The Formation of a Cyclohexadienone at a Dimolybdenum Centre; *X*-Ray Crystal Structure of $[Mo_2(\mu\text{-}\{\eta^4\text{-}\overline{CMe_2 \cdot CH \cdot CH \cdot CH \cdot C(Bu^t)CO}\})(CO)_2(\eta\text{-}C_5H_5)_2]$, and Evidence for an Unusual Bonding Mode for a Bridging 1,3-Diene Ligand

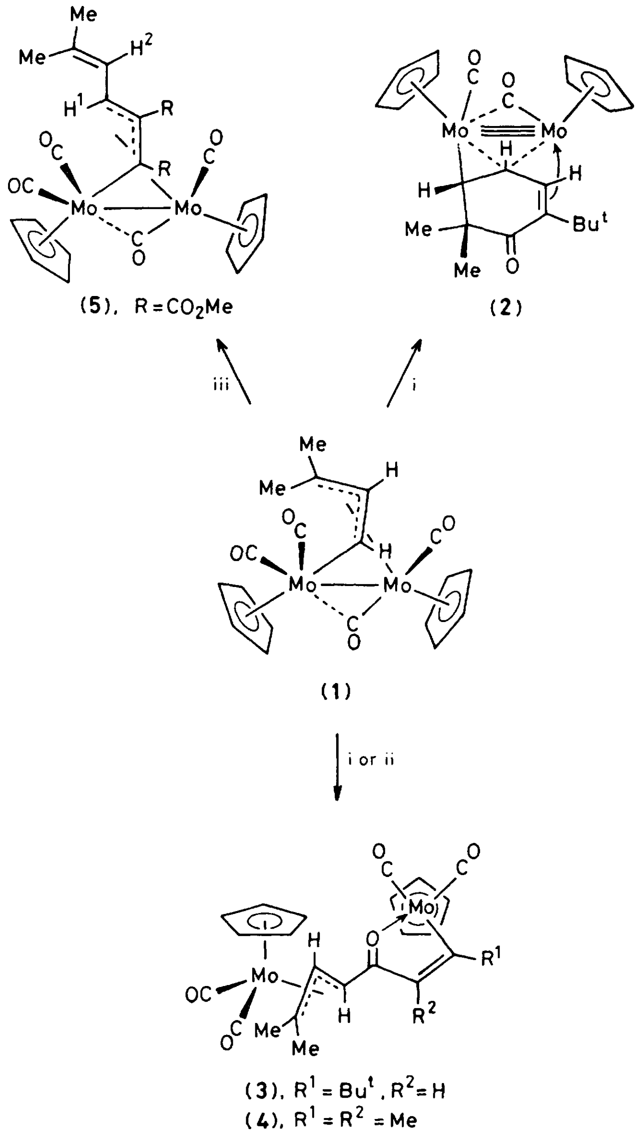
Michael Green, A. Guy Orpen, Colin J. Schaverien, and Ian D. Williams

Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

Reaction of $[Mo_2(CO)_4(\mu\text{-}CH{\cdot}CH{\cdot}CMe_2)(\eta\text{-}C_5H_5)_2]$ with Bu^tC_2H affords $[Mo_2(\mu\text{-}\{\eta^4\text{-}\overline{CMe_2{\cdot}CH{\cdot}CH{\cdot}CH{\cdot}C(Bu_t)CO}\})(CO)_2(\eta\text{-}C_5H_5)_2]$ containing a bridging 1,3-diene ligand with an unusual bonding mode and an η^3-allylic complex in which the Mo-Mo bond has been broken, whereas but-2-yne afords only the η^3-allylic type of complex, and $C_2(CO_2Me)_2$ gives a vinyl substituted μ-allylidene complex.

The current interest[1] in the chemistry of transition-metal compounds containing μ-alkylidene ligands has been partially stimulated by the possible[2,3] involvement of such species in Fischer–Tropsch reductions of carbon monoxide, and recently μ-allylidene complexes of di-iron,[4,5] diruthenium,[5] and ditungsten[6] have been implicated in the linear oligomerisation of alkynes. In investigating the chemistry of the μ-allylidene complex (1)[7] $[Mo_2(CO)_4(\mu\text{-}CH{\cdot}CH{\cdot}CMe_2)(\eta\text{-}C_5H_5)_2]$ (Scheme 1), which is formed on reaction of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with 3,3-dimethylcyclopropene, we have observed an unusual cyclisation reaction at a di-metal centre.

3,3-Dimethylbut-1-yne reacts (50 °C; 5 h) with (1) in CH_2Cl_2 as solvent to afford (20% yield) a dark green crystalline complex (2).† A single-crystal *X*-ray diffraction study elucidated the structure of (2) as its dichloromethane solvate.‡



Scheme 1. i, Bu^tC_2H; ii, MeC_2Me; iii, $C_2(CO_2Me)_2$.

The structure of (2) is shown in Figure 1, and consists of an $Mo_2(\eta\text{-}C_5H_5)_2$ fragment linked by two asymmetrically bridging CO ligands (one of which is much more asymmetric than the other). The Mo_2 unit is also bridged by a 2-t-butyl-6,6-dimethylcyclohexa-2,4-dienone ligand (see Figure 1 for bond lengths), which adopts an asymmetric bonding mode in marked contrast to that observed[8] in μ-(η^4-cyclohexa-1,3-diene)-μ-carbonyl-bis-(η^5-indenyl)dirhodium(*Rh–Rh*). As

---

† Spectroscopic data for (2): ν_{CO} 1 803 m, br., 1 705 m, and 1 595 m cm^{-1} (CH_2Cl_2); n.m.r. (CD_2Cl_2): ^1H, δ 5.33 (5 H, s, C_5H_5), 5.20 (1 H, m, CH), 5.04 (5 H, s, C_5H_5), 4.33 (1 H, m, CH), 4.13 (1 H, m, CH), 1.47 (3 H, s, CH_3) 1.06 [9 H, s, $C(CH_3)_3$], and 0.83 (3 H, s, CH_3); the resonances at δ 5.20, 4.33, and 4.13 form an ABX spin system with J_{AX} −0.75 Hz, J_{BX} 6.31 Hz, and J_{AB} 7.25 Hz (simulation); ^{13}C, δ 262.7 (s, CO), 253.6 (s, CO), 204.6 (s, CO, ketonic), 94.6 (s, C_5H_5), 92.7 (s, C_5H_5), 85.9 [s, $C(CMe_3)$], 62.3 (s, CH), 56.4 (s, CH), 55.9 (s, CH), 42.9 (s, CMe_2 or CMe_3), 35.4 (s, CH_3), 31.4 [s, $C(CH_3)_3$], and 26.7 p.p.m. (s, CH_3).

‡ *Crystal data* for (2): $C_{24}H_{28}Mo_2O_3.CH_2Cl_2$, F. wt. = 556.2 + 84.9 = 641.1, monoclinic, space group $P2_1$ (No. 4), $a = 8.745(5)$, $b = 14.571(7)$, $c = 10.909(4)$ Å, $\beta = 112.87(3)°$, $U = 1281(1)$ Å^3, $Z = 2$, $D_c = 1.66$ g cm^{-3}, $F(000) = 444$, $\mu(Mo\text{-}K_\alpha) = 11.64$ cm^{-1}, Mo-K_α, *X*-radiation, $\bar{\lambda} = 0.710\,69$ Å. Current R 0.031 (R_w 0.035) for 3 228 unique observed [$I > 2\sigma(I)$] reflections measured in the range $3° \leqslant 2\theta \leqslant 60°$ at 293 K on a Syntex P3m diffractometer. The structure was solved by heavy atom (Patterson, Fourier) methods and refined by full-matrix blocked-cascade least squares. Hydrogen atoms were given fixed geometries excepting H(8), H(9), and H(10) which were refined freely with isotropic thermal parameters, all other atoms being anisotropic.

Crystal Data for (4): $C_{24}H_{25}Mo_2O_5$, $M = 584.1$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.591(2)$, $b = 8.906(3)$, $c = 15.071(4)$ Å, $\alpha = 89.10(2)$, $\beta = 99.65(2)$, $\gamma = 99.06(2)°$, $U = 1169.5(6)$ Å^3, $Z = 2$, $D_c = 1.66$ g cm^{-3}, $F(000) = 584$, $\mu(Mo\text{-}K_\alpha) = 10.77$ cm^{-1}, Mo-K_α, *X*-radiation, $\bar{\lambda} = 0.710\,69$ Å. Current R 0.031 (R_w 0.034) for 3543 unique, observed [$I > 2\sigma(I)$] reflections collected as for (2) in the range $3° \leqslant 2\theta \leqslant 50°$. Analysis was as for (2) with only H(6) and H(7) of the hydrogen atoms refined without positional constraints.

The atomic co-ordinates for this work 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.

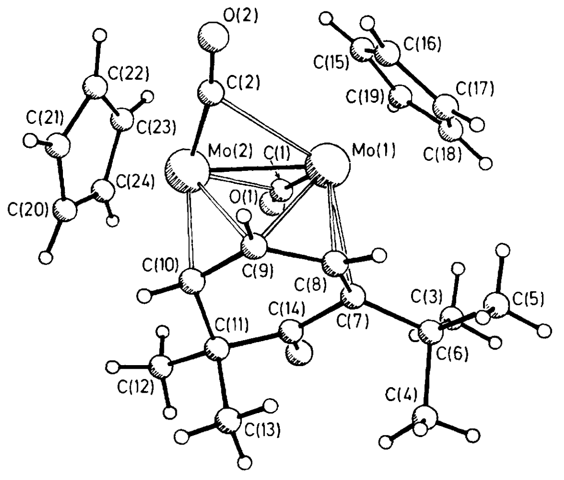


Figure 1. Molecular structure of $[\mathrm{Mo_2}(\mu\text{-}\{\eta^4\text{-}\overline{\mathrm{CMe_2 \cdot CH \cdot CH \cdot CH \cdot C(Bu^t)CO}}\})(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})_2]$ (**2**). Important molecular parameters not given in the text are: bond lengths Mo(1)–C(1) 1.951(4), Mo(2)–C(1) 2.335(5), Mo(2)–C(2) 1.918(6), Mo(1)–C(2) 2.654(5), Mo(1)–C(7) 2.396(4), Mo(1)–C(8) 2.222(4), Mo(1)–C(9) 2.530(5), Mo(2)–C(9) 2.534(4), and Mo(2)–C(10) 2.232(5) Å; bond angles Mo(1)–C(9)–Mo(2) 59.8(1), Mo(1)–C(1)–O(1) 163.2(5), Mo(2)–C(2)–O(2) 168.4(7), C(7)–C(8)–C(9) 119.3(3), C(8)–C(9)–C(10) 123.6(3), and C(9)–C(10)–C(11) 114.3(4)°.

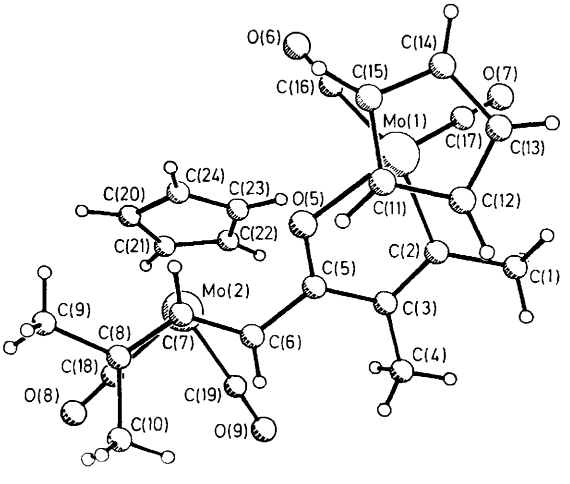


Figure 2. Molecular structure of $[\mathrm{Mo(CO)_2}(\eta\text{-}\mathrm{C_5H_5})(\mu\text{-}\{\eta^2,\eta^3\text{-}\mathrm{C(Me)C(Me)C(O) \cdot CH \cdot CH \cdot CMe_2}\})\text{-}\mathrm{Mo(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$(**4**). Important molecular parameters are: Mo(1) . . . . Mo(2) 5.809(2), Mo(1)–C(2) 2.158(4), Mo(1)–O(5) 2.132(5), Mo(1)–C(16) 2.008(5), Mo(1)–C(17) 1.969(5), Mo(2)–C(6) 2.349 (4), Mo(2)–C(7) 2.239(4), Mo(2)–C(8) 2.463(4), Mo(2)–C(18) 1.971(4), Mo(2)–C(19) 1.954(4), C(2)–C(3) 1.378(6), C(3)–C(5) 1.420(5), C(5)–O(5) 1.286(4), C(5)–C(6) 1.481(6), C(6)–C(7) 1.409(5), and C(7)–C(8) 1.411(6) Å.

shown in Figure 1 carbon atom C(9) is apparently pentacoordinate being equidistant from Mo(1) and Mo(2) [at 2.532(5) Å] and linked to one hydrogen and two carbon atoms. In previously characterised[8,9] μ-η^4-diene complexes the bridged metal atoms each interact with just two carbon atoms, which atoms behave as olefinic ligands in the classical sense; the new diene bonding mode found in (2) is more complex. The C–C bond lengths within the diene fragment show little variation [C(7)–C(8) 1.439(5), C(8)–C(9) 1.428(7), C(9)–C(10) 1.420(6) Å] indicating considerable delocalisation in its bonding to the $\mathrm{Mo_2}$ moiety. The origin of the asymmetry in the diene bonding in (**2**) would appear to be steric, the bulk of the t-butyl substituent at C(7) preventing the attainment of the orientation observed for μ-(η^4-cyclohexa-1,3-diene)-μ-carbonyl-bis(η^5-indenyl)dirhodium, where the central C–C bond lies parallel to the metal–metal vector. The 23.3° rotation of the C–C bond relative to this orientation in (**2**) is therefore indicative of some flexibility in the electronic requirements of the μ-diene ligand in bonding to the $\mathrm{Mo_2}$ unit. The short Mo–Mo distance [2.524(1) Å] is similar to that seen[9] in $[\mathrm{Mo_2(CO)_2}(\mu\text{-}\mathrm{C_{10}H_{10}})(\eta\text{-}\mathrm{C_5H_5})_2]$ [2.504(1) Å] which has, as does (**2**), a 30 valence electron count for the $\mathrm{Mo_2}$ unit, implying a formal Mo–Mo triple bond.

The lability of the cyclohexadienone ligand in (**2**) is illustrated by its smooth reaction with carbon monoxide (1 atm; room temperature) to give $[\mathrm{Mo_2(CO)_6}(\eta\text{-}\mathrm{C_5H_5})_2]$ and the free ligand.

Although the formation of (**2**) is the first example of a cyclisation occurring on reaction of a μ-allylidene or μ-alkylidene complex with an alkyne, the reaction is not selective, a second deep-red crystalline complex (**3**) being formed (40% yield) The structural identity of (**3**) was established by comparing n.m.r. parameters with those of an analogous complex (**4**),§ which was the only product (50% yield) formed on reaction of (**1**) with but-2-yne, and which was characterised by *X*-ray crystallography.‡ As shown in Figure 2 a very different type of reaction has occurred. Although a carbonyl 'insertion' reaction has again taken place the CO is bonded to the opposite end of the μ-allylidene fragment $\mathrm{CH \cdot CH \cdot CMe_2}$ to that found in the cyclic complex (**2**). Moreover, the Mo–Mo bond in (**1**) has been completely broken. Each Mo atom carries an η^5-$\mathrm{C_5H_5}$ and two carbonyl ligands; the complex ligand formed acts as an *exo*-η^3-allyl ligand to one metal, and an η^2-vinyl ketone to the other.

Finally, reaction (50 °C; 3 h) of (**1**) with the electronegatively substituted alkyne $\mathrm{C_2(CO_2Me)_2}$ was found to give only one product (40% yield), the red crystalline complex (**5**), which on the basis of n.m.r. parameters, analysis, and i.r. and mass spectrometry,¶ is assigned the illustrated structure where the alkyne has apparently 'inserted' into a carbon–metal bond of the μ-allylidene system, a type of reaction which has been observed[4,5,6] in $\mathrm{Fe_2}$, $\mathrm{Ru_2}$, and $\mathrm{W_2}$ chemistry.

Thus, these observations demonstrate the potentially rich chemistry of μ-alkylidene systems and serve to emphasise the

---

§ Spectroscopic data for (**3**): ν_{CO} 1 955 s, 1 935 s, 1 909 m, 1 861 s, and 1 611 w $\mathrm{cm^{-1}}$; n.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 7.03 (1 H, s, CH), 5.41 (5 H, s, $\mathrm{C_5H_5}$), 5.12 (5 H, s, $\mathrm{C_5H_5}$), 4.98 (1 H, d, CH, $^3J_{\mathrm{HH}}$ 10 Hz), 2.82 (1 H, d, CH, $^3J_{\mathrm{HH}}$ 10 Hz), 1.82 (3 H, s, $\mathrm{CH_3}$), 1.33 [9 H, s, $\mathrm{C(CH_3)_3}$], and 1.13 (3 H, s, $\mathrm{CH_3}$); ^{13}C, δ 274.2 [s, $C\mathrm{C(CH_3)_3}$], 253.7, 251.9, 242.2, 238.2 (s, CO × 4), 201.4 (s, CO, ketonic), 129.6 (s, CH), 93.4, 93.3 (s, $\mathrm{C_5H_5}$ × 2), 81.1 [s, $C\mathrm{(CH_3)_2}$], 70.8 (s, CH), 48.9 (s, CH), 46.8 [s, $C\mathrm{(CH_3)_3}$], 32.6 [s, $\mathrm{C}(C\mathrm{H_3})_3$], 30.4 (s, $\mathrm{CH_3}$), and 23.0 p.p.m. (s, $\mathrm{CH_3}$).

Spectroscopic data for (**4**): ν_{CO} 1 940 s, 1 865 s, and 1 605 m $\mathrm{cm^{-1}}$; n.m.r. ($\mathrm{CDCl_3}$), δ 5.30 (5 H, s, $\mathrm{C_5H_5}$), 5.10 (1 H, d, CH, $^3J_{\mathrm{HH}}$ 10 Hz), 5.08 (5 H, s, $\mathrm{C_5H_5}$), 2.87 (1 H, d, CH, $^3J_{\mathrm{HH}}$ 10 Hz), 2.84 (3 H, s, $\mathrm{CH_3}$), 2.04 (3 H, s, $\mathrm{CH_3}$), 1.92 (3 H, s, $\mathrm{CH_3}$), and 1.18 (3 H, s, $\mathrm{CH_3}$), ^{13}C, δ 250.7 [s, $C\mathrm{(CH_3)}$], 243.8 (s, CO × 2), 239.2 (s, CO × 2), 199.8 (s, CO, ketonic), 135.8 [s, $C\mathrm{(CH_3)}$], 93.8, 93.4 (s, $\mathrm{C_5H_5}$ × 2), 83.7 [s, $C\mathrm{(CH_3)_2}$], 73.0 (s, CH), 47.0 (s, CH), 33.6, 30.5, 23.3, and 12.9 p.p.m. (s, $C\mathrm{H_3}$ × 4).

¶ Spectroscopic data for (**5**): ν_{CO} 1 949 s, 1 909 s, 1 837 s, 1 769 m, 1 711 m, and 1 681 m $\mathrm{cm^{-1}}$; mass spectrum: m/z 532 (M^+ −4CO); n.m.r. ($\mathrm{CD_2Cl_2}$), δ 5.28 (5 H, s, $\mathrm{C_5H_5}$), 5.20 (5 H, s, $\mathrm{C_5H_5}$), 3.82 (3 H, s, $\mathrm{CO_2CH_3}$), 3.74 (3 H, s, $\mathrm{CO_2CH_3}$), 2.80 (1 H, d, CH, $^3J_{\mathrm{HH}}$ 12 Hz), 1.81 (3 H, d, $\mathrm{CH_3}$, $^4J_{\mathrm{HH}}$ 1 Hz), and 1.77 (3 H, d, $\mathrm{CH_3}$, $^4J_{\mathrm{HH}}$ 1 Hz); ^{13}C, δ 250.0, 245.9, 241.2, 236.9, (s, CO × 4), 179.0, 174.9, 170.0 [s, $C\mathrm{O_2CH_3}$ × 2 and $C\mathrm{(CO_2CH_3)}$], 140.7 [s, $C\mathrm{(CO_2CH_3)}$], 122.5 (s, CH), 105.1 [s, $C\mathrm{(CH_3)_2}$], 97.4 (s, $\mathrm{C_5H_5}$), 95.3 (s, $\mathrm{C_5H_5}$), 80.9 (s, CH), 53.3 (s, $\mathrm{CO_2}C\mathrm{H_3}$), 53.1 (s, $\mathrm{CO_2}C\mathrm{H_3}$), 26.6 (s, $\mathrm{CH_3}$), and 18.5 p.p.m. (s, $\mathrm{CH_3}$).

delicate balance of the factors controlling access to competing reaction paths.

We thank the S.E.R.C. for support and for research studentships (C.J.S. and I.D.W.).

Received, 22nd November 1982; Com. 1333

References

1 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159.
2 R. C. Brady, III, and R. Pettit, *J. Am. Chem. Soc.*, 1981, **103**, 1287.
3 C. E. Sumner, Jr., P. E. Riley, and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 1752.
4 C. E. Sumner, Jr., J. A. Collier, and R. Pettit, *Organometallics*, 1982, **1**, 1350.
5 A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 803.
6 J. Levisalles, H. Rudler, F. Daham, and Y. Jeannin, *J. Organomet. Chem.*, 1980, **188**, 193; J. Levisalles, F. Rose-Munch, H. Rudler, J. Davan, and Y. Dromzee, *J. Chem. Soc., Chem. Commun.*, 1981, 152.
7 G. K. Barker, W. E. Carroll, M. Green, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1980, 1071.
8 Y. N. Al-Obaidi, M. Green, N. D. White, J.-M. Bassett, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 494.
9 S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward., *J. Chem. Soc., Chem. Commun.*, 1979, 934.