Formation of Cationic Molybdenum η^2-Vinyl Complexes; Structural Evidence for the Coupling of η^2-Vinyl and Alkyne Ligands

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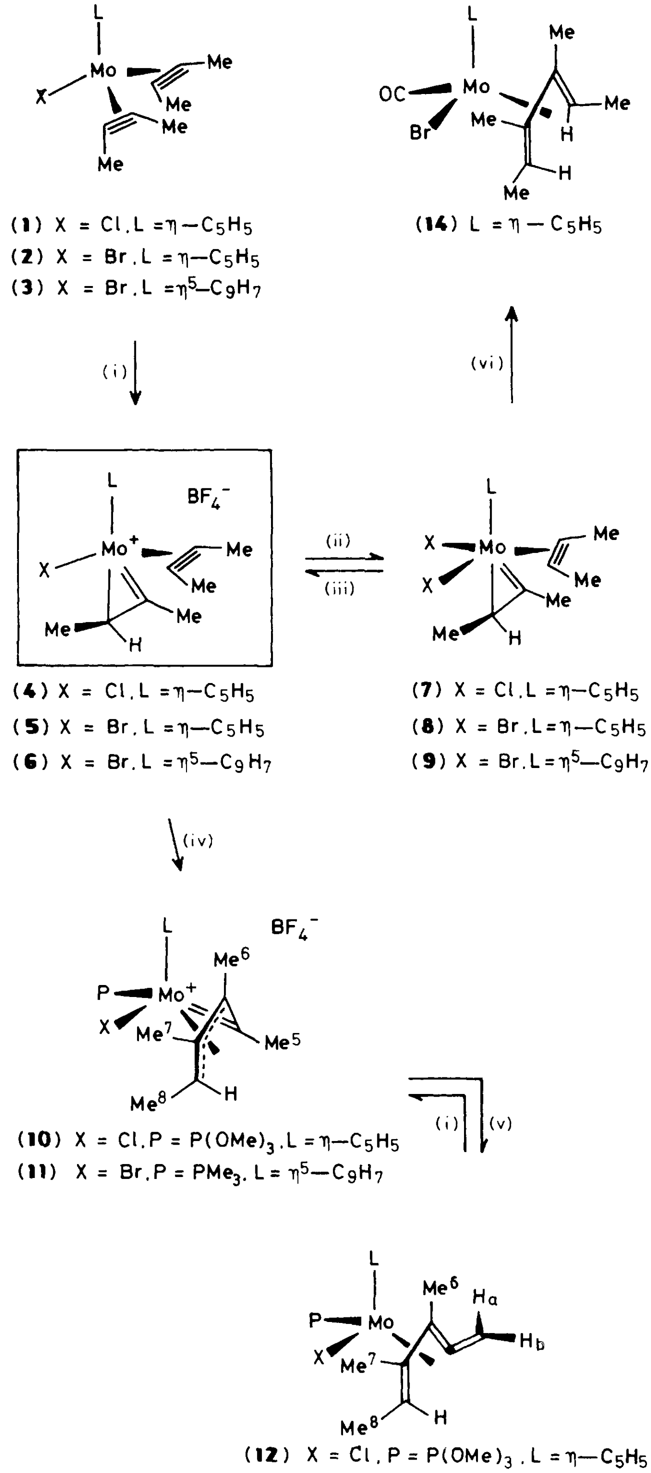
Protonation ($HBF_4 \cdot Et_2O$) of $[MoX(\eta^2\text{-}MeC_2Me)_2L]$ (X = Cl, Br, I; L = $\eta\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7$) affords the cations $[X\overline{Mo{=}C(Me)C}HMe(\eta^2\text{-}MeC_2Me)L]$ $[BF_4]$, which react with LiX to give $[X_2\overline{Mo{=}C(Me)C}HMe(\eta^2\text{-}MeC_2Me)L]$ or with PR_3 (R = Me, or OMe) to give the C–C coupled products $[XMo{=}C(Me)\text{-}\eta^3\text{-}\{C(Me)C(Me)CHMe\}(PR_3)(L)][BF_4]$, the latter being structurally identified by *X*-ray crystallography; carbon–carbon coupling also occurs on reduction of $[Br_2\overline{Mo{=}C(Me)C}HMe(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)]$ with Mg/Hg in the presence of CO to form $[MoBr(CO)\{\eta^4\text{-}CHMe{=}C(Me){\cdot}C(Me){=}CHMe\}(\eta\text{-}C_5H_5)]$, and treatment of the phosphine promoted coupled products with $Li[N(SiMe_3)_2]$ leads to reversible deprotonation reactions affording $[MoX\{\eta^4\text{-}CHMe{=}C(Me){\cdot}C(Me){=}C{=}CH_2\}(PR_3)L]$.

The synthesis and structural characterisation of complexes containing η^2(3e)-vinyl ligands[1—3] has interesting implications for catalysis, in that co-ordinatively unsaturated η^1(1e)-vinyl species can in principle be stabilised, and in a sense stored, by an η^1(1e) to η^2(3e) transformation of the bonding mode of the vinyl ligand. However, the development of this chemistry has so far been centred around the neutral η^2-vinyl complexes prepared by nucleophilic attack on three- or four-electron donor alkyne complexes, and therefore has been restricted in its scope. In this paper we describe how protonation of neutral bis(alkyne)molybdenum† complexes provides access to reactive cationic η^2-vinyl/alkyne species.

The neutral halogeno-complexes (**1**) to (**3**)‡ containing three-electron donor alkyne ligands can be readily synthesised as yellow to orange crystalline materials by reaction (refluxing tetrahydrofuran, thf) of LiX with the cations [Mo(NCMe)(η^2-MeC_2Me)$_2$(η-C_5H_5 or η^5-C_9H_7)][BF_4].[4] Protonation (−78 °C, CH_2Cl_2) of (**1**), (**2**), and (**3**) with $HBF_4 \cdot Et_2O$ affords the orange to red crystalline cations (**4**), (**5**), and (**6**), characterised by ^{1}H and ^{13}C-{^{1}H} n.m.r. spectroscopy‡ as complexes containing η^2(4e)-alkyne and η^2(3e)-vinyl ligands. The ^{13}C-{^{1}H} n.m.r. spectrum of, for example (**5**), showed a low-field resonance at 297.6 p.p.m. characteristic[1] of the α-carbon or carbene carbon of an η^2-vinyl complex, and at room temperature there were resonances due to a non-rotating but-2-yne ligand. In view of the isolobal relationship[1,3] between HC_2H and $CHCH_2^-$ it is likely that these cations have a structure analogous to that found[5] in [WCl(η^2-$CF_3C_2CF_3$)$_2$(η-C_5H_5)] with the C–C vector of both the but-2-yne and C(Me)CHMe η^2-vinyl fragments in (**4**)—(**6**) lying approximately parallel to the Mo–X axis.

Treatment of solutions of (**4**), (**5**), and (**6**) with lithium halides in CH_2Cl_2/thf results in the formation of the neutral purple crystalline complexes (**7**), (**8**), and (**9**)‡ (Scheme 1). These molecules show low-field ^{13}C resonances due to the η^2-vinyl fragment; however, in contrast with the parent cations the η^2-MeC_2Me ligands donate only two electrons to the molybdenum, and it is interesting that relatively lower barriers to alkyne rotation are observed, as is illustrated by the coalescence of the MeC_2Me ^{1}H resonances [$\Delta G^{\ddagger}_{288K}$ 58.5



Scheme 1. *Reagents and conditions:* (i) + $HBF_4 \cdot Et_2O$, CH_2Cl_2; (ii) + LiX, CH_2Cl_2/thf (1 : 1); (iii) + $AgBF_4$, −AgX, CH_2Cl_2; (iv) + P, CH_2Cl_2; (v) + LiN($SiMe_3$)$_2$, thf, −78 °C; (vi) Mg/Hg, + CO, thf.

† It is interesting that protonation (HX) of [Pt(η^2-RC_2R)(PPh_3)$_2$] affords *trans*-[PtX{η^1-C(R)=CHR}(PPh_3)$_2$]. See B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc.* (A), 1971, 2667.

‡ *Selected spectroscopic data* for (**2**): n.m.r. ^{13}C-{^{1}H} (CD_2Cl_2), δ 180.3 (Me*C*≡), 165.4 (Me*C*≡), 101.3 (*C*$_5$H$_5$), 20.2 (*Me*C), 15.7 (*Me*C). Compound (**5**): n.m.r. ^{1}H (CD_3NO_2), δ 6.0 (s, 5H, C_5H_5), 2.8 (s, 3H, *Me*C≡), 2.4 (s, 3H, *Me*C≡), 2.15 (s, 3H, *Me*C≡), 2.0 [d, 3H, CH*Me*, ^3J(HH) 6.0 Hz]; ^{13}C-{^{1}H} (CD_3NO_2), δ 297.6 [Mo=*C*(Me)], 134.6 (br.s Me*C*≡), 104.0 (C_5H_5), 73.6 (*C*HMe) [^1J(CH) 66.2 Hz from off-resonance spectrum of η^5-C_9H_7 analogue], 31.0 [Mo=C(*Me*)], 16.6 (*Me*C≡), 16.1 (CH*Me*), 12.2 (*Me*C≡). Compound (**7**): n.m.r. ^{1}H (CD_2Cl_2), δ 5.70 (s, 5H, C_5H_5), 2.80 (s, 3H, MeC≡), 2.08 (s, 6H, *Me*C≡), 2.03 [d, 3H, CH*Me*, ^3J(HH) 6.04 Hz], 1.90 [q, 1H, C*H*Me, ^3J(HH) 6.07 Hz]; ^{13}C-{^{1}H} (CD_2Cl_2), δ 291.3 [Mo=*C*(Me)], 134.2 (Me*C*≡), 113.6 (Me*C*≡), 102.6 (C_5H_5), 70.0 (*C*HMe), 27.5 (Me), 16.8 (*Me*C≡), 16.4 (*Me*C≡), 11.1 (Me). Compound (**11**) (major isomer): ^{1}H n.m.r. (CD_2Cl_2), δ 7.7—7.35 (m, 4H, C_6H_4), 6.15, 5.96, 5.55 (m, 3H, C_5H_3), 2.89 [d, 3H, Me^5, ^4J(HP) 5.37 Hz], 2.36 [m, 1H, CHMe^8, *J*(HH) 5.90 Hz], 2.32 (s, 3H, Me^7), 1.98 (s, 3H, Me^6), 1.56 [d, 9H, P*Me*$_3$, *J*(HP) 10.36 Hz], 1.18 [m, 3H, CH*Me*^{8}, ^3J(HH) 5.86 Hz]; ^{13}C-{^{1}H} (CD_2Cl_2), δ 298.1 [d, Mo=C(Me), ^3J(CP) 16.9 Hz], 127.1 (Me*C*), 115.8 (Me*C*), 132.6, 131.7, 127.3, 127.0 (C_9H_7), 117.1, 107.3 (C_9H_7), 92.7, 92.4, 88.6 (C_9H_7), 77.3 (*C*HMe), 30.3 (Me), 18.0 [d, P*Me*$_3$, ^1J(CP) 33.0 Hz], 17.6 (Me), 15.5 (Me), 10.9 (Me); ^{31}P-{^{1}H} (CD_2Cl_2) δ − 0.17 p.p.m. Compound (**12**): n.m.r. ^{1}H (C_6D_6), δ 5.39 [dd, 1H, C*H*^{b}H, ^4J(HP) 3.30, ^2J(HH) 0.94 Hz], 4.55 [d, 5H, C_5H_5, ^3J(HP) 1.43 Hz], 3.69 [dd, 1H, CH*H*^{a}, ^4J(HP) 1.96, ^2J(HH) 0.94], 3.33 [d, 9H, PO*Me*, ^3J(HP) 10.36 Hz], 2.39 [dd, 3H, Me^7, ^4J(HP) 1.6, ^4J(HH) 1.01], 2.07 [dqq, ^{1}H, C*H*Me, C*H*Me^8, ^3H(HH) 6.05, ^3J(HP) 2.5, ^4J(HH) 1.0 Hz], 1.91 (s, 3H, Me^6), 1.86 [d, 3H, Me^8, *J*(HP) 6.09 Hz]; ^{13}C-{^{1}H} (C_6D_6), δ 196.5 [d, CH_2=*C*, ^2J(CP) 10.5 Hz], 129.1 (Me*C*), 103.6 (Me*C*), 93.0 (C_5H_5), 91.7 (*C*H$_2$), 65.2 (*C*HMe), 52.6 [d, PO*Me*, ^2J(CP) 6.1 Hz], 17.8 (Me^8), 15.9 (Me^6), 14.3 (Me^7); ^{31}P-{^{1}H} (CD_2Cl_2), δ 168.6 p.p.m. Compound (**14**): ν_{CO} (Et_2O) 1945s cm^{-1}; n.m.r. ^{1}H (CD_2Cl_2), δ 4.94 (s, 5H, C_5H_5), 2.47 [q, 1H, C*H*Me, ^3J(HH) 5.95 Hz], 2.41 (s, 3H, *Me*C), 1.99 (s, 3H, *Me*C), 1.70 [d, 3H, *Me*CH, ^3J(HH) 5.95 Hz], 1.34 [d, 3H, *Me*CH, ^3J(HH) 5.97 Hz], 0.84 [q, 1H, MeC*H*, ^3J(HH) 6.00 Hz]; ^{13}C-{^{1}H} (CD_2Cl_2), δ 244.6 (CO), 123.6 (Me*C*), 109.6 (Me*C*), 92.3 (C_5H_5), 69.1 (*C*HMe), 59.4 (*C*HMe), 19.1 (*Me*C), 17.5 (*Me*C), 15.9 (*Me*CH), 15.6 p.p.m. (*Me*CH).

($\pm$ 0.5) kJ mol^{-1}] in the dichloro-complex (**7**). It was confirmed that in the formation of (**7**)—(**9**) from (**4**)—(**6**), coupling of the η^2(3e)-vinyl and η^2-alkyne ligands had not occurred because when (**7**)—(**9**) were treated with $AgBF_4$, a precipitate of AgX was produced and the parent cations (**4**)—(**6**) were reformed in good yield.

In contrast, linking of the η^2-vinyl and but-2-yne ligands does occur on treatment of, for example, (**4**) with trimethyl phosphite and (**6**) with trimethylphosphine. In both reactions orange crystalline products are formed, the reaction with $P(OMe)_3$ and (**4**) giving (**10**), and PMe_3 and (**6**) affording two isomeric complexes of (**11**) in the ratio of (6:1). These materials all showed‡ low-field ($\approx$ 300 p.p.m.) ^{13}C resonances attributable to Mo=C. In addition there were ^{13}C and ^1H signals‡ present in the respective n.m.r. spectra consistent with the presence of η^4(5e)-butadienyl,[6,7,8] *i.e.* Mo=C(Me)-η^3-{C(Me)C(Me)CHMe}, ligands. This was confirmed by a single crystal *X*-ray crystallographic study with the major isomeric complex of (**11**).§

As is shown in Figure 1 the molecule contains a molybdenum atom to which are co-ordinated a slipped η^5-indenyl, PMe_3 and Br ligands. In addition there is an η^4-bonded four-carbon fragment C(11)·C(12)·C(13)·C(14) beginning with a molybdenum to carbon double bond to C(11) [1.91(1) Å], and terminating with a CHMe group [Mo–C(14)] at 2.32(1) Å from the molybdenum. The other two carbons C(12) and C(13) are also bonded to the metal with Mo–C(12) and Mo–C(13) distances of 2.36(2) and 2.48(1) Å respectively. Thus, twisting of the C_4 chain, reflected in the torsion angles (see Figure 1), allows η^4-bonding. Interestingly, the C(11)–C(12) and C(13)–C(14) distances of 1.35(2) and 1.40(2) Å respectively suggest that the butadienyl fragment adopts an η^3(3e) bonding mode.[9,10] However, this is clearly inconsistent with the short Mo–C(11) distance and the presence of a low field ^{13}C resonance. Whatever the precise details of the mode of bonding of the C_4 fragment to the molybdenum it is clear that coupling of the η^2-vinyl and but-2-yne ligands has occurred suggesting that the recently reported[7] formation of an η^4(5e)-C_4R_4H ligand by protonation of the bis(alkyne)dithiocarbamate complexes $[M(R^1C_2R^2)_2(S_2CNR_2)]$ (M = Mo, W) might also involve a stepwise[11] process. As shown in Figure 1 the hydrogen substituent of the η^4(5e)-butadienyl fragment, which has its origin in the proton source $HBF_4{\cdot}Et_2O$, occupies an inside or pseudo-*anti* position.

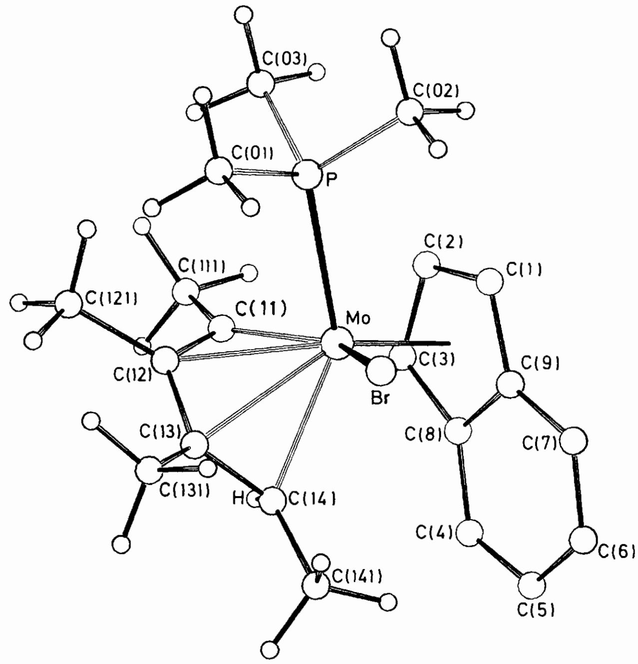


Figure 1. Molecular structure of cation in (**11**). Selected bond lengths (Å): Mo(1)–Br 2.641(1); Mo(1)–P 2.531(4); Mo(1)–C(11) 1.91(1); Mo(1)–C(12) 2.36(2); Mo(1)–C(13) 2.48(1); Mo(1)–C(14) 2.32(1); mean Mo(1)–C_9H_7 2.36(2); P–C(01) 1.82(2); P–C(02) 1.79(2); P–C(03) 1.81(2); C(11)–C(12) 1.35(2); C(11)–C(111) 1.52(2); C(12)–C(13) 1.42(2); C(12)–C(121) 1.57(3); C(13)–C(14) 1.40(2); C(14)–C(141) 1.53(2).

It is interesting that whilst the carbon–carbon coupling reaction initiated by reaction with $P(OMe)_3$ is selective, the reaction with PMe_3 forms two isomers presumably *via* attack on either of the two XMoL faces.

These cationic η^4(5e)-butadienyl complexes are reactive towards nucleophilic reagents, and of particular interest is their reaction with the sterically demanding reagent Li[N-$(SiMe_3)_2$]. Reaction at low temperature leads to a regioselective deprotonation of the methyl group, which is bonded to the carbenoid or α carbon atom, and formation in good yield of the neutral complexes (**12**) and (**13**).‡ These molecules can be represented as η^4(4e)-vinylallene complexes and it is interesting that (**12**) and (**13**) can be regioselectively reprotonated [$HBF_4{\cdot}Et_2O$] on the 'allenic' methylene carbon to reform the cations (**10**) and (**11**) in quantitative yield. This suggests a possible general route to other η^4(5e)-butadienyl complexes *via* protonation of species carrying η^4-vinylallene ligands.

Finally, in exploring the reduction of the neutral η^2-vinyl/alkyne complexes (**7**)—(**9**), it was found that treatment of, for example, (**8**) with magnesium amalgam suspended in thf in the presence of carbon monoxide (1 atm) leads to a novel carbon–carbon coupling reaction and the formation (43% yield) of the η^4-1,3-diene complex (**14**).‡

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§ *Crystal data:* for [BrMo=C(Me)-η^3-{C(Me)C(Me)CHMe}-$(PMe_3)(C_9H_7)$] $[BF_4]{\cdot}\{0.5(CH_2Cl_2)\}$ (**11**): M = 576.05, monoclinic, space group $C2/c$, a = 26.765(4), b = 13.310(2), c = 15.482(3) Å, β = 117.587(2)°, U = 4888.29 Å^3, $F(000)$ = 2424, μ(Mo-K_α) = 22.71 cm^{-1}, Z = 8, D_c = 1.63 g cm^{-3}. Data were collected on a Philips PW1100 diffractometer in the θ-range 3—25 °, with a scan width of 0.70 °, using the technique described previously.[1] Lorentz and polarisation corrections were applied,[1] and equivalent reflections were merged to give 3020 data with $I/\sigma(I) > 3.0$. The co-ordinates of the molybdenum atom were deduced from a Patterson synthesis, and all remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. There appears to be some rotational disorder of the BF_4^- anion, shown by regions of extended electron density in the vicinity of three of the fluorine atoms, resulting in high anisotropic thermal parameters for these atoms. Half a dichloromethane solvent molecule is present per asymmetric unit, with the central carbon lying on a 2-fold axis (0,y,0.25). The hydrogen atom H(1), attached to carbon atom C(14) of the organic fragment, was located in a difference Fourier synthesis using data with sin θ <0.35. The parameters of this atom were included in the structure factor calculations but were not refined. The remaining hydrogen atoms were included in geometrically idealised positions and were constrained to 'ride' on the relevant carbon atoms with isotropic thermal parameters fixed at 0.80 Å^2. The molybdenum, phosphorus, and bromine atoms, and all five atoms of the counter ion were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement which gave R 0.0639 and R' 0.0680, with weights of $w = 1/\sigma^2F_o$ assigned to the individual reflections. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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11 It is also important to note that thermolysis or u.v. irradiation of $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)S_2CNR_2\}(CF_3C_2CF_3)(\eta\text{-}C_5H_5)]$ gives the coupled complex $[Mo\{\eta^3\text{-}C(CF_3)C(CF_3)C(CF_3){=}C(CF_3)S\}(\eta^2\text{-}R_2NCS)(\eta\text{-}C_5H_5)]$, J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1987, 2715.