

Formation of an Alkyne and a 1,3-Diene at a Dimolybdenum Centre by Isomerisation of a μ -Allylidene Complex; Synthesis and X-Ray Structure of $[\text{Mo}_3(\mu_3\text{-}\{\eta^4\text{-C}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\})\text{(CO)}_4(\eta\text{-C}_5\text{H}_5)_3]$

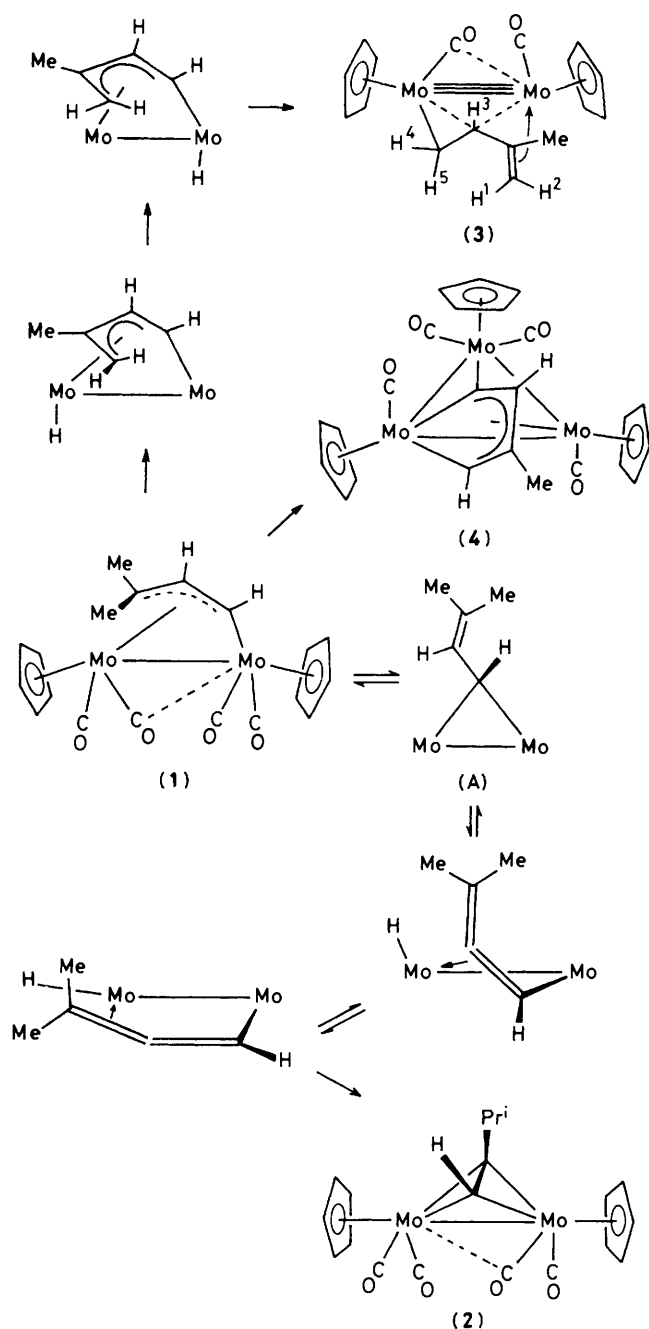
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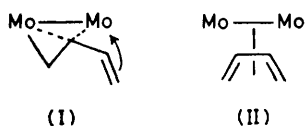
Thermolysis of $[\text{Mo}_2(\mu\text{-CH}\cdot\text{CH}\cdot\text{CMe}_2)\text{(CO)}_4(\eta\text{-C}_5\text{H}_5)_2]$ in toluene-hexane gives $[\text{Mo}_2(\mu\text{-HC}_2\text{Pri})\text{(CO)}_4(\eta\text{-C}_5\text{H}_5)_2]$, $[\text{Mo}_2(\mu\text{-}\{\eta^4\text{-CH}_2\cdot\text{CH}\cdot\text{C}(\text{Me})\text{CH}_2\})\text{(CO)}_2(\eta\text{-C}_5\text{H}_5)_2]$, alkyne and isoprene complexes, respectively, and in addition the trinuclear complex $[\text{Mo}_3(\mu_3\text{-}\{\eta^4\text{-C}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\})\text{(CO)}_4(\eta\text{-C}_5\text{H}_5)_3]$, identified by X-ray crystallography.

Bridged carbene complexes have recently attracted considerable interest because of their possible role in alkene metathesis, alkyne polymerisation, and carbon monoxide reduction chemistry.¹ However, relatively little attention has been paid

to isomerisation reactions involving hydrogen shift processes within the bridged carbene ligand,²⁻⁴ although of course a great deal is known about isomerisation reactions of organic fragments co-ordinated to one metal centre.⁵ With the objec-



Scheme 1. Ligands omitted for clarity.



tive of establishing such reactions at dinuclear centres we have examined the thermolysis of the μ -allylidene complex $[\text{Mo}_2(\mu\text{-CH}\cdot\text{CH}\cdot\text{CMe}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (1).⁶

Thermolysis of (1) in refluxing 1:1 toluene-hexane (3 h) affords red (2) (40%), green (3) (20%), and green (4) (10%) crystalline products, which were separated by column chromatography. Examination of the analytical, mass spectral (m.s.),

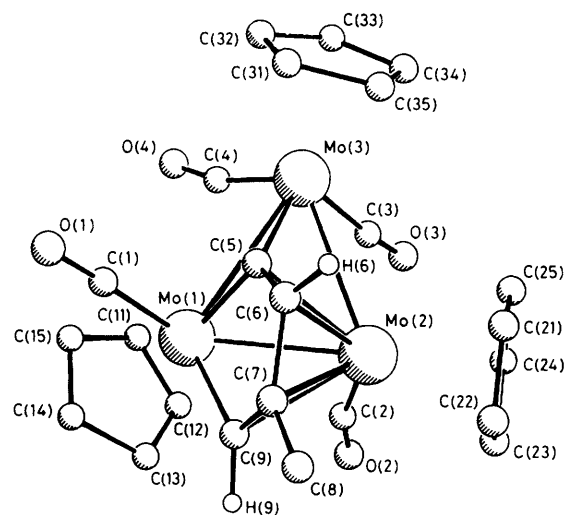


Figure 1. Molecular structure of $[\text{Mo}_3(\mu_3\text{-C}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_3]$ (4). Important molecular parameters are Mo(1)–Mo(2) 2.929(1), Mo(1)–Mo(3) 3.079(1), Mo(2)–Mo(3) 3.049(1), Mo(1)–C(1) 1.942(4), Mo(2)–C(2) 1.954(5), Mo(3)–C(3) 1.969(5), Mo(3)–C(4) 1.937(5), Mo(1)–C(5) 2.079(5), Mo(2)–C(5) 2.200(5), Mo(3)–C(5) 2.048(4), Mo(2)–C(6) 2.263(4), Mo(2)–C(7) 2.346(4), Mo(1)–C(9) 2.151(4), Mo(2)–C(9) 2.361(4), C(5)–C(6) 1.405(6), C(6)–C(7) 1.435(6), C(7)–C(9) 1.403(7) Å.

i.r., and n.m.r. data† for (2) revealed that the complex was, surprisingly, $[\text{Mo}_2(\mu\text{-HC}_2\text{Pr}^1)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$, a type of molecule which has previously^{7,8} been prepared by the direct reaction of the appropriate alkyne with the unsaturated dimolybdenum species $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$. The green complex (3) was identified by analytical, m.s., i.r., and n.m.r. data† as a bridged isoprene complex.

In this complex $[\text{Mo}_2(\mu\text{-}\{\eta^4\text{-CH}_2\cdot\text{CH}\cdot\text{C}(\text{Me})\text{CH}_2\})](\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ (3), there are two possible orientations (I) and (II), which the 1,3-diene fragment can adopt relative to the $\text{Mo}\cdots\text{Mo}$ vector. An asymmetric arrangement of the kind illustrated in Scheme 1, which we have established⁹ by X-ray crystallography for the related green complex $[\text{Mo}_2(\mu\text{-}\{\eta^4\text{-CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{Bu}^t)\text{CO}\})](\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$, and a symmetrical arrangement (II), which has been suggested¹⁰ for a *trans*-penta-1,3-diene complex obtained in low yield (2%) from the reaction of the diene with $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$.

As is illustrated in Scheme 1 the formation of (2) and (3) is consistent with the existence of at least two competing metal-assisted hydrogen shift processes, which require the presence of two metal centres. The first of these involves an unusual

† Spectroscopic data, for (2): ν_{CO} (CH_2Cl_2) 1 977s, 1 953sh, 1 901 vs. and 1 825s cm^{-1} ; n.m.r. (CDCl_3): ^1H , δ 6.04 [d, 1 H, CH, $^4J(\text{HH})$ 0.7 Hz], 5.28 (s, 10 H, $2 \times \text{C}_5\text{H}_5$), 2.65 [septet, 1 H, CH, $^3J(\text{HH})$ 6.6 Hz], and 0.95 [d, 6 H, $2 \times \text{Me}$, $^3J(\text{HH})$ 6.6 Hz]; ^{13}C -{ ^1H }, δ 233.2 (CO), 226.5 (CO), 91.0 (C_5H_5), 85.1 (HC), 65.3 (CPr¹), 31.9 (CHMe₂), and 25.8 p.p.m. (CHMe₂); for (3): ν_{CO} (CH_2Cl_2) 1 777m and 1 745m cm^{-1} ; n.m.r. (CDCl_3): ^1H , δ 5.14 (s, 5 H, C_5H_5), 5.05 (s, 5 H, C_5H_5), 4.34 [dd, 1 H, H³, $^2J(\text{H}^3\text{H}^4)$ 7.33, $^3J(\text{H}^3\text{H}^5)$ 10.8 Hz], 2.99 [dd, 1 H, H², $^4J(\text{H}^2\text{H}^3)$ 0.74, $^2J(\text{H}^2\text{H}^5)$ 3.3 Hz], 2.19 [dd, 1 H, H¹, $^2J(\text{H}^1\text{H}^5)$ 4.4, $^2J(\text{H}^1\text{H}^3)$ 7.33 Hz], 2.04 (s, 3 H, Me), 0.485 [dd, 1 H, H⁵, $^2J(\text{H}^5\text{H}^4)$ 4.4, $^3J(\text{H}^5\text{H}^3)$ 10.8 Hz], and 0.163 [d, 1 H, H⁴, $^2J(\text{H}^4\text{H}^3)$ 3.3 Hz]; ^{13}C { ^1H } (CD_2Cl_2) δ 268.1 (CO), 266.4 (CO), 97.6 (CMe), 93.6 (C_5H_5), 92.8 (C_5H_5), 57.4 (CH), 33.9 (CH_2), 30.8 (Me), and 26.8 p.p.m. (CH_2); for (4): ν_{CO} (CH_2Cl_2) 1 881br. vs. 1 799m cm^{-1} ; n.m.r. (CD_2Cl_2): ^1H , δ 6.49 [d, 1 H, CH, $^4J(\text{HH})$ 2.3 Hz], 5.78 [d, 1 H, CH, $^4J(\text{HH})$ 2.3 Hz], 5.10 (s, 5 H, C_5H_5), 4.95 (s, 5 H, C_5H_5), 4.89 (s, 5 H, C_5H_5), and 1.92 (s, 3 H, Me).

abstraction of the olefinic hydrogen in an intermediate (A) (see Scheme 1) where the allylidene ligand adopts a μ - η^1 bonding mode. The resultant μ -allenyl fragment would be capable of a change in bonding mode, bringing the second π -system into co-ordination thus giving access to a species in which an 'insertion' reaction could take place. This 'insertion' process forms the isopropyl alkyne ligand observed, which subsequently¹¹ adopts its preferred bonding mode giving (2). In contrast to the above reaction, the second isomerisation proceeds with concomitant loss of CO to form (3). In this process a net 1,4-hydrogen shift is promoted, possibly *via* the β -hydrogen abstraction, inter-metal hydrogen transfer, reductive elimination steps illustrated (Scheme 1).

That such intramolecular rearrangements are not exclusive is demonstrated by the formation of (4). This trinuclear complex was identified by n.m.r. and i.r. spectroscopy,[†] and fully characterised by an X-ray structure analysis.[‡] The molecular structure of (4) is illustrated in Figure 1. The three molybdenum atoms are separated by single bond distances [2.929(1)–3.079(1) Å]. The allylidene moiety of (1) has lost three hydrogen atoms, one from the bridging carbon atom, and two from a methyl group. The resultant organic fragment bridges all three molybdenum atoms, forming a methyl substituted metallacyclopentadienyl unit incorporating Mo(1), which is η^4 -bonded to Mo(2), and metallated by Mo(3) at the carbon [C(5)] α to Mo(1). Thus C(5) asymmetrically bridges the Mo₃ triangle in a manner reminiscent of the μ_3 -carbon in, for example, [H₂O₃(CO)₃(CCH₂)].¹²

[†] *Crystal data:* (4), C₂₄H₂₀Mo₃O₄, *M* = 660.1, monoclinic, space group *P*2₁/*n*, *a* = 8.066(1), *b* = 17.557(5), *c* = 15.754(5) Å, β = 101.35(2)°, *U* = 2 187(1) Å³, *Z* = 4, *D*_c = 2.00 g cm⁻³, *F*(000) = 1 288, μ (Mo-*K* α) = 16.8 cm⁻¹, Mo-*K* α X-radiation, λ = 0.710 69 Å. The structure was solved by heavy atom (Patterson and difference Fourier) methods and refined by a least-squares procedure. For 2 888 unique observed [*I* > 2 σ (*I*)] data measured at 293 K on a Nicolet P3m diffractometer in the range 3 < 2 θ < 50°, the current residual *R* is 0.026. All hydrogen atoms were located directly and ascribed isotropic thermal parameters and idealised geometries, except H(6) and H(9) which were refined freely; all other atoms were refined without constraints and with anisotropic thermal parameters. The atomic co-ordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The formation of (4) implies a degree of fragmentation of the dinuclear species present during the thermolysis of (1). Although the mechanism of this reaction is obscure, it is interesting to note that a loss of two hydrogens from a dinuclear (Fe₂) μ -allylidene species giving a metallacyclopentadienyl fragment has been reported.³

In contrast to the variety of transformations observed in these polynuclear complexes containing an allylidene (vinylcarbene) moiety, mononuclear complexes of similar ligands¹³ have shown no tendency towards formation of alkyne or diene units.

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