Syntheses and Molecular Structures of Molybdenum Complexes containing an η^3-Butadienyl Ligand and its Hydromethoxylated Derivative

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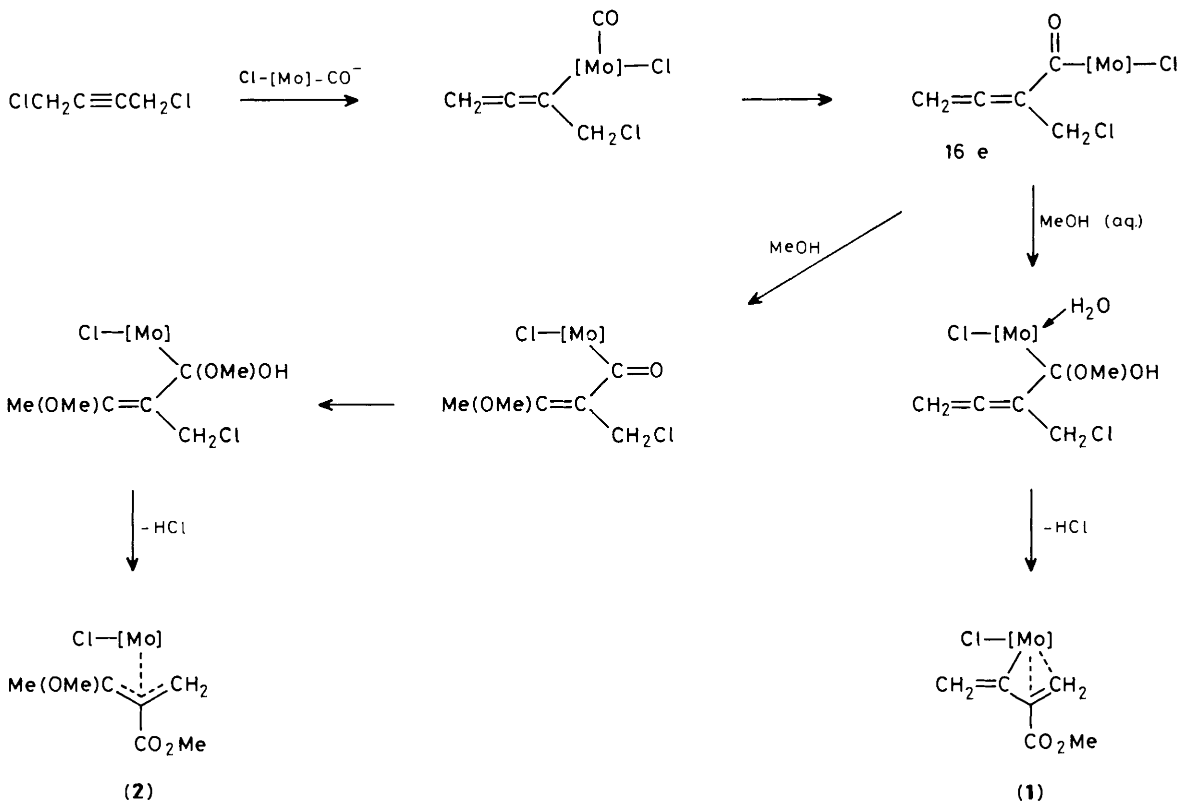
Reaction of $Ph_4P[Mo(bipy)Cl(CO)_3]$ (bipy = bipyridine) with $ClCH_2C{\equiv}CCH_2Cl$ in wet methanol yields $[Mo(bipy)Cl(CO)_2\{\eta^3\text{-}CH_2{\cdots}C{\cdots}(CO_2Me){\cdots}C{=}CH_2\}]$ (**1**), which contains an η^3-bonded *trans*-butadienyl ligand; under anhydrous conditions in methanol–tetrahydrofuran $[Mo(bipy)Cl(CO)_2\{\eta^3\text{-}CH_2{\cdots}C(CO_2Me){\cdots}C(Me)(OMe)\}]$ (**2**) is formed: the η^3-allyl ligand in (**2**) can be formally derived by addition of MeOH across the non-co-ordinated $C{=}CH_2$ entity in (**1**), so yielding –Me and –OMe substituents in *syn*- and *anti*-conformations respectively.

In an attempt to extend the known synthetic potential of allylmolybdenum complexes,[1] we have been investigating the interaction of the strongly nucleophilic $[Mo(bipy)Cl(CO)_3]^-$ anion (bipy = 2,2′-bipyridine) with unsaturated halogenated hydrocarbons under conditions which may generate novel, functionalised metal allyls.

Treatment of a suspension of $Ph_4P[Mo(bipy)Cl(CO)_3]$[2] in wet MeOH held at −17 °C with $ClCH_2C{\equiv}CCH_2Cl$ produced a red microcrystalline precipitate of $[Mo(bipy)Cl(CO)_2\{\eta^3\text{-}CH_2{\cdots}C(CO_2Me){\cdots}C{=}CH_2\}]$ (**1**) in high yield (≥70%) (Scheme 1). Under anhydrous conditions, in 1:1 MeOH–tetrahydrofuran (THF), $[Mo(bipy)Cl(CO)_2\{\eta^3$-



Scheme 1. Formation of the two alkoxycarbonylated products (**1**) and (**2**) from $Ph_4P[Mo(bipy)Cl(CO)_3]$ and $ClCH_2C{\equiv}CCH_2Cl$ in wet and anhydrous MeOH respectively. [Mo] represents the $Mo(bipy)(CO)_2$ moiety.

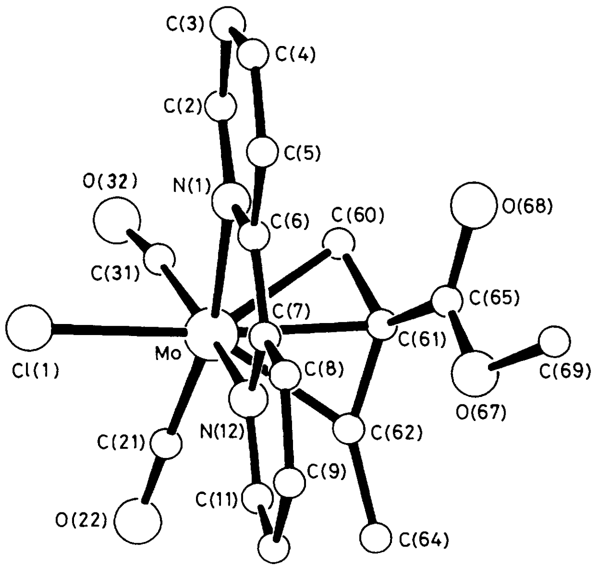


Figure 1. Structure of (**1**). Pertinent distances (Å) and angles (°); Mo–C(60), 2.32(4); Mo–C(61), 2.22(3); Mo–C(62), 2.22(3); C(60)–C(61), 1.44(5); C(61)–C(62), 1.41(5); C(62)–C(64), 1.45(5); C(60)–C(61)–C(62), 116.2(31); C(61)–C(62)–C(64), 148.3(35).

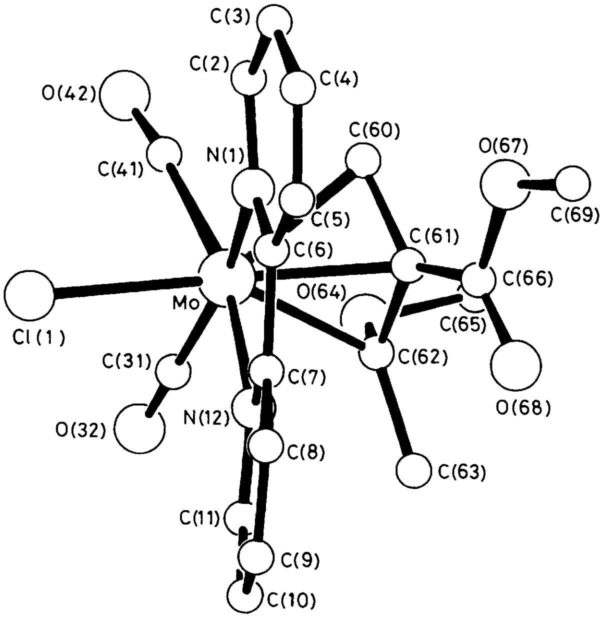
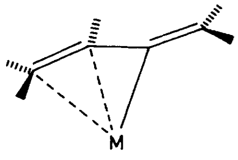


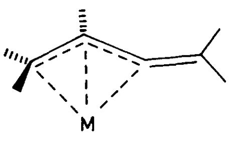
Figure 2. Structure of (**2**). Pertinent distances (Å) and angles (°); Mo–C(60), 2.262(19); Mo–C(61), 2.226(15); Mo–C(62), 2.343(18); C(60)–C(61), 1.415(26); C(61)–C(62), 1.409(22); C(62)–C(63), 1.465(24); C(60)–C(61)–C(62), 110.3(15); C(61)–C(62)–C(63), 123.5(16); C(61)–C(62)–O(64), 115.5(14).

$CH_2\cdots C(CO_2Me)\cdots C(Me)(OMe)\}]$ (**2**) was formed in 65% yield.† In the absence of THF, a mixture of (**1**) and (**2**) was produced. The presence of the unco-ordinated $C{=}CH_2$ moiety in (**1**) was indicated by the appearance of doublets of equal intensity centred at δ 5.66 and 6.28 in the ^1H n.m.r. spectrum of this complex. Corresponding signals were absent in the spectrum of (**2**).‡ Single crystal *X*-ray diffraction studies§ revealed the molecular structures of (**1**) and (**2**) as shown in Figures 1 and 2. In both molecules the molybdenum atom occupies a pseudo-octahedral site, being bonded to two carbonyl groups and a bipyridine ligand in an equatorial plane. One axial position is occupied by a chlorine atom and the other by three carbon atoms. Of particular interest are the dimensions associated with the η^3-$CH_2\cdots C(CO_2Me)\cdots C{=}CH_2$ ligand found in (**1**). The metal atom is bonded to the three carbon atoms C(60), C(61), C(62) at distances of 2.32(4), 2.22(3), 2.22(3) Å. The Mo–C(62) distance is shorter than other reported Mo–terminal allyl carbon distances in analogous complexes,[3] and this asymmetry in the bonding of the unsaturated C_4 unit, together with the C(60)–C(61), C(61)–C(62), and C(62)–C(64) bond lengths of 1.44(5), 1.41(5), and 1.45(5) Å respectively are indicative of a distorted η^3-butadienyl ligand whose bonding extremes are represented by (A) and (B).

Structural studies have confirmed that the short-long-short C–C bond sequence of free butadiene is frequently reversed in η^4-butadiene metal carbonyl complexes,[4] as a consequence of the simultaneous donor/acceptor interactions of such ligands.[5] Despite the uncertainties in the C–C bond lengths in (**1**), which preclude accurate comparisons, it appears likely that the abnormally long unco-ordinated $C{=}CH_2$ bond distance results from analogous interactions which populate anti-bonding diene orbitals, even though the $C_4H_4CO_2Me$ ligand is η^3-bonded in order that the d^4-metal ion achieves an 18-electron configuration. Although this mode of bonding appears to be extremely rare for an open C_4 system, it is the preferred mode of bonding in some pentadienyl complexes.[6]



(A)



(B)

The allyl ligand in (**2**) is formally derived from that in (**1**) by regio- and stereo-selective addition of MeOH across the $C{=}CH_2$ entity, yielding *syn*-Me and *anti*-OMe substituents with unexceptional C(61)–C(62)–C(63) and C(61)–C(62)–O(64) bond angles of 123.5(16) and 115.5(14)° respectively.[3] The conformation of the $-CO_2Me$ substituent on C(61) as revealed by *X*-ray crystallography, is reversed relative to that in (**1**), in agreement with a mechanism in which alcoholysis of the terminal $C{=}CH_2$ group precedes η^3-bonding of the ligand. In keeping with previous studies,[7] we consider that initial attack of the substituted carbonylate anion occurs at the β-carbon atom (S_N2') with concomitant oxidative addition. Carbonyl insertion followed by alcoholysis yields either (**1**) or (**2**) (Scheme 1).

A search using the Cambridge Data Centre files has revealed only two crystallographic studies on η^3-butadienyl complexes.[8,9] Both complexes are formed from σ-butadienyl precursors containing highly electron-withdrawing substituents. It has been suggested that the tungsten complex $cpW(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2]$ (cp = η^5-C_5H_5) is best regarded as a methylenetungstabicyclobutane derivative,[8] whereas the organic moiety of $cpFe(PPh_3)[\eta^3\text{-}CF_2C(CF_3)C{=}C(CF_3)_2]$ was formulated as an η^3-allylidene ligand.[9]

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† Satisfactory C, H, N, and Cl elemental analyses were obtained for (**1**) and (**2**).

‡ Selected n.m.r. data for (**1**): ^1H (CD_2Cl_2) δ 7.6—8.9 (m, 8H, aromatics), 6.28 (d, 1H, *J* 2.0 Hz, $=CH_2$), 5.66 (d, 1H, *J* 2.0 Hz, $=CH_2$), 3.60 (s, 1H, *syn*-H), 2.82 (s, 3H, OMe), 1.96 (s, 1H, *anti*-H). Because of the low solubility of (**1**), ^{13}C n.m.r. data were not recorded.

The corresponding ethoxy derivative $[Mo(bipy)Cl(CO)_2\{\eta^3\text{-}CH_2C(CO_2Et)C{=}CH_2\}]$ (**3**), produced by an analogous procedure, was more soluble: ^1H (CD_2Cl_2) δ 7.5—8.8 (m, 8H, aromatics), 6.26 (d, 1H, *J* 2.0 Hz, $=CH_2$), 5.63 (d, 1H, *J* 2.0 Hz, $=CH_2$), 3.61 (s, 1H, *syn*-H), 3.28 (qd, 1H, *J* 7.1, 10.5 Hz, CH_2), 3.11 (qd, 1H, *J* 7.1, 10.5 Hz, CH_2) 1.95 (s, 1H, *anti*-H), 0.65 (t, 3H, *J* 7.1 Hz, CH_3); ^{13}C-$\{^1H\}$ δ 152.7, 152.4, 139.8, 139.2, 126.6, 126.2, 122.6, 122.3 (aromatics), 106.2 ($=CH_2$), 60.6 (CH_2), 50.5 (CH_2), 13.8 (CH_3).

For (**2**): ^1H (CD_2Cl_2) δ 7.6—8.8 (m, 8H, aromatics), 3.34 (d, 1H, *J* 3.5 Hz, *syn*-H), 3.20 (s, 3H, CO_2Me), 2.88 (s, 3H, OMe), 2.31 (d, 1H, *J* 3.5 Hz, *anti*-H), 2.30 (s, 3H, CMe).

§ *Crystal data:* (**1**) $C_{18}H_{15}N_2O_4ClMo$, M = 434.7, orthorhombic, space group *Pcab*, (No. 61), Z = 8, a = 12.590(11), b = 13.537(12), c = 20.801(17) Å, U = 3545.2 Å^3, $F(000)$ = 1824, D_m = 1.64, D_c = 1.70 g cm^{-3}, μ = 9.06 cm^{-1}, Mo-K_α radiation, λ = 0.7107 Å.

(**2**) $C_{19}H_{19}N_2O_5ClMo$, M = 486.8, orthorhombic, space group *Pbca*, Z = 8, a = 13.591(11), b = 14.414(8), c = 20.169(11) Å, U = 3951.1 Å^3, $F(000)$ = 1968, D_m = 1.64, D_c = 1.64 g cm^{-3}, μ = 8.23 cm^{-1}, Mo-K_α radiation, λ = 0.7107 Å.

For (**1**) 881 independent reflections with $I > 2\sigma(I)$ and for (**2**) 1721 reflections with $I > 3\sigma(I)$ were measured on a diffractometer. The data for (**1**) were of poor quality because the crystals were small and therefore in the refinement only Mo and Cl were refined anisotropically with C, O, N, H isotropic. The final R was 0.084. (**2**) refined to R 0.073 with Mo, Cl, C, O, N anisotropic and H isotropic. 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, 1986.

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