Organic Chemistry of Dinuclear Metal Centres. Part 2.[1] Combination of Dimethyl Acetylenedicarboxylate with Carbon Monoxide at a Ditungsten Centre: Crystal Structure of $[W_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(O)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ *

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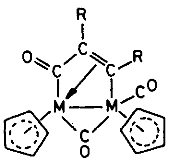
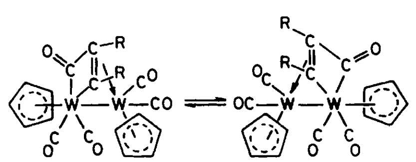
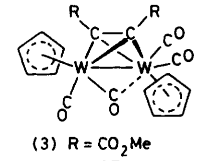
Under u.v. radiation dimethyl acetylenedicarboxylate reacts with $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ to produce $[W_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(O)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ in 55% yield. An *X*-ray diffraction study has revealed that the molecule contains a unique bridging ligand composed of linked alkyne and CO. Crystals are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions a = 9.419(5), b = 8.089(2), c = 14.561(4) Å, α = 91.16(2), β = 81.96(4), and γ = 106.81(3)°. The structure was solved by heavy-atom methods and refined by least squares to R 0.033 for 5 045 diffractometer-measured reflection intensities. The molecule contains a ditungsten unit, one atom of which is part of a metallocyclobutenone ring whose ethylenic bond is η^2-co-ordinated to the other tungsten. The compound is fluxional, n.m.r. spectra identifying a process ($\Delta G^\ddagger$ 77 kJ mol^{-1}) which appears to involve an oscillation of the bridging unit with retention of the alkyne–carbonyl link. Cleavage of this link is evident in the thermal and photochemical instability of the complex with respect to CO liberation and formation of $[W_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)_2]$. The latter is the major product after prolonged irradiation of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with $MeO_2CC_2CO_2Me$, but also formed is $[W_2(CO)_2\{\mu\text{-}C_4(CO_2Me)_4CO\}(\eta\text{-}C_5H_5)_2]$, containing a bridging unit of two alkyne molecules linked *via* CO. Protonation of $[W_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(O)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ with HBF_4 occurs at exocyclic ketonic oxygen to give $[W_2(CO)_4\{\mu\text{-}C(OH)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ quantitatively. The μ-alkyne complex $[W_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)_2]$ reacts in boiling octane with $MeO_2CC_2CO_2Me$ to produce $[W_2\{\mu\text{-}C_8(CO_2Me)_8(\eta\text{-}C_5H_5)_2]$, containing four linked molecules of alkyne bridging the ditungsten centre.

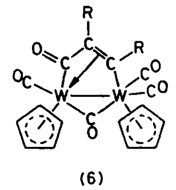
In the previous part [1] of this Series we described the reactions of alkynes with the di-iron and diruthenium complexes $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$. These gave dimetallocycles $[M_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ (1), derived by linking of CO and alkyne, whose chemistry is dominated by the fragility of this link. In an extension of these studies we have investigated the reaction of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with dimethyl acetylenedicarboxylate ($MeO_2CC_2CO_2Me$), finding that linking of CO and alkyne occurs here also, but in a subtly different manner. A preliminary account of this work has appeared.[2]


(1) M = Fe or Ru


(a) (b)

(2) R = CO_2Me


(3) R = CO_2Me
(4) R = CF_3
(5) R = H
(10) R = Ph


(6)

Results and Discussion

U.v. irradiation of a toluene solution of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $MeO_2CC_2CO_2Me$ for a few hours provides a 55% yield of air-stable hydrocarbon-soluble orange crystalline $[W_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(O)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (2) and a 20% yield of the known $[W_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)_2]$ (3). The latter was obtained previously by heating together $[WH(CO)_3(\eta\text{-}C_5H_5)]$ and $MeO_2CC_2CO_2Me$;[3] like $[W_2(CO)_4(\mu\text{-}CF_3C_2CF_3)(\eta\text{-}C_5H_5)_2]$ (4)[4] its spectroscopic properties are indicative of a structure analogous to that established by *X*-ray diffraction for $[W_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ (5).[5]

The i.r. spectrum of (2) revealed that, unlike (3), the complex contained only terminal CO ligands and none of semi-bridging character. In addition to characteristic absorption from the C=O bonds of the CO_2Me groups at 1 693 cm^{-1} there was also, however, a band at 1 601 cm^{-1}. The possibility that this was due to a carbonyl which had linked to the alkyne led us to initiate an *X*-ray diffraction study, which established that this was indeed the case.

The structure of (2) is presented in Figure 1, with the atom-numbering scheme; Figure 2 provides a stereoscopic view of the molecule. Interatomic distances and interbond angles are given in Tables 1 and 2. The molecule is based on two tungsten atoms at a single bond distance, each bearing two terminal carbonyl ligands and a cyclopentadienyl group, with the latter in a mutually *trans* arrangement with respect to the metal–metal axis. The tungsten–tungsten distance of 3.017(1) Å is

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* μ-[1,3-σ 1—2-η-1,2-Bis(methoxycarbonyl)-3-oxopropene-1,3-diyl-$C^{1,3}$:C^{1-2}]-bis[dicarbonyl(η-cyclopentadienyl)tungsten] (*W*–*W*).

Supplementary data available (No. SUP 23338, 27 pp.): thermal, parameters, observed and calculated structure factors, molecular planes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: atm = 101 325 Pa.

Table 1. Interatomic distances (Å) for $[W_2(CO)_4\{\mu-\eta^2:\eta^2-C(O)C_2(CO_2Me)_2\}(\eta-C_5H_5)_2]$ (2) *

W(1)-W(2)	3.017(1)	W(2)-C(16)	2.350(6)
W(1)-C(4)	2.197(6)	W(1)-C(3)	2.782(8)
W(1)-C(7)	2.238(8)	W(2)-C(7)	2.721(8)
W(1)-C(8)	2.015(8)	C(7)-O(5)	1.236(9)
W(1)-C(9)	1.964(8)	C(7)-C(3)	1.455(9)
W(1)-C(17)	2.299(5)	C(3)-C(4)	1.446(10)
W(1)-C(18)	2.303(6)	C(2)-C(3)	1.511(9)
W(1)-C(19)	2.332(6)	C(2)-O(1)	1.327(8)
W(1)-C(20)	2.345(5)	C(2)-O(2)	1.206(9)
W(1)-C(21)	2.325(5)	C(1)-O(1)	1.462(9)
W(2)-C(3)	2.220(7)	C(4)-C(5)	1.483(10)
W(2)-C(4)	2.124(7)	C(5)-O(3)	1.350(9)
W(2)-C(10)	2.002(8)	C(5)-O(4)	1.215(8)
W(2)-C(11)	1.987(8)	C(6)-O(3)	1.455(9)
W(2)-C(12)	2.364(6)	C(8)-O(6)	1.156(10)
W(2)-C(13)	2.341(6)	C(9)-O(7)	1.152(9)
W(2)-C(14)	2.313(6)	C(10)-O(8)	1.143(9)
W(2)-C(15)	2.319(6)	C(11)-O(9)	1.165(9)

* Throughout the tables of crystallographic data, estimated standard deviations are given in parentheses.

Table 2. Interbond angles (°) for (2)

W(2)-W(1)-C(8)	84.7(2)	W(1)-C(4)-C(3)	97.4(4)
W(2)-W(1)-C(9)	80.3(2)	W(1)-C(4)-W(2)	88.5(2)
W(2)-W(1)-C(7)	60.2(2)	C(5)-C(4)-C(3)	127.1(6)
W(2)-W(1)-C(4)	44.7(2)	C(5)-C(4)-W(2)	137.8(5)
C(8)-W(1)-C(9)	85.3(3)	W(2)-C(4)-C(3)	72.4(2)
C(8)-W(1)-C(7)	144.9(3)	C(4)-C(3)-W(2)	67.0(4)
C(8)-W(1)-C(4)	92.4(3)	C(4)-C(3)-C(2)	127.0(6)
C(9)-W(1)-C(7)	89.9(3)	C(4)-C(3)-C(7)	104.8(6)
C(9)-W(1)-C(4)	124.9(3)	W(2)-C(3)-C(2)	120.0(5)
C(7)-W(1)-C(4)	62.4(2)	W(2)-C(3)-C(7)	93.2(4)
W(1)-W(2)-C(10)	88.0(2)	C(2)-C(3)-C(7)	125.4(6)
W(1)-W(2)-C(11)	127.6(2)	C(3)-C(7)-O(5)	129.8(7)
W(1)-W(2)-C(3)	62.0(2)	C(3)-C(7)-W(1)	95.4(5)
W(1)-W(2)-C(4)	46.7(2)	O(5)-C(7)-W(1)	134.7(5)
C(10)-W(2)-C(11)	78.6(3)	C(3)-C(2)-O(2)	123.7(6)
C(10)-W(2)-C(3)	127.5(3)	C(3)-C(2)-O(1)	113.3(6)
C(10)-W(2)-C(4)	89.0(3)	O(1)-C(2)-O(2)	123.0(7)
C(11)-W(2)-C(3)	87.2(3)	C(2)-O(1)-C(1)	116.2(7)
C(11)-W(2)-C(4)	82.3(3)	C(4)-C(5)-O(4)	125.2(7)
C(3)-W(2)-C(4)	78.6(3)	C(4)-C(5)-O(3)	112.8(3)
W(1)-C(8)-O(6)	172.2(7)	O(3)-C(5)-O(4)	122.0(7)
W(1)-C(9)-O(7)	173.8(6)	C(5)-O(3)-C(6)	114.4(6)
W(1)-C(4)-C(5)	118.8(5)		

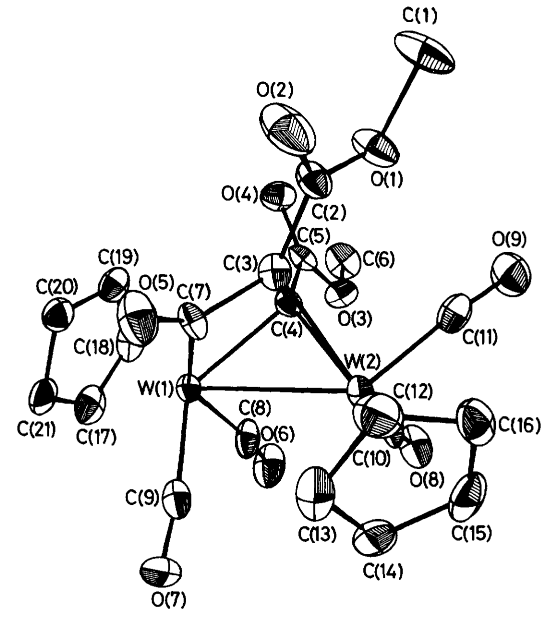


Figure 1. Molecular structure of (2), with atomic numbering scheme. Thermal ellipsoids are constructed at the 50% probability level

considerably shorter than that found in $[W_2(CO)_6(\eta-C_5H_5)_2]$ [3.222(1) Å][6] but near that of the bridged interaction in $[W_2(CO)_4(\mu-HC_2H)(\eta-C_5H_5)_2]$ (5) [2.987(1) Å].[5] Bridging the W-W bond in (2) is a group derived by combination of $MeO_2CC_2CO_2Me$ and CO, such that tungsten W(1) can be seen as a component of a metallocyclobutenone ring $\overline{W(1)-C(7)-C(3)=C(4)}$ which interacts with the other metal atom W(2) *via* the C(3)=C(4) double bond. In this way the bridging group is η^2 bound to each of W(1) and W(2). Bond lengths within the metallocyclobutenone ring are W(1)-C(7) 2.238(8), C(7)-C(3) 1.455(9), C(3)-C(4) 1.446(10), and C(4)-W(1) 2.197(6) Å, and this portion of the molecule, including O(5), is essentially planar; it makes an angle of 86.6° with the plane formed by W(2), C(3), and C(4). The exact nature of the interaction between C(3)-C(4) and W(2) is uncertain because of the severe strain imposed at atoms C(3) and C(4) by the metallocycle, but the considerable rotation of the substituent planes at these two atoms (27.6°) is certainly compatible with loss of π character in a co-ordinated C(3)=C(4) bond according to the classic Chatt-Dewar model.

There are thus three systems now known in which a bridging unit of linked alkyne and CO molecules spans a metal-metal bond. These are (2), the complexes (1), and the dirhodium species $[Rh_2(CO)_2\{\mu-\sigma:\sigma-C(O)C_2(CF_3)_2\}(\eta-C_5H_5)_2]$;[7] the

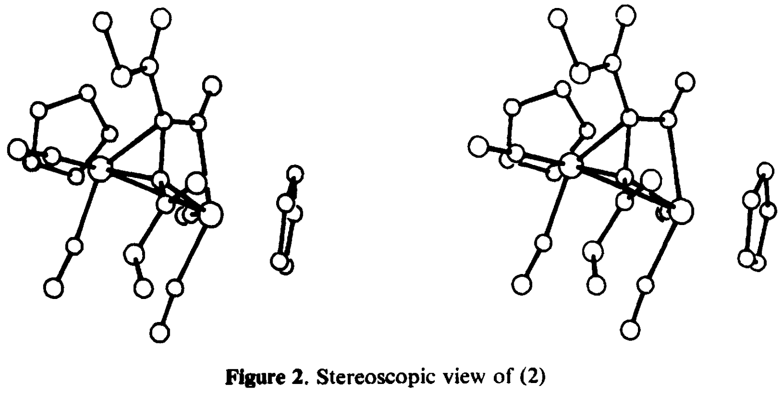
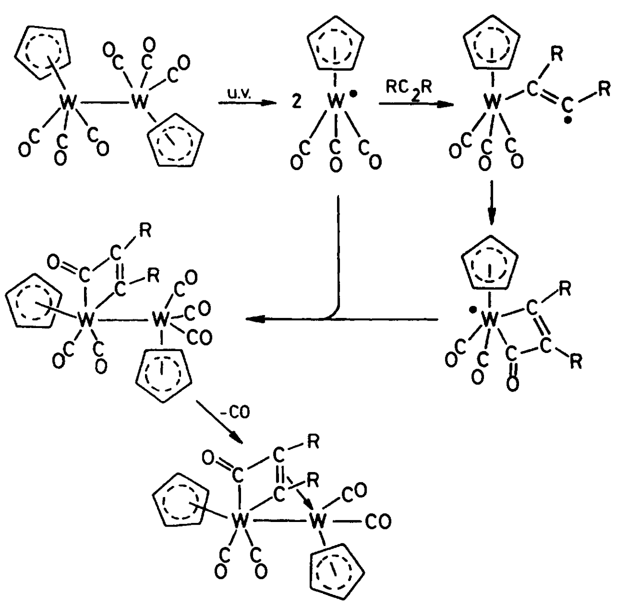
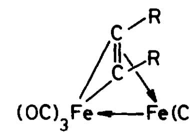


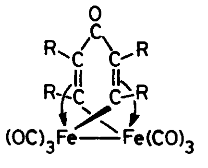
Figure 2. Stereoscopic view of (2)



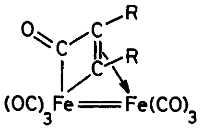
Scheme



(7)



(8)



(9)

latter contains a bridge similar to that in (1), but with the double bond unco-ordinated.

We turn now to the question of why complex (2) adopts the structure it does rather than the one depicted as (6), with the type of $\sigma:\eta^3$-bound bridging ligand found in the iron and ruthenium complexes (1).[1] Two reasons immediately suggest themselves: first, (6) requires a symmetrically bridging carbonyl ligand which is highly disfavoured by the long tungsten–tungsten bond and, secondly, one of the tungstens in (6) is effectively nine-co-ordinate. Further, each metal atom in the tungsten compound must bear an additional carbonyl, when compared with (1), in order to satisfy the 18-electron rule. There is evidence that the extra steric demands these make are also important in favouring structure (2). The existence of steric pressure can be seen in the pair of carbonyls C(8)O(6) and C(10)O(8) (torsion angle 8.3°), which are bowed towards one another such that each W–C–O angle is 172.2(7)°. An examination of a space-filling model reveals that this pressure about the metal atoms pushes the carbonyl carbons together while the oxygen atoms are unaffected. In (2) the cage-like grouping W(1), W(2), C(3), C(4), and C(7) (see Figure 2) occupies only a small portion of the co-ordination spheres of the metals and leaves more space for the extra carbonyl group each tungsten requires than does the undoubtedly less strained grouping in (6).

The primary photoprocess occurring upon u.v. irradiation of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ has been shown to be homolytic fission of the metal–metal bond, generating $[W(CO)_3(\eta\text{-}C_5H_5)_2]$ radicals.[8] We therefore propose that the formation of (2) occurs by the path laid out in the Scheme, a path essentially identical to that which was invoked for the complexes (1), and supported by the existence of mononuclear metallocyclobutenone complexes.

One consequence of structure (2) being adopted rather than (6), analogous to (1), is that the exocyclic ketonic CO is effectively within a four-membered rather than a three-membered ring, explaining the very different i.r. stretching bands of 1 601 cm^{-1} for (2) and *ca.* 1 750 cm^{-1} for the iron and ruthenium complexes (1).

The determination of the structure of (2) resurrects an old problem in alkyne–iron carbonyl chemistry. Hübel [9] observed that $[Fe_2(CO)_9]$ and certain alkynes reacted together to form unstable complexes formulated as $[Fe_2(CO)_7(RC_2R)]$, to which the unlikely structure (7) was assigned. Later it was suggested that the heptacarbonyl formulation was incorrect and that Hübel had, in fact, been dealing with the iron–iron double-bonded μ-alkyne complexes $[Fe_2(CO)_6(\mu\text{-}RC_2R)]$.[10] However, '$[Fe_2(CO)_7(RC_2R)]$' was observed to react with alkynes to afford (8) in high yield, and '$[Fe_2(CO)_7(PhC_2Ph)]$' with methanol to give *trans*-PhCH=C(Ph)CO$_2$Me, reactions which suggest that an alkyne is linked with CO in the complexes. Taken with the established structure of (2), this leads us to propose that there could indeed be di-iron heptacarbonyls, but with structure (9). Their high reactivity would be accounted for by the required iron–iron double bond.

One of the most striking features of the chemistry of the complexes (1) is their fluxionality, which involves rapidly reversible cleavage of the alkyne–carbonyl link. The complex (2) appears also to be fluxional, but with retention of this link. At 30 °C the ^1H n.m.r. spectrum of (2) accords with the structure determined for the solid state in having signals for two inequivalent η-C_5H_5 ligands and two inequivalent CO_2Me groups. On warming, the spectrum becomes complicated by the growth of signals resulting from the decarbonylation of (2) to give (3), but it is clear that the η-C_5H_5 signals coalesce near 65 °C while the CO_2Me group signals remain sharp and distinct up to 85 °C. Above this temperature decarbonylation is rapid. Figure 3 displays the η-C_5H_5 ligand resonance of (2) at temperatures up to and including coalescence. Based on a coalescence temperature of 62 °C, calculation of the free energy of activation of the fluxional process provides a value of 77 kJ mol^{-1}.

These observations require that the η-C_5H_5 ligands exchange their environments on the n.m.r. time-scale and that the CO_2-Me groups do not, which in turn suggests that the alkyne–carbonyl link remains intact in the process. In order to render the η-C_5H_5 ligands equivalent it is then necessary for the tungsten–carbon(ketonic) bond [W(1)–C(7) of Figure 1] to break and for the ketonic carbonyl to be transferred reversibly from one tungsten to the other. Associated movements of the η-C_5H_5 and CO ligands must also occur in this unusual process, which is illustrated as (2a) $\rightleftharpoons$ (2b).

It is possible to envisage another process for the fluxionality of (2) which equally well accounts for the changes in the n.m.r. spectrum. In this, the alkyne–carbonyl link is broken and the ketonic CO becomes terminally bound to W(1), while a terminal carbonyl on W(2) regenerates the alkyne–carbonyl bond specifically with carbon C(3) of the alkyne. A transfer of CO from W(1) to W(2) must occur in association. Such a process is considered unlikely because rupture of the alkyne–carbonyl link has been observed to result in CO elimination

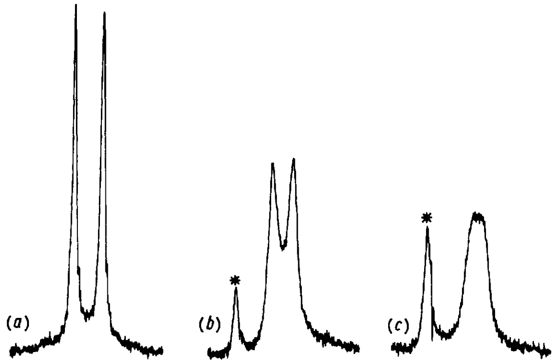
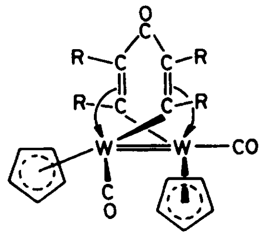


Figure 3. Proton n.m.r. spectrum (η-C_5H_5 signals) of (2) at (*a*) 35, (*b*) 55, and (*c*) 62 °C in [$^2H_5$]pyridine solution. The asterisk denotes the η-C_5H_5 resonance of (3) produced by decarbonylation of (2)

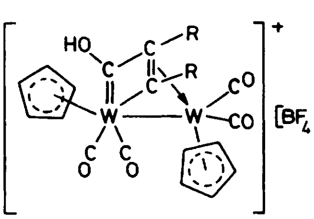


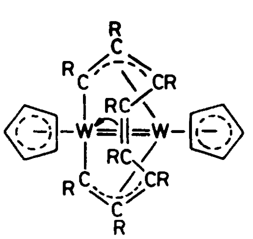
(11) R = CO_2Me

and formation of (3), and because transfer of CO between third-row transition metals is very unfavourable. The thermal instability of (2) thwarted attempts to establish the nature of the fluxional process more firmly using ^{13}C n.m.r. spectroscopy.

High-yield formation of (3) occurs on either brief heating of (2) at hexane reflux temperature or on prolonged u.v. irradiation, and even under 150 atm of CO pressure (3) resists the regeneration of (2). Each of these results may be seen, in the light of the structural determination, as a consequence of the steric pressures in (2). Reactions of other alkynes (HC_2H, PhC_2Ph, and $CF_3C_2CF_3$) with $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ under u.v. irradiation (at −78 °C for $CF_3C_2CF_3$) provided i.r. evidence for the formation of (4), (5), and (10) alone. It is possible that in these cases complexes of type (2) are also formed initially, but that higher thermal instability precludes even their observation.

Prolonged u.v. irradiation of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with $MeO_2CC_2CO_2Me$ for 2 d gives not only a much increased quantity of (3) (50%) and decreased amount of (2) (2%) than is obtained after a few hours, but also a new dark purple crystalline complex $[W_2(CO)_2\{\mu\text{-}C_4(CO_2Me)_4CO\}(\eta\text{-}C_5H_5)_2]$ in 1% yield. On the basis of its i.r. (two strong terminal carbonyl bands) and temperature-independent (down to −90 °C) ^1H n.m.r. (one η-C_5H_5 and two CO_2Me signals of relative intensity 10 : 6 : 6) spectra the complex is assigned the structure (11), with a metal–metal double bond as required by the 18-electron rule. Precedent is available for this form of ' fly-over ' bridging in the structurally established [11] complexes (8) discussed previously;[9] these have a ketonic CO stretching frequency in the i.r. at *ca.* 1 660 cm^{-1}, and a similar absorption is seen for (11) at 1 649 cm^{-1}. It may be noted that the probable formation of (11) from (2) provides another indication that the complexes $[Fe_2(CO)_7(RC_2R)]$, discussed earlier, and which react with alkynes to yield (8), do indeed have the structure (9).





(12) R = CO_2Me (13)

An important reaction of the complexes (1) is protonation, which effects a fission of the alkyne–carbonyl link and formation of synthetically useful cationic μ-vinyl complexes.[12] No such fission occurred upon treating (2) with HBF_4. Instead, quantitative formation of stable yellow crystalline $[W_2(CO)_4\{\mu\text{-}C(OH)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ was observed, isolated as a dichloromethane solvate. Strong evidence for protonation at the ketonic oxygen and, therefore, a structural representation (12), comes from the i.r. spectrum which displays no band near 1 600 cm^{-1} which, by comparison with (2), could be attributed to an exocyclic ketonic bond. Moreover, broad absorption is observed in the region typical of a hydroxyl group. In accord with structure (12) the ^1H n.m.r. spectrum has signals from two CO_2Me groups, but only a single η-C_5H_5 ligand resonance when inequivalent environments are to be expected. On cooling, however, the η-C_5H_5 resonance at δ 5.87 broadens and at −90 °C it is replaced by two sharp signals of equal intensity at δ 6.00 and 6.03, while the CO_2Me signals remain unchanged. The cation (12) is therefore fluxional, like its precursor (2), and a similar process is indicated. No ^{13}C resonance characteristic of the formerly ketonic carbon, now carbene-like, could be clearly identified. Also, no hydroxyl proton resonance was observed in the ^1H n.m.r. spectrum, in this case probably due to rapid exchange with traces of water in the acetone solvent required to dissolve (12). Regeneration of (2) occurs rapidly on treatment of an acetone solution of (12) with $NaHCO_3$, behaviour consistent with (2) being protonated at oxygen, and with little overall structural change. Deprotonation of (12) also occurs with $NaBH_4$, but this reagent produces some decarbonylation to give (3), which is formed quantitatively when an aqueous solution of (12) is boiled briefly.

As might be expected, the reaction of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with $MeO_2CC_2CO_2Me$ in boiling octane affords no (2), but reasonable yields of (3) and a new complex, purple $[W_2\{\mu\text{-}C_8(CO_2Me)_8\}(\eta\text{-}C_5H_5)_2]$, are obtained. The presence of two η-C_5H_5 and four CO_2Me signals (ratio 5 : 5 : 6 : 6 : 6 : 6) in the ^1H n.m.r. spectrum of the latter readily identifies the complex as being of structure (13), like that established by *X*-ray diffraction for the molybdenum analogue.[13] It was shown that (13) is formed *via* (3) by heating the latter with $MeO_2CC_2CO_2Me$ in boiling octane, and it is therefore apparent that the sequential linking of alkynes at dichromium and dimolybdenum centres [14] can equally well be achieved at a ditungsten centre. Efforts to intercept tungsten complexes containing two and three linked molecules of $MeO_2CC_2CO_2Me$ as intermediates between (3) and (13) were unsuccessful. Even at short reaction times only (13) was observed as a product and it is clear that such intermediates must be traversed very rapidly.

Experimental

Techniques and instrumentation were as described in Part 1 of this Series.[1] U.v. irradiation was with a 250-W mercury lamp, the solutions being held in a silica glass vessel. Chromatography was on silica. The complex $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ was prepared by a literature method.[15]

Reactions of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ *with Dimethyl Acetylenedicarboxylate*.—(*a*) A toluene (150 cm^3) solution of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (2 g, 3 mmol) and $MeO_2CC_2CO_2Me$ (1.4 g, 9.8 mmol) was subjected to u.v. radiation for 3 h. After removal of solvent under reduced pressure, chromatography, eluting with dichloromethane, gave an orange band from which 0.48 g (20%) of known [3] orange crystalline (3) was obtained, identified through its i.r., ^{1}H n.m.r., and mass spectra and analyses (Found: C, 32.7; H, 2.5%; *M*, 752. $C_{20}H_{16}O_8W_2$ requires C, 31.9; H, 2.1%; *M*, 752). Further elution with dichloromethane–acetone (1 : 1) developed a yellow band which provided 1.2 g (55%) of orange crystalline (2) {m.p. 135—145 °C (decomp.); ν(CO) (CH_2Cl_2) 2 026s, 1 979s, 1 906m, 1 693m, and 1 601m cm^{-1}; ^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.) 3.68 (s, 3 H, CO_2Me), 3.74 (s, 3 H, CO_2Me), 5.24 (s, 5 H, C_5H_5), and 5.34 (s, 5 H, C_5H_5); ^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.) 5.13 (Me), 52.3 (Me), 74.7 (*C*CO_2Me), 89.7 (C_5H_5), 93.8 (C_5H_5), 105.4 (*C*CO_2Me), 171.0 (CO_2Me), 176.9 (*C*O_2Me), 193.5 (WC=O), 207.6 (CO), 210.4 (CO), 213.6 (CO), and 222.3 (CO). Found: C, 32.0, H, 2.2%; *M*, 752 [(P − CO)$^+$]. $C_{21}H_{16}O_9W_2$ requires C, 32.3; H, 2.1%; *M*, 780}.

(*b*) An identical reaction mixture, irradiated for 2 d, gave 1.2 g (50%) of (3) and 35 mg (2%) of (2) after chromatography, but also, on elution with dichloromethane, a purple band which contained 20 mg (1%) of purple-black powdery (11) [m.p. >200 °C; ν(CO) (CH_2Cl_2) 2 029s, 1 959s, 1 694m, and 1 649m cm^{-1}; ^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.) 3.57 (s, 6 H, 2CO_2Me), 3.68 (s, 6 H, 2CO_2Me), and 5.55 (s, 10 H, 2C_5H_5). Found: C, 32.0; H, 2.5%; *M*, 866. $C_{25}H_{22}O_{11}W_2$ requires C, 34.6; H, 2.5%; *M*, 866].

(*c*) A mixture of $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (2 g, 3 mmol) and $MeO_2CC_2CO_2Me$ (1.4 g, 9.8 mmol) was heated in boiling octane (170 cm^3) for 10 d. Chromatography, eluting with dichloromethane–acetone (5 : 1), then gave a yellow band which afforded 0.31 g (14%) of orange crystalline (3). This was followed, on elution with dichloromethane–acetone (3 : 1), by a faint pink band (uncharacterised) and a purple band. The latter yielded 0.25 g (8%) of (13) as a purple powder [m.p. >200 °C; ν(CO) (CH_2Cl_2) 1 721s and 1 701s m^{-1}; ^{1}H n.m.r. ($CDCl_3$), δ (p.p.m.) 3.58 (s, 6 H, 2CO_2Me), 3.62 (s, 6 H, 2CO_2Me), 3.77 (s, 6 H, 2CO_2Me), 4.04 (s, 6 H, 2CO_2Me), 5.34 (s, 5 H, C_5H_5), and 5.36 (s, 5 H, C_5H_5); ^{13}C n.m.r. ($CDCl_3$), δ (p.p.m.) 51.1 (2Me), 52.0 (2Me), 52.5 (2Me), 53.5 (2Me), 56.0 (2*C*CO_2Me), 64.4 (2*C*CO_2Me), 97.2 (C_5H_5), 103.0 (C_5H_5), 109.1 (2*C*CO_2Me), 159.1 (2*C*CO_2Me), 169.0 (2*C*O_2Me), 174.9 (4*C*O_2Me), and 177.2 (2*C*O_2Me). Found: C, 39.0; H, 3.5%; *M*, 1 066. $C_{34}H_{34}O_{16}W_2$ requires C, 38.3; H, 3.2%; *M*, 1 066].

Reactions of $[W_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(O)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (2).—*Conversion into* (3). Either heating a hexane solution of (2) to boiling for 1 h or subjecting it to u.v. irradiation overnight resulted in high-yield formation of (3).

Protonation. Dropwise addition of HBF_4 [1 cm^3 of 40% aqueous solution in acetone (20 cm^3)] to a solution of (2) (0.13 g, 0.17 mmol) in acetone (150 cm^3), followed by evaporation and recrystallisation from dichloromethane, yielded 0.15 g (97%) of yellow crystalline (12) as a CH_2Cl_2 solvate {m.p. >200 °C; ν(CO) (CH_2Cl_2) 2 061vs, 2 025vs, 1 962s, 1 713m, and 1 685m cm^{-1}; ^{1}H n.m.r. ([$^2H_6$]acetone) (30 °C), δ (p.p.m.) 3.68 (s, 3 H, Me), 3.72 (s, 3 H, Me), 5.60 (s, 2 H, CH_2Cl_2), and 5.87 (s, 10 H, 2C_5H_5); ^{13}C n.m.r. ([$^2H_6$]acetone) (−80 °C), δ (p.p.m.) 51.5 (Me), 52.3 (Me), 73.0 (*C*CO_2Me), 90.1 (C_5H_5), 95.5 (C_5H_5), 111.4 (*C*CO_2Me), 167.7 (*C*O_2Me), 174.0 (*C*O_2Me), 197.7 (CO), 202.1 (CO), 209.4 (CO), and 215.4 (CO). Found: C, 27.6; H, 2.0; Cl, 7.0%. $C_{22}H_{19}BCl_2F_4O_9W_2$ requires C, 27.7; H, 2.0; Cl, 7.4%}.

Table 3. Atomic positional (fractional co-ordinates) parameters for (2)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W(1)	0.467 3(1)	0.323 7(1)	0.193 5(1)
W(2)	0.168 8(1)	0.050 2(1)	0.227 4(1)
C(1)	−0.137 4(11)	0.328 6(14)	0.450 2(6)
C(2)	0.037 6(8)	0.359 1(9)	0.313 4(5)
C(3)	0.176 6(8)	0.319 6(9)	0.265 4(5)
C(4)	0.280 8(8)	0.255 9(9)	0.308 0(5)
C(5)	0.314 4(8)	0.282 6(9)	0.404 7(4)
C(6)	0.405 8(11)	0.180 9(13)	0.528 3(5)
C(7)	0.257 8(8)	0.390 0(9)	0.175 6(5)
C(8)	0.550 9(9)	0.136 1(10)	0.230 7(6)
C(9)	0.466 6(8)	0.215 0(9)	0.071 7(5)
C(10)	0.272 8(8)	−0.101 8(10)	0.280 4(6)
C(11)	0.039 4(9)	−0.023 5(9)	0.348 0(5)
C(12)	−0.000 7(6)	0.058 9(6)	0.123 6(4)
C(13)	0.136 6(6)	0.053 2(6)	0.071 0(4)
C(14)	0.161 7(6)	−0.105 7(6)	0.092 3(4)
C(15)	0.040 0(6)	−0.198 1(6)	0.158 1(4)
C(16)	−0.060 4(6)	−0.096 3(6)	0.177 4(4)
C(17)	0.715 3(5)	0.482 2(7)	0.168 2(4)
C(18)	0.660 7(5)	0.498 4(7)	0.262 9(4)
C(19)	0.549 8(5)	0.586 6(7)	0.266 4(4)
C(20)	0.535 9(5)	0.624 9(7)	0.174 0(4)
C(21)	0.638 2(5)	0.560 4(7)	0.113 2(4)
O(1)	−0.000 4(7)	0.301 1(8)	0.400 6(4)
O(2)	−0.031 6(7)	0.437 3(9)	0.276 9(4)
O(3)	0.352 7(7)	0.149 8(7)	0.438 6(3)
O(4)	0.312 2(7)	0.410 2(7)	0.449 7(4)
O(5)	0.218 0(6)	0.461 5(7)	0.113 7(4)
O(6)	0.614 6(8)	0.041 0(8)	0.248 2(5)
O(7)	0.477 3(8)	0.163 4(7)	−0.002 6(4)
O(8)	0.316 2(7)	−0.201 0(8)	0.313 5(5)
O(9)	−0.039 2(8)	−0.079 8(8)	0.416 1(4)

Reactions of $[W_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)_2]$ (3) *with Dimethyl Acetylenedicarboxylate*.—A mixture of (3) (0.5 g, 0.67 mmol) and $MeO_2CC_2CO_2Me$ (0.9 g, 6.7 mmol) was heated in boiling octane (60 cm^3) for 4 d. Chromatography then gave, on elution with dichloromethane–hexane (1 : 4), an orange band due to unreacted (3) and, with dichloromethane–acetone (1 : 2), a purple band from which 50 mg (7%) of purple powdery (13) was obtained.

With CO. An acetone solution of (3) was subjected to 150 atm of CO pressure at 70 °C for 12 h without any change being effected. Decomposition of (3) did occur under 300 atm of CO pressure at 130 °C for 12 h, but no products were isolated.

X-Ray Data Collection and Structure Determination.—A crystal of $[W_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(O)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (2) of dimensions 0.24 × 0.21 × 0.08 mm was mounted and centred on a Syntex $P2_1$ diffractometer according to methods described earlier.[16] After cooling to 240 K, and recentring of the crystal, 6 170 independent reflections were measured in the range $2.9 \leqslant 2\theta \leqslant 60°$; of these 5 045 were deemed observed according to the criterion $I \geqslant 3.0\sigma(I)$ and were retained for subsequent structure solution and refinement.

Crystal data. $C_{21}H_{16}O_9W_2$, *M* 779.7, Triclinic, space group $P\bar{1}$, $a = 9.419(5)$, $b = 8.089(2)$, $c = 14.561(4)$ Å, $\alpha = 91.16(2)$, $\beta = 81.96(4)$, $\gamma = 106.81(3)°$, $U = 1\,051.3(7)$ Å^3, $D_m = 2.44$ g cm^{-3}, $Z = 2$, $D_c = 2.46$ g cm^{-3}, $F(000) = 724$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 105.2 cm^{-1}.

The intensities were corrected for the effects of decay, *X*-ray absorption, Lorentz, and polarisation. All computation was carried out on the South Western Universities network using the SHELX-76 system of programs.[17]

The location of the tungsten atoms in a Patterson map provided sufficient phasing information to allow subsequent location of all the other non-hydrogen atoms. A further map provided some of the hydrogen atoms of the cyclopentadienyl rings but not the methyl hydrogens. The carbon and hydrogen atoms of the cyclopentadienyl rings were refined as rigid groups of D_{5h} symmetry with C–C 1.396 and C–H 1.08 Å. All non-hydrogen atoms were refined with anisotropic thermal parameters. The reflections were assigned weights according to the scheme $w = 1.30[\sigma^2(F_o) + 0.0007|F_o|^2]^{-1}$ to equate, as far as possible, the sums of the variances for different classes of reflections sorted on $|F_o|$. The full-matrix least-squares refinements converged at R 0.033 (R' 0.031). The final electron-density synthesis showed several peaks with densities of between 2.0 and 4.0 e Å^{-3} in the vicinity of the metal atoms. These were presumed to arise from absorption effects and the general residual level of the difference density was $<$1.0 e Å^{-3}. Atomic scattering factors were those of ref. 18 for hydrogen and ref. 19 for all other atoms. Corrections for the real and imaginary parts of anomalous scattering were applied for all atoms.[20] Table 3 lists the derived atomic co-ordinates.

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