Cleavage of M≡C (M = Mo or W) Bonds in the Formation of the Complexes $[Fe_2M(\mu\text{-}C_2R)(CO)_8(\eta\text{-}C_5H_5)]$: *X*-Ray Crystal Structure of $[Fe_2W(\mu\text{-}C_2C_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$

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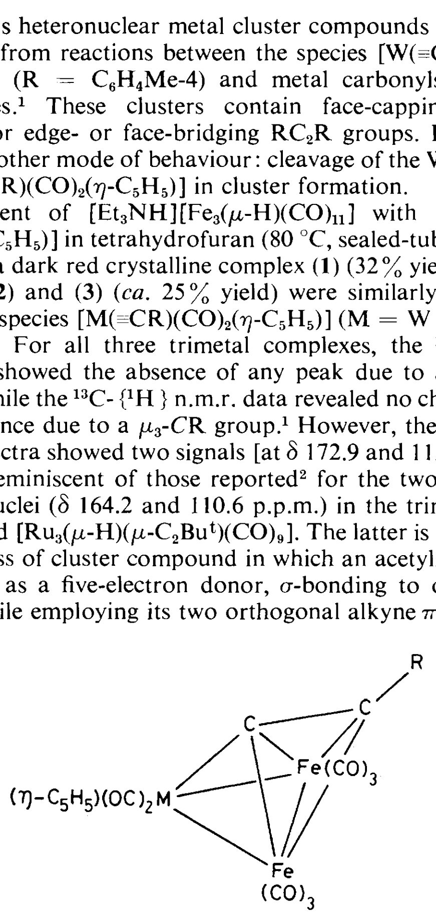
The compounds $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Mo, R = Me; M = W, R = Me or C_6H_4Me-4) react with $[Et_3NH][Fe_3(\mu\text{-}H)(CO)_{11}]$ in tetrahydrofuran at 80 °C to afford bridged-acetylide complexes $[Fe_2M(\mu\text{-}C_2R)(CO)_8(\eta\text{-}C_5H_5)]$; the structure of the species M = W and R = C_6H_4Me-4 has been established by *X*-ray diffraction.

Numerous heteronuclear metal cluster compounds have been obtained from reactions between the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) and metal carbonyls or their derivatives.[1] These clusters contain face-capping μ_3-CR ligands, or edge- or face-bridging RC_2R groups. Herein we report another mode of behaviour: cleavage of the W≡C bond of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ in cluster formation.

Treatment of $[Et_3NH][Fe_3(\mu\text{-}H)(CO)_{11}]$ with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ in tetrahydrofuran (80 °C, sealed-tube, 4 days) afforded a dark red crystalline complex (**1**) (32% yield). Compounds (**2**) and (**3**) (*ca.* 25% yield) were similarly obtained using the species $[M(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = W or Mo) as reactants. For all three trimetal complexes, the ^1H n.m.r. spectra† showed the absence of any peak due to a hydrido ligand, while the ^{13}C-{^1H} n.m.r. data revealed no characteristic resonance due to a μ_3-CR group.[1] However, the ^{13}C-{^1H} n.m.r. spectra showed two signals [at δ 172.9 and 112.7 p.p.m. for (**1**)] reminiscent of those reported[2] for the two acetylide carbon nuclei (δ 164.2 and 110.6 p.p.m.) in the triruthenium compound $[Ru_3(\mu\text{-}H)(\mu\text{-}C_2Bu^t)(CO)_9]$. The latter is a member of the class of cluster compound in which an acetylide ligand functions as a five-electron donor, σ-bonding to one metal centre while employing its two orthogonal alkyne π-bonds to bridge an edge of the metal–metal triangle.[3] In order to establish the structures of (**1**)—(**3**) an *X*-ray diffraction study was carried out on (**1**).



	M	R
(**1**)	W	C_6H_4Me-4
(**2**)	W	Me
(**3**)	Mo	Me

The molecular configuration is shown in Figure 1 with the molecular dimensions.‡ The WFe_2 triangle is near-isosceles, while the *p*-tolylethyne moiety is σ-bonded to the W atom but also forms a transverse bridge over the Fe–Fe bond. Each Fe atom carries three approximately mutually orthogonal terminal CO ligands; the W atom carries the cyclopentadienyl ring and two terminal CO ligands of which one lies approximately perpendicular to the metal atom plane. The asymmetric unit of the crystal structure comprises two molecules, and although these are closely similar in their bond distances, they are markedly different in the torsion angles relating to peripheral groups. In neither molecule are the $Fe(CO)_3$ moieties

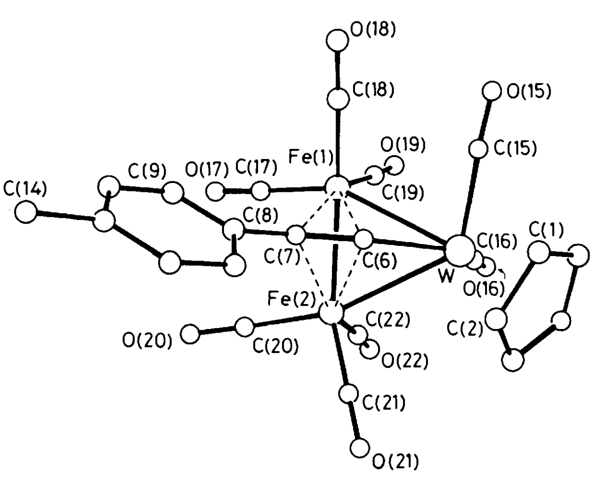


Figure 1. Molecular structure of one of the independent molecules of $[Fe_2W(\mu\text{-}C_2C_6H_4Me\text{-}4)(CO)_8(\eta\text{-}C_5H_5)]$. Dimensions: W–Fe(1) 2.897(2), W–Fe(2) 2.874(3), Fe(1)–Fe(2) 2.503(3), W–C(6) 1.999(15), Fe(1)–C(6) 2.025(11), Fe(2)–C(6) 2.011(11), Fe(1)–C(7) 2.091(13), Fe(2)–C(7) 2.086(12), C(6)–C(7) 1.30(2), C(7)–C(8) 1.47(2) Å; W–C(6)–C(7) 163, C(6)–C(7)–C(8) 141°.

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† Selected spectroscopic data [i.r. measured in cyclohexane, n.m.r. in $CDCl_3$ (^1H) or CD_2Cl_2–CH_2Cl_2 (^{13}C-{^1H}), unless otherwise stated]: (**1**), i.r. ν_{CO} 2 064m, 2 057s, 2 021s, 2 009vs, 2 002vs, 1 987m(br.), 1 959m, and 1 945m cm^{-1}; n.m.r.: ^1H [$(CD_3)_2CO$], δ 2.38 (s, 3 H, 4-Me), 6.01 (s, 5 H, C_5H_5), and 7.28 and 7.62 [$\{AB\}_2$ quart., 4 H, C_6H_4, *J*(AB) 8 Hz]; ^{13}C-{^1H}, δ 212.9 (3 × CO, FeCO), 208.3 [1 × CO, WCO, *J*(WC) 180 Hz], 172.9 (W*C*CR), 139.3, 131.6, 129.8 (C_6H_4), 112.7 (WC*C*R), 88.8 (C_5H_5), and 21.6 p.p.m. (Me-4). (**2**), i.r. ν_{CO} 2 064(sh), 2 057s, 2 014(sh), 2 008vs, 1 999s, 1 985m(br.), 1 961m, and 1 943m cm^{-1}; n.m.r.: ^1H, δ 2.88 (s, 3 H, Me) and 5.57 (s, 5 H, C_5H_5); ^{13}C-{^1H}, δ 213.1 (3 × CO, FeCO), 208.6 [1 × CO, WCO, *J*(WC) 171 Hz], 165.7 (W*C*CMe), 108.3 (WC*C*Me), 88.2 (C_5H_5), and 18.0 p.p.m. (Me). (**3**), i.r. ν_{CO} 2 065s, 2 058w, 2 019vs, 2 009m, 2 001vs, 1 987m, 1 959m, and 1 946vw cm^{-1}; n.m.r.: ^1H, δ 2.97 (s, 3 H, Me) and 5.30 (s, 5 H, C_5H_5); ^{13}C-{^1H}, δ 227.6 and 223.6 (1 × CO, MoCO), 214.1 and 212.8 (3 × CO, FeCO), 181.8 (Mo*C*CMe), 95.9 (MoC*C*Me), 92.0 (C_5H_5), and 21.2 p.p.m. (Me).

‡ *Crystal data* for (**1**): $C_{22}H_{12}Fe_2O_8W$, M = 699.9, triclinic, a = 11.511(5), b = 12.121(7), c = 17.247(10) Å, α = 90.60(5), β = 99.77(5), γ = 109.91(4)°, U = 2 223(2) Å^3, D_m not measured, Z = 4, D_c = 2.09 g cm^{-3}, $F(000)$ = 1 336. Space group $P\bar{1}$ (No. 2), Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 65.9 cm^{-1}. Intensities [6 496 with $I \geqslant 3\sigma(I)$] were measured on a Nicolet *P*3*m* four-circle diffractometer at room temperature and corrected for Lorentz, polarisation, and absorption effects. Structure refined to R 0.065 (R' 0.062) by blocked cascade least squares.

The atomic co-ordinates 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.

precisely eclipsed when viewed along the Fe–Fe bond, and the two molecules differ from one another by some 20° in the orientation of the $W(CO)_2(\eta\text{-}C_5H_5)$ moiety relative to the rest of the molecule. Furthermore, the *p*-tolyl group adopts a different twist in the two molecules, neither symmetrical.

The establishment of the structure of (**1**) allows discussion of the $^{13}C\text{-}\{^1H\}$ n.m.r. data.† The pattern of CO signals for (**1**) and (**2**) is not consistent with the solid state structure of the former, which has no plane of symmetry. A dynamic process is evidently causing the two tungsten-bonded CO ligands to become equivalent on the n.m.r. timescale. The data can be explained by proposing that the $W(CO)_2(\eta\text{-}C_5H_5)$ moiety rotates around an axis through the tungsten atom and a triangular face formed by C(6)Fe(1)Fe(2). The spectra are unchanged at −90 °C, so this process must have a low activation energy. Structural evidence for the existence of rotamers involving the $W(CO)_2(\eta\text{-}C_5H_5)$ group is provided by the abovementioned observation of significantly different torsion angles in the two independent molecules of (**1**) in the unit cell, suggesting extreme molecular flexibility. The proposed rotation, previously also invoked to account for the n.m.r. data for $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ and $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$,[1] also causes the two sets of carbonyls on the iron atoms to appear equivalent in the n.m.r. spectrum; but to explain the observed singlet resonance a further dynamic process involving site exchange of CO groups on the iron atoms must occur. Interestingly, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**3**) shows two distinct resonances for the molybdenum-bound CO groups and one peak for each $Fe(CO)_3$ group. Evidently rotation of the $Mo(CO)_2(\eta\text{-}C_5H_5)$ moiety does not occur, although site exchange of CO on Fe takes place.

In order to demonstrate that the M≡C bonds are broken in these reactions, complex (**2**) was prepared using $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ having both the alkylidyne carbon and CO ligands ^{13}C enriched. Examination of the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of the labelled product (**2**) showed that the resonance for the acetylide–carbon bonded to the Me group retained its enrichment, but the peaks due to the μ_3-C acetylide carbon and the CO ligands were all enriched to a much lesser extent. Evidently a complete scrambling of CO groups between tungsten and iron takes place before the acetylide cluster is formed, and also the μ_3-C atom is derived from a CO ligand.

Formation of acetylenic linkages from CO and carbyne groups on metal centres has not been previously reported, but may be related to certain heterogeneous reactions involving CO reduction.

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