Reactions Between μ-Alkylidyne Iron–Molybdenum Complexes and But-2-yne: Unusually Facile C–C Bond Forming Processes Accompanied by Hydrogen Migration Between Carbon Centres

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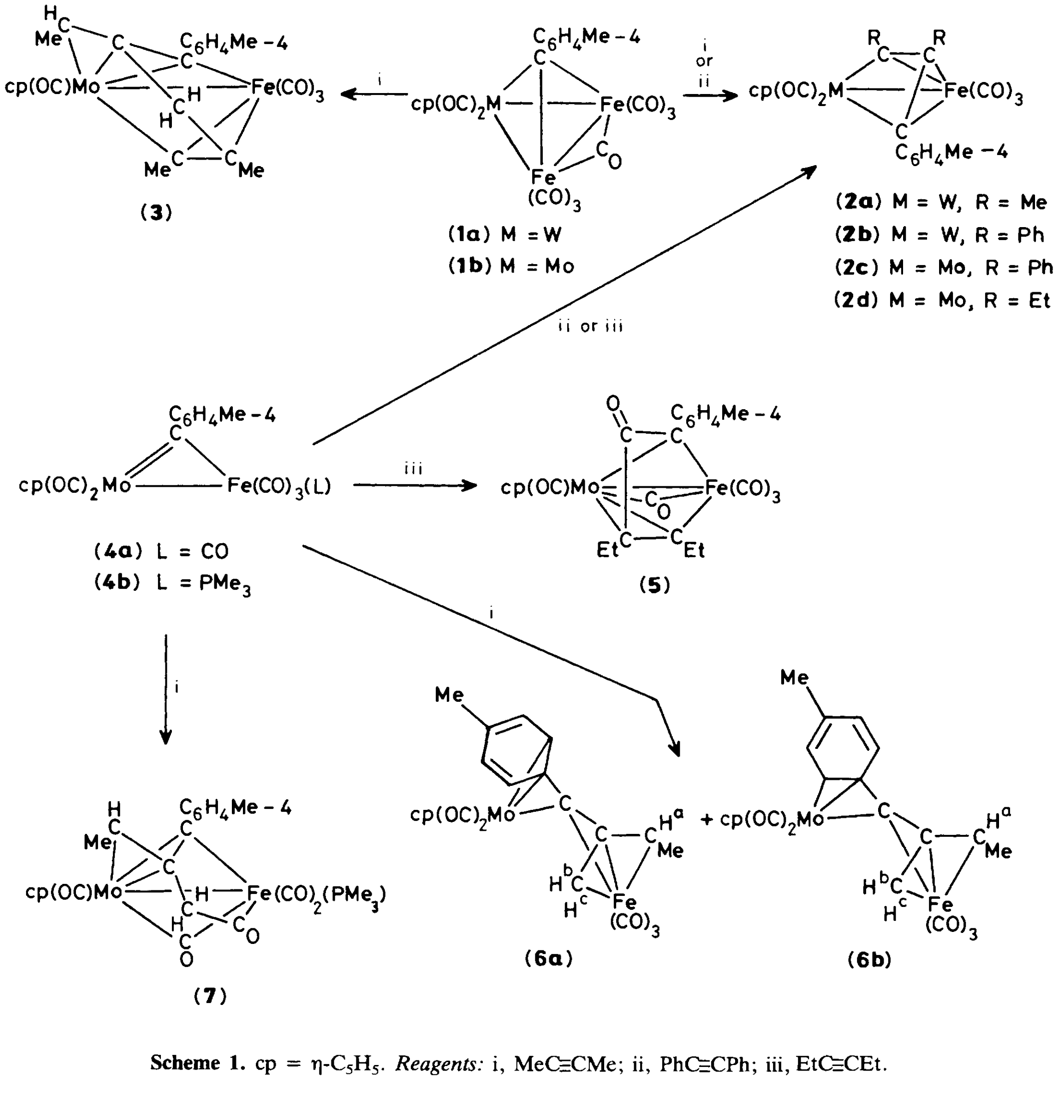
The molybdenum–di-iron complex [MoFe$_2$(μ_3-CR)(μ-CO)(CO)$_8$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4) (**1b**) reacts with MeC≡CMe to give [FeMo{μ-C(R)$\overline{\mathrm{C(CHMe)C}}H_2$C(Me)C(Me)}(CO)$_4$($\eta$-C$_5H_5$)] (**3**), while the dimetal compound [FeMo(μ-CR)(CO)$_6$(η-C$_5$H$_5$)] affords with EtC≡CEt and MeC≡CMe the complexes [FeMo{μ-C(R)C(O)C(Et)C(Et)}(μ-CO)(CO)$_4$(η-C$_5$H$_5$)] (**5**) and [FeMo{μ-C(R)$\overline{\mathrm{C(CHMe)C}}H_2$}(CO)$_5$($\eta$-C$_5H_5$)] (**6**) respectively; the structures of (**3**), (**5**), and (**6**) have been established by *X*-ray diffraction.

There is currently general interest in the reactions of hydrocarbon fragments bonded simultaneously to two or to three metal centres.[1] If these groups link different transition elements there is the possibility of observing ligand transformations not found with homopolynuclear metal species. The presence in close proximity of two or more metal centres possessing their own unique bonding properties should result in unusual reactivity towards substrate molecules. Herein we report unprecedented reactions of but-2-yne with complexes having iron–molybdenum bonds.

The tungsten–di-iron complex (**1a**) is known to react in toluene at 80 °C with the alkynes RC≡CR (R = Me or Ph) to give the dimetal compounds (**2a**) and (**2b**) (Scheme 1); an iron carbonyl fragment being released in these processes.[2] Compound (**1b**), the molybdenum analogue of (**1a**), also reacts with PhC≡CPh under similar conditions to yield the related



Scheme 1. cp = η-C$_5$H$_5$. *Reagents:* i, MeC≡CMe; ii, PhC≡CPh; iii, EtC≡CEt.

species (**2c**).† In contrast, however, (**1b**) and MeC≡CMe at room temperature afford complex (**3**),† the structure of which (Figure 1) has been established by an *X*-ray diffraction study.‡ Formation of (**3**) results from a coupling of the tolylmethylidyne ligand in (**1b**) with two molecules of but-2-yne, together with hydrogen migration from a C*Me* group to a *C*Me carbon atom.

The ready availability of the complexes (**4**)[3] allowed examination of the reactions of these heteronuclear dimetal

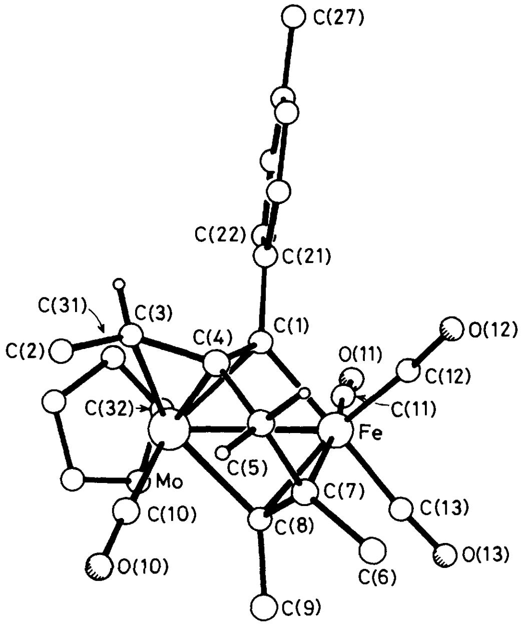


Figure 1. Molecular structure of [FeMo{μ-C(C_6H_4Me-4)-C(CHMe)CH$_2$C(Me)C(Me)}(CO)$_4$(η-C_5H_5)] (**3**). Dimensions Mo–Fe 2.784(1), Mo–C(1) 2.172(3), Mo–C(3) 2.337(4), Mo–C(4) 2.204(3), Mo–C(8) 2.176(3), Fe–C(1) 1.999(3), Fe–C(7) 2.172(3), Fe–C(8) 2.056(3), C(1)–C(4) 1.435(4), C(3)–C(4) 1.429(4), C(7)–C(8) 1.415(4) Å; C(1)–C(4)–C(3) 111.8(2), C(3)–C(4)–C(5) 130.1(3), C(1)–C(4)–C(5) 117.2(3), C(1)–Mo–C(4) 38.3(1), C(3)–Mo–C(4) 36.5(1), C(7)–Fe–C(8) 39.0(1), Mo–C(1)–C(21) 127.6(2), Fe–C(1)–C(21) 125.3(2)°.

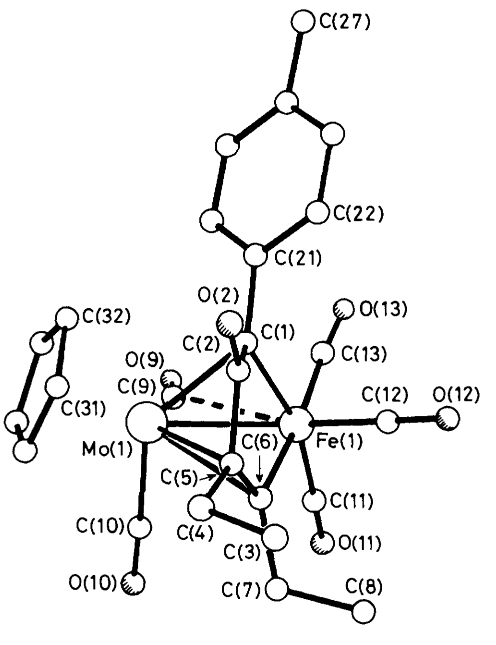


Figure 2. Molecular structure of [FeMo{μ-C(C_6H_4Me-4)C(O)-C(Et)C(Et)}(μ-CO)(CO)$_4$(η-C_5H_5)] (**5**). Dimensions Mo(1)–Fe(1) 2.694(1), Mo(1)–C(1) 2.244(7), Mo(1)–C(5) 2.441(7), Mo(1)–C(6) 2.390(7), Mo(1)–C(9) 2.021(9), Fe(1)–C(1) 2.006(7), Fe(1)–C(6) 1.984(8), Fe(1) · · · C(9) 2.55, C(1)–C(2) 1.478(11), C(2)–O(2) 1.259(9), C(2)–C(5) 1.506(11), C(5)–C(6) 1.384(10) Å; C(1)–Mo(1)–C(6) 68.3(3), C(1)–Fe(1)–C(6) 81.5(3), C(1)–C(2)–O(2) 127.7(7), C(5)–C(2)–O(2) 122.4(7), Mo(1)–C(9)–O(9) 164.2(8)°.

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† Selected spectroscopic data, with i.r. measurements in light petroleum unless otherwise stated. For n.m.r. data the chemical shifts are in p.p.m. and coupling constants are in Hz with ^{1}H spectra recorded in CD_2Cl_2 and ^{13}C{^{1}H} spectra in CD_2Cl_2–CH_2Cl_2. Compound (**2c**) (red), ν_{CO}(max) at 2 051vs, 1 992s, 1 966w, and 1 940w cm^{-1}; compound (**2d**) (red), ν_{CO}(max) at 2 048, 1 988s, 1 958w, and 1 937w cm^{-1}; compound (**3**) (green), ν_{CO}(max) at 2 031vs, 1 979s, 1 955m, and 1 924s cm^{-1}; n.m.r., ^{1}H, δ 1.57 [d, 3 H, CH*Me*, *J*(HH) 6], 1.74 (s, 3 H, CMe), 2.29 (s, 3 H, Me-4), 2.40 [q, 1 H, C*H*Me, *J*(HH) 6], 2.47 [d, 1 H, CH_2, *J*(HH) 15], 2.95 [d, 1 H, CH_2, *J*(HH) 15], 3.00 (s, 3 H, μ-CMe), 5.45 (s, 5 H, C_5H_5), and 6.99, 7.13 [(AB)$_2$, 4 H, C_6H_4, *J*(AB) 8]; ^{13}C{^{1}H}, δ 234.4 (MoCO), 213.5 (FeCO), 212.0 (μ-*C*Me), 185.7 (μ-*C*C_6H_4Me-4), 149.5, 136.3, 130.8, 128.3 (C_6H_4), 102.8 (C), 98.1 (*C*Me), 95.5 (C_5H_5), 48.9 (*C*HMe), 45.8 (CH_2), 33.8 (μ-C*Me*), 23.5 (C*Me*), 21.1 (Me-4), and 18.5 (CH*Me*). Compound (**5**) (yellow), ν_{CO}(max) at 2 058s, 1 997w, 1 977w, 1 885w, and 1 599w cm^{-1}; ^{13}C {^{1}H} n.m.r. ($CDCl_3$), δ 239.2, 226.0 (MoCO), 207.1 (FeCO), 186.2 (C=O), 183.4 (*C*Et), 147.4, 134.8 (C_6H_4), 136.6 (μ-*C*C_6H_4Me-4), 129.2 (μ-*C*Et), 128.3, 128.1 (C_6H_4), 95.3 (C_5H_5), 38.6, 24.8 (*C*H$_2$Me), 21.1 (Me-4), 19.6 and 15.1 (CH$_2$*Me*). Compound (**6**) (red), ν_{CO}(max) at 2 041s, 1 979s, 1 968s, 1 958vs, and 1 892s cm^{-1}; ^{1}H n.m.r., (**6a**), δ 1.57 [d, 3 H, CH*Me*, *J*(H^{a}H) 7], 2.29 (s, 3 H, Me-4), 2.73 [d, 1 H^b, CH_2, *J*(H^{a}H^b) 1], 2.82 (s, 1 H^c, CH_2), 3.90 [d of q, 1 H^a, C*H*Me, *J*(HH^a) 7, *J*(H^{b}H^a) 1], 5.48 (s, 5H, C_5H_5), 5.70 (m, 1 H, C_6H_4), and 6.98 (m, 3 H, C_6H_4); (**6b**), δ 1.44 [d, 3 H, CH*Me*, *J*(H^{a}H) 7], 2.29 (s, 3 H, Me-4), 2.88 [d, 1 H^b, CH_2, *J*(H^{a}H^b) 1], 2.96 (s, 1 H^c, CH_2), 3.61 [d of q, 1 H^a, C*H*Me, *J*(HH^a) 7, *J*(H^{b}H^a) 1], 5.48 (s, 5 H, C_5H_5), 5.70 (m, 1 H, C_6H_4), and 6.98 (m, 3 H, C_6H_4). Compound (**7**) (orange), ν_{CO}(max) at 2 000s, 1 933s, 1 783wbr, and 1 606wbr cm^{-1} (CH_2Cl_2); ^{13}C {^{1}H} n.m.r. (−60 °C), δ 279.1 [d, C=O, *J*(PC) 29], 254.2 [d, μ-CO, *J*(PC) 6], 234.2 (MoCO), 214.6 [d, FeCO, *J*(PC) 15], 208.1 [d, FeCO, *J*(PC) 13], 177.2 [d, μ-*C*C_6H_4Me-4, *J*(PC) 20], 152.6, 135.8, 133.1, 129.7, 128.5, 126.2 (C_6H_4), 110.0 (C), 97.8 (C_5H_5), 66.3 (*C*HMe), 57.3 (CH_2), 21.3 (Me-4), 17.6 [d, MeP, *J*(PC) 32], and 17.2 (CH*Me*).

‡ *Crystal data* for (**3**): $C_{25}H_{24}FeMoO_4$, $M = 540.23$, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.166(3)$, $b = 8.714(1)$, $c = 18.645(3)$ Å, $\beta = 100.95(1)°$, $U = 2\,259.8(6)$ Å^3, $Z = 4$, $D_c = 1.59$ g cm^{-3}, $F(000) = 1\,096$, μ(Mo-K_α) = 12.11 cm^{-1}, $R = 0.032$ ($R_w = 0.032$) for 3 866 unique absorption-corrected intensities [293 K, ω/2θ scans, $2\theta \leqslant 55°$, $I \geqslant 2.5\sigma(I)$, Mo-K_α ($\bar{\lambda} = 0.710\,69$ Å)]. Data were collected on a Nicolet *P3m* diffractometer and the structure solved by Patterson and Fourier methods, with refinement by blocked-cascade least squares.

Crystal data for (**5**): $C_{25}H_{22}FeMoO_6$, $M = 570.23$, orthorhombic, space group $Pna2_1$ (No. 33), $a = 18.407(3)$, $b = 11.480(2)$, $c = 22.813(4)$ Å, $U = 4\,821(1)$ Å^3, $Z = 8$, $D_c = 1.57$ g cm^{-3}, $F(000) = 2\,304$, μ(Mo-K_α) = 11.45 cm^{-1}, $R = 0.045$ ($R_w = 0.042$) for 4 300 absorption-corrected intensities, $2\theta \leqslant 60°$, $I \geqslant 2.0\sigma(I)$. Data collection as for (**3**). The structure was solved by direct and Fourier methods and refined by blocked cascade least squares. There are two independent molecules in the asymmetric unit and only one is shown in Figure 2.

Crystal data for (**6a**): $C_{22}H_{18}FeMoO_5$, $M = 514.2$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), $a = 7.950(1)$, $b = 26.558(7)$, $c = 9.889(4)$ Å, $\beta = 99.67(3)°$, $U = 2\,058(1)$ Å^3, $Z = 4$, $D_c = 1.66$ g cm^{-3}, $F(000) = 1\,032$, μ(Mo-K_α) = 13.28 cm^{-1}, $R = 0.038$ ($R_w = 0.032$) for 2 575 absorption-corrected intensities, $2\theta \leqslant 50°$, $I \geqslant 2.0\sigma(I)$. Data collection and structure refinement as for (**3**).

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

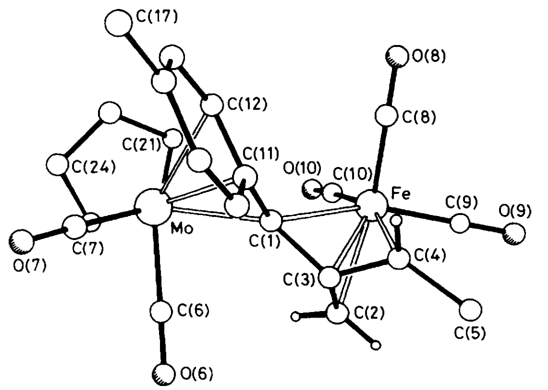

Figure 3. Molecular structure of [FeMo{μ-C(C_6H_4Me-4)-$\overline{\mathrm{C(CHMe)C}}\mathrm{H_2}$}$(CO)_5(\eta$-$C_5H_5)$] (**6a**). Dimensions Mo · · · Fe 4.027, Mo–C(1) 2.188(4), Mo–C(11) 2.393(4), Mo–C(12) 2.520(5), Fe–C(1) 2.188(4), Fe–C(2) 2.122(5), Fe–C(3), 1.945(5), Fe–C(4) 2.142(5), C(1)–C(11) 1.449(5), C(1)–C(3) 1.441(6), C(2)–C(3) 1.407(6), C(3)–C(4) 1.418(7) Å; Mo–C(1)–Fe 133.9(2), C(11)–C(1)–C(3) 124.1(4), C(1)–C(3)–C(2) 115.3(4), C(1)–C(3)–C(4) 114.9(4), C(2)–C(3)–C(4) 116.5(4), C(3)–C(4)–C(5) 124.6(4)°.

species with alkynes. Not surprisingly, compound (**4a**) with PhC≡CPh in light petroleum (b.p. 40—60 °C) at ambient temperatures affords (**2c**) quantitatively. Similarly, (**4a**) and EtC≡CEt yield (**2d**) (50%) but a CO insertion product (**5**) (30%)† is also formed in this reaction. The structure of the latter has been established by *X*-ray diffraction (Figure 2),‡ and evidently results from a coupling of μ-CC_6H_4Me-4, CO, and EtC≡CEt groups at the Fe–Mo centre of (**4a**).

Compound (**4a**) reacts rapidly with MeC≡CMe in light petroleum at room temperature to give (**6**) in quantitative yield. N.m.r. studies revealed that in solution (**6**) exists as a mixture of isomers [(**6a**) and (**6b**), *ca.* 3:2]. An *X*-ray diffraction study‡ showed that in the crystal (**6a**) is the preferred form (Figure 3). The molecular structure is especially interesting since there is no metal–metal bond, and if a fragment formalism is adopted the $Fe(CO)_3$ moiety may be regarded as being ligated by a molybdenum-substituted 'trimethylenemethane' group.

The reaction between (**4b**) and MeC≡CMe further illustrates the variety of insertion, coupling, and hydrogen migration reactions which may be possible by altering a ligand (*e.g.* PMe_3 for CO) on one of the heteronuclear metal centres. The product (**7**)† has an Fe–Mo bond bridged by a C_5 fragment derived from the tolylmethylidyne group, a but-2-yne molecule, and a CO ligand; this being established by *X*-ray diffraction.[4] The hydrogen migration processes which produce the $\overline{\mathrm{C(CHMe)C}}\mathrm{H_2}$ moieties present in (**3**), (**6**), and (**7**) probably involve transient Fe(μ-H)Mo intermediates, since the protons on the resulting C(H)Me groups are *anti* with respect to their parent CH_2 carbon atoms.

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