The Chemistry of Cycloheptatrienyl Complexes of Molybdenum and Tungsten: the Synthesis and Reactions of some Vinylidene and Alkynyl Derivatives

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Reaction of the terminal alkyne HC≡CPh with [Mo(sol)(dppe)(η-C_7H_7)][PF_6] [(**2a**), sol = NCMe; (**2b**), sol = acetone; dppe = $Ph_2PCH_2CH_2PPh_2$] in refluxing acetone yields the phenylvinylidene complex [Mo(C=CHPh)(dppe)(η-C_7H_7)][PF_6] (**3**) which is readily deprotonated to give the alkynyl complex [Mo(C≡CPh)(dppe)(η-C_7H_7)] (**4**). A similar reaction sequence starting from HC≡CBu^t and (**2b**) yields [Mo(C≡CBu^t)(dppe)(η-C_7H_7)] (**6**). Protonation of (**4**) with H[BF_4]·Et_2O reforms [Mo(C=CHPh)(dppe)(η-C_7H_7)]$^+$. Electrochemical studies show that (**4**) and (**6**) undergo a reversible one-electron oxidation at a glassy carbon electrode in CH_2Cl_2 and chemical oxidation with [Fe(η-C_5H_5)$_2$][BF_4] yields the radical cations [Mo(C≡CR)(dppe)(η-C_7H_7)][BF_4] [(**5**), R = Ph; (**7**), R = Bu^t] which have been studied by e.s.r. spectroscopy. Reaction of LiC≡CPh with [MX(CO)$_2$(η-C_7H_7)] (M = Mo or W; X = I or Cl) affords the parent dicarbonylalkynyl complexes [M(C≡CPh)(CO)$_2$(η-C_7H_7)] [(**8**), M = Mo; (**9**), M = W].

The organometallic chemistry of the cycloheptatrienyl ligand (C_7H_7) has been relatively neglected by comparison with the extensive investigations on closely related systems containing the cyclopentadienyl (C_5H_5) and pentamethylcyclopentadienyl ligands. However cycloheptatrienyl is an extremely versatile ligand readily adopting η^7, η^5, η^3, or σ hapticities which may, in certain cases, interconvert,[1] thus providing a mechanism for 'ring slippage' and formation of vacant co-ordination sites at the metal centre. A further point of interest is the proposed close similarity between the steric requirements of the cycloheptatrienyl and pentamethylcyclopentadienyl ligands.[2]

Our studies on cycloheptatrienyl complexes of Group 6 transition metals were prompted by the existence of a series of analogous complexes {such as [MoCl(CO)$_2$(η-C_7H_7)] and [RuCl(CO)$_2$(η-C_5H_5)]} resulting from the formally isoelectronic nature of the fragments Mo(η-C_7H_7) and Ru(η-C_5H_5). Moreover, if the η-C_7H_7 ligand is considered to possess a unipositive charge† then, in the examples chosen, both Mo and Ru have a formal d^6 configuration. As part of a programme of work to investigate the chemistry of M(η-C_7H_7) complexes (M = Cr, Mo, or W) and to compare the results with the reactions of analogous M′(η-C_5R_5) complexes (M′ = Fe or Ru; R = H or Me) we report[4] the synthesis of the phenylvinylidene complex [Mo(C=CHPh)(dppe)(η-C_7H_7)][PF_6] (**3**) [dppe = 1,2-bis(diphenylphosphino)ethane] and the alkynyl complexes (**4**)—(**9**) (see Table 1). The special properties of the Mo(η-C_7H_7) complexes are demonstrated by the isolation and stability of the radical cations (**5**) and (**7**).

Results and Discussion

The rearrangement of a 1-alkyne to a vinylidene at a metal d^6 or d^8 centre has proved to be a highly effective route to vinylidene complexes such as *mer*-[W(C=CHPh)(CO)$_3$(dppe)],[5] [Ru(C=CHPh)(dppe)(η-C_5H_5)][PF_6],[6] and [Rh_2(μ-C=CH_2)(CO)$_2$-(η^5-C_9H_7)$_2$] (C_9H_7 = indenyl).[7] In this work [Mo(NCMe)-(dppe)(η-C_7H_7)][PF_6][8] (**2a**) (Scheme) reacted with HC≡CPh under acetone reflux over a period of 10 d to give the cationic, orange-red, phenylvinylidene complex [Mo(C=CHPh)(dppe)-(η-C_7H_7)][PF_6] (**3**), which was separated from unreacted (**2a**), in low yield, by recrystallisation from methanol–diethyl ether. The identity of (**3**) as a mononuclear phenylvinylidene complex was established by elemental analysis (Table 1), by ^1H and ^{13}C n.m.r. spectroscopy (Table 2), and by i.r. spectroscopy. A signal centred at 372.8 p.p.m. in the ^{13}C n.m.r. spectrum is characteristic of the low-field resonance of C_α in the phenylvinylidene ligand whilst the hydrogen attached to C_β is clearly observed in the ^1H n.m.r. spectrum. The i.r. spectrum of (**3**), recorded in Nujol, exhibits bands at 1 620 (broad), 1 585, and 1 560 cm^{-1}, in the region characteristic of the vinylidene C_α–C_β stretching mode, but a precise assignment is precluded by the similar carbon–carbon stretches of the phenyl carbons in the dppe ligand.

Deprotonation of the phenylvinylidene complex (**3**) occurs readily upon treatment with sodium methoxide or 1,8-bis-(dimethylamino)naphthalene to give the neutral phenylalkynyl complex [Mo(C≡CPh)(dppe)(η-C_7H_7)] (**4**) which was isolated as a deep brown-purple solid after purification by column chromatography on alumina. Characterisation details for complex (**4**), by elemental analysis, i.r. and mass spectroscopy are given in Table 1. The ^1H and ^{13}C n.m.r. spectra of (**4**) are generally uninformative and, in common with the closely related halide complexes [MoX(dppe)(η-C_7H_7)] (X = I or Cl), fail to show a signal attributable to the cycloheptatrienyl ligand.[3]

Although pure samples of the phenylvinylidene complex (**3**), free from traces of paramagnetic impurity, are best synthesised from the acetonitrile complex (**2a**), the long reaction times, due to difficulty in displacing the acetonitrile ligand, and the low yield obtained by this method made it inconvenient for the large scale preparation of complexes derived from (**3**). However, the reaction of the sandwich complex (**1**) with dppe in acetone has been reported[3] to produce a material which, although unobtainable as a pure complex, undergoes further reactions which advocate its formulation as [Mo(OCMe$_2$)(dppe)(η-C_7H_7)][PF_6] (**2b**). Treatment of a refluxing acetone solution of the proposed acetone complex (**2b**) [prepared *in situ* from (**1**) and dppe] with HC≡CPh produced a rapid colour change from brown to deep orange and termination of the reaction after 2 h led to the isolation of (**3**) as an orange-brown solid. Samples of complex (**3**) prepared by this method contained traces of inseparable paramagnetic impurity which precluded characterisation by n.m.r. spectroscopy; however the i.r. spectrum was identical to that of an authentic sample of (**3**) [prepared from

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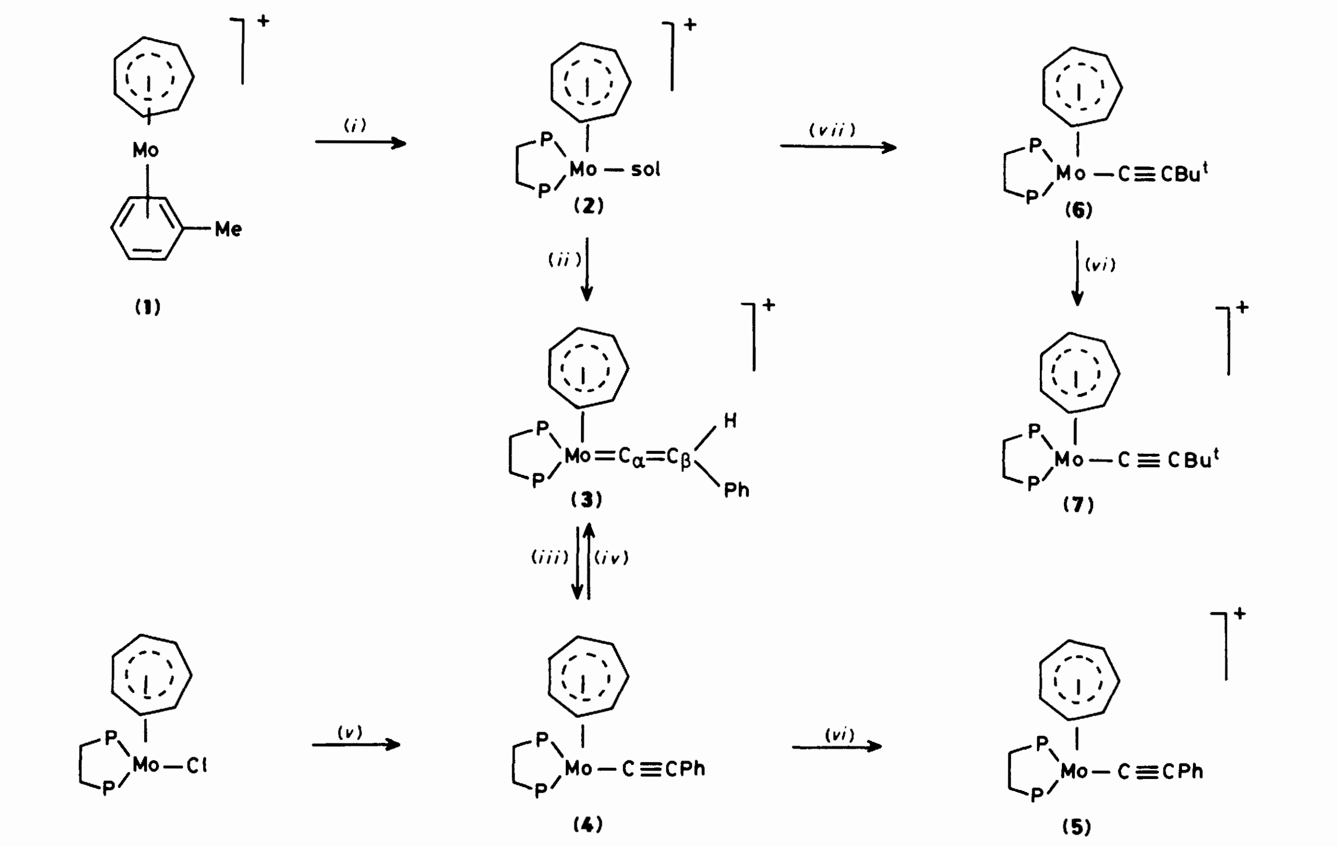
† A referee has pointed out that the η-C_7H_7 ligand may also be considered as a trinegative system as discussed in ref. 3.



Scheme. $\overset{\frown}{P\quad P}$ = dppe. (*i*) dppe in MeCN or acetone; (*ii*) sol = MeCN or acetone, HC≡CPh in acetone; (*iii*) Na in methanol or 1,8-bis(dimethylamino)naphthalene in acetone; (*iv*) H[BF$_4$]·Et$_2$O in CH$_2$Cl$_2$; (*v*) HC≡CPh in methanol followed by Na; (*vi*) [Fe(η-C$_5$H$_5$)$_2$][BF$_4$] in CH$_2$Cl$_2$; (*vii*) sol = acetone, HC≡CBu^t in acetone followed by KOBu^t

Table 1. Infrared, analytical, and electrochemical data

Complex	*M*[a]	ν(C≡C)[b]/cm^{-1}	Analysis[c] (%) C	Analysis[c] (%) H	$E^\ominus$/V
(3) [Mo(C=CHPh)(dppe)(η-C$_7$H$_7$)][PF$_6$]			58.9 (59.1)	4.7 (4.5)	
(4) [Mo(C≡CPh)(dppe)(η-C$_7$H$_7$)]	688	2 045[d]	71.7 (71.7)	5.4 (5.3)	−0.15
(5) [Mo(C≡CPh)(dppe)(η-C$_7$H$_7$)][BF$_4$]		2 032	63.2 (63.7)	4.8 (4.7)	−0.16
(6) [Mo(C≡CBu^t)(dppe)(η-C$_7$H$_7$)]	668	2 057	70.5 (70.3)	6.0 (6.0)	−0.28
(7) [Mo(C≡CBu^t)(dppe)(η-C$_7$H$_7$)][BF$_4$]		2 044	61.3 (62.2)	5.3 (5.4)	−0.28
(8) [Mo(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)]	346[e]	2 078[f]	59.4 (59.3)	3.5 (3.5)	
(9) [W(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)]	432[g]	2 080[h]	47.0 (47.2)	2.8 (2.8)	

[a] By electron impact mass spectroscopy; values for ^{98}Mo and ^{184}W. [b] In CH$_2$Cl$_2$. [c] Calculated values are given in parentheses. [d] Misreported in ref. 3 as 2 025 cm^{-1}. [e] *m/z* 318 (M^+ − CO), 290 (M^+ − 2CO). [f] ν(CO) 2 012, 1 962 cm^{-1}. [g] *m/z* 404 (M^+ − CO), 376 (M^+ − 2CO). [h] ν(CO) 2 000, 1 940 cm^{-1}.

Table 2. Proton and ^{13}C n.m.r. spectral data[a]

Complex	^{1}H (δ)[b]	^{13}C (p.p.m.)[c]
(3) [Mo(C=CHPh)(dppe)(η-C$_7$H$_7$)][PF$_6$][d]	8.16, 7.68, 7.29, 7.23, 6.80 (m, 25 H, Ph), 5.66 [t, *J*(P–H) 3, 7 H, η-C$_7$H$_7$], 5.57 [t, *J*(P–H) 12, 1 H, C=C*H*Ph], 3.01 (br, 4 H, CH$_2$)	372.8 [t, *J*(P–C) 32, C$_\alpha$], 136.7—126.7 (Ph), 120.0 [t, *J*(P–C) 11, C$_\beta$], 93.2 (s, η-C$_7$H$_7$) 26.8 [m, AA′X, |^1*J*(P–C) + ^{2}*J*(P–C)| 40.5, CH$_2$]
(8) [Mo(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)][e]	7.38 (m, 2 H, Ph), 7.23 (m, 2 H, Ph), 7.15 (m, 1 H, Ph), 5.42 (s, 7 H, η-C$_7$H$_7$)	215.3 (CO), 131.5, 127.7, 127.2, 125.2 (Ph), 113.1, 111.1 (C$_\alpha$, C$_\beta$), 94.5 (η-C$_7$H$_7$)
(9) [W(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)][e]	7.34 (m, 2 H, Ph), 7.20 (m, 2 H, Ph), 7.13 (m, 1 H, Ph), 5.30 (s, 7 H, η-C$_7$H$_7$)	208.1 (CO), 131.8, 127.8, 127.0, 125.5 (Ph), 111.4, 99.6 (C$_\alpha$, C$_\beta$), 91.0 (η-C$_7$H$_7$)

[a] Chemical shifts downfield from SiMe$_4$; *J* values in Hz. [b] 300-MHz spectra. [c] 75-MHz spectra. [d] In [^{2}H$_6$]acetone. [e] In CDCl$_3$.

the acetonitrile complex (**2a**)] and, most importantly, reaction with sodium methoxide in methanol gave, after purification, the phenylalkynyl complex (**4**). In this way complex (**4**) was obtained in sufficiently large quantities to permit further investigation of its chemistry. A similar *in situ* reaction between the acetone complex (**2b**) and $HC{\equiv}CBu^t$ followed by treatment of the resulting material with $KOBu^t$ yielded the t-butylalkynyl complex $[Mo(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_7H_7)]$ (**6**) which was isolated as a brown solid after purification by column chromatography on alumina and characterised as shown in Table 1.

We have also investigated an alternative synthesis of the phenylalkynyl complex (**4**) which closely parallels the familiar synthesis of complex $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$ from $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $HC{\equiv}CPh$ in methanol.[6] Thus a green solution of $[MoCl(dppe)(\eta\text{-}C_7H_7)]$[3] reacts with $HC{\equiv}CPh$ in refluxing methanol to give a red solution from which pure (**4**) is precipitated upon treatment with sodium methoxide. We suggest that the reaction proceeds *via* ready dissociation of chloride from $[MoCl(dppe)(\eta\text{-}C_7H_7)]$ dissolved in methanol, in a manner analogous[9] to that reported for $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$. However, in the cycloheptatrienylmolybdenum system the usefulness of this route to alkynyl complexes is, in our experience, restricted by the difficulty in preparing large quantities of $[MoCl(dppe)(\eta\text{-}C_7H_7)]$.

In common with related diphosphine-substituted vinylidene and alkynyl complexes such as $[M(C{=}CHPh)(dppe)(\eta\text{-}C_5H_5)]^+$ and $[M(C{\equiv}CPh)(dppe)(\eta\text{-}C_5H_5)]$ (M = Fe or Ru), the vinylidene complex (**3**) and alkynyl complex (**4**) constitute a reversible acid–base system.[10] Thus whilst (**4**) is formed *via* deprotonation of (**3**) with sodium methoxide, treatment of alkynyl complex (**4**) with $H[BF_4]\cdot Et_2O$ in dichloromethane results in facile protonation at C_β of the alkynyl ligand and, after addition of diethyl ether precipitation of $[Mo(C{=}CHPh)(dppe)(\eta\text{-}C_7H_7)][BF_4]$ which was identified by elemental analysis and ^1H n.m.r. spectroscopy.

Reports[3] of the isolation of radical cation halide complexes $[MoX(dppe)(\eta\text{-}C_7H_7)][PF_6]$ (X = I, Br, or Cl) prompted us to investigate the electrochemistry and synthetic redox chemistry of the alkynyl complexes (**4**) and (**6**). Cyclic voltammetric studies at a glassy carbon electrode in dichloromethane reveal that (**4**) and (**6**) undergo a reversible one-electron oxidation; values obtained for the electrode potential $E^\ominus$ of each process are given in Table 1. We have also remeasured the cyclic voltammetry of $[MoCl(dppe)(\eta\text{-}C_7H_7)]$ and, in our system in dichloromethane, determined $E^\ominus = -0.05$ V *vs.* a saturated calomel electrode (s.c.e.). For each of the alkynyl complexes (**4**) and (**6**) the electron-transfer process is diffusion controlled ($i_p^{ox}/v^{\frac{1}{2}}$ constant) for scan rates v = 50—500 mV s^{-1} and chemically reversible with the ratio of cathodic to anodic peak currents equal to unity over the same scan range. Moreover, the observed separation between the cathodic and anodic peak potentials compared well with that measured for ferrocene under identical conditions.

The magnitudes of $E^\ominus$ for (**4**) and (**6**), and the reversibility of the electron-transfer process suggested that chemical oxidation to the corresponding monocations might be achieved by one-electron oxidants such as the ferrocenium ion for which the value of $E^\ominus$, measured under identical conditions to (**4**) and (**6**), is 0.56 V *vs.* s.c.e. Thus addition of $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ to a brown solution of the phenylalkynyl complex (**4**) in dichloromethane immediately produced a deep blue solution, which afforded good yields of the radical cation $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)][BF_4]$ (**5**) as a deep purple solid. Similarly $[Mo(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_7H_7)][BF_4]$ (**7**) was isolated as an orange solid from the reaction of $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ with (**6**) in dichloromethane. The radical cation alkynyl complexes (**5**) and (**7**) are readily characterised by elemental analysis, i.r. spectroscopy, and cyclic voltammetry (Table 1) and by e.s.r. spectroscopy. In dichloromethane the cyclic voltammetry of complexes (**5**) and (**7**) is complementary to that of the corresponding neutral alkynyl precursor complexes (**4**) and (**6**) and $E^\ominus$ values within each redox pair [(**4**) and (**5**), (**6**) and (**7**)] are virtually identical.

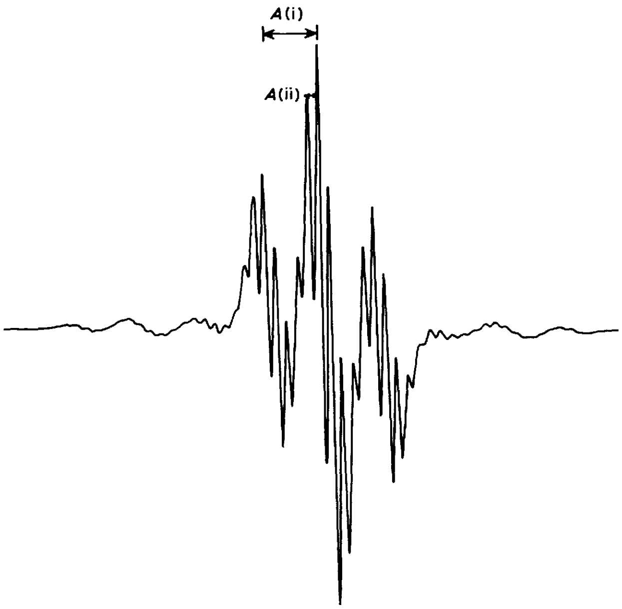
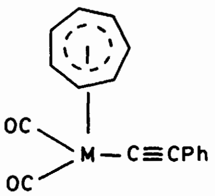


Figure. The e.s.r. spectrum of $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)][BF_4]$ (**5**) in CH_2Cl_2

The fluid solution e.s.r. spectrum of the cationic phenylalkynyl complex (**5**) in dichloromethane (Figure) reveals incompletely resolved structure due to $^{95,97}Mo$, ^{31}P, and a further small coupling, which might be attributable to the phenyl hydrogens of the dppe ligand although a definitive assignment could not be made. Extraction of e.s.r. parameters for (**5**) specified in the Figure gave values [$g_{av.}$ 1.996, A(i) 22.5 G, A(ii) 4.3 G (G = 10^{-4} T)] closely comparable with those reported for $[MoCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$ measured in acetone–methanol (1 : 1). It must be emphasised however that the e.s.r. spectra of (**5**) and $[MoCl(dppe)(\eta\text{-}C_7H_7)][PF_6]$, both in dichloromethane, are clearly distinct. The solution e.s.r. spectrum of (**7**) was virtually identical to that of (**5**) and gave parameters $g_{av.}$ 1.996, A(i) 22 G, A(ii) 4.2 G; for both (**5**) and (**7**) the coupling to $^{95,97}Mo$ was estimated to be *ca.* 32 G. The almost identical nature of the solution e.s.r. spectra of the alkynyl cations (**5**) and (**7**) was unexpected in view of the results of cyclic voltammetric studies for which $E^\ominus$ was clearly dependent upon the identity of the substituent on the alkynyl ligand. However it must be concluded that the e.s.r. spectra of (**5**) and (**7**) provide no evidence for significant localisation of the highest occupied molecular orbital (h.o.m.o.) on the alkynyl ligand.

The details of bonding between a transition metal and the alkynyl ligand have been the subject of several recent studies. Symmetry arguments suggest that the bonding interaction could involve back donation from filled, metal-based orbitals to π^* orbitals of the alkynyl ligand but molecular orbital calculations on $[Fe(C{\equiv}CH)L_2(\eta\text{-}C_5H_5)]$ (L = CO or PH_3) conclude[11] that the π^* level of the alkynyl ligand is of too high energy for effective back donation from the metal. Although the results of these molecular orbital studies are supported by an *X*-ray crystallographic comparison of the pertinent bond lengths[12] in the ruthenium complexes $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$, we believe that an additional, more direct, experimental probe for the



(**8**), M = Mo

(**9**), M = W

nature of metal–alkynyl bonding is provided by the redox pairs (**4**) and (**5**), (**6**) and (**7**).

First we have examined i.r. spectra for the change in the alkynyl stretching frequency ν(C≡C) upon one-electron oxidation. In the case of metal carbonyl complexes which form stable radical cations with a metal based h.o.m.o., ν(CO) (average) is typically shifted to higher wavenumber by 100 cm^{-1} upon one-electron oxidation[13] due to decreased back donation from the metal to π^* orbitals of the carbonyl ligands. However one-electron oxidation of the alkynyl complexes (**4**) to (**5**) or (**6**) to (**7**) in each instance results in a small *decrease* in ν(C≡C) thus supporting the absence of a metal $\rightarrow$ alkynyl π^* interaction in the h.o.m.o. We are also investigating the possibility of a structural comparison of the redox pair (**4**) and (**5**) to determine the effect of one-electron oxidation upon the molybdenum–alkynyl bond length. It is notable that the cycloheptatrienylmolybdenum system provides a rare opportunity for such an investigation; to further this work we have investigated the synthesis and redox properties of a wide range of alkynyl complexes [M(C≡CR)(dppe)(η-C$_5$R′$_5$)] (M = Fe or Ru; R = alkyl or aryl; R′ = H or Me) including new pentamethylcyclopentadienyl complexes (R′ = Me; M = Ru, R = Ph or Bu^t; M = Fe, R = Ph). Our preliminary results[14] show that, although many of the complexes [M(C≡CR)(dppe)(η-C$_5$R′$_5$)] exhibit cyclic voltammetry consistent with a chemically reversible one-electron oxidation at scan rates of 50 mV s^{-1}, in no case is it possible to isolate the corresponding cations [M(C≡CR)(dppe)(η-C$_5$R′$_5$)]$^+$ by chemical oxidation.

The chemistry of alkynyl complexes of the cycloheptatrienyl system has been further extended through the synthesis of the parent dicarbonyl complexes [Mo(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)] (**8**) and [W(C≡CPh)(CO)$_2$(η-C$_7$H$_7$)] (**9**). The synthesis of [MoR(CO)$_2$(η-C$_7$H$_7$)] (R = Me or Ph) from [MoBr(CO)$_2$(η-C$_7$H$_7$)] and the appropriate lithium reagent has been reported[15] previously; similarly in the present work reaction of [MX(CO)$_2$(η-C$_7$H$_7$)] (M = Mo or W; X = I or Cl) with a preformed tetrahydrofuran (thf) solution of LiC≡CPh at −78 °C resulted in the rapid formation of brown solutions which afforded moderate yields of the dicarbonylalkynyl complexes (**8**) and (**9**) after purification by chromatography on alumina. Complexes (**8**) and (**9**) were fully characterised by elemental analysis, i.r. and mass spectroscopy (Table 1), and by ^{1}H and ^{13}C n.m.r. spectroscopy (Table 2). On two occasions synthesis of the molybdenum complex (**8**) was achieved in *ca.* 60% yield by a procedure analogous to that reported by Bruce *et al.*[16] for [Fe(C≡CPh)(CO)$_2$(η-C$_5$H$_5$)]. Thus reaction of [MoCl(CO)$_2$(η-C$_7$H$_7$)] with HC≡CPh in triethylamine in the presence of a trace of copper(I) iodide gave complex (**8**) after 2 h stirring but, in the case of the cycloheptatrienylmolybdenum system, the method proved unreliable.

We are currently continuing work in this area by investigation of the reactions of alkynyl complexes (**4**), (**6**), (**8**), and (**9**) with electrophiles and the substitution chemistry of the dicarbonyl complexes (**8**) and (**9**).

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. All solvents were dried by standard methods, distilled, and deoxygenated before use. The complexes [Mo(η-C$_6$H$_5$Me)(η-C$_7$H$_7$)][PF$_6$] (**1**),[17] [Mo(NCMe)(dppe)(η-C$_7$H$_7$)][PF$_6$] (**2a**),[8] [MoCl(dppe)(η-C$_7$H$_7$)],[3] [MoI(CO)$_2$(η-C$_7$H$_7$)],[18] and [WCl(CO)$_2$(η-C$_7$H$_7$)][19] were prepared by published procedures. The compounds HC≡CPh, 1,8-bis(dimethylamino)naphthalene, KOBu^t, and H[BF$_4$]·Et$_2$O were supplied by the Aldrich Chemical Co.; HC≡CBu^t was purchased from Lancaster Synthesis. Alumina (Brockmann activity II) for column chromatography was purchased from B.D.H. Chemicals Ltd.

Infrared spectra were recorded on a Perkin-Elmer FT 1710 instrument. Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates SC 300 spectrometer and ^{13}C n.m.r. spectra were recorded at 75 MHz on a Varian Associates XL 300 instrument. *X*-Band e.s.r. spectra were recorded in dichloromethane solution on a Varian Associates E112 spectrometer and electron impact mass spectra were obtained using an AEI MS 30 instrument. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Cyclic voltammetric studies were made using a Princeton Applied Research model 173 potentiostat in conjunction with a model 175 signal waveform generator and a three-electrode cell. The working electrode was glassy carbon and a platinum wire served as the auxiliary; the reference electrode was an aqueous saturated calomel electrode (s.c.e.) which was separated from the test solution by a bridge tube fitted with a porous glass membrane. Test solutions were made up under a purge of dry nitrogen using solvents containing 1×10^{-3} mol dm^{-3} of complex and 0.2 mol dm^{-3} [NBu$^n_4$][BF$_4$] as supporting electrolyte. All potentials are standardised and quoted *vs.* the s.c.e.; under these conditions E° for the couple [Fe(η-C$_5$H$_5$)$_2$]$^+$–[Fe(η-C$_5$H$_5$)$_2$] is 0.56 V.

Preparation of [Mo(C=CHPh)(dppe)(η-C$_7$H$_7$)][PF$_6$] (**3**).—A mixture of [Mo(NCMe)(dppe)(η-C$_7$H$_7$)][PF$_6$] (**2a**) (0.85 g, 1.1 mmol) and HC≡CPh (0.45 g, 4.4 mmol) in acetone (100 cm^3) was refluxed for 4 d after which additional HC≡CPh (0.22 g, 2.2 mmol) was added and the reflux continued for a further 6 d. The resulting red-brown solution, which contains small quantities of unreacted (**2a**), was evaporated to dryness, the residue dissolved in methanol, filtered and diethyl ether added to precipitate (**3**) as a brown solid. Further recrystallisations from methanol–diethyl ether and finally acetone–diethyl ether gave pure (**3**) as an orange-red solid, yield 0.06 g (7%).

Large quantities of crude (**3**), suitable for the subsequent preparation of the phenylalkynyl complex (**4**), were more conveniently prepared as follows. The sandwich complex [Mo(η-C$_6$H$_5$Me)(η-C$_7$H$_7$)][PF$_6$] (**1**) (2.00 g, 4.73 mmol) in acetone (100 cm^3) was refluxed with stirring for 15 min to give a deep red solution which, on addition of dppe (1.88 g, 4.73 mmol), gave a green-brown solution. After further reflux for 18 h, resulting in formation of the complex tentatively formulated as (**2b**), HC≡CPh (0.96 g, 9.4 mmol) was added and reflux continued to give a deep orange solution. After 2 h, filtration and removal of solvent *in vacuo* gave an oily residue which was dried, dissolved in dichloromethane (8 cm^3) and added dropwise to vigorously stirred diethyl ether (150 cm^3) to afford crude (**3**) (3.9 g) as an orange-brown solid.

Preparation of [Mo(C≡CPh)(dppe)(η-C$_7$H$_7$)] (**4**).—*Method A*. To a stirred solution of (**3**) (0.20 g, 0.24 mmol) [prepared from (**2a**)] in methanol (55 cm^3) was added dropwise a solution of NaOMe [prepared from 0.02 g (0.87 mmol) Na in methanol

(5 cm^3)]. After 45 min the resulting dark brown solution was evaporated to dryness and the residue, dissolved in CH_2Cl_2 (5 cm^3), was transferred to an alumina–n-hexane column. Elution with n-hexane–acetone (1:1) gave a brown band which was collected, reduced in volume and n-hexane added to precipitate (**4**) as a deep brown-purple solid, yield 0.034 g (21%).

A similar preparation from (**3**) (2.00 g, 2.40 mmol) and 1,8-bis(dimethylamino)naphthalene (0.50 g, 2.34 mmol), stirred in acetone (200 cm^3) for 1 h and subsequent purification by column chromatography also gave (**4**), yield 0.39 g (24%).

Method B. A mixture of $[MoCl(dppe)(\eta\text{-}C_7H_7)]$ (0.30 g, 0.48 mmol) and $HC\equiv CPh$ (0.15 g, 1.5 mol) was stirred in refluxing methanol (80 cm^3) for 1 h to give a deep red solution. After filtration and cooling, addition of Na (0.06 g, 2.4 mmol) in methanol (10 cm^3) produced a brown solution. After 20 min, reduction in volume to 30 cm^3 afforded a brown-purple precipitate of (**4**) which was recrystallised from dichloromethane–n-hexane, yield 0.17 g (51%).

Preparation of $[Mo(C\equiv CBu^t)(dppe)(\eta\text{-}C_7H_7)]$ (**6**).—A stirred solution of (**2b**) [prepared from (**1**) (1.98 g, 4.68 mmol)] in acetone (80 cm^3) was treated with $HC\equiv CBu^t$ (1.15 g, 14.0 mmol) and refluxed for 5 h. The resulting brown solution was filtered, evaporated to dryness, and the residue washed with diethyl ether then dried *in vacuo*, dissolved in dichloromethane (8 cm^3), and added dropwise to vigorously stirred diethyl ether (150 cm^3). The orange-brown solid obtained by this procedure was dissolved in acetone (80 cm^3) and treated with $KOBu^t$ (1.09 g, 9.7 mmol) to give a deep brown solution. After 30 min solvent was removed *in vacuo* and the residue, dissolved in dichloromethane (5 cm^3), was transferred to an alumina–n-hexane column (20 cm × 3 cm). Elution with n-hexane–acetone (1:1) gave a brown band which after collection, removal of solvent and recrystallisation of the residue from diethyl ether–n-hexane afforded (**6**) as a brown solid, yield 1.04 g [33%, based on (**1**)].

Reaction of $[Mo(C\equiv CPh)(dppe)(\eta\text{-}C_7H_7)]$ (**4**) *with* $H[BF_4]\cdot Et_2O$.—Addition of $H[BF_4]\cdot Et_2O$ (0.47 g, 2.90 mmol) to a stirred solution of (**4**) (0.40 g, 0.58 mmol) in dichloromethane (40 cm^3) at 0 °C gave a rapid colour change from brown to deep red. After stirring for 10 min the solution was filtered, reduced in volume and diethyl ether added to give a red-brown precipitate. Recrystallisation from dichloromethane–n-hexane, followed by washing with methanol (5 cm^3) and drying *in vacuo* gave pure $[Mo(C{=}CHPh)(dppe)(\eta\text{-}C_7H_7)][BF_4]$, yield 0.15 g (33%) (Found: C, 63.0; H, 4.9. $C_{41}H_{37}BF_4MoP_2$ requires C, 63.6; H, 4.8%).

Preparation of $[Mo(C\equiv CPh)(dppe)(\eta\text{-}C_7H_7)][BF_4]$ (**5**).—Treatment of a stirred solution of (**4**) (0.345 g, 0.50 mmol) with $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ (0.137 g, 0.50 mmol) in dichloromethane (50 cm^3) produced an immediate colour change from brown to deep blue. After 30 min the solution was filtered, reduced in volume and diethyl ether added to precipitate (**5**) as a deep purple solid, yield 0.24 g (62%).

Similarly $[Mo(C\equiv CBu^t)(dppe)(\eta\text{-}C_7H_7)][BF_4]$ (**7**) was obtained as an orange solid in 15% yield from (**6**) (0.31 g, 0.46 mmol) and $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ (0.13 g, 0.46 mmol) after several recrystallisations of the initially formed product from dichloromethane–n-hexane.

Preparation of $[Mo(C\equiv CPh)(CO)_2(\eta\text{-}C_7H_7)]$ (**8**).—A hexane solution of n-butyl-lithium (1.7 cm^3, 1.6 mol dm^{-3}) was added to a solution of $HC\equiv CPh$ (0.29 g, 2.8 mmol) in thf (50 cm^3) at −78 °C. After warming to 0 °C the solution was stirred for 1.5 h then transferred to a cooled (−78 °C) flask containing $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ (0.90 g, 2.43 mmol). The resulting brown solution was warmed to 0 °C in an ice-bath, stirred for 1.5 h then evaporated to dryness. The residue, dissolved in dichloromethane (8 cm^3), was transferred to an alumina–n-hexane column (15 cm × 3 cm) and eluted with dichloromethane to give a dark green band which, on collection, reduction in volume and addition of n-hexane, yielded (**8**) as a dark green solid. Recrystallisation from diethyl ether–n-hexane gave the analytical sample, yield 0.31 g (37%).

A similar procedure starting from n-butyl-lithium (0.9 cm^3 of a 1.6 mol dm^{-3} solution in hexane), $HC\equiv CPh$ (0.14 g, 1.37 mmol), and $[WCl(CO)_2(\eta\text{-}C_7H_7)]$ (0.45 g, 1.23 mmol) gave dark green $[W(C\equiv CPh)(CO)_2(\eta\text{-}C_7H_7)]$ (**9**), yield 0.076 g (14%).

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