_3)(\eta\text{-}C_7H_7)][BF_4]$ (R'' = OMe or Ph). The first examples of stable cycloheptatrienylmolybdenum carbene complexes $[Mo(\overline{CCH_2CH_2CH_2O})(CO)(PR'_3)(\eta\text{-}C_7H_7)][PF_6]$ (R' = Me or Ph), have been obtained *via* respective reaction of **1** and **2** with a but-3-yn-1-ol–$[NH_4][PF_6]$ mixture in methanol.

The chemistry of cycloheptatrienylmolybdenum complexes has expanded considerably in recent years but there are few reports on the synthesis and properties of derivatives of the type $[MoR(L)_2(\eta\text{-}C_7H_7)]$ (R = σ-C ligand, L = CO or P-donor ligand). The known examples of such complexes comprise $[MoR(CO)_2(\eta\text{-}C_7H_7)]$ (R = Me, Ph,[1] C_6F_5 [2] or $C{\equiv}CPh$[3]), of which the Me and Ph derivatives are very unstable and decompose rapidly in the solid state at ambient temperatures, and $[MoR(dppe)(\eta\text{-}C_7H_7)]^{z+}$ [dppe = $Ph_2PCH_2CH_2PPh_2$; $z = 0$, R = Me[4] or $C{\equiv}CBu^n$;[5] $z = 0$ or 1, R = $C{\equiv}CPh$ or $C{\equiv}CBu^t$; $z = 1$, R = $C{=}CHR''$ (R'' = Ph, Bu^t or Bu^n)[3,5]]. The poor stability of $[MoR(CO)_2(\eta\text{-}C_7H_7)]$ (R = Me or Ph) contrasts with the relative stability of analogous cyclopentadienyl complexes such as $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ and $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ and may account for the limited development of this area in cycloheptatrienylmolybdenum chemistry. However the phosphine-substituted complex $[MoMe(dppe)(\eta\text{-}C_7H_7)]$ is a readily isolable species suggesting that substitution of carbonyl by phosphorus-donor ligands substantially enhances the stability of $[MoR(L)_2(\eta\text{-}C_7H_7)]$ and surprisingly, therefore, there are no previous accounts of derivatives of the type $[MoR(CO)(PR'_3)(\eta\text{-}C_7H_7)]$. Accordingly we now report the synthesis and properties of a series of readily accessible complexes $[MoR(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R = Me, aryl, vinyl or alkynyl; R' = Me or Ph) and the application of these species in the formation of cationic vinylidene and carbene derivatives.

Results and Discussion

Two simple strategies are generally employed in the synthesis of metal to carbon σ bonds. Taking as an example the synthesis of $[FeR(CO)_2(\eta\text{-}C_5H_5)]$, the commonly used methods involve either reaction of the anion $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ with an organic halide RX or alternatively treatment of the halide complex $[FeX(CO)_2(\eta\text{-}C_5H_5)]$ with a Grignard or organolithium reagent.[6] However in the chemistry of cycloheptatrienylmolybdenum complexes the former method is not a productive strategy since the anion $[Mo(CO)_2(\eta\text{-}C_7H_7)]^-$ {although implicated as an intermediate in the formation of $[Mo(SnPh_3)(CO)_2(\eta\text{-}C_7H_7)]$[7]} is, in our experience, a highly unstable species. Moreover, our attempts to generate phosphine-substituted derivatives $[Mo(CO)(PR'_3)(\eta\text{-}C_7H_7)]^-$, crucial to the stability of the required Mo–C σ bonds, were uniformly unsuccessful. Consequently our investigations focused on the reactions of $[MoX(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (X = halide) with Grignard or organolithium reagents.

Although the synthesis of a series of complexes $[MoI(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ *via* reaction of $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ with PR'_3 has been reported previously,[8] we have developed analogous syntheses of the new bromide derivatives $[MoBr(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ [R' = Me **1** or Ph **2** (see Scheme 1)] since the relative lability of the Mo–Br bond should ensure milder reaction conditions in the formation of the Mo–C σ bonds. A further, unforeseen advantage was that carbonyl substitution in $[MoX(CO)_2(\eta\text{-}C_7H_7)]$ proceeds more readily for X = Br than for I leading to milder reaction conditions and improved yields in the current work. Thus treatment of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ with 1 equivalent of PMe_3 in toluene at room temperature led to rapid precipitation of an orange solid which was identified as the salt $[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)]Br$ and fully characterised as the hexafluorophosphate salt $[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)][PF_6]$ **3**, following anion exchange with $[NH_4][PF_6]$ in acetone. When the suspension of $[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)]Br$ in toluene was warmed to 80 °C it redissolved leading to the formation of a green solution of **1**. Reaction of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ with 2 equivalents of PMe_3 in toluene also results in the initial formation of $[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)]Br$ and subsequent heating affords the disubstituted cationic complex $[Mo(CO)(PMe_3)_2(\eta\text{-}C_7H_7)]Br$ **4**. The reaction between $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ and a small excess of PPh_3 proceeds only at elevated temperatures leading to the direct, high-yield formation of **2** with no detectable intermediates. Details of the characterisation of **1**–**4** and of subsequently described complexes are given in Tables 1 (elemental analysis, infrared and mass spectroscopy) and 2 (^1H and ^{13}C NMR spectroscopy). We have also investigated the

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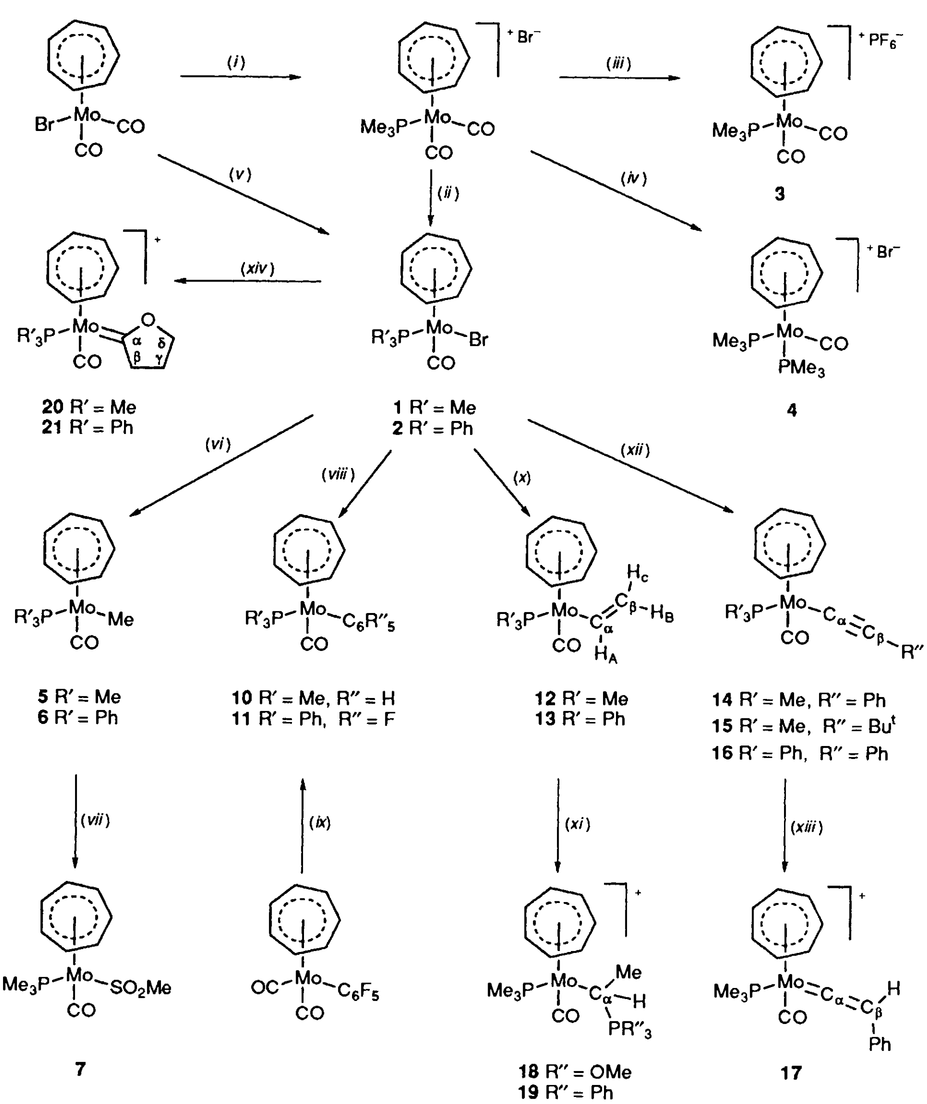
* *Non-SI unit employed:* G = 10^{-4} T.



Scheme 1 Reagents and conditions: (*i*) PMe_3 in toluene, 5 min; (*ii*) toluene, 1 h, 80 °C; (*iii*) $[NH_4][PF_6]$ in acetone, 30 min; (*iv*) PMe_3 in toluene, 2 h, 80 °C; (*v*) PPh_3 in toluene, 1 h, 80 °C; (*vi*) LiMe in thf; R' = Me, 30 min, −78 °C; R' = Ph, 90 min, −40 °C; (*vii*) SO_2 in thf; (*viii*) R' = Me, R'' = H; LiPh in thf, 1 h, −78 °C; R' = Ph, R'' = F; $Mg(C_6F_5)Br$ in thf, 5 h, 50 °C; (*ix*) PPh_3 in refluxing toluene, 3 h; (*x*) $Li(CH{=}CH_2)$ in thf, −78 °C; R' = Me, 10 min; R' = Ph, 90 min; (*xi*) $HBF_4{\cdot}Et_2O$ in thf, −78 °C, then PR''_3; (*xii*) $Li(C{\equiv}CR'')$ in thf; R' = Me or Ph, R'' = Ph, 1 h; R' = Me, R'' = Buᵗ, 2 h, 60 °C; (*xiii*) $HBF_4{\cdot}Et_2O$ in diethyl ether, 10 min, −78 °C; (*xiv*) $[NH_4][PF_6]$ and $HC{\equiv}CCH_2CH_2OH$ in refluxing methanol; R' = Me, 90 min; R' = Ph, 4 h

redox chemistry of selected complexes in this work by cyclic voltammetry and the results are summarised in Table 3. The halide complexes **1** and **2** and the majority of σ-carbon ligand complexes $[MoR(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ undergo irreversible oxidation processes for which E_P^A values at a scan rate of 100 mV s^{-1} are reported.

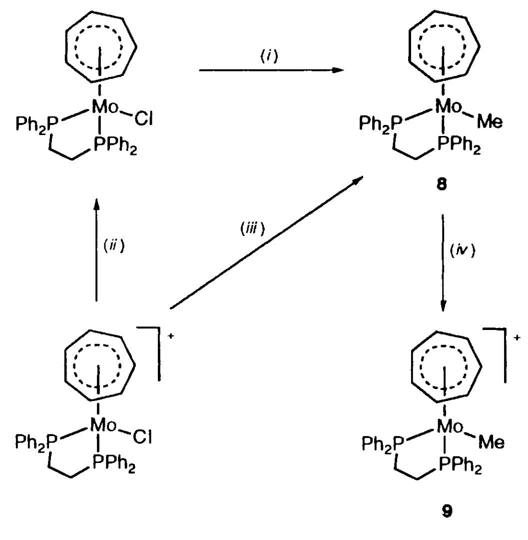
Methyl Complexes.—Treatment of complexes **1** and **2** with an excess of methyllithium at low temperature generates $[MoMe(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R' = Me **5** or Ph **6**) which were isolated in good yield as green solids following chromatography of the whole reaction mixture on alumina at −78 °C. Attempts to prepare **5** and **6** *via* reaction of **1** and **2** with the Grignard reagent MgMeBr were unsuccessful. In contrast to $[MoMe(CO)_2(\eta\text{-}C_7H_7)]$,[1] complexes **5** and **6** are stable indefinitely in the solid state under an inert atmosphere but they are unstable in chlorinated solvents and decompose rapidly if chromatographic purification is attempted at ambient temperature. Their hydrogen-1 and ^{13}C NMR spectra exhibit characteristic high-field resonances for the methyl ligand, each signal appearing as a doublet due to coupling to ^{31}P of the PR'_3 ligand. The hexane solution infrared spectrum of **5** exhibits a single ν(CO) band at 1903 cm^{-1}, but the corresponding spectrum of the PPh_3 derivative **6** displays two carbonyl-stretching bands [ν(CO) (hexane) 1922 and 1906 cm^{-1}] of approximately relative intensity 1 : 1.9, although in more polar solvents, such as thf, a single unresolved band is observed. Similar effects have been observed previously in complexes such as $[MoI(CO)\{P(OMe)_3\}(\eta\text{-}C_7H_7)]$[8] and $[FeI(CO)(PPh_3)(\eta\text{-}C_5H_4Me)]$[9] and have been attributed to conformational isomerism of the P-donor ligand rather than a property associated with the asymmetric metal centre.

Methyl complexes such as $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ and $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ act as precursors to acyl complexes *via* migratory insertion processes induced by co-ordinating ligands L' (L' = CO or P-donor ligand).[10] There are no reports of the corresponding formation of the cycloheptatrienyl acyl complexes $[Mo(COMe)(CO)L'(\eta\text{-}C_7H_7)]$ from $[MoMe(CO)_2(\eta\text{-}C_7H_7)]$, but insertion of SO_2 into the Mo–Me bond has been demonstrated.[1] Similarly we have shown that treatment of **5** with SO_2 readily produces air-stable $[Mo(SO_2Me)(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ **7** which was assigned as an S-sulfinate[11] on the basis of infrared-active sulfur–oxygen stretching frequencies [KBr disc, $\nu_{asym}(SO_2)$ 1135, $\nu_{sym}(SO_2)$ 1024 cm^{-1}]. Hydrogen-1

Table 1 Microanalytical, infrared and mass spectroscopic data

	Analysis (%)[a]		Infrared, $\tilde{\nu}$(CO)/cm^{-1} [b]		
Complex	C	H	thf	Hexane	Mass spectral data[c]
1	35.8 (35.6)	4.0 (4.3)	1924	1943	372 (M^+), 344 ($[M - \text{CO}]^+$), 268 ($[M - \text{CO} - \text{PMe}_3]^+$)
2	55.8 (56.0)	4.1 (4.0)	1944		
3	30.7 (31.0)	3.6 (3.4)	2020, 1975[d]		321 (M^+), 293 ($[M - \text{CO}]^+$)
4	37.4 (37.6)	5.7 (5.6)	1904		369 (M^+), 341 ($[M - \text{CO}]^+$), 265 ($[M - \text{CO} - \text{PMe}_3]^+$)
5	46.7 (47.1)	6.2 (6.3)	1884	1903	308 (M^+), 280 ($[M - \text{CO}]^+$), 265 ($[M - \text{CO} - \text{Me}]^+$)[e]
6	65.8 (65.8)	5.1 (5.1)	1893	1922, 1906 (1 : 1.9)	
7	39.0 (38.9)	5.4 (5.2)[f]	1918		371 (M^+), 344 ($[M - \text{CO}]^+$), 293 ($[M - \text{SO}_2\text{Me}]^+$), 265 ($[M - \text{CO} - \text{SO}_2\text{Me}]^+$)
8	68.3 (68.0)	5.8 (5.7)			602 (M^+), 587 ($[M - \text{Me}]^+$)
9	54.8 (54.8)	4.5 (4.6)			602 (M^+), 587 ($[M - \text{Me}]^+$)
10	54.9 (55.4)	5.6 (5.7)	1888	1904	369 (M^+), 341 ($[M - \text{CO}]^+$)
11	59.5 (59.6)	3.5 (3.4)	1933	1947	645 (M^+), 617 ($[M - \text{CO}]^+$)
12	48.7 (49.1)	5.8 (6.0)	1893	1909	320 (M^+), 292 ($[M - \text{CO}]^+$)[g]
13	65.9 (66.7)	5.0 (5.0)	1913	1939, 1927 (1 : 1.0)	506 (M^+), 478 ($[M - \text{CO}]^+$)[g]
14	58.3 (58.2)	5.6 (5.4)	1916[h]	1936	366 ($[M - \text{CO}]^+$), 290 ($[M - \text{CO} - \text{PMe}_3]^+$)
15	55.2 (54.8)	6.6 (6.8)	1913[i]	1932	374 (M^+), 346 ($[M - \text{CO}]^+$), 270 ($[M - \text{CO} - \text{PMe}_3]^+$)
16	70.3 (70.6)	5.0 (4.7)	1935[j]		580 (M^+), 552 ($[M - \text{CO}]^+$)
17	47.4 (47.5)	4.5 (4.6)	2023[k]		367 ($[M - \text{CO}]^+$), 291 ($[M - \text{CO} - \text{PMe}_3]^+$)
18	36.4 (36.3)	5.7 (5.5)	1894		445 (M^+), 417 ($[M - \text{CO}]^+$), 369 ($[M - \text{PMe}_3]^+$), 341 ($[M - \text{CO} - \text{PMe}_3]^+$)
19	55.7 (55.7)	5.3 (5.3)	1887		583 (M^+), 507 ($[M - \text{PMe}_3]^+$), 479 ($[M - \text{CO} - \text{PMe}_3]^+$)
20	35.2 (35.6)	4.2 (4.4)	1963[d]		363 (M^+), 335 ($[M - \text{CO}]^+$)
21	52.0 (52.0)	4.2 (4.1)	1963[d]		549 (M^+), 521 ($[M - \text{CO}]^+$), 451 ($[M - \text{CO} - \overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}]^+$)

[a] Calculated values in parentheses. [b] Solution spectra in thf or hexane (where soluble) unless stated otherwise; parentheses indicate relative intensities of bands. [c] By FAB mass spectroscopy unless stated otherwise, *m/z* values based on ^{98}Mo. [d] In CH_2Cl_2. [e] By electron-impact mass spectroscopy. [f] S, 8.7 (8.7)%. [g] By chemical ionisation mass spectroscopy. [h] ν(C≡C) (thf) 2067 cm^{-1}. [i] ν(C≡C) (thf) 2077 cm^{-1}. [j] ν(C≡C) (thf) 2069 cm^{-1}. [k] Solid-state CsI disc spectrum.



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Scheme 2 Reagents and conditions: (*i*) LiMe in thf, 3 h; (*ii*) [Co(η-$C_5H_5)_2$] in toluene, 2 h; (*iii*) LiMe in thf, 2 h, 40 °C; (*iv*) [Fe(η-$C_5H_5)_2$]PF_6 in thf, 1 h; [Ph_3C][PF_6] in CH_2Cl_2, 1 h

and ^{13}C NMR spectra reveal a shift to low field of the methyl resonance on generation of **7** from **5**.

Having demonstrated the feasibility of insertion into the Mo–Me bond of complex **5**, attempts were made to effect insertion of CO. Although [FeMe(CO)(PPh_3)(η-C_5H_5)] reacts slowly with CO to give [Fe(COMe)(CO)(PPh_3)(η-C_5H_5)],[12] no reaction was observed on passage of CO through a tetrahydrofuran (thf) solution of **5**. An alternative approach involving reaction of **6** with PMe_3 at room temperature in thf, resulted, not in the formation of [Mo(COMe)(PMe_3)(PPh_3)(η-C_7H_7)], but in simple substitution of PPh_3 by PMe_3 to give **5**.

Redox catalysis of migratory insertion in [FeMe(CO)(PPh_3)(η-C_5H_5)] is well established[12] and there is also some evidence to support redox-induced migratory insertion in [Mo(C_6F_5)-$(CO)_2$(η-C_7H_7)] although no confirmatory organometallic products were isolated.[13] Accordingly we have investigated the reaction of **5** with CO in the presence of catalytic quantities of the one-electron oxidant [Fe(η-$C_5H_5)_2$][PF_6] but the major isolated product was cationic [Mo(CO)$(PMe_3)_2$(η-C_7H_7)]$^+$, of which the bromide salt **4**, has been fully characterised. The contrasting behaviour of [FeMe(CO)(PPh_3)(η-C_5H_5)] and [MoMe(CO)(PMe_3)(η-C_7H_7)] towards redox-promoted migratory insertion may in part be rationalised by cyclic voltammetric data. Whereas the 17-electron radical cation generated from [FeMe(CO)(PPh_3)(η-C_5H_5)] is relatively stable on the electrochemical time-scale,[12] cyclic voltammetry on **5** in thf reveals an irreversible oxidation process (E_p^A = 0.17 V, scan rate = 100 mV s^{-1}) and even at a scan rate of 500 mV s^{-1} the ratio of peak currents $i_p^C : i_p^A$ is still less than 0.2 : 1. It is possible therefore that the 17-electron radical cation derived from **5** is activated towards processes such as ligand exchange in preference to migratory insertion.

Further to extend the chemistry of alkyl derivatives of cycloheptatrienylmolybdenum complexes we have also examined the redox chemistry and a new synthesis of the known complex [MoMe(dppe)(η-C_7H_7)] **8** (see Scheme 2). In the current work complex **8** has been obtained in 36% yield *via* reaction of [MoCl(dppe)(η-C_7H_7)] with methyllithium by a procedure similar to that employed for the synthesis of **5** and **6**. Alternatively, **8** has been prepared in 47% yield *via* reaction of the more readily available[14] 17-electron radical cation [MoCl(dppe)(η-C_7H_7)]$^+$ with a large excess of methyllithium in thf; presumably in this latter reaction LiMe acts both as a reducing agent and as a source of the methyl ligand.

Our previous investigations have demonstrated that a wide range of complexes of general formulation [MoL′(dppe)(η-

Table 2 Proton and ^{13}C NMR spectral data

Complex	^1H NMR (δ)[a]	^{13}C NMR (δ)[a]
1[b]	5.14 [d, 7 H, C_7H_7, *J*(H–P) 2.5], 1.48 [d, 9 H, PMe_3, *J*(H–P) 8.4]	236.5 [d, CO, *J*(C–P) 20.6], 91.2 (s, C_7H_7), 18.3 [d, PMe_3, *J*(C–P) 26.9]
2[b]	7.53 (m, 6 H, Ph), 7.39 (m, 9 H, Ph), 4.98 [d, 7 H, C_7H_7, *J*(H–P) 2.0]	234.9 [d, CO, *J*(C–P) 18.1], 134.7 [d, Ph, *J*(C–P) 37.7], 133.8 [d, Ph, *J*(C–P) 10.7], 130.0 (s, Ph), 128.2 [d, Ph, *J*(C–P) 9.3], 92.5 (s, C_7H_7)
3[c]	6.19 [d, 7 H, C_7H_7, *J*(H–P) 2.5], 1.79 [d, 9 H, PMe_3, *J*(H–P) 9.7]	215.7 [d, CO, *J*(C–P) 17.8], 97.5 (s, C_7H_7), 20.0 [d, PMe_3, *J*(C–P) 30.6]
4[d]	5.53 [t, 7 H, C_7H_7, *J*(H–P) 2.7], 1.57 [m, 18 H, PMe_3, $A_9XX'A_9'$, $\lvert$*J*(H–P) + *J*(H–P′)$\rvert$ 8.1]	229.2 [t, CO, *J*(C–P) 21.0], 92.5 (s, C_7H_7), 21.6 [at, PMe_3, AA′X, $\lvert$*J*(C–P) + *J*(C–P′)$\rvert$ 29.1]
5	4.67 [d, 7 H, C_7H_7, *J*(H–P) 2.6], 0.90 [d, 9 H, PMe_3, *J*(H–P) 7.6], 0.11 [d, 3 H, Me, *J*(H–P) 8.1]	242.4 [d, CO, *J*(C–P) 19.0], 89.3 (s, C_7H_7), 17.8 [d, PMe_3, *J*(C–P) 23.7], −16.6 [d, Me, *J*(C–P) 15.2]
6	7.57 (m, 6 H, Ph), 7.09 (m, 9 H, Ph), 4.63 [d, 7 H, C_7H_7, *J*(H–P) 2.1], 0.34 [d, 3 H, Me, *J*(H–P) 7.3]	240.0 [d, CO, *J*(C–P) 17.6], 136.5 [d, Ph, *J*(C–P) 34.1], 133.9 [d, Ph, *J*(C–P) 11.7], 129.5, 128.2 (Ph), 90.9 (s, C_7H_7), −13.9 [d, Me, *J*(C–P) 14.2]
7[b]	5.28 [d, 7 H, C_7H_7, *J*(H–P) 2.4], 2.70 (s, 3 H, Me), 1.54 [d, 9 H, PMe_3, *J*(H–P) 8.8]	233.1 [d, CO, *J*(C–P) 21.3], 92.3 (s, C_7H_7), 57.7 (s, Me), 19.2 [d, PMe_3, *J*(C–P) 27.3]
10	7.75 (m, 2 H, Ph), 7.17 (m, 3 H, Ph), 4.65 [d, 7 H, C_7H_7, *J*(H–P) 2.5], 0.79 [d, 9 H, PMe_3, *J*(H–P) 7.8]	242.2 [d, CO, *J*(C–P) 20.5], 174.0 [d, Ph, *J*(C–P) 18.4], 142.1 [d, Ph, *J*(C–P) 5.0], 125.8 (s, Ph), 122.2 (s, Ph), 90.4 (s, C_7H_7), 18.2 [d, PMe_3, *J*(C–P) 25.4]
11	7.40–7.15 (m, 15 H, Ph), 5.01 [d, 7 H, C_7H_7, *J*(H–P) 2.1][b]	236.5 [d, CO, *J*(C–P) 14.3], 149.4–136.9 (C_6F_5), 134.5 [d, Ph, *J*(C–P) 36.8], 133.7 [d, Ph, *J*(C–P) 10.6], 130.2 (s, Ph), 128.4 [d, Ph, *J*(C–P) 9.3], 92.0 (s, C_7H_7)[d]
12	8.03 [ddd, 1 H, H_A, *J*(H_A–H_B) 12.8, *J*(H_A–H_C) 19.1, *J*(H_A–P) 7.1], 6.62 [ddd, 1 H, H_B, *J*(H_B–H_A) 12.8, $\lvert$*J*(H_B–H_C)$\rvert$ 4.9, *J*(H_B–P) 2.4], 5.93 [ddd, 1 H, H_C, *J*(H_C–H_A) 19.1, $\lvert$*J*(H_C–H_B)$\rvert$ 4.9, *J*(H_C–P) 1.6], 4.69 [d, 7 H, C_7H_7, *J*(H–P) 2.5], 0.95 [d, 9 H, PMe_3, *J*(H–P) 7.8]	240.5 [d, CO, *J*(C–P) 19.3], 163.2 [d, C_α, *J*(C–P) 20.1], 126.5 [d, C_β, *J*(C–P) 6.4], 89.9 (s, C_7H_7), 18.2 [d, PMe_3, *J*(C–P) 24.5]
13	8.15 [m, 1 H, H_A, *J*(H_A–H_B) 12.4, *J*(H_A–H_C) 18.5, *J*(H_A–P) 13.3], 7.51 (m, 6 H, Ph), 7.11 (m, 9 H, Ph), 6.56 [ddd, 1 H, H_B, *J*(H_B–H_A) 12.4, $\lvert$*J*(H_B–H_C)$\rvert$ 4.5, *J*(H_B–P) 2.0], 6.01 [dd, 1 H, H_C, *J*(H_C–H_A) 18.5, $\lvert$*J*(H_B–H_C)$\rvert$ 4.5], 4.67 [d, 7 H, C_7H_7, *J*(H–P) 2.1]	235.0 [d, CO, *J*(C–P) 17.1], 170.5 [d, C_α, *J*(C–P) 15.1], 136.1 [d, Ph, *J*(C–P) 34.6], 134.0 [d, Ph, *J*(C–P) 10.9], 129.6 (s, Ph), 128.8 [d, Ph, *J*(C–P) 6.9], 125.4 [d, C_β, *J*(C–P) 4.4], 91.0 (s, C_7H_7)
14	7.61 (m, 2 H, Ph), 7.16 (m, 2 H, Ph), 7.01 (m, 1 H, Ph), 4.77 [d, 7 H, C_7H_7, *J*(H–P) 2.6], 1.13 [d, 9 H, PMe_3, *J*(H–P) 8.3]	235.1 [d, CO, *J*(C–P) 18.9], 131.1 (s, Ph), 129.7 (s, Ph), 128.3 (s, Ph), 126.3 [d, C_α, *J*(C–P) 27.2], 124.5 (s, Ph), 112.7 (s, C_β), 90.6 (s, C_7H_7), 18.6 [d, PMe_3, *J*(C–P) 26.6]
15	4.73 [d, 7 H, C_7H_7, *J*(H–P) 2.6], 1.46 (s, 9 H, Bu^t), 1.16 [d, 9 H, PMe_3, *J*(H–P) 8.3]	236.6 [d, CO, *J*(C–P) 18.9], 119.0 (s, C_β), 102.1 [d, C_α, *J*(C–P) 28.2], 90.4 (s, C_7H_7), 33.3 (CMe_3), 29.5 (s, CMe_3), 18.5 [d, PMe_3, *J*(C–P) 26.3]
16[d]	7.68–6.77 (20 H, Ph), 4.95 [d, 7 H, C_7H_7, *J*(H–P) 2.2]	233.4 [d, CO, *J*(C–P) 18.0], 136.5 [d, Ph, *J*(C–P) 37.6], 134.2 [d, Ph, *J*(C–P) 10.9], 130.7 (s, Ph), 130.1 (s, Ph), 129.0 (s, Ph), 128.4 [d, Ph, *J*(C–P) 9.5], 128.1 (s, Ph), 127.5 [d, C_α, *J*(C–P) 24.9], 124.6 (s, Ph), 117.1 (s, C_β), 92.7 (s, C_7H_7)
18[d–g]	5.08 [d, 7 H, C_7H_7, *J*(H–P) 2.4], 3.99 [d, 9 H, $P(OMe)_3$, *J*(H–P) 10.6], 1.35 [d, 9 H, PMe_3, *J*(H–P) 8.0], 1.29 [dd, 3 H, Me, *J*(H–P) 24.9, *J*(H–H) 6.9], 1.12 (m, 1 H, CH)	241.1 [dd, CO, *J*(C–P) 21.0, 5.9], 90.8 (s, C_7H_7), 56.8 [d, $P(OMe)_3$, *J*(C–P) 7.4], 18.6 [d, PMe_3, *J*(C–P) 25.8], 18.2 [at, Me, $\lvert$*J*(C–P) + *J*(C–P′)$\rvert$ 9.8], −8.4 [dd, C_α, *J*(C–P) 91.6, 9.7]
19[e,f,h]	Major isomer: 7.98–7.79 (m, 18 H, Ph), 5.27 [d, C_7H_7, *J*(H–P) 2.7], 3.13 [m, 1 H, CH, *J*(H–P) 17.4, 2.8, *J*(H–H) 7.3], 1.78 [ddd, 3 H, Me, *J*(H–P) 22.8, 1.4, *J*(H–H) 7.3], 1.27 [d, PMe_3, *J*(H–P) 8.0][c] Minor isomer:[i] 5.13 [d, C_7H_7, *J*(H–P) 2.8], 1.66 [d, PMe_3, *J*(H–P) 8.0][c]	Major isomer: 241.2 [dd, CO, *J*(C–P) 22.6, 4.0], 134.5–133.8 (m, Ph), 130.2 [d, Ph, *J*(C–P) 11.0], 124.4 [d, Ph, *J*(C–P) 79.7], 91.6 (s, C_7H_7), 24.7 [at, Me, $\lvert$*J*(C–P) + *J*(C–P′)$\rvert$ 12.1], 19.1 [d, PMe_3, *J*(C–P) 25.7], −2.6 [at, C_α, $\lvert$*J*(C–P) + *J*(C–P′)$\rvert$ 21.3][d] Minor isomer:[i] 130.1 [d, Ph, *J*(C–P) 10.6], 124.1 [d, Ph, *J*(C–P) 80.1], 90.6 (s, C_7H_7), 25.0 [dd, Me, *J*(C–P) 8.0, 5.3], 18.1 [d, PMe_3, *J*(C–P) 25.9], −1.0 [dd, C_α, *J*(C–P) 14.6, 9.3][d]
20[d,e]	5.32 [d, 7 H, C_7H_7, *J*(H–P) 2.8], 4.93 [dt, 1 H, $C_\delta H$, $\lvert ^1J$(H–H)$\rvert$ 6.7, ^2J(H–H) 8.8], 4.74 [m, 1 H, $C_\delta H$, $\lvert ^1J$(H–H)$\rvert$ 6.7, ^2J(H–H) 9.1], 3.56 [m, 1 H, $C_\beta H$, $\lvert ^1J$(H–H)$\rvert$ 20.0, ^2J(H–H) + ^2J(H–H) 15.7], 3.42 [m, 1 H, $C_\beta H$, $\lvert ^1J$(H–H)$\rvert$ 20.0, ^2J(H–H) + ^2J(H–H) 15.8, *J*(H–P) 1.2], 2.07 (m, 2 H, $C_\gamma H_2$), 1.41 [d, 9 H, PMe_3, *J*(H–P) 8.7]	333.1 [d, C_α, *J*(C–P) 17.1], 215.5 [d, CO, *J*(C–P) 17.2], 93.1 (s, C_7H_7), 85.7 (s, C_δ), 59.9 (s, C_β), 22.5 (s, C_γ), 19.8 [d, PMe_3, *J*(C–P) 28.0]
21[d,e]	7.91–7.29 (m, 15 H, Ph), 5.21 [d, 7 H, C_7H_7, *J*(H–P) 2.5], 4.74 [dt, 1 H, $C_\delta H$, $\lvert ^1J$(H–H)$\rvert$ 6.5, ^2J(H–H) 8.9], 3.64 [m, 1 H, $C_\delta H$, $\lvert ^1J$(H–H)$\rvert$ 6.5, ^2J(H–H) 9.2], 3.47 [m, 1 H, $C_\beta H$, $\lvert ^1J$(H–H)$\rvert$ 19.1, ^2J(H–H) + ^2J(H–H) 15.0], 3.27 [m, 1 H, $C_\beta H$, $\lvert ^1J$(H–H)$\rvert$ 19.1, ^2J(H–H) + ^2J(H–H) 15.6, *J*(H–P) 1.1], 1.79 (m, 1 H, $C_\gamma H$), 1.40 (m, 1 H, $C_\gamma H$)	333.9 [d, C_α, *J*(C–P) 15.9], 218.0 [d, CO, *J*(C–P) 16.5], 134.6 [d, PPh_3, *J*(C–P) 41.2], 133.4 [d, PPh_3, *J*(C–P) 10.9], 131.4 (s, PPh_3), 129.4 [d, PPh_3, *J*(C–P) 9.1], 94.4 (s, C_7H_7), 86.3 (s, C_δ), 59.8 (s, C_β), 21.8 (s, C_γ)

[a] 300 MHz for ^1H, 75 MHz for ^{13}C; s = singlet, d = doublet, t = triplet, at = apparent triplet, m = multiplet; chemical shifts downfield from $SiMe_4$, coupling constants in Hz, in C_6D_6 solution unless stated otherwise; numbering/lettering as in Scheme 1. [b] In $CDCl_3$. [c] In $(CD_3)_2CO$. [d] In CD_2Cl_2. [e] Proton NMR assignments made with the aid of ^1H–^1H double-irradiation experiments. [f] Carbon-13 NMR assignments made with the aid of DEPT experiments. [g] ^{31}P NMR (CD_2Cl_2): δ 69.1 [s, $P(OMe_3)$] and −5.8 (s, PMe_3). [h] ^{31}P NMR (CD_2Cl_2): major isomer, δ 42.0 (s, PPh_3) and −10.6 (s, PMe_3); minor isomer, δ 41.8 [d, PPh_3, *J*(P–P) 16.2] and −6.0 [d, PMe_3, *J*(P–P) 16.2]. [i] Data for minor isomer where distinct signals observed.

C_7H_7)]$^{z+}$(z = 0, L′ = C≡CPh, Cl[3] or C≡N;[15] z = 1, L′ = NCMe[14]) undergo reversible one-electron oxidation processes leading to relatively stable, isolable, 17-electron radical cations. In contrast to **5** and **6**, the dppe derivative **8** is stable in

Table 3 Cyclic voltammetric data

Complex	$E^{\circ a}$/V	E_p^{Aa}/V (100 mV s^{-1})	$i_p^C:i_p^A$ (500 mV s^{-1})
1		0.43	0.4
2		0.56	0.4
5		0.17^b	0.15
6		0.32^b	0.3
8	−0.37	−0.34	1.0
9	−0.37	−0.34	1.0
10		0.33^b	0.6
11	0.60	0.64	1.0
12		0.25^b	0.3
13		0.36^b	0.25
14		0.28	0.0
15	0.22	0.25	1.0
16		0.41	0.2

[a] At a carbon electrode in CH_2Cl_2 unless stated otherwise. Solutions 10^{-3} mol dm^{-3} in complex and 0.2 mol dm^{-3} in supporting electrolyte $[NBu^n{}_4][BF_4]$. Potentials relative to SCE at scan rates 100 mV s^{-1} and standardised with respect to the ferrocene–ferrocenium couple for which $E^\circ = 0.56$ V in CH_2Cl_2 and 0.59 V in thf; E° values quoted only for fully reversible processes. [b] In thf.

solution in CH_2Cl_2 for short periods and cyclic voltammetric investigations on it in CH_2Cl_2 for scan rates 50–500 mV s^{-1} reveal a reversible, diffusion-controlled, one-electron oxidation process with the ratio of peak currents ($i_p^C:i_p^A$) unity over the scan-rate range investigated. The measured formal redox potential ($E^\circ = -0.37$ V) is the most negative that we have observed in this series of complexes and the results of the cyclic voltammetric study prompted an investigation of the chemical synthesis of 17-electron $[MoMe(dppe)(\eta\text{-}C_7H_7)][PF_6]$ **9**. Chemical oxidation of **8** with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in thf produced a brown-orange solution from which **9** was isolated as a beige solid. Cyclic voltammetry of **9** in CH_2Cl_2 is complementary to that of the 18-electron precursor **8**. The fluid solution ESR spectrum is characteristic for radical cations of the type $[MoL'(dppe)(\eta\text{-}C_7H_7)]^{z+}$ and closely resembles that previously reported[3] for $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)]^+$ with resolved coupling $A(i)$ to 2 equivalent ^{31}P nuclei and a further small coupling, $A(ii)$, probably attributable to the hydrogens of the cycloheptatrienyl ring. The parameters for **9** in solution in CH_2Cl_2 have been calculated as $g_{av} = 2.002$, $A(i) = 24$ G, $A(ii) = 5$ G.

Aryl Complexes.—Reaction of $[MoBr(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ with phenyllithium yields $[MoPh(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ **10** which was isolated as an air-stable green solid following chromatography of the crude reaction mixture on alumina at −78 °C. However attempts to isolate the PPh_3 analogue *via* an analogous synthesis were unsuccessful; infrared spectra of the crude reaction mixture exhibited a single carbonyl-stretching band [ν(CO)(thf) 1903 cm^{-1}] consistent with the formation of $[MoPh(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ but the product appears to decompose on attempted isolation.

By contrast the pentafluorophenyl derivative $[Mo(C_6F_5)(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ **11**, in common with the dicarbonyl derivative $[Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)]$,[2] is a stable, isolable species. It is accessible *via* two routes: (*a*) treatment of $[MoBr(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ **2** with $Mg(C_6F_5)Br$ in thf at 50 °C followed by column chromatography at room temperature gave an air-stable green solid in 42% yield; (*b*) a toluene reflux of readily accessible $[Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)]$ with PPh_3 gave the complex in 72% yield. It is probable that the latter synthesis proceeds *via* simple substitution of CO by PPh_3 and when the reaction was carried out in either toluene or methylcyclohexane and monitored by solution infrared spectroscopy no evidence was obtained for the formation of a complex of the type $[Mo(COC_6F_5)(CO)(PPh_3)(\eta\text{-}C_7H_7)]$.

Reports on the redox chemistry of $[Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)]$[13] prompted an investigation of the cyclic voltammetry of complex **11** since, in general, substitution of CO by PPh_3 results in more facile oxidative chemistry and enhanced stability of 17-electron radical cations. At a carbon electron in CH_2Cl_2, over the scan-rate range 50–500 mV s^{-1}, **11** undergoes a diffusion-controlled, reversible, one-electron oxidation process with $E^\circ = 0.60$ V. Attempts to generate the radical cation resulting from one-electron oxidation of **11** met with some success. Treatment of a green solution of **11** in CH_2Cl_2 with $AgBF_4$ afforded a bright red solution and spectroscopic data, recorded *in situ* [infrared ν(CO) 2080 cm^{-1}; ESR, $g_{av} = 2.001$, $A(^{31}P) = 23.5$ G] were consistent with the presence of the radical cation $[Mo(C_6F_5)(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$. However isolation attempts were frustrated by rapid decomposition.

Vinyl Complexes.—Treatment of complexes **1** and **2** with an excess of vinyllithium in thf affords the vinyl complexes $[Mo(CH{=}CH_2)(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R' = Me **12** or Ph **13**); as with the methyl complexes **5** and **6**, the alternative Grignard synthesis of **12** and **13** was unsuccessful. In common with **5** and **6**, the hexane-solution infrared spectrum of the PMe_3 derivative **12** exhibits a single carbonyl-stretching frequency, but that of the PPh_3 derivative **13** shows two bands which are not resolved in thf.

The procedure for assignment of the ^1H and ^{13}C NMR resonances associated with the vinyl ligand of complexes **12** and **13** merits further discussion. In the ^1H NMR spectrum of **12** each of the three vinyl protons exhibits a doublet of doublet of doublets pattern. The three discrete couplings originate from coupling to the other two vinyl protons and additionally to ^{31}P of the PMe_3 ligand. The proton H_A, attached to C_α (the carbon bound directly to the Mo), is readily assigned from the magnitude of $J(H_A\text{–}P)$ (7.1 Hz); this is significantly greater than J(H–P) observed for protons H_B and H_C which are attached to C_β. The protons H_B and H_C can be distinguished from the size of their coupling to H_A. Thus the proton *trans* to H_A, that is H_C, exhibits $J(H_A\text{–}H_C) = 19.1$ Hz, whilst the proton *cis* to H_A (that is H_B) has $J(H_A\text{–}H_B) = 12.8$ Hz. In the ^{13}C NMR spectrum C_α and C_β appear as doublets at δ 163.2 and 126.5 respectively and are readily distinguished by the magnitude of the phosphorus–carbon coupling [$J(C_\alpha\text{–}P) = 20.1$, $J(C_\beta\text{–}P) = 6.4$ Hz]. The NMR resonances assignable to the vinyl ligand of **13** are similar to those of **12** except that $J(H_A\text{–}P)$ is significantly greater and no resolved coupling was observed between H_C and ^{31}P of the PPh_3 ligand.

Alkynyl Complexes.—We have previously reported two synthetic routes to alkynyl derivatives of cycloheptatrienyl complexes. The first involves the reaction of $[Mo(solv)(dppe)(\eta\text{-}C_7H_7)]^+$ (solv = NCMe or Me_2CO) with terminal alkynes $HC{\equiv}CR''$ (R'' = Ph, Bu^t or Bu^n) to give the intermediate vinylidenes $[Mo(C{=}CHR'')(dppe)(\eta\text{-}C_7H_7)]^+$ which are subsequently deprotonated to the alkynyls $[Mo(C{\equiv}CR'')(dppe)(\eta\text{-}C_7H_7)]$.[3,5] Alternatively reaction of $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ with $Li(C{\equiv}CPh)$ has been shown to give $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$.[3] Owing to the inherent instability of vinylidene complexes of the type $[Mo(C{=}CHR'')(CO)(PR'_3)(\eta\text{-}C_7H_7)]^+$ (see below), it is unlikely that the former strategy would succeed in the synthesis of $[Mo(C{\equiv}CR'')(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ but a series of complexes of this formulation (R' = Me, R'' = Ph **14** or Bu^t **15**; R' = R'' = Ph **16**) has been prepared by reaction of **1** or **2** with $Li(C{\equiv}CR'')$ in thf followed by low-temperature chromatography of the reaction mixture. In contrast to the methyl complexes **5** and **6** and the vinyl complexes **12** and **13**, the alkynyl complexes **14**–**16** are relatively stable to column chromatography at room temperature, but superior yields were obtained when low-temperature chromatography of the crude reaction mixture was employed; indeed the relatively low-yield synthesis of $[Mo(C{\equiv}CPh)(CO)_2(\eta\text{-}C_7H_7)]$ was also significantly improved by the application of such techniques. Spectroscopic features of note are the characteristic alkynyl

$C{\equiv}C$ stretching frequency in the region 2060–2080 cm^{-1} in the infrared spectra and, in the ^{13}C NMR spectra, phosphorus–carbon coupling between C_α of the alkynyl ligand and the phosphorus of PR'_3. Distinction of the resonances due to C_α and C_β is easily made on the basis of the observed phosphorus–carbon coupling; thus C_α appears as a doublet whilst C_β shows no resolved coupling to phosphorus and appears as a singlet. We are thus able further to substantiate the observation that the relative chemical shift ordering of C_α and C_β in alkynyl complexes exhibits some dependence upon the alkynyl substituent R″[16] {compare the Ph derivative **14**, δ 126.3 [J(C–P) = 27.2, C_α] and 112.7 (C_β), with the Bu^t analogue **15**, δ 102.1 [J(C–P) 28.2 Hz, C_α] and 119.0 (C_β)}.

We have previously reported an extensive redox chemistry of the alkynyl complexes $[Mo(C{\equiv}CR'')(dppe)(\eta\text{-}C_7H_7)]$ leading to the isolable 17-electron radical cations $[Mo(C{\equiv}CR'')(dppe)(\eta\text{-}C_7H_7)]^+$ (R″ = Ph or Bu^t)[3] and the diamagnetic products of radical–radical coupling $[\{Mo(dppe)(\eta\text{-}C_7H_7)\}_2(\mu\text{-}C_4R''_2)]^{2+}$ (R″ = Ph or Bu^n)[5] and, subsequent to our early reports, an extensive redox chemistry of organometallic alkynyl complexes has developed. Accordingly we have investigated the cyclic voltammetry and synthetic redox chemistry of **14**–**16**. Cyclic voltammetric investigations on $[Mo(C{\equiv}CBu^t)(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ **15** in CH_2Cl_2 reveal a reversible one-electron oxidation ($E°$ = 0.22 V) which is diffusion controlled over the scan-rate range 50–500 mV s^{-1} with the ratio of peak currents equal to unity. However, as with **11**, although the radical cation $[Mo(C{\equiv}CBu^t)(CO)(PMe_3)(\eta\text{-}C_7H_7)]^+$ appears stable on the electrochemical time-scale, attempts to isolate the complex were unsuccessful. Chemical oxidation of **15** with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2 produced a bright red solution that faded to brown after a few minutes. Spectroscopic data recorded *in situ* [infrared, ν(CO) 2071 cm^{-1}; fluid solution ESR in CH_2Cl_2, g_{av} = 1.999, $A(^{31}P)$ = 22 G] were consistent with the presence of the radical cation $[Mo(C{\equiv}CBu^t)(CO)(PMe_3)(\eta\text{-}C_7H_7)]^+$, but monitoring by infrared spectroscopy revealed the steady decay of the carbonyl-stretching band at 2071 cm^{-1} and the growth of new bands attributable to $[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)]^+$ **3**. Thus, in contrast to the radical cations $[Mo(C{\equiv}CR'')(dppe)(\eta\text{-}C_7H_7)]^+$, which are activated towards the formation of vinylidene products, the radical cation derived from $[Mo(C{\equiv}CBu^t)(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ appears to decay with loss of the alkynyl ligand. In contrast with the redox behaviour of the *tert*-butyl alkynyl complex **15**, the phenylalkynyl derivatives, **14** and **16**, exhibit irreversible oxidation processes in their cyclic voltammograms. The PMe_3 derivative **14** shows no reverse reduction peak, even at a scan rate of 1000 mV s^{-1} whereas, at this scan rate, the PPh_3 derivative **16** exhibits a peak current ratio $i_p{}^C : i_p{}^A$ of 0.3 : 1.

Vinylidene and Carbene Complexes.—Alkynyl complexes are convenient precursors to vinylidene complexes and we have previously shown that HBF_4 protonation of $[Mo(C{\equiv}CR'')(dppe)(\eta\text{-}C_7H_7)]$ (R″ = Ph, Bu^t or Bu^n) affords the corresponding vinylidenes $[Mo(C{=}CHR'')(dppe)(\eta\text{-}C_7H_7)]^+$.[3,5] Addition of $HBF_4{\cdot}Et_2O$ to a solution of **14** in diethyl ether leads to the immediate formation of an orange precipitate which, without further work-up, has been characterised as the vinylidene complex $[Mo(C{=}CHPh)(CO)(PMe_3)(\eta\text{-}C_7H_7)]^+$ **17** on the basis of microanalytical, mass and infrared spectroscopic data (see Table 1). The solid-state, CsI disc, infrared spectrum exhibits a single carbonyl-stretching band at 2023 cm^{-1} and bands at 1588 and 1569 cm^{-1} in the region characteristic of the vinylidene C_α–C_β stretching mode. However **17** appears to be extremely short-lived in solution and all attempts further to characterise it by solution techniques were unsuccessful.

There are no reported examples of carbene derivatives of cycloheptatrienylmolybdenum complexes although the vinylidenes $[Mo(C{=}CHR'')(dppe)(\eta\text{-}C_7H_7)]^+$ (R″ = Ph, Bu^t or Bu^n) are closely related species. Although our attempts to produce acyl derivatives, which are commonly employed as carbene precursors, were unsuccessful, examination of synthetic routes to carbene complexes suggested that $[MoMe(dppe)(\eta\text{-}C_7H_7)]$ **8** and the vinyl complexes $[Mo(CH{=}CH_2)(CO)(PR'_3)(\eta\text{-}C_7H_7)]$ (R′ = Me **12** or Ph **13**) might serve as carbene precursors.

Reaction of $[RuMe(dppe)(\eta\text{-}C_5H_5)]$ with the hydride-abstraction agent $[Ph_3C][AsF_6]$ affords the methylene complex $[Ru(CH_2)(dppe)(\eta\text{-}C_5H_5)]^+$[17] but, by contrast, treatment of **8** with $[Ph_3C][PF_6]$ in CH_2Cl_2 resulted in the formation of the 17-electron radical cation **9** which was identified by microanalytical, mass and ESR spectroscopic data. It appears that, in the case of **8**, $[Ph_3C][PF_6]$ acts as a one-electron oxidant in preference to its function as a hydride-abstraction agent; this observation might be rationalised by a consideration of the extremely facile one-electron oxidation of **8** [$E°(CH_2Cl_2)$ = −0.37 V].

Vinyl complexes have also been shown to act as carbene precursors *via* protonation at C_β.[18] Treatment of a solution of **12** in diethyl ether with $HBF_4{\cdot}Et_2O$ at −78 °C gave a yellow precipitate of proposed formulation $[Mo(CHMe)(CO)(PMe_3)(\eta\text{-}C_7H_7)][BF_4]$, but all confirmatory characterisation attempts were precluded by rapid decomposition. An alternative strategy, which has been employed to implicate the formation of unstable carbenes, is to generate the carbene complex in the presence of a P-donor ligand which adds efficiently to the carbene carbon to produce a 'trapped' carbene adduct.[19] Accordingly, reaction of **12** with $HBF_4{\cdot}Et_2O$ in thf gave a yellow solution, which on immediate treatment with $P(OMe)_3$ or PPh_3 led to the respective isolation of $[Mo\{CH(PR''_3)Me\}(CO)(PMe_3)(\eta\text{-}C_7H_7)][BF_4]$ (R″ = OMe **18** or Ph **19**) as lime-green solids.

The PPh_3 derivative **19** exhibits two isomeric forms and a more detailed discussion warrants further consideration of the NMR spectroscopic data for **18** and **19**. Interpretation of the spectra of **18** is relatively straightforward although coupling to ^{31}P nuclei of both PMe_3 and $P(OMe)_3$ is observed. In the ^{1}H NMR spectrum of **18** the methyl group attached to C_α of the carbene-derived ligand exhibits a doublet of doublets pattern due to coupling to ^{31}P of $P(OMe)_3$ and the C_α proton [J(H–P) = 24.9, J(H–H) = 6.9 Hz]. In the ^{13}C NMR spectrum both the carbonyl carbon and C_α appear as doublet of doublet signals due to phosphorus–carbon coupling, whilst the methyl group attached to C_α [which was distinguished from C_α by a distortionless enhancements of polarisation transfer (DEPT) experiment] is an apparent triplet. The ^{31}P NMR spectrum exhibits two sharp singlet resonances; surprisingly, and in contrast to the related complexes[20] $[Fe(CH_2PR''_3)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (R″ = Me or Ph), coupling between the two discrete phosphorus environments was not observed. The NMR spectra of **19** are much more complex and have been interpreted as consistent with the presence of two conformational isomers, in a 3.75 : 1 ratio. In the ^{1}H NMR spectrum two sets of signals for the cycloheptatrienyl ring and for the PMe_3 are observed and, in the ^{13}C NMR spectrum, discrete signals for the cycloheptatrienyl ring, the PMe_3 ligand, C_α and the methyl carbon attached to C_α were observed for each of the two isomers. The existence of two isomeric forms is further confirmed by the ^{31}P NMR spectrum. In common with **18**, the major isomer of **19** exhibits two sharp singlet resonances but the minor isomer gives rise to two doublets with J(P–P) = 16.2 Hz; a further small, unassigned splitting of the low-field resonance associated with the metal-co-ordinated PMe_3 ligand was also observed. The precise origin of the isomeric forms of **19** remains a matter for speculation but its absence in **18**, which is formed from the same intermediate, suggests that the effect may be due to conformational isomerism within the PPh_3 ligand itself or alternatively restricted rotation about the Mo–C_α bond arising from interaction of the bulky PPh_3 group with the cycloheptatrienyl ligand.

The generation of the 'trapped' carbene adducts **18** and **19** provides strong evidence for the intermediacy of the unstable carbene $[Mo(CHMe)(CO)(PMe_3)(\eta\text{-}C_7H_7)]^+$ and, in the search for a stable carbene derivative of a cycloheptatrienylmolybdenum complex, we turned our attention to cyclic oxycarbene ligands. A number of routes are available for the synthesis of cyclic oxycarbene complexes[21,22] but the most useful strategy for application in the current work is exemplified by the formation of $[Ru(\overline{CCH_2CH_2CH_2O})(PPh_3)_2(\eta\text{-}C_5H_5)][PF_6]$ *via* reaction of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ with the hydroxyalkyne $HC{\equiv}CCH_2CH_2OH$ in methanol in the presence of $[NH_4][PF_6]$. This reaction is thought to proceed with initial alkyne to vinylidene rearrangement at the Ru followed by facile intramolecular attack at the vinylidene C_α by the hydroxyl group accompanied by a proton shift. Although less well documented, there is some evidence to suggest that terminal alkyne to vinylidene isomerisation may also be promoted by the $Fe(CO)(PPh_3)(\eta\text{-}C_5H_5)$ fragment[23] and therefore the possibility of an analogous reaction based on $Mo(CO)(PR'_3)(\eta\text{-}C_7H_7)$ (R' = Me or Ph) was investigated. Reaction of **1** or **2** with the hydroxyalkyne $HC{\equiv}CCH_2CH_2OH$ in methanol in the presence of $[NH_4][PF_6]$ provides a synthesis of the cyclic oxycarbenes $[Mo(\overline{CCH_2CH_2CH_2O})(CO)(PR'_3)(\eta\text{-}C_7H_7)][PF_6]$ (R' = Me **20** or Ph **21**). The formulation of **20** and **21** as carbenes is confirmed in each case by the characteristic low-field resonance of the carbenoid carbon at δ *ca.* 333 in the ^{13}C NMR spectra. Both the syntheses proceed in relatively low yield and, in the case of **20**, the major side product was identified as $[Mo(CO)(PMe_3)_2(\eta\text{-}C_7H_7)]^+$. However **20** and **21** represent the first examples of stable cycloheptatrienylmolybdenum carbene complexes and the further reactions of these and related dppe-substituted complexes will form the subject of a future report.

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 $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$,[24] $[Mo(C_6F_5)(CO)_2(\eta\text{-}C_7H_7)]$,[2] $[MoCl(dppe)(\eta\text{-}C_7H_7)]$,[14] $[MoCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$[14] and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$,[25] and $Mg(C_6F_5)Br$,[26] $Li(CH{=}CH_2)$[27] and $[Ph_3C][PF_6]$[28] were prepared by published procedures. Column chromatography was carried out on alumina (Brockmann activity II) and silica (230–400 mesh) supplied by Merck. The chemicals $[NH_4][PF_6]$, PMe_3, PPh_3, $P(OMe)_3$, $HBF_4{\cdot}Et_2O$, LiMe, LiPh, $Sn(CH{=}CH_2)_4$, C_6F_5Br, $PhC{\equiv}CH$ and $HC{\equiv}CCH_2CH_2OH$ were supplied by Aldrich Chemical Co.; $Bu^tC{\equiv}CH$ was obtained from Lancaster Synthesis and $LiBu^n$ from Fluka.

The 300 MHz ^1H and 75 MHz ^{13}C NMR spectra were recorded on Bruker AC 300 E or Varian Associates XL 300 spectrometers, 122 MHz ^{31}P NMR spectra on the Varian Associates XL 300 with positive chemical shifts quoted downfield from H_3PO_4. Infrared spectra were obtained on a Perkin-Elmer FT 1710 spectrometer, mass spectra on Kratos Concept 1S or VG Trio 2000 instruments and X-band ESR spectra on a Varian Associates E4 spectrometer. Cyclic voltammetric studies were carried out, as described previously,[3] at a carbon working electrode using 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ as supporting electrolyte. All potentials are referenced to an aqueous calomel electrode and, under these conditions, $E°$ for the ferrocene–ferrocenium couple is 0.56 V in CH_2Cl_2 and 0.59 V in thf. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

$[MoBr(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ **1**.—Treatment of a stirred solution of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ (3.00 g, 9.29 mmol) in toluene (100 cm^3) with PMe_3 (9.30 mmol, 9.3 cm^3 of a 1.0 mol dm^{-3} solution in toluene) resulted in rapid formation of an orange precipitate of $[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)]Br$. On warming the reaction mixture to 80 °C the precipitate dissolved to give a green solution. After 1 h the solution was filtered then evaporated to dryness. Recrystallisation of the residue from CH_2Cl_2–hexane gave complex **1** as a green solid, yield 2.81 g (82%).

$[MoBr(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ **2**.—The complex $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ (2.10 g, 6.50 mmol) and a slight excess of PPh_3 (1.87 g, 7.13 mmol) were heated together in toluene (60 cm^3) at 80 °C for 1 h. The product **2** formed as a green precipitate which was isolated and recrystallised from CH_2Cl_2–hexane; yield 3.04 g (84%).

$[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)][PF_6]$ **3**.—A sample of $[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)]Br$, formed *via* treatment of a toluene solution of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ (0.324 g, 1.00 mmol) with PMe_3 (2.00 mmol, 2.0 cm^3 of a 1.0 mol dm^{-3} solution in toluene), was collected and dried *in vacuo*. The complex was dissolved in a solution of AR acetone containing $[NH_4][PF_6]$ (0.164 g, 1.01 mmol) and stirred for 30 min. Removal of solvent and recrystallisation of the residue from CH_2Cl_2–diethyl ether gave complex **3** as an orange-red solid, yield 0.18 g (39%).

$[Mo(CO)(PMe_3)_2(\eta\text{-}C_7H_7)]Br$ **4**.—A suspension of $[Mo(CO)_2(PMe_3)(\eta\text{-}C_7H_7)]Br$ was prepared by treatment of a stirred solution of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ (0.50 g, 1.55 mmol) in toluene (20 cm^3) with PMe_3 (3.10 mmol, 3.1 cm^3 of a 1.0 mol dm^{-3} solution in toluene). The reaction mixture was then warmed to 80 °C for 2 h resulting in the formation of **4** as a light green precipitate. After cooling to room temperature the product was collected and recrystallised from CH_2Cl_2–hexane; yield 0.56 g (81%).

$[MoMe(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ **5**.—A stirred solution of complex **1** (1.13 g, 3.05 mmol) in thf (40 cm^3) was cooled to −78 °C and treated with LiMe (4.62 mmol, 3.3 cm^3 of a 1.4 mol dm^{-3} solution in diethyl ether). The stirred reaction mixture was maintained at −78 °C for 30 min and then transferred in entirety to an alumina–hexane chromatography column maintained at −78 °C. Elution of the reaction mixture with hexane led to the collection of a green fraction which was reduced in volume and hexane added to precipitate complex **5** as a green solid, yield 0.65 g (70%). The complex $[MoMe(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ **6** was prepared in 59% yield from **2** (2.00 g, 3.59 mmol) and LiMe (7.0 mmol, 5.0 cm^3 of a 1.4 mol dm^{-3} solution in diethyl ether) in thf (80 cm^3) by an identical procedure except that reaction occurred at −40 °C over a period of 1.5 h.

$[Mo(SO_2Me)(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ **7**.—A solution of $[MoMe(CO)(PMe_3)(\eta\text{-}C_7H_7)]$ **5** was prepared by treatment of complex **1** (0.50 g, 1.35 mmol) in thf with LiMe (2.10 mmol, 1.5 cm^3 of a 1.4 mol dm^{-3} solution in diethyl ether) and subsequent chromatography on alumina. Sulfur dioxide was bubbled through the solution of **5** as it was collected off the column. The resulting reaction mixture was evaporated to dryness and the residue recrystallised from thf–diethyl ether to give the product **7** as a lime-green solid, yield 0.25 g (50% based on **1**).

$[MoMe(dppe)(\eta\text{-}C_7H_7)]$ **8**.—*Method* (*a*). A solution of $[MoCl(dppe)(\eta\text{-}C_7H_7)]$ (0.40 g, 0.64 mmol) in thf (100 cm^3), maintained at −78 °C, was treated with LiMe (7.0 mmol, 5.0 cm^3 of a 1.4 mol dm^{-3} solution in diethyl ether). Gradual warming to room temperature resulted in an orange solution. After 3 h the reaction mixture was recooled to −78 °C and transferred to a cold (−78 °C) alumina–hexane chromatography column. Elution of the reaction mixture with hexane gave an orange-red band which was collected, reduced in volume and treated with hexane to precipitate the product **8** as a red-brown solid which was recrystallised from diethyl ether–hexane; yield 0.14 g (36%).

Method (*b*). Treatment of a yellow solution of [MoCl(dppe)(η-C_7H_7)][PF_6] (0.30 g, 0.39 mmol) in thf at −78 °C with LiMe (7.0 mmol, 5.0 cm^3 of a 1.4 mol dm^{-3} solution in diethyl ether) resulted in its immediate darkening. Subsequent warming to 40 °C for 2 h gave an orange solution of complex **8** which was recooled and the product isolated as described in (*a*); yield 0.11 g (47%).

[MoMe(dppe)(η-C_7H_7)][PF_6] **9**.—*Method* (*a*). A solution of complex **8** (0.124 g, 0.206 mmol) in thf (40 cm^3) was treated with [Fe(η-C_5H_5)$_2$][PF_6] (0.068 g, 0.205 mmol). After 1 h the solvent was removed *in vacuo* and the residue washed with toluene (3 × 15 cm^3). After drying, the brown residue was recrystallised from thf–diethyl ether to give complex **9** as a beige solid, yield 0.062 g (40%).

Method (*b*). The salt [Ph_3C][PF_6] (10.1 mg, 0.026 mmol) was added to a solution of complex **8** (15.2 mg, 0.025 mmol) in CH_2Cl_2 (10 cm^3) at −78 °C. After stirring at room temperature for 1 h the solvent was removed *in vacuo* and the residue washed with toluene (3 × 10 cm^3), dried and recrystallised from CH_2Cl_2–diethyl ether; yield 5.0 mg (26%) (Found: C, 55.3; H, 4.9. $C_{34}H_{34}F_6MoP_3$ requires C, 54.8; H, 4.6%).

[MoPh(CO)(PMe_3)(η-C_7H_7)] **10**.—A stirred solution of complex **1** (1.54 g, 4.15 mmol) in thf (60 cm^3) was cooled to −78 °C and treated with LiPh [8.28 mmol, 4.6 cm^3 of a 1.8 mol dm^{-3} solution in cyclohexane–diethyl ether (70:30)]. The solution was maintained at −78 °C for 1 h after which time the entire reaction mixture was transferred to a cold (−78 °C) alumina–hexane chromatography column. Elution with hexane led to the collection of a green fraction which, on reduction in volume and addition of hexane, precipitated complex **10** as a green solid, yield 0.74 g (48%).

[Mo(C_6F_5)(CO)(PPh_3)(η-C_7H_7)] **11**.—*Method* (*a*). A stirred solution of complex **2** (0.49 g, 0.88 mmol) in thf (15 cm^3) was cooled to −78 °C and treated with a solution of Mg(C_6F_5)Br [prepared from Mg (0.08 g, 3.29 mmol) and C_6F_5Br (0.62 g, 2.51 mmol)] in thf (5 cm^3). The reaction mixture was then warmed to 50 °C and maintained at this temperature for 5 h after which time the solvent was removed *in vacuo*. The residue, dissolved in CH_2Cl_2 (8 cm^3), was transferred to a silica–hexane chromatography column and a green band, eluted with CH_2Cl_2–hexane (1:2), was collected and reduced in volume resulting in the precipitation of complex **11** as a bright green solid, yield 0.24 g (42%).

Method (*b*). A mixture of [Mo(C_6F_5)(CO)$_2$(η-C_7H_7)] (0.22 g, 0.54 mmol) and PPh_3 (0.15 g, 0.57 mmol) in toluene (40 cm^3) was refluxed for 3 h followed by evaporation to dryness. Subsequent work-up followed the procedure described in (*a*) except that an alumina column was used; yield 0.25 g (72%).

[Mo(CH=CH_2)(CO)(PMe_3)(η-C_7H_7)] **12**.—A stirred solution of complex **1** (0.82 g, 2.21 mmol) in thf (60 cm^3) was cooled to −78 °C and treated with a solution of vinyllithium [prepared from Sn(CH=CH_2)$_4$ (1.13 g, 4.98 mmol), LiBu^n (12.0 mmol, 7.5 cm^3 of a 1.6 mol dm^{-3} solution in hexane) and thf (15 cm^3)]. After 10 min the entire reaction mixture was transferred to a cold (−78 °C) alumina–hexane chromatography column. Elution of the reaction mixture with hexane gave a green band which was collected, reduced in volume, and hexane added to precipitate complex **12** as a green solid, yield 0.37 g (53%). Complex [Mo(CH=CH_2)(CO)(PPh_3)(η-C_7H_7)] **13** was prepared in 45% yield by an identical procedure starting from a solution of **2** (1.00 g, 1.79 mmol) in thf (40 cm^3) and a solution of vinyllithium [prepared from Sn(CH=CH_2)$_4$ (1.18 g, 5.20 mmol), LiBu^n (12.8 mmol, 8.0 cm^3 of a 1.6 mol dm^{-3} solution in hexane) and thf (15 cm^3)] except that the reaction occurred over a period of 90 min.

[Mo(C≡CPh)(CO)(PMe_3)(η-C_7H_7)] **14**.—A solution of complex **1** (1.20 g, 3.23 mmol) in thf (50 cm^3) at −78 °C was treated with a solution of Li(C≡CPh) [prepared from HC≡CPh (0.97 g, 9.50 mmol), LiBu^n (9.12 mmol, 5.7 cm^3 of a 1.6 mol dm^{-3} solution in hexane) and thf (10 cm^3)]. The reaction mixture was allowed to warm to room temperature giving a green-brown solution. After 1 h it was recooled to −78 °C and transferred to a cold (−78 °C) alumina–hexane chromatography column. Subsequent purification by an identical procedure to that described for **5** resulted in the isolation of **14** as a green solid, yield 0.80 g (63%). The complex [Mo(C≡CPh)(CO)(PPh_3)(η-C_7H_7)] **16** was obtained as a brown solid in 65% yield by an identical procedure starting from **2** (1.51 g, 2.71 mmol) in thf (80 cm^3) and a solution of Li(C≡CPh) [prepared from PhC≡CH (1.22 g, 11.94 mmol), LiBu^n (11.84 mmol, 7.4 cm^3 of a 1.6 mol dm^{-3} solution in hexane) and thf (30 cm^3)]. A similar method was employed for the synthesis of [Mo(C≡CBu^t)(CO)(PMe_3)(η-C_7H_7)] **15** in 48% yield from a solution of **1** (1.00 g, 2.69 mmol) in thf (50 cm^3) and a solution of Li(C≡CBu^t) [prepared from Bu^{t}C≡CH (0.68 g, 8.28 mmol), LiBu^n (7.68 mmol, 4.8 cm^3 of a 1.6 mol dm^{-3} solution in hexane) and thf (10 cm^3)] except that the reaction mixture was warmed to 60 °C for 2 h and the final product was obtained as a brown solid following recrystallisation from hexane at −78 °C.

[Mo(C=CHPh)(CO)(PMe_3)(η-C_7H_7)][BF_4] **17**.—A solution of [Mo(C≡CPh)(CO)(PMe_3)(η-C_7H_7)] **14** (0.061 g, 0.16 mmol) in diethyl ether (20 cm^3) was cooled to −78 °C and treated with $HBF_4 \cdot Et_2O$ (0.030 g, 0.16 mmol) to give an orange-red suspension of complex **17**. The reaction mixture was warmed to room temperature permitting removal of the mother-liquors and the product was washed with diethyl ether (4 × 20 cm^3); yield 0.048 g (64%).

[Mo{CH[P(OMe)$_3$]Me}(CO)(PMe_3)(η-C_7H_7)][BF_4] **18**.—A solution of [Mo(CH=CH_2)(CO)(PMe_3)(η-C_7H_7)] **12** (0.22 g, 0.69 mmol) in thf (40 cm^3) was cooled to −78 °C and $HBF_4 \cdot Et_2O$ (0.16 g, 0.84 mmol) added to form a yellow solution which was immediately treated with P(OMe)$_3$ (0.10 g, 0.81 mmol). After 5 min the reaction mixture had turned green, it was then treated with diethyl ether resulting in the precipitation of complex **18**. Subsequent recrystallisation from CH_2Cl_2–diethyl ether gave the product as a lime-green solid, yield 0.18 g (49%). The complex [Mo{CH(PPh_3)Me}(CO)(PMe_3)(η-C_7H_7)][BF_4] **19** was prepared in 73% yield by an identical procedure starting from **12** (0.19 g, 0.60 mmol), $HBF_4 \cdot Et_2O$ (0.13 g, 0.68 mmol) and PPh_3 (0.16 g, 0.61 mmol) in thf (25 cm^3).

[Mo($\overline{CCH_2CH_2CH_2O}$)(CO)($PMe_3$)(η-$C_7H_7$)][$PF_6$] **20**.—A mixture of complex **1** (0.51 g, 1.37 mmol), [NH_4][PF_6] (0.39 g, 2.39 mmol) and but-3-yn-1-ol (0.53 g, 7.56 mmol) in methanol (50 cm^3) was refluxed for 90 min to give an orange solution which was evaporated to dryness. The residue consists of a mixture of **20** and the side product [Mo(CO)(PMe_3)$_2$(η-C_7H_7)]$^+$ which were separated *via* fractional precipitation on addition of diethyl ether to a CH_2Cl_2 solution of the mixture; [Mo(CO)(PMe_3)$_2$(η-C_7H_7)]$^+$ is precipitated first. The second precipitate so obtained, consisting mainly of **20**, was further purified by a second fractional precipitation and finally recrystallised from acetone–diethyl ether to give **20** as a yellow-orange solid, yield 0.057 g (8%). The complex [Mo($\overline{CCH_2CH_2CH_2O}$)(CO)($PPh_3$)(η-$C_7H_7$)][$PF_6$] **21** was prepared as an orange solid in 11% yield from **2** (0.71 g, 1.27 mmol), [NH_4][PF_6] (0.30 g, 1.84 mmol) and but-3-yn-1-ol (0.50 g, 7.13 mmol) in methanol (50 cm^3) refluxed for 4 h. The purification method, including separation of an unidentified impurity by fractional precipitation, was identical to that described for **20**.

Acknowledgements

We are grateful to the SERC for the award of a research studentship (to R. W. G.).

References

1 W. H. Dell and M. L. Ziegler, *Z. Naturforsch., Teil B*, 1982, **37**, 1.

2 M. D. Rausch, A. K. Ignatowicz, M. R. Churchill and T. A. O'Brien, *J. Am. Chem. Soc.*, 1968, **90**, 3242.

3 J. S. Adams, C. Bitcon, J. R. Brown, D. Collison, M. Cunningham and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1987, 3049.

4 M. L. H. Green and R. B. A. Pardy, *Polyhedron*, 1985, **4**, 1035.

5 R. L. Beddoes, C. Bitcon, A. Ricalton and M. W. Whiteley, *J. Organomet. Chem.*, 1989, **367**, C21.

6 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104.

7 E. E. Isaacs and W. A. G. Graham, *Can. J. Chem.*, 1975, **53**, 975.

8 T. W. Beall and L. W. Houk, *Inorg. Chem.*, 1972, **11**, 915.

9 D. A. Brown, H. J. Lyons and A. R. Manning, *Inorg. Chim. Acta*, 1970, **4**, 428.

10 A. Wojcicki, *Adv. Organomet. Chem.*, 1973, **11**, 87.

11 A. Wojcicki, *Adv. Organomet. Chem.*, 1974, **12**, 31.

12 R. H. Magnuson, R. Meirowitz, S. J. Zulu and W. P. Giering, *Organometallics*, 1983, **2**, 460.

13 S. L. Gipson and K. Kneten, *Inorg. Chim. Acta*, 1989, **157**, 143.

14 C. Bitcon, R. Breeze, P. F. Miller and M. W. Whiteley, *J. Organomet. Chem.*, 1989, **364**, 181.

15 R. L. Beddoes, C. Bitcon and M. W. Whiteley, *J. Organomet. Chem.*, 1991, **402**, 85.

16 N. G. Connelly, M. P. Gamasa, J. Gimeno, C. Lapinte, E. Lastra, J. P. Maher, N. Le Narvor, A. L. Rieger and P. H. Rieger, *J. Chem. Soc., Dalton Trans.*, 1993, 2575.

17 W. B. Studabaker and M. Brookhart, *J. Organomet. Chem.*, 1986, **310**, C39.

18 C. P. Casey, W. H. Miles, H. Tukada and J. M. O'Connor, *J. Am. Chem. Soc.*, 1982, **104**, 3761.

19 V. Guerchais and D. Astruc, *J. Chem. Soc., Chem. Commun.*, 1985, 835.

20 S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton and M. Whittaker, *J. Am. Chem. Soc.*, 1987, **109**, 5711.

21 N. A. Bailey, P. L. Chell, C. P. Manuel, A. Mukhopadhyay, D. Rogers, H. E. Tabbron and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1983, 2397.

22 M. I. Bruce, A. G. Swincer, B. J. Thomson and R. C. Wallis, *Aust. J. Chem.*, 1980, **33**, 2605.

23 D. L. Reger and C. A. Swift, *Organometallics*, 1984, **3**, 876.

24 G. Hoch, R. Panter and M. L. Ziegler, *Z. Naturforsch., Teil B*, 1976, **31**, 294.

25 J. C. Smart and B. L. Pinsky, *J. Am. Chem. Soc.*, 1980, **102**, 1009.

26 C. Tamborski, E. J. Soloski and J. P. Ward, *J. Org. Chem.*, 1966, **31**, 4230.

27 C. S. Johnson, M. A. Weiner, J. S. Waugh and D. Seyferth, *J. Am. Chem. Soc.*, 1961, **83**, 1306.

28 H. J. Dauben, L. R. Honnen and K. M. Harmon, *J. Org. Chem.*, 1960, **25**, 1442.

Received 7*th February* 1994; *Paper* 4/00723I