Facile [1,2] Hydrogen-shift Reaction Promoted by Metal–Metal Bond Rupture; *X*-Ray Crystal Structure of $W_2(CO)_8[C_9H_{14}]$

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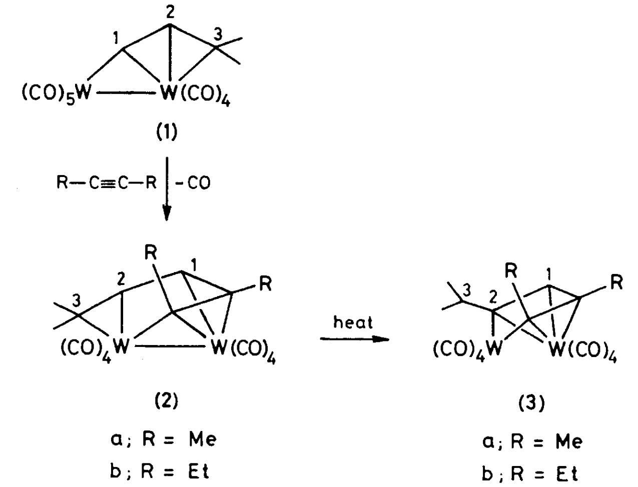
Summary The insertion product, $W_2(CO)_8[C_9H_{14}]$, of but-2-yne into the μ-alkylidene complex $W_2(CO)_9[\mu$-$CHCHCMe_2]$ rearranges easily to the tungstole–tungsten derivative $W_2(CO)_8[C_9H_{14}]$, possibly *via* a mechanism which involves α- and β-elimination reactions promoted by metal–metal bond rupture.

In an earlier paper[1] we described the synthesis of complex (**2a**) starting from the μ-alkylidene complex (**1**). The same reaction pathway allowed us to synthesize complex (**2b**).

Although the complexes (**2**) are stable at room temperature they rearrange smoothly, when refluxed in hexane under argon for 1 h, to give quantitatively, the complexes (**3**). The complexes (**3**) contain, according to ^1H n.m.r.[†] spectroscopy and an *X*-ray crystal structure determination, a metallacycle co-ordinated to a second metal centre (Figure).



Scheme 1

Crystal Data: $C_{17}H_{14}O_8W_2$, $M = 714$, monoclinic, space group $P2_1/c$, $a = 9{\cdot}175(6)$, $b = 12{\cdot}500(14)$, $c = 17{\cdot}550(17)$ Å,

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[†] Complex (**3a**), m.p. 130—132 °C (decomp.); ν_{CO} (CCl_4) 1935, 1965, 1970, 1990, 2030, and 2070 cm^{-1}; δ (CCl_4) 7·20 (s, 1-H), 2·50 (3 H, s, 6-H), 2·35 (3 H, s, 9-H), 2·15 (m, 3-H), 1·05 (3 H, s, 4-H), and 0·95 (3 H, s, 5-H); δ (C_6D_6) 6·50 (s, 1-H), 2·10 (3 H, s, 6-H), 1·95 (m, 3-H), 1·85 (3 H, s, 9-H), 0·95 (3 H, d, 4-H), and 0·85 (3 H, d, 5-H); *m/e* 714. (The numbering is given in the Figure.)

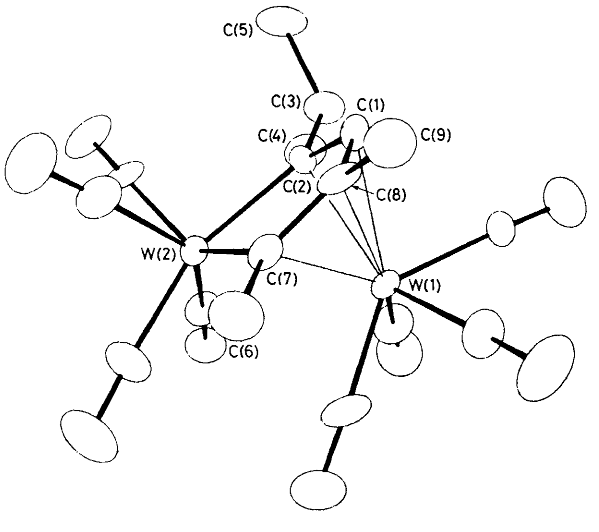
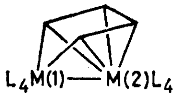


FIGURE. ORTEP view of the structure (**3a**). Important bond lengths (Å): W(1)–W(2) 2·90(2), W(1)–C(7) 2·31(2), W(1)–C(8) 2·36(2), W(1)–C(1) 2·34(2), W(1)–C(2) 2·40(2), W(2)–C(2) 2·15(2), W(2)–C(7) 2·18(2), C(7)–C(8) 1·40(3), C(8)–C(1) 1·48(3), and C(1)–C(2) 1·43(3). Important bond angles (°): W(2)–C(7)–C(8) 117(2), C(7)–C(8)–C(1) 114(2), C(8)–C(1)–C(2) 116(2), C(1)–C(2)–W(2) 116(2), C(2)–W(2)–C(7) 76(1), W(2)–C(7)–C(6) 127(2), C(6)–C(7)–C(8) 115(2), W(2)–C(7)–C(8) 117(2), C(7)–C(8)–C(9) 127(2), C(9)–C(8)–C(1) 119(2), C(1)–C(2)–C(3) 111(2), W(2)–C(2)–C(3) 132(2), C(2)–C(3)–C(4) 115(2), C(2)–C(3)–C(5) 111(2), and C(4)–C(3)–C(5) 112(2).

β = 90·7(1)°, Z = 4, D_c = 2·36, D_m = 2·35 g cm^{-3}, μ(Mo-K_α) = 121·3 cm^{-1}. Data were collected on a Philips PW 1100 diffractometer at room temperature. The structure was solved by standard Patterson–Fourier techniques. Full-matrix least-squares refinements of all atoms, except hydrogen, have converged to an agreement factor of R 0·071.‡

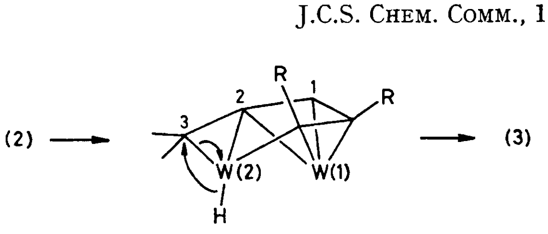


(**5**)

Although complexes of the general structure (**5**) are known, with M(1) = M(2) = Fe,[2,3,4] M(1) = M(2) = Mo,[5] M(1) = M(2) = Cr,[6] and M(1) = W, M(2) = Co,[7] their formation is usually due to the dimerization of an alkyne on two metal centres.

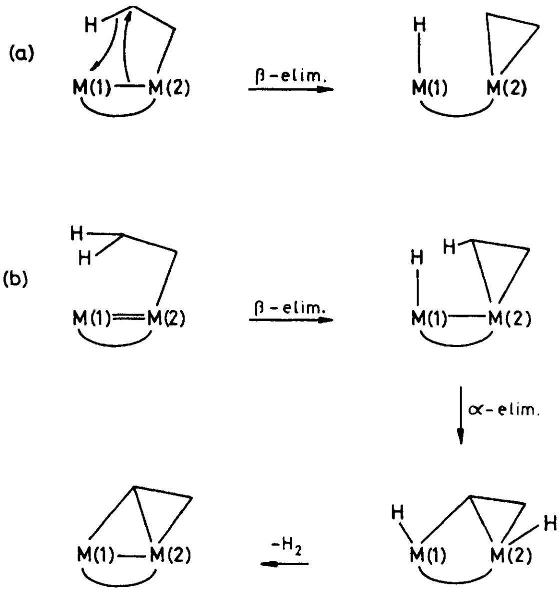
The formation of complex (**3**) from complex (**2**) follows another pathway and, therefore, needs some comment.

An explanation which accounts for such a transformation might be that a β-elimination [with respect to W(1)] or an α-elimination [with respect to W(2)] promoted by the M–M bond takes place according to Scheme 2. An oxidative addition of the C$_2$H bond across the W(1)–W(2) bond[8,9] gives the intermediate (**4**) which, upon reductive elimination, leads to complex (**3**). If such a mechanism takes place, it would illustrate a new type of β-elimination on two metal centres, the driving force of which would be the rupture of the metal–metal bond (Scheme 3a). Such a reaction would be of importance in the mechanistic interpretation of metal–alkyl reactions on metal surfaces and in homogeneous-cluster catalysis reactions.



(**4**)

SCHEME 2



SCHEME 3. Elim. = elimination.

Support for such a mechanism is found in the literature. On the one hand, Knox *et al.*[10] observed the formation of compound (**10**) from compound (**6**), but the fate of the hydrogen has not been established. A possible mechanism, depicted in Scheme 4, involves a β-elimination [with respect to Fe(2)] followed by an α-elimination [with respect to Fe(2)] induced by a multiple metal–metal bond. This could

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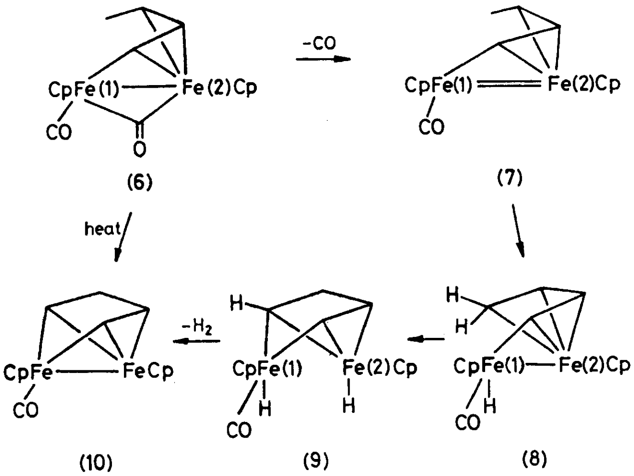
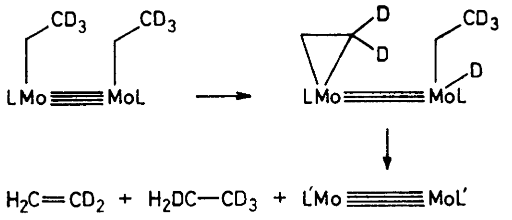
‡ As the crystal was broken at the end of the data collection, the usual absorption correction could not be made. However, it was found that some thermal anisotropic components had negative values. The structure factor was then multiplied by the empirical factor exp $[-(A_1h^2 + A_2k^2 + A_3l^2 + A_4hk + A_5hl + A_6kl)]$ and the six parameters A_i were refined by least squares. Thus we obtained more consistent anisotropic thermal parameters. Structure factors were weighted by $w = (4{\cdot}2 + 0{\cdot}235F_0 + 0{\cdot}0052F_0^2)^{-1}$. In the final cycle of least squares no shift was larger than one tenth of its corresponding standard deviation. 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. The structure factor table is available as Supplementary Publication No. 23180 (15 pp) from the British Library, Lending Division (for details see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans.* 1, 1979, Index issue).



SCHEME 4. Cp = η-C_5H_5.

easily account for the transformation and would be in good agreement with the general mechanism of Scheme 3b. On the other hand, the observations of Chisholm and Haitko[11] during the decomposition of labelled *vic*-dialkyl di-metal complexes (Scheme 5) is in accord with our hypohesis.



SCHEME 5

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