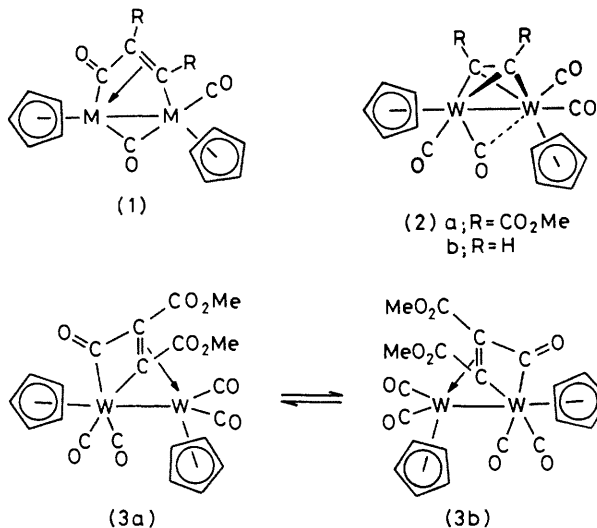


## Making and Breaking of Carbon–Carbon Bonds at a Di-tungsten Centre: X-Ray Structure of $[\text{W}_2(\text{CO})_4\{\mu\text{-}\eta^2,\eta^2\text{-C}(\text{O})\text{C}_2(\text{CO}_2\text{Me})_2\}(\eta\text{-C}_5\text{H}_5)_2]$

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**Summary** Dimethyl acetylenedicarboxylate reacts with  $[\{\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$  under u.v. irradiation to yield the dimetalocycle  $[\text{W}_2(\text{CO})_4\{\mu\text{-}\eta^2,\eta^2\text{-C}(\text{O})\text{C}_2(\text{CO}_2\text{Me})_2\}(\eta\text{-C}_5\text{H}_5)_2]$ , which ejects CO readily to give  $[\text{W}_2(\text{CO})_4\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\eta\text{-C}_5\text{H}_5)_2]$ ; in both structure, determined by X-ray diffraction, and reactivity  $[\text{W}_2(\text{CO})_4\{\mu\text{-}\eta^2,\eta^2\text{-C}(\text{O})\text{C}_2(\text{CO}_2\text{Me})_2\}(\eta\text{-C}_5\text{H}_5)_2]$  is subtly different from the complexes  $[\text{M}_2(\text{CO})_4(\mu\text{-CO})\{\mu\text{-}\eta^1,\eta^3\text{-C}(\text{O})\text{C}_2\text{R}_2\}(\eta\text{-C}_5\text{H}_5)_2]$  ( $\text{M} = \text{Fe}$  or  $\text{Ru}$ ).

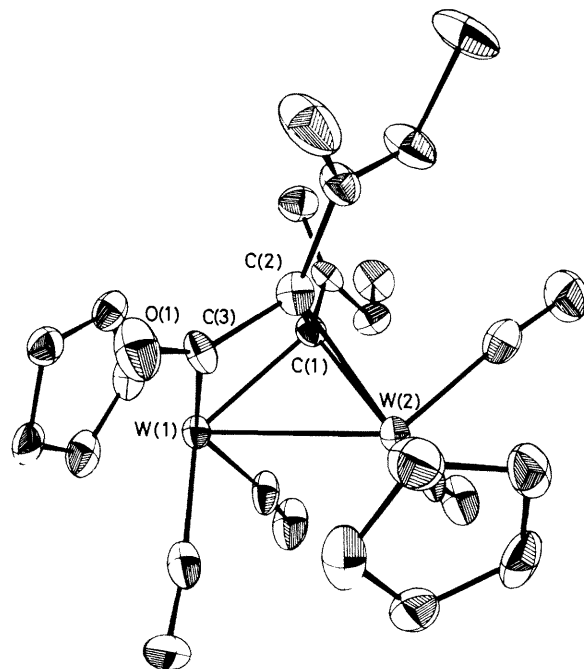
In the preceding communication, di-iron and di-ruthenium complexes  $[\text{M}_2(\text{CO})_4(\mu\text{-CO})\{\mu\text{-}\eta^1,\eta^3\text{-C}(\text{O})\text{C}_2\text{R}_2\}(\eta\text{-C}_5\text{H}_5)_2]$  (**1**) were described, whose chemistry was marked by an ease of carbon–carbon bond-making and -breaking.<sup>1</sup> We have also obtained a di-tungsten metalocycle with an intriguingly related structure and chemistry which are reported here.



U.v. irradiation (250 W mercury lamp, toluene solution, silica glass flask, 3 h) of a mixture of  $[\{\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$  and dimethyl acetylenedicarboxylate at room temperature provides a 55% yield of orange crystalline  $[\text{W}_2(\text{CO})_4\{\mu\text{-}\eta^2,\eta^2\text{-C}(\text{O})\text{C}_2(\text{CO}_2\text{Me})_2\}(\eta\text{-C}_5\text{H}_5)_2]$  (**3**) [m.p. 135–145 °C (decomp.);  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$  2 026s, 1 979s, 1 906m, 1 693m, and 1 601m  $\text{cm}^{-1}$ ] together with a 20% yield of  $[\text{W}_2(\text{CO})_4\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}(\eta\text{-C}_5\text{H}_5)_2]$  (**2a**). The latter has been prepared previously<sup>2</sup> by heating dimethyl acetylenedicarboxylate with  $[\text{W}(\text{HCO})_3(\eta\text{-C}_5\text{H}_5)]$ , and from its spectroscopic properties it is structurally analogous to  $[\text{W}_2(\text{CO})_4\{\mu\text{-C}_2(\text{H}_2)\}(\eta\text{-C}_5\text{H}_5)_2]$  (**2b**), the subject of an X-ray diffraction study.<sup>3</sup> If the reactants are irradiated for 2 days a greatly reduced yield (2%) of (**3**) is obtained and (**2a**) becomes the major product. This clear indication that (**3**) is a precursor of (**2a**) was confirmed by warming the former in hexane,

when rapid CO evolution occurred and (**2a**) was formed quantitatively. Reactions of other alkynes ( $\text{HC}_2\text{H}$ ,  $\text{PhC}_2\text{Ph}$ , or  $\text{CF}_3\text{C}_2\text{CF}_3$ ) with  $[\{\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$  under u.v. irradiation (at  $-78^\circ\text{C}$  for  $\text{CF}_3\text{C}_2\text{CF}_3$ ) provided only the analogues of (**2a**). Probably complexes of type (**3**) are formed initially, but in these cases the thermal instability is even more marked. The structure of (**3**) was established by X-ray diffraction.

**Crystal data:**  $\text{C}_{21}\text{H}_{16}\text{O}_9\text{W}_2$ ,  $M$  780.0, triclinic, space group  $P\bar{1}$ ,  $a = 9.419(5)$ ,  $b = 8.089(2)$ ,  $c = 14.561(4)$  Å,  $\alpha = 91.16(2)$ ,  $\beta = 81.96(4)$ ,  $\gamma = 106.81(4)^\circ$ ,  $U = 1051.3(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 724$ ,  $\bar{\lambda} = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 105.2$   $\text{cm}^{-1}$ . The structure was solved by conventional heavy atom methods from data collected on a Syntex  $P2_1$  diffractometer to  $2\theta_{\text{max}} = 60^\circ$  at 233 K. For 5045 independent reflections [ $I \geq 3\sigma(I)$ ]  $R = 0.033$ .†



**FIGURE.** Molecular structure of  $[\text{W}_2(\text{CO})_4\{\mu\text{-}\eta^2,\eta^2\text{-C}(\text{O})\text{C}_2(\text{CO}_2\text{Me})_2\}(\eta\text{-C}_5\text{H}_5)_2]$  (**2**). Bond lengths:  $\text{W}(1)\text{-W}(2)$  3.017(1),  $\text{W}(1)\text{-C}(1)$  2.197(6),  $\text{W}(1)\text{-C}(3)$  2.238(8),  $\text{W}(2)\text{-C}(1)$  2.124(7),  $\text{W}(2)\text{-C}(2)$  2.220(7),  $\text{C}(1)\text{-C}(2)$  1.450(10),  $\text{C}(2)\text{-C}(3)$  1.455(9),  $\text{C}(3)\text{-O}(1)$  1.236(9) Å.

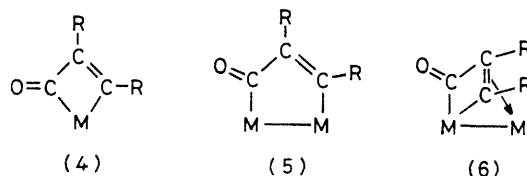
The molecular structure, shown in the Figure, contains a pair of tungsten atoms singly bonded to one another [ $\text{W}(1)\text{-W}(2)$  3.017(1) Å] with each bearing an  $\eta^5$ -cyclopentadienyl ligand and two terminal carbonyls. Bridging the tungsten–tungsten bond is a group derived from the

† 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.

combination of a molecule of dimethyl acetylenedicarboxylate with CO. This group is  $\eta^2$ -bonded to W(1) through  $\sigma$ -bonds to the ketonic carbon C(3) and to C(1) and  $\eta^2$ -bonded to W(2) via an olefinic link C(1)-C(2) [1.45(1) Å] as depicted in (3). The complexes (1) and (3) are thus related but subtly different in that although each contains a C(O)C<sub>2</sub>R<sub>2</sub> bridge between two metals this is  $\eta^1 \eta^3$ -bound in (1) and  $\eta^2, \eta^2$ -bound in (3). One consequence is that the ketonic CO is effectively within a three-membered ring in (1) and a four-membered ring in (3) with very different  $\nu$  stretching frequencies of ca 1750 and 1601 cm<sup>-1</sup>, respectively.

The most notable feature of the complexes (1) is the lability of the carbon-carbon (ketonic) bond. Similar behaviour is apparent in the thermal instability of (3) with respect to formation of the  $\mu_2$ -alkyne complex (2a). However, unlike the complexes (1), the fluxionality of (3) appears to involve cleavage of the metal-carbon (ketonic) bond rather than the carbon-carbon (ketonic) bond. At 30 °C the <sup>1</sup>H n.m.r. spectrum of (3) accords with the structure determined for the solid state in having signals for two inequivalent  $\eta$ -C<sub>5</sub>H<sub>5</sub> ligands ( $\tau$  4.52 and 4.55) and for the two inequivalent CO<sub>2</sub>Me groups ( $\tau$  6.24 and 6.37). On warming above 30 °C the spectrum becomes complicated by the rapid growth of signals resulting from the formation of (2a), but it can clearly be seen that the  $\eta$ -C<sub>5</sub>H<sub>5</sub> signals of (3) coalesce at ca 65 °C while the CO<sub>2</sub>Me signals remain sharp and distinct. These observations requiring that the  $\eta$ -C<sub>5</sub>H<sub>5</sub> ligands exchange their environments while the CO<sub>2</sub>Me groups do not, suggest that the bond between C(2) and C(3) is retained throughout the fluxional process, and that the ketonic carbonyl is transferred reversibly from one tungsten to the other via cleavage and regeneration of the tungsten-carbon bond. Associated movements of the  $\eta$ -C<sub>5</sub>H<sub>5</sub> and CO ligands on the tungsten atoms must also occur in this unusual process, which is illustrated as (3a)  $\rightleftharpoons$  (3b). An alternative process, in which the C(2)-C(3) bond is broken for the ketonic carbonyl to become terminal while

a terminal CO on W(2) inserts specifically into the C(2)-W(2) bond and a CO is transferred from W(1) to W(2), would also retain the distinct identities of the two CO<sub>2</sub>Me groups. However, such a process seems improbable because (a) rupture of the C(2)-C(3) bond has already been seen to coincide with CO elimination and formation of (2a), (b) even under 300 atm of CO the W-C(alkyne) bonds of (2a) resist insertion to give (3) and (c) CO transfers between third row transition metals are very unfavourable. Attempts to establish the nature of the fluxional process unequivocally by <sup>13</sup>CO n.m.r. spectroscopy were thwarted by the thermal instability of (3).



The combination of carbon monoxide with alkynes in the presence (often catalytic) of transition metal carbonyls has attracted study for forty years. Much of the chemistry remains obscure mechanistically but there has been speculation that metallocycles (4) are involved with mono-metal carbonyls and (5) or (6) with di-metal carbonyls.<sup>4</sup> Stable examples of (4) are known (e.g. [Ru(CO)<sub>2</sub>{P(OMe)<sub>3</sub>}<sub>2</sub>{C(O)C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>}]<sup>5</sup>) and now in the complexes (1) and (3) there are the first examples of the postulated dimetallo-cycles. Experiments are continuing in an attempt to establish their intermediacy in the synthesis of a variety of organic compounds.

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<sup>1</sup> A. F. Dyke, S. A. R. Knox, P. J. Naish and G. E. Taylor preceding communication.

<sup>2</sup> R. M. Laine and P. C. Ford *J. Organomet. Chem.* 1977, **124**, 29.

<sup>3</sup> D. S. Ginley, C. R. Bock, M. S. Wrighton, B. Fischer, D. L. Tipton and R. Bau *J. Organomet. Chem.* 1978, **157**, 41.

<sup>4</sup> P. Pino and G. Braca in 'Organic Syntheses via Metal Carbonyls', Vol. II, eds I. Wender and P. Pino, Wiley-Interscience, New York, 1977, p. 419, and references therein.

<sup>5</sup> R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. (A)*, 1970, 2981.