

Synthesis and Reactivity of Cationic Alkene–Alkyne Molybdenum Complexes; Structural Evidence for the Formation of an η^3, η^3 -Bonded Hexatriene Ligand by Coupling of a Co-ordinated Alkyne and a 1,3-Diene

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The synthesis and reactions of the simple alkene/(4e)-alkyne complex $[\text{Mo}(\eta^2\text{-C}_2\text{H}_4)(\eta^2\text{-MeC}_2\text{Me})(\text{CO})(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ is described; reaction with isoprene leads to a novel coupling reaction and the formation of an η^3, η^3 -bonded hexatriene cation identified by X-ray crystallography.

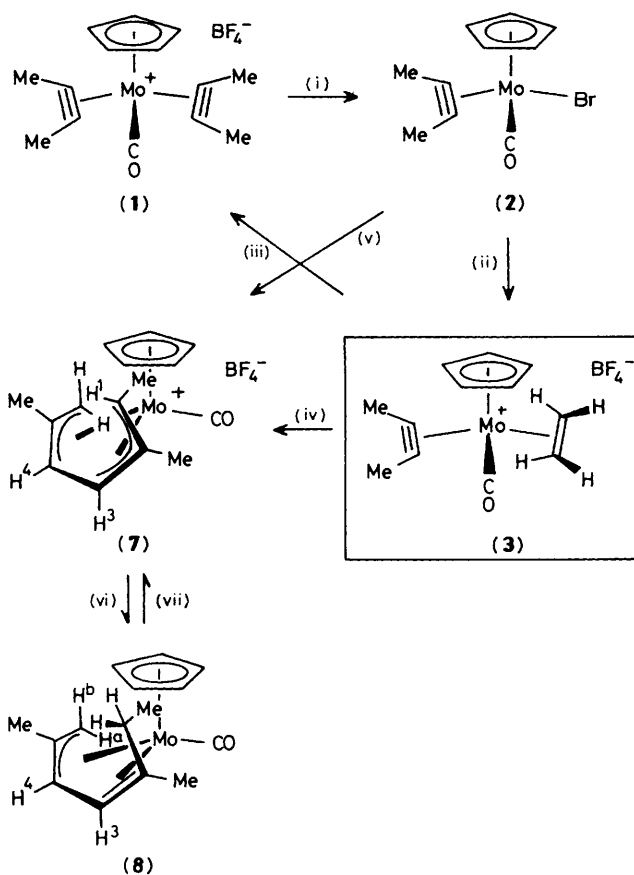
Although mixed four-electron donor alkene–alkyne complexes are a potentially interesting group of molecules, relatively little is known about their chemistry. An indication of this potential was the observation¹ that when the cation $[\text{Mo}(\eta^2\text{-MeC}_2\text{Me})(\eta^2\text{-}o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH=CH}_2)(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ was refluxed in acetonitrile carbon–carbon coupling occurred between the but-2-yne and alkene. This suggested that if related species could be synthesised containing simple alkenes or 1,3-dienes instead of the sterically constrained chelating ligand *o*-styryl-diphenylphosphine, then such molecules might

show unusual chemical reactivity. However, at the beginning of this study the only other mixed alkene–alkyne complexes to have been described² were the neutral species $[\text{M}(\eta^2\text{-alkene})(\eta^2\text{-alkyne})(\text{S}_2\text{CNR}_2)_2]$ ($\text{M} = \text{Mo, W}$), which could only be isolated if the alkene was electron poor, *e.g.* maleic anhydride, tetracyanoethylene, or *trans*-dicyanoethylene.

It was, therefore, interesting to observe that treatment of $[\text{Mo}(\eta^2\text{-MeC}_2\text{Me})_2(\text{CO})(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (**1**) with EtMgBr led unexpectedly^{3,4} to displacement by a bromide anion of one but-2-yne molecule, and the formation (65%) of the green

crystalline air-sensitive neutral complex $[\text{MoBr}(\eta^2\text{-MeC}_2\text{Me})(\text{CO})(\eta\text{-C}_5\text{H}_5)]^\dagger$ (**2**) (Scheme 1). The molybdenum-halogen bond in (**2**) is labile and addition of AgBF_4 to a solution of (**2**) in CH_2Cl_2 saturated with ethylene resulted in the immediate precipitation of AgBr and the formation (60%) of the mixed alkene/(4e)-alkyne cation $[\text{Mo}(\eta^2\text{-C}_2\text{H}_4)(\eta^2\text{-MeC}_2\text{Me})(\text{CO})(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]^\dagger$ (**3**). This cation proved to be relatively unstable in solution and could only be recrystallised from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ in the presence of an excess of C_2H_4 . Examination of the variable temperature ^1H and $^{13}\text{C}\text{-}\{^1\text{H}\}$ n.m.r. spectra revealed that in the temperature range 180–300 K only the but-2-yne ligand rotates $[\Delta G_{T_c}^\ddagger 53(\pm 2) \text{ kJ mol}^{-1}$, T_c 260 K].

The cation (**3**) proved to be highly reactive. Because previous studies⁵ had shown that nucleophiles can react with molybdenum cationic complexes carrying four-electron donor alkynes either at a metal or alkyne carbon centre, it was obviously interesting to examine the corresponding reactions of (**3**) where there is the additional possibility of competitive attack on co-ordinated ethylene. Treatment with $\text{K}[\text{BHBu}_3]$ led to apparent regioselective attack on the co-ordinated ethylene and formation of $[\text{MoEt}(\eta^2\text{-MeC}_2\text{Me})(\text{CO})(\eta\text{-C}_5\text{H}_5)]$ (**4**).[†] However, reaction of (**3**) with methyl-lithium resulted in the displacement of ethylene and formation of $[\text{MoMe}(\eta^2\text{-MeC}_2\text{Me})(\text{CO})(\eta\text{-C}_5\text{H}_5)]$ (**5**)[†] suggesting that the reaction with 'H⁻' might also involve initial attack on the metal centre followed by a migratory insertion reaction. Neutral donor ligands also rapidly react with (**3**) with selective displacement of ethylene. For example, treatment with but-2-yne gives (**1**), and carbon monoxide forms $[\text{Mo}(\eta^2\text{-MeC}_2\text{Me})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (**6**).[†] When (**3**) was treated with isoprene, or (**2**) was treated with AgBF_4 in the presence of isoprene, a particularly interesting reaction occurred. The product (**7**)[†] (50% yield) was obtained as a yellow crystalline monocarbonyl cation, and examination of the ^1H and $^{13}\text{C}\text{-}\{^1\text{H}\}$ n.m.r. spectra suggested that a carbon-carbon coupling reaction and a hydrogen shift process had taken place. This was confirmed by single crystal X-ray crystallo-



Scheme 1. Reagents and conditions: (i) EtMgBr , tetrahydrofuran (thf), r; (ii) AgBF_4 , C_2H_4 , CH_2Cl_2 ; (iii) MeC_2Me , CH_2Cl_2 ; (iv) isoprene, CH_2Cl_2 , r.t.; (v) AgBF_4 , isoprene, CH_2Cl_2 , r.t.; (vi) $\text{Li}[\text{BHEt}_3]$, thf, -78°C ; (vii) Ph_3CBF_4 , CH_2Cl_2 (r.t. = room temperature).

[†] Selected spectroscopic data for (**2**): n.m.r. ^1H (CDCl_3), δ 5.55 (s, 5H, C_5H_5), 3.15 (br.s, 6H, MeC_2Me); $^{13}\text{C}\text{-}\{^1\text{H}\}$ (CD_2Cl_2), δ 232.0 (CO), 202.0 ($\text{MeC}\equiv\text{C}$), 196.0 ($\text{MeC}\equiv\text{C}$); ν (CO) 1935 cm^{-1} (CH_2Cl_2). (**3**): n.m.r. ^1H (CD_2Cl_2), δ 5.97 (s, 5H, C_5H_5), 3.19 (s, 6H, $\text{MeC}\equiv\text{C}$), 2.75 (m, 1H, J 12.1 Hz), 2.61 (m, 1H, J 10.4 Hz), 2.46 (m, 1H, J 12.3 Hz), 1.15 (m, 1H, J 11.0 Hz); $^{13}\text{C}\text{-}\{^1\text{H}\}$ (CD_2Cl_2), δ 223.5 (CO), 100.7 (C_5H_5), 63.0 (CH_2), 46.2 (CH_2), 22.1 (Me). The resonances of the corresponding η^5 -indenyl cation are more fully resolved showing co-ordinated ethylene signals at δ 2.32 [ddd, 1H, H^2 , $^3J(\text{H}^2\text{H}^3)$ 14.34, $^3J(\text{H}^2\text{H}^4)$ 11.53, $^2J(\text{H}^2\text{H}^1)$ 2.85 Hz], 1.46 [ddd, 1H, H^3 , $^3J(\text{H}^3\text{H}^2)$ 14.51, $^3J(\text{H}^3\text{H}^1)$ 10.58, $^2J(\text{H}^3\text{H}^4)$ 2.06 Hz], 1.31 [ddd, 1H, H^4 , $^3J(\text{H}^4\text{H}^1)$ 16.98, $^3J(\text{H}^4\text{H}^2)$ 11.82, $^2J(\text{H}^4\text{H}^3)$ 2.00 Hz], 0.03 [1H, H^1 , $^3J(\text{H}^1\text{H}^4)$ 17.04, $^3J(\text{H}^1\text{H}^3)$ 10.69, $J(\text{H}^1\text{H}^2)$ 2.88 Hz]. (**4**): ν (CO) 1910 cm^{-1} (hexane). (**5**): ν (CO) 1915 cm^{-1} (hexane). (**6**): n.m.r. ^1H (CD_2Cl_2), δ 6.26 (s, 5H, C_5H_5), 3.38 (s, 6H, $\text{MeC}\equiv\text{C}$); ν (CO) 2050 cm^{-1} , 1995 s cm^{-1} (CH_2Cl_2). (**7**): n.m.r. ^1H [$(\text{CD}_3)_2\text{CO}$], δ 5.69 (s, 5H, C_5H_5), 4.75 [q, 1H, H^1 , $^3J(\text{MeH}^1)$ 5.85 Hz], 3.64 [d, 1H, H^4 , $^3J(\text{H}^3\text{H}^4)$ 4.76 Hz], 2.75 [d, 1H, H^{6a} , $^2J(\text{H}^{6a}\text{H}^{6b})$ 1.75 Hz], 2.55 [d, 1H, H^{6a} , $^2J(\text{H}^{6a}\text{H}^{6b})$ 1.65 Hz], 2.31 (s, 3H, Me), 2.15 (s, 3H, Me), 1.78 [d, 3H, Me, $^3J(\text{MeH})$ 6.05 Hz]; $^{13}\text{C}\text{-}\{^1\text{H}\}$ [$(\text{CD}_3)_2\text{CO}$], δ 221.8 (CO), 118.6 (C^5Me), 114.5 (C^2Me), 101.3 (C^1HMe), 95.6 (C_5H_5), 85.0 (C^4H), 76.4 (C^3H), 38.4 (C^6H_2), 22.6 (C^9H_3), 17.9 (C^8H_3), 16.1 (C^7H_3); ν (CO) 2000 cm^{-1} (CH_2Cl_2). (**8**): n.m.r. ^1H (CD_2Cl_2), δ 4.89 (s, 5H, C_5H_5), 3.44 [br.d, 1H, H^4 , $^3J(\text{H}^3\text{H}^4)$ 5.98 Hz], 2.56 [dd, 1H, H^{6b} , $^2J(\text{H}^{6a}\text{H}^{6b})$ 2.53, $^4J(\text{HH})$ 1.02 Hz], 1.94 (s, 3H, Me), 1.71 [q, 2H, CH_2^1 , $^3J(\text{MeH})$ 7.34 Hz], 1.68 (s, 3H, Me), 1.18 [d, 1H, H^3 , $^3J(\text{H}^3\text{H}^4)$ 6.0 Hz], 0.95 (m, 1H, H^{6a}), 0.95 [t, 3H, C^1H_3 , $^3J(\text{MeH})$ 7.3 Hz]; $^{13}\text{C}\text{-}\{^1\text{H}\}$ (CD_2Cl_2), δ 234.8 (CO), 101.9 (C^5Me), 91.4 (C_5H_5), 76.6 (C^4H), 75.5 (C^2Me), 69.3 (C^3H), 42.7 (C^6H_2), 33.7 ($\text{C}^1\text{H}_2\text{Me}$), 28.6 (C^9H_3), 24.7 (C^8H_3), 18.1 p.p.m. (C^7H_3); ν (CO) 1910 cm^{-1} (hexane).

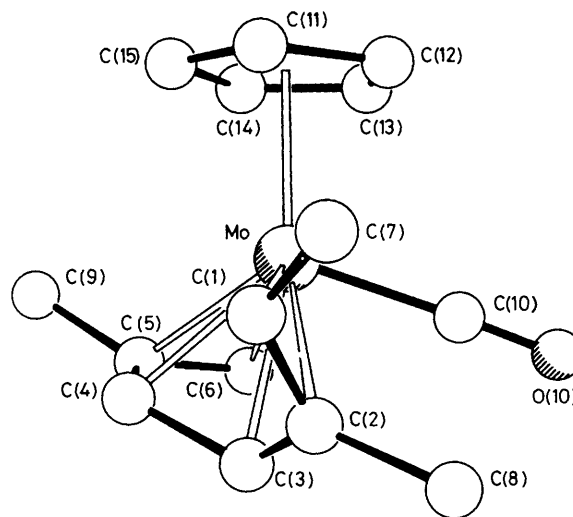


Figure 1. Molecular structure of (**7**). For clarity hydrogen atoms have been omitted. Selected bond lengths (Å): Mo-C(1) 2.491(8), Mo-C(2) 2.348(10), Mo-C(3) 2.232(8), Mo-C(4) 2.198(7), Mo-C(5) 2.317(8), Mo-C(6) 2.372(8), C(1)-C(2) 1.417(16), C(2)-C(3) 1.340(12), C(3)-C(4) 1.474(12), C(4)-C(5) 1.372(12), C(5)-C(6) 1.431(12).

graphy.‡ As is shown in Figure 1, a carbonyl(η -cyclopentadienyl)molybdenum cation is complexed onto an organic fragment, which in the uncomplexed state would be a hexa-1,3,5-triene; however, its co-ordinated mode is best described as two linked allyl units [C(1)–C(2)–C(3) and C(4)–C(5)–C(6)]. The planes of the two allyls are twisted about the C(3)–C(4) bond (dihedral angle 126.4°), and there is no conjugation through this bond, evidence for which is the bond length of 1.474(12) Å, which is the longest in the C₆ chain. All four allylic bonds are co-ordinated to the metal (6-electron donor), but the C(2)–C(3) and C(4)–C(5) bonds interact more strongly than C(1)–C(2) and C(5)–C(6). It is possible that this occurs because to bring C(1) and C(6) closer to the metal would produce unfavourable non-bonding interactions between the methyl groups and the cyclopentadienyl ring. The η^3, η^3 -bonding mode for a mononuclear hexa-1,3,5-triene complex has not been previously observed, and it is suggested that this unusual arrangement, in which the C₆ chain is wrapped around the metal, is imposed by the geometries of the transition states of reactions involved in the formation of (7). In other words, it might not be possible to gain access to molecules like (7) by simply treating hexa-1,3,5-trienes with a source of a [Mo(CO)(η -C₅H₅)]⁺ fragment.

From a synthetic standpoint the formation of a hexa-1,3,5-triene ligand from a 1,3-diene and an alkyne is without precedent. Although there are known examples⁶ of 1,3-diene-alkyne coupling reactions, these have not been accompanied by a facile H-shift and reductive elimination reaction. In beginning to explore the chemistry of (7), the reactivity towards nucleophilic reagents was examined. Treatment with Li[BHET₃] led to regioselective attack on the most substituted

terminus of the C₆ chain with formation of the η^5 -pentadienyl complex (8).† Reversal of this reaction by treatment of (8) with Ph₃CBF₄ afforded only (7), there being no evidence for the formation of an isomer of (7) with *trans*-vicinal methyl groups. The molecule (8) is related to the species [M(CO)(η -C₅H₅)₂] (M = Mo, W),^{7,8} and it is interesting that the conformation of the η^5 -pentadienyl ligand present in (8) is different from that adopted by all other previously described η^5 -pentadienyl complexes.^{9,10} As is illustrated, the ligand is wrapped around the molybdenum such that compared with other systems the opposite face of the alkene part of the pentadienyl ligand is bonded to the metal. It will be interesting to see how this relates to the chemistry of (8), and in this context it is worth noting that the terminal carbonyl stretching frequency of (8) (1910 cm⁻¹) is similar to that in the electron rich species [Mo(CO)(η -C₅H₅)₂] (1905 cm⁻¹).

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‡ Crystal data: (7) C₁₅H₁₉OBF₄Mo, *M* = 398.1, orthorhombic, *a* = 10.872(3), *b* = 11.487(4), *c* = 12.992(4), *U* = 1622 Å³, space group *P2₁cn*, *Z* = 4, *D_c* = 1.63 g cm⁻³, $\mu(\text{Cu-K}\alpha)$ = 71 cm⁻¹. Data were measured on a Nicolet R3m diffractometer with Cu-K α radiation (graphite monochromator) using ω -scans. The structure was solved by the heavy-atom method and refined anisotropically using absorption corrected data to give *R* = 0.034, *R_w* = 0.043 for 1113 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$], $\theta \leq 58^\circ$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.