

A Molybdenum-centred (6 + 2) π Addition of Alkynes to Cyclo-octatetraene and Cycloheptatriene; Structural Evidence for an Arrested 1,3-Hydrogen Shift

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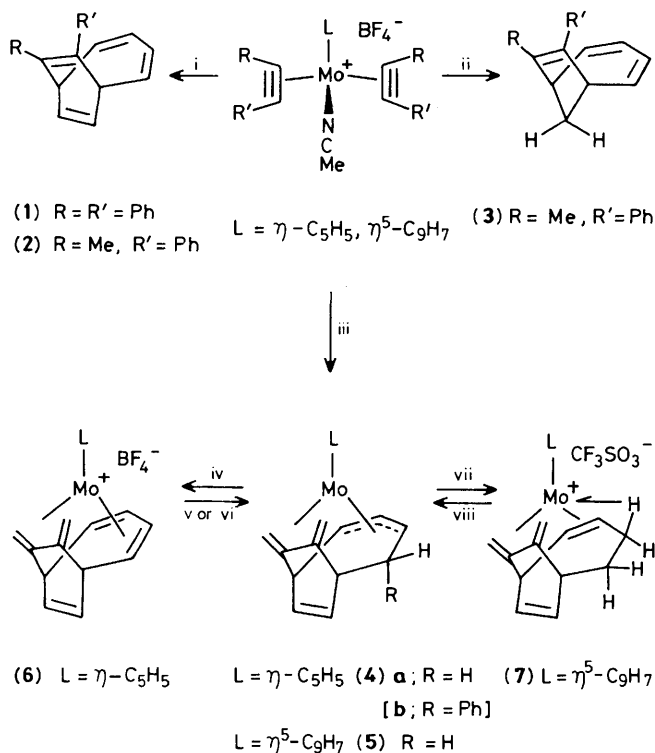
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Depending on the choice of the alkyne, reaction of $[\text{Mo}(\text{NCMe})(\eta^2\text{-RC}_2\text{R}')_2(\eta\text{-C}_5\text{H}_5 \text{ or } \eta^5\text{-C}_9\text{H}_7)][\text{BF}_4]$ with cyclo-octatetraene or cycloheptatriene in MeCN affords either bicyclo[4.2.2]decatetraenes and bicyclo[4.2.1]nonatrienes or neutral complexes containing both η^3 -allyl and η^4 -1,3-diene ligands; X-ray crystallographic studies show that protonation of one of these neutral complexes affords a cation which models the initial stage of a 1,3-hydrogen shift process.

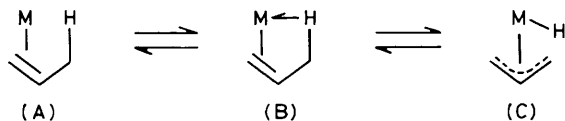
Alkyne-alkene metal complexes have been implicated¹ in the cyclocotrimerisation of alkynes and alkenes, and recently we reported² that the cation of $[\text{Mo}(\eta^2\text{-}o\text{-diphenylphosphinostyrene})(\eta^2\text{-MeC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ containing a co-ordinated four-electron alkyne and alkene undergoes a thermal reaction in acetonitrile which results in the formation of a 1,3-diene *via* C-C coupling and a hydrogen shift process. In exploring related chemistry we have observed an unusual (6 + 2) π addition reaction and the formation of 1,3-diene(η^3 -allyl)(η -cyclopentadienyl or η^5 -indenyl)molybdenum complexes. Protonation of the latter η^5 -indenyl species provides

insight into the mechanism of the metal-promoted 1,3-isomerisation of alkenes.

When the cations of $[\text{Mo}(\text{NCMe})(\eta^2\text{-PhC}_2\text{Ph})_2(\eta\text{-C}_5\text{H}_5 \text{ or } \eta^5\text{-C}_9\text{H}_7)][\text{BF}_4]^3$ were reacted with an excess of cyclo-octatetraene in refluxing acetonitrile an organic compound was formed which was identified as the substituted bicyclo[4.2.2]decatetraene (**1**) (Scheme 1). Both the η -cyclopentadienyl- and the corresponding η^5 -indenyl-molybdenum cations are catalysts for the transformation of diphenylacetylene and cyclo-octatetraene into (**1**). The catalytic reaction was also extended to the synthesis of (**2**) using



Scheme 1. i, Alkyne + C_8H_8 , reflux MeCN; ii, alkyne + C_7H_8 , reflux MeCN; iii, bis(but-2-yne) cation + C_8H_8 , reflux MeCN; iv, $[\text{Ph}_3\text{C}][\text{BF}_4](\text{CH}_2\text{Cl}_2)$; v, $\text{Na}[\text{BH}_3\text{CN}]$; vi, LiCuPh_2 ; vii, $\text{CF}_3\text{SO}_3\text{H}$; viii, base.



Scheme 2

1-phenylprop-2-yne, and significantly an analogous reaction occurred between $[\text{Mo}(\text{NCMe})(\eta^2\text{-PhC}_2\text{Me})_2(\eta^5\text{-C}_5\text{H}_5)][\text{BF}_4]$ and cycloheptatriene affording the bicyclo[4.2.1]nona-2,4,7-triene (3). Thus, these observations suggest that a formally forbidden $6\pi_s + 2\pi_s$ reaction is occurring at a molybdenum centre, and it is probable that this involves a stepwise rather than concerted addition of the alkyne to co-ordinated cyclo- C_8H_8 or C_7H_8 . Recently,⁴ it has been reported that norbornadiene(cycloheptatriene)ruthenium(0) reacts with ethyne in a stoichiometric reaction to afford norbornadiene(bicyclo[4.2.1]nona-2,4,7-triene)ruthenium(0).

In contrast, the but-2-yne complex $[\text{Mo}(\text{NCMe})(\eta^2\text{-MeC}_2\text{Me})_2(\eta^5\text{-C}_5\text{H}_5)][\text{BF}_4]$ ³ reacted (refluxing MeCN) with cyclo-octatetraene to form (31% yield) a neutral air-stable yellow crystalline molybdenum complex (4a). Analysis, mass spectrometry, and n.m.r. spectroscopy suggested for (4a) the molecular formula $[\text{Mo}(\text{C}_{12}\text{H}_{13})(\eta^5\text{-C}_5\text{H}_5)]$, but surprisingly, examination of both the ^1H and ^{13}C spectra revealed the absence of resonances which could be assigned to methyl groups having their origin in the but-2-yne ligands. In order to resolve the structural problem a single crystal X-ray diffrac-

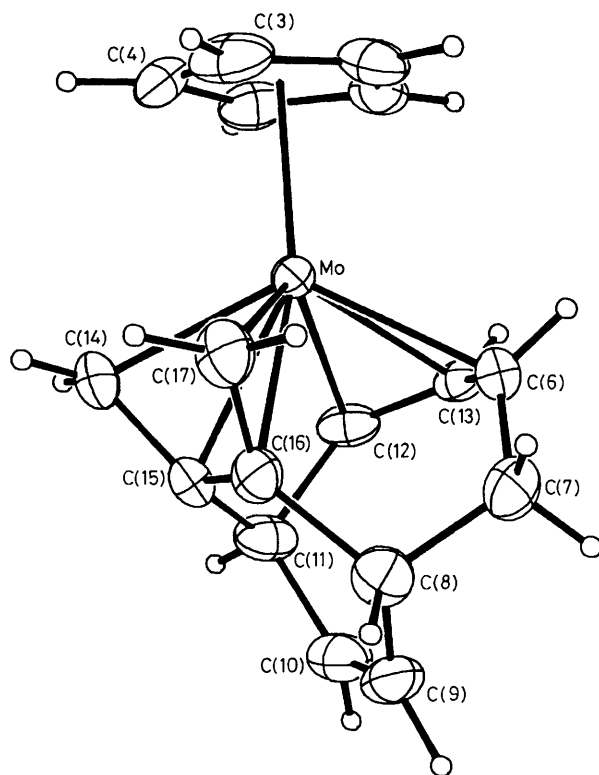


Figure 1. Molecular structure of (4a) showing atomic labelling scheme. Important geometric parameters include: lengths, Mo-C(6) 2.265(7), Mo-C(13) 2.235(5), Mo-C(12) 2.315(7), Mo-C(14) 2.266(8), Mo-C(15) 2.284(7), Mo-C(16) 2.287(7), Mo-C(17) 2.244(7), C(6)-C(13) 1.421(10), C(13)-C(12) 1.403(10) Å. Angles: Mo-C(13)-C(6) 72.8(3), Mo-C(13)-C(12) 75.2(4), C(6)-C(13)-C(12) 130.5(6)°.

tion study[†] was carried out. This established the structure shown in Figure 1, and reveals that a complex C_{12} ligand has been formed by formal $(6+2)\pi$ addition of but-2-yne to co-ordinated cyclo-octatetraene; however, instead of a 7,8-disubstituted bicyclo[4.2.2]decatetraene being displaced, as is the case with the corresponding reactions of PhC_2Ph and PhC_2Me , hydrogen migration occurs *via* the metal, followed by proton loss to give complexes containing η^2 -1,3-diene and η^3 -allyl ligands. This is an unusual reaction which can be extended to the η^5 -indenyl analogue (5) (55% yield), and provides synthetic access to the first examples of η^3 -allyl(η^4 -1,3-diene)(η -cyclopentadienyl or η^5 -indenyl)molybdenum complexes. This provided an opportunity to begin to study their reactivity.

[†] Crystal data for (4a): $\text{C}_{17}\text{H}_{18}\text{Mo}$, $M = 318$, orthorhombic, space group $P2_12_12_1$, $a = 7.848(6)$, $b = 11.339(7)$, $c = 14.378(13)$ Å, $U = 1279(2)$ Å³, $Z = 4$, $D_c = 1.65$ g cm⁻³, $F(000) = 648$, $\mu(\text{Mo-K}\alpha) = 9.78$ cm⁻¹, $T = 295$ K. (7): $\text{C}_{21}\text{H}_{21}\text{Mo} \cdot \text{CF}_3\text{O}_3\text{S}$, $M = 518.4$, monoclinic, space group $P2_1/c$, $a = 10.558(6)$, $b = 15.605(8)$, $c = 12.023(7)$ Å, $\beta = 94.37(4)^\circ$, $U = 1975(2)$ Å³, $Z = 4$, $D_c = 1.74$ g cm⁻³, $F(000) = 1048$, $\mu(\text{Mo-K}\alpha) = 7.98$ cm⁻¹, $T = 200$ K. Data were collected for unique volumes of reciprocal space on a Nicolet P3m diffractometer for $3^\circ < 2\theta < 60^\circ$ and 55° for (4a) and (7) respectively. All atoms were directly located and refined, final residuals R being 0.049 and 0.045 for 1959 and 3563 unique, observed [$I > 2\sigma(I)$ and $1.5\sigma(I)$] intensity data respectively. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

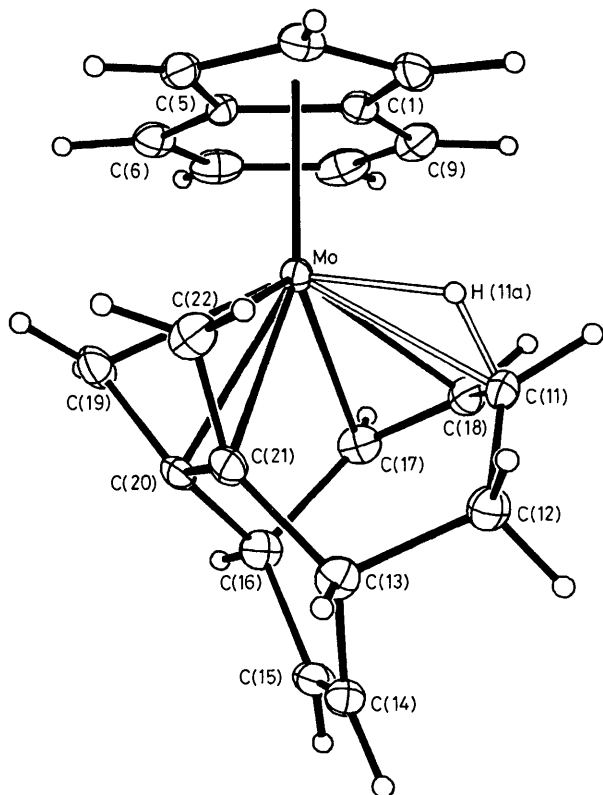


Figure 2. Molecular structure of cation of (7) showing atomic labelling scheme. Important geometric parameters include: lengths, Mo–C(11) 2.391(4), Mo–H(11a) 1.80(6), Mo–C(17) 2.342(4), Mo–C(18) 2.218(4), Mo–C(19) 2.296(5), Mo–C(20) 2.284(4), Mo–C(21) 2.287(4), Mo–C(22) 2.246(4), C(18)–C(17) 1.412(6), C(11)–C(18) 1.471(8), C(11)–H(11a) 1.08(6) Å. Angles: Mo–H(11a)–C(11) 110(4), Mo–C(18)–C(11) 77.9(2), Mo–C(18)–C(17) 76.8(2), C(11)–C(18)–C(17) 132.4(4)°.

Treatment (CH_2Cl_2 , room temperature) of (4a) with $[\text{Ph}_3\text{C}][\text{BF}_4]$ affords the bis(η^4 -1,3-diene)(η -cyclopentadienyl)molybdenum cation of (6) where the 1,3-diene fragments adopt *exo* and *endo* conformations. It is interesting that reaction of (6) with $\text{Na}[\text{BH}_3\text{CN}]$ in tetrahydrofuran reforms (4a), and the corresponding reaction with LiCuPh_2 gives (4b), there being no evidence for products originating from nucleophilic attack on the *endo*-orientated 1,3-diene moiety.

Complexes (4a) and (5) clearly present a number of sites for electrophilic attack; we have studied these by protonation: for example, treatment of (5) with $\text{CF}_3\text{SO}_3\text{H}$ in CH_2Cl_2 (-78°C) affords dark brown crystals of $[\text{Mo}(\text{C}_{12}\text{H}_{14})(\eta^5\text{-C}_5\text{H}_7)][\text{CF}_3\text{SO}_3]$ (7),[‡] showing a high field ^1H n.m.r. signal (-80°C , CD_2Cl_2) at $\delta -7.83$. A low temperature X-ray structural analysis[†] of (7) showed the cation geometry illustrated in

[‡] Selected spectroscopic data for (7): ^1H n.m.r. (CD_2Cl_2 , -80°C), δ 7.25 (m, 4 H, indenyl), 6.17 (d, 2 H, indenyl, J 7.3 Hz), 3.77 (t, 1 H, indenyl, J 7.3 Hz), -7.83 (s, 1 H, $\mu\text{-CHMo}$).

Figure 2. Protonation has occurred at one of the terminal allyl carbons [C(11) in Figure 2]. As a result the allyl moiety of (5) is formally converted on protonation into an alkene functionality in (7). The resultant co-ordinative unsaturation at molybdenum is then relieved by co-ordination of an *endo*-C–H bond [C(11)–H(11a)]. This agostic interaction shows geometry appropriate for a three-centre two electron $\mu\text{-MoHC}$ bond [Mo–H(11a) 1.80(6), Mo–C(11) 2.391(4), C(11)–H(11a) 1.08(6) Å, Mo–H(11a)–C(11) 110(4)°]. Related β -hydrogen–metal bonds have been spectroscopically and structurally characterized for alkyl, allyl, and 1,3-diene moieties⁵ but *not* for alkenes. These agostic interactions model the intermediate stages of the β -hydrogen elimination reaction, and in the case of (7) the reaction in question is that postulated to explain the initial stage of the metal-assisted isomerization of alkenes (Scheme 2), *i.e.* a 1,3-hydrogen shift.⁶ In other words complex (7) represents an arrested 1,3-H shift. In this context it is interesting to note the shortening of C(11)–C(18) [to 1.471(8) Å] prior to C–H bond cleavage, and the non-planar geometry in the four-centre system Mo–C(18)–C(11)–H(11a) [dihedral angle 27(3)°]. This latter feature is in marked contrast to the other β -agostic systems⁵ where M–C $_{\alpha}$ –C $_{\beta}$ –H $_{\mu}$ angles are $<17^\circ$, but rather close to that in $[\text{IrCl}(\text{PPh}_3)_2(\eta^5\text{-C}_3\text{H}_4\text{Ph})(\text{H})]$ ⁷ a model for (C) in Scheme 2 where Ir–C $_{\alpha}$ –C $_{\beta}$ –H $\approx 32^\circ$.

Examination of the variable temperature ^1H spectrum of (7) in CD_2Cl_2 reveals that a dynamic process is occurring in solution at room temperature, which involves reversible transfer of the hydrogen from C(11) to C(22). Details of this will be discussed in a full paper.

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