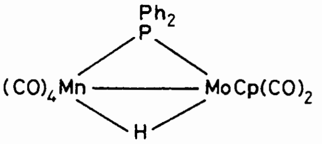
Formation of Complexes with C · · · H · · · Mn Interactions from Reactions of Dienes or Acetylene with a μ-Hydrido Heterometallic Dimer; *X*-Ray Crystal Structures of $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$, $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}\sigma : \eta^3\text{-}CH_2C(Me)CHMe\}(\mu\text{-}PPh_2)(CO)_4]$, and $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}\sigma : \eta^4\text{-}CHCHCH_2CHPPh_2\}(CO)_4]$

Andrew D. Horton, Martin J. Mays,* and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.

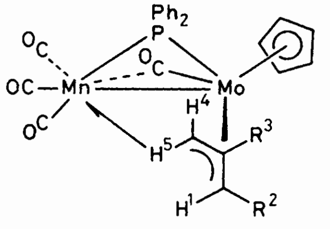
The heterodimetallic complex $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$, the structure of which has been established by *X*-ray analysis, reacts with dienes and with acetylene under photolysis; two of the products, $[(\eta^5\text{-}C_5H_5(MoMn\{\mu\text{-}\sigma : \eta^3\text{-}CH_2C(Me)CHMe\}(\mu\text{-}PPh_2)(CO)_4]$ and $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}\sigma : \eta^4\text{-}CHCHCH_2CHPPh_2\}(CO)_4]$ have been characterised by *X*-ray analysis and show unusual bonding modes for the organic ligands.

Relatively little is known about the organic chemistry of heterodimetallic complexes.[1–4] In particular, the organic chemistry of complexes of this type in which the two metal centres are bridged by a hydrogen atom remains virtually unexplored.[5] We have recently reported on the reactivity of the homodimetallic hydrogen-bridged complex $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$[6] and, in this communication, we describe some reactions of a related heterodimetallic complex, $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$, with dienes and with acetylene. These illustrate the different chemistry that may be expected for such systems and give rise to complexes in which unusual modes of bonding are observed for the organic ligands formed.

Addition of an equimolar quantity of Ph_2PH to the

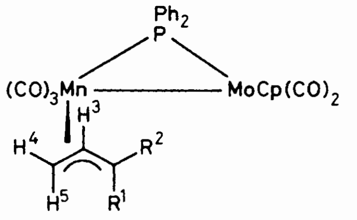


(1)



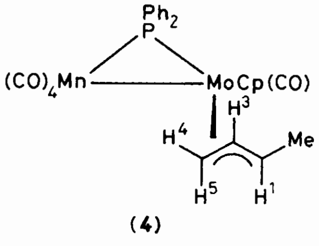
(2)

a; $R^2 = R^3 = Me$
b; $R^2 = Me, R^3 = H$
c; $R^2 = R^3 = H$

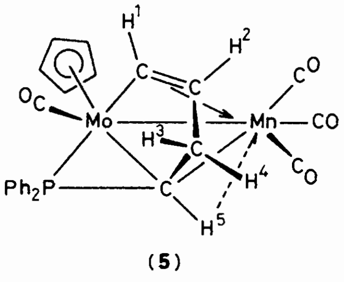


(3)

a; $R^1 = R^2 = Me$
b; $R^1 = H, R^2 = Me$
c; $R^1 = R^2 = H$



(4)



(5)

$Cp = \eta^5\text{-}C_5H_5$

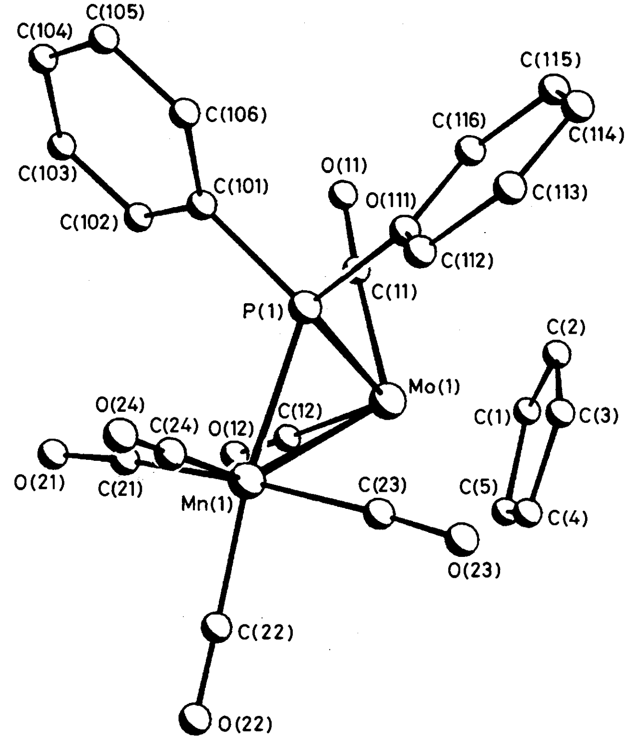


Figure 1. The molecular structure of $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$ (**1**). Bond lengths: Mn(1)–Mo(1), 3.088(1); Mn(1)–P(1), 2.294(2); Mo(1)–P(1), 2.435(1); Mo(1)–C(11), 1.950(6); Mo(1)–C(12), 1.954(7); Mn(1)–C(21), 1.842(6); Mn(1)–C(22), 1.820(6); Mn(1)–C(23), 1.853(6); Mn(1)–C(24), 1.811(5); Mo(1)–C(Cp, av.), 2.34(2) Å. Bond angle: Mn(1)–P(1)–Mo(1), 81.5(1)°.

mixed-metal dimer $[(\eta^5\text{-}C_5H_5)MoMn(CO)_8]$[7] in benzene solution gives, on photolysis, $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6]$ (**1**)† in *ca.* 40% yield. Complex (**1**) has been characterised by a single crystal *X*-ray determination.‡ The structure is shown in Figure 1 which includes some important bond parameters. The synthesis, by a different route, of a complex closely related to (**1**) has been recently described by Casey[8] but no structural details or reactions were reported.

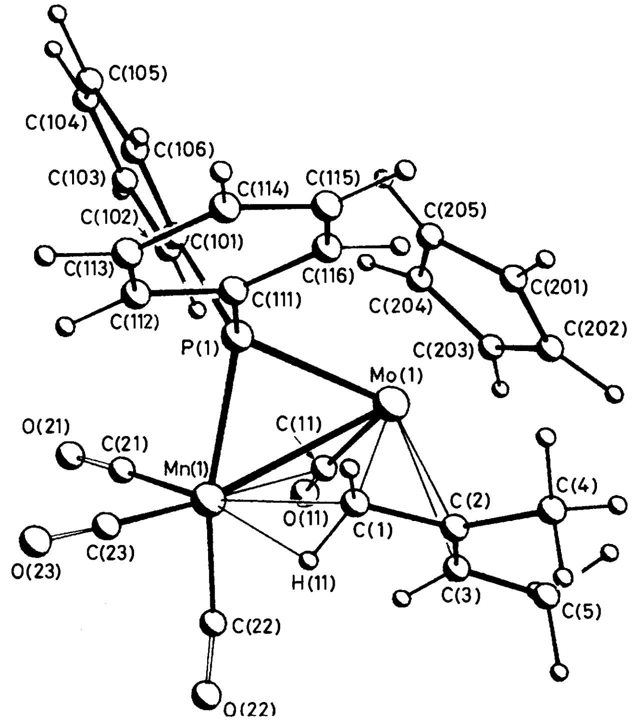


Figure 2. The molecular structure of $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH_2C(Me)CHMe\}(\mu\text{-}PPh_2)(CO)_4]$ (**2a**). Bond lengths: Mn(1)–Mo(1), 2.800(1); Mn(1)–P(1), 2.267(1); Mo(1)–P(1), 2.428(1); Mo(1)–C(11), 1.944(4); Mn(1) · · · C(11), 2.507(4); Mn(1)–C(21), 1.776(4); Mn(1)–C(22), 1.838(4); Mn(1)–C(23), 1.790(4); Mo(1)–C(Cp, av.), 2.34(2); Mo(1)–C(1), 2.276(4); Mo(1)–C(2), 2.239(4); Mo(1)–C(3), 2.397(4); Mn(1)–C(1), 2.346(4); C(1)–C(2), 1.431(5); C(2)–C(3), 1.392(6); C(2)–C(4), 1.517(5); C(3)–C(5), 1.497(6) Å. Bond angles: Mn(1)–P(1)–Mo(1), 73.1(1); Mo(1)–C(11)–O(11), 161.9(3); Mn(1)–C(11)–O(11), 121.1(3); Mn(1)–C(1)–Mo(1), 74.5(1); C(1)–C(2)–C(3), 117.9(3); C(1)–C(2)–C(4), 118.2(4); C(3)–C(2)–C(4), 123.9(4); C(2)–C(3)–C(5), 125.3(4)°.

Complex (**1**) in hexane solution reacts under photolysis with a wide variety of dienes at room temperature or below. With

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† *Selected spectroscopic data* [i.r. (ν_{CO} cm^{-1}) measured in hexane solution; ^1H and ^{13}C n.m.r. in $CDCl_3$ or $[^2H_6]$acetone solution for (**1**); couplings in Hz]: (**1**), ν_{CO} 2072m, 2001m, 1979s, 1964s, 1903m; ^1H n.m.r. (298 K) δ −13.91 [d, *J*(PH) 32.2, 1H, MoMnH]; (**2a**), ν_{CO} 2012s, 1933m, 1924m/s, 1828w; ^1H n.m.r. (298 K), δ 2.29 [q, *J* (H^1Me^2) 6.3, 1H, H^1], 1.94 (s, 3H, Me^3), 1.68 (d, 3H, Me^2), −0.66 [dd, *J*(PH) 18.2, *J*(H^4H^5) 7.2, 1H, H^4], −7.68 (d, 1H, H^5); $^{13}C\{^1H\}$ n.m.r. (238 K) δ 99.2 [s, 1H, $CH_2\mathit{C}(Me)CHMe$], 70.0 [s, $CH_2C(Me)\mathit{C}HMe$], 23.6 [s, $CH_2C(\mathit{Me})CHMe$], 16.0 [s, $CH_2C(Me)CH\mathit{Me}$], 9.9 (br., CH_2); (**2b**), ν_{CO} 2012s, 1937m, 1921m/s, 1831w; ^1H n.m.r. (298 K) δ 4.49 [ddd, *J*(H^1H^3) 10.2, *J*(H^3H^4) 6.3, *J*(H^3H^5) 6.3, 1H, H^3], 2.58 [dq, *J* (H^1 Me) 6.2, 1 H, H^1], 1.65 (d, 3H, *Me*), −0.71 [ddd, *J*(PH) 16.8, *J* (H^4H^5) 7.3, 1H, H^4], −7.51 (dd, 1H, H^5); (**3a**), ν_{CO} 2026m/w, 1948m/s, 1942s, 1918m, 1875m; ^1H n.m.r. (298 K): major isomer (70%) δ 4.65 [dd, *J*(H^3H^5) 12.2, *J*(H^3H^4) 6.7, 1H, H^3], 3.68 [ddd, *J*(PH) 4.6, *J*(H^4H^5) 2.9, 1H, H^4], 2.08 (s, 3H, Me^2), 1.36 (s, 3H, Me^1), 1.26 (dd, 1H, H^5); minor isomer (30%) 4.21 [dd, *J*(H^3H^5) 11.5, *J*(H^3H^4) 6.9, 1H, H^3], 3.04 [dd, *J*(PH) 4, 1H, H^4], 2.63 (d, 1H, H^5), 2.06 (s, 3H, Me^2), 1.52 (s, 3H, Me^1); (**3b**), ν_{CO} 2029m/w, 1952sh, 1946s, 1923m, 1876m; (**4**), ν_{CO} 2049s, 1984m, 1958s, 1947m/s; ^1H n.m.r. (298 K) δ 3.95 [ddd, *J*(H^3H^5) 11.8, *J*(H^1H^3) 11.0, *J*(H^3H^4) 7.8, 1H, H^3], 2.12 [dq, *J*(H^1Me) 6.3, 1H, H^1], 1.74 (d, 3H, Me), 1.46 [ddd, *J*(PH) 2.31, *J*(H^4H^5) 4.9, 1H, H^4], −0.44 [ddd, *J*(PH) 9.7, 1H, H^5]; (**5**), ν_{CO} 1994m/s, 1915s, 1901vs; ^1H n.m.r. (298 K) δ 8.71 [dd, *J*(H^1H^2) 6.9, *J*(H^1H^4) 1.5, 1H, H^1], 5.68 [dddd, *J*(PH) 7, *J*(H^2H^4) 3, *J*(H^2H^3) 2.7, 1H, H^2], 3.11 [dddd, *J*(H^3H^4) 13.6, *J*(H^3H^5) 7.9, *J*(PH) 7.5, 1H, H^3], 1.00 [ddddd, *J*(PH), 18.3, *J*(H^4H^5) 10.0, 1H, H^4], −3.76 [ddd, *J*(PH) 10, 1H, H^5]; $^{13}C\{^1H\}$ n.m.r. (243 K) δ 189.3 [d, *J*(PC) 6.0, $\mathit{C}HCHCH_2CH$], 88.9 [d, *J*(PC) 8.6, $CH\mathit{C}HCH_2CH$], 39.4 (s, $CHCH\mathit{C}H_2CH$), −11.5 (br., $CHCHCH_2\mathit{C}H$).

‡ *Crystal data:* (**1**) $C_{23}H_{16}MnMoO_6P$, $M = 570.21$, monoclinic, space group *P*2/*a* (non-standard setting of *P*2/*c*, No. 13), $a = 15.922(2)$, $b = 8.544(1)$, $c = 18.330(2)$ Å, $\beta = 113.78(1)°$, $U = 2281.9(11)$ Å^3, $D_c = 1.66$ g cm^{-3}, $Z = 4$, $F(000) = 1136$, $\mu(Mo\text{-}K_\alpha) = 11.39$ cm^{-1}, $F \geqslant 4\sigma(F)$, 2θ range 5—50°, $R = 0.048$, $R_w = 0.047$ for 3281 absorption corrected diffractometer data. (**2a**) $C_{26}H_{24}MnMoO_4P$, $M = 581.90$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.337(1)$, $b = 15.743(1)$, $c = 15.282(1)$ Å, $\beta = 102.49(1)°$, $U = 2428.1(6)$ Å^3, $D_c = 1.59$ g cm^{-3}, $Z = 4$, $F(000) = 1176$, $\mu(Mo\text{-}K_\alpha) = 11.49$ cm^{-1}, $F \geqslant 4\sigma(F)$, 2θ range 5—50°, $R = 0.037$, $R_w = 0.042$ for 3772 absorption corrected diffractometer data. (**5**) $C_{25}H_{20}MnMoO_4P$, $M = 566.26$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), $a = 11.709(1)$, $b = 15.857(1)$, $c = 12.670(1)$ Å, $\beta = 100.45(1)°$, $U = 2313.4(6)$ Å^3, $D_c = 1.63$ g cm^{-3}, $Z = 4$, $F(000) = 1136$, $\mu(Mo\text{-}K_\alpha) = 11.18$ cm^{-1}, $F \geqslant 4\sigma(F)$, 2θ range 5—50°, $R = 0.029$, $R_w = 0.031$ for 3725 absorption corrected diffractometer data.

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.

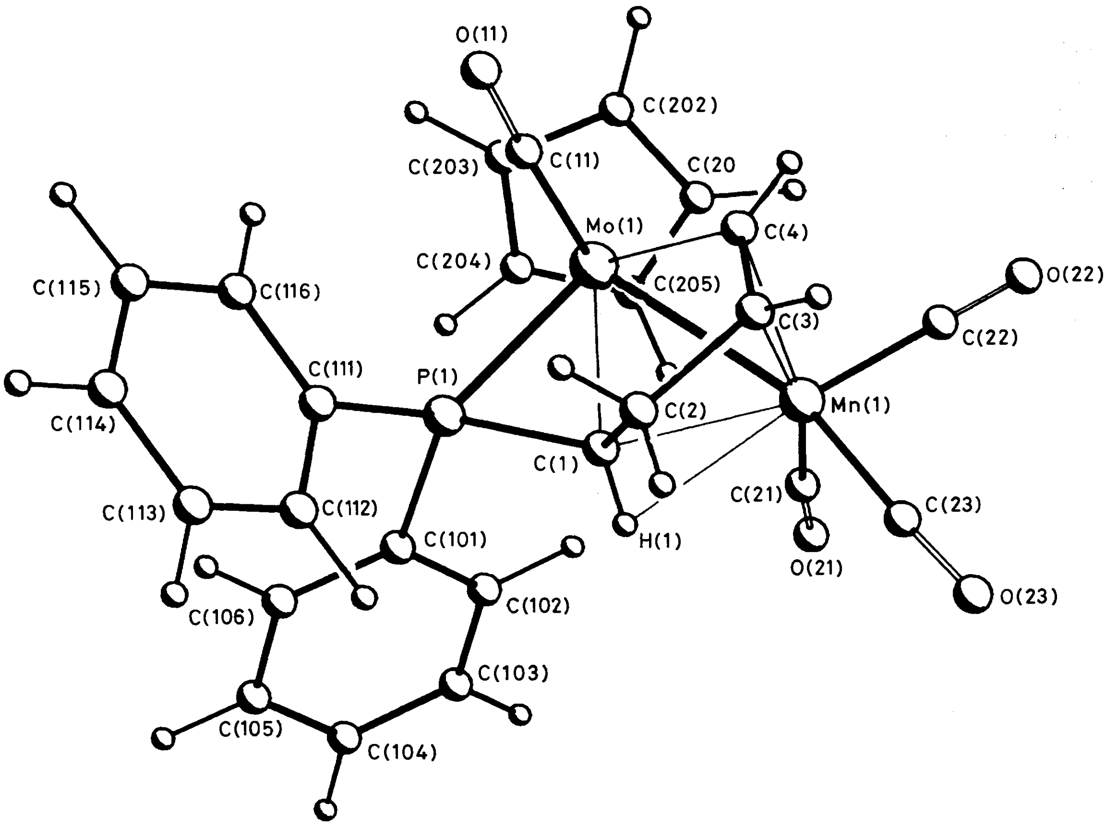

Figure 3. The molecular structure of $[(\eta^5\text{-}C_5H_5)MoMn\{\mu\text{-}\sigma:\eta^4\text{-}CHCHCH_2CHPPh_2\}(CO)_4]$ (**5**). Mn(1)–Mo(1), 2.680(1); Mo(1)–P(1), 2.329(1); Mo(1)–C(11), 1.935(3), Mn(1)–C(21), 1.795(3); Mn(1)–C(22), 1.777(3); Mn(1)–C(23), 1.791(4); Mo(1)–C(Cp, av.), 2.34(2); Mo(1)–C(1), 2.364(3); Mo(1)–C(4), 2.154(3); Mn(1)–C(1), 2.245(3); Mn(1)–C(3), 2.190(3); Mn(1)–C(4), 2.081(3); P(1)–C(1), 1.787; C(1)–C(2), 1.521(4); C(2)–C(3), 1.512(5); C(3)–C(4), 1.374(4) Å. Bond angles: Mn(1)–C(1)–Mo(1), 71.1(1); P(1)–C(1)–C(2), 121.7(2); C(1)–C(2)–C(3), 103.8(2); C(2)–C(3)–C(4), 116.7(3); Mn(1)–C(4)–Mo(1), 78.5(1); Mo(1)–P(1)–C(1), 68.7(1)°.

2-methylbutadiene (isoprene) only one major product was present in solution after 4 h at −20 °C and this was isolated by t.l.c. in 45% yield as an orange crystalline complex (**2a**),† which has been characterised by a single crystal *X*-ray analysis.‡ The structure is illustrated in Figure 2 which includes some important bond parameters. Carbon atoms C(1), C(2), and C(3) are all bonded to the Mo atom but C(1) is also bonded to Mn. The C(1)–Mn bond is bridged by H(11) which has been located 2.02(4) Å from Mn. The hydrogen–metal interaction is clearly also present in solution, as revealed by the high field ^1H n.m.r. signal (δ −7.64) characteristic of this type of bonding.[9—11] Overall, the complex is 2 electrons short of the number required to satisfy the E.A.N. (effective atomic number) rule, if the organic ligand is counted as a 3-electron donor. The unsaturation is mainly centred on the Mn atom and is presumably responsible for the C · · · H · · · Mn interaction. The presence of a semi-bridging carbonyl group and the short Mn–Mo bond [*ca.* 0.3 Å shorter than in (**1**)] suggests that electron donation from this CO group and from the Mo atom may also be important. However, the differing nature of the bridging ligands in (**2a**) as compared to (**1**) makes an assessment of the relative metal–metal bond order difficult.

The only other product present in significant yield, (**3a**),† has not been fully characterised but, on the basis of spectroscopic data, it is tentatively formulated as a mixture of two isomeric allyl complexes in which the allyl groups are η^3-bonded to the manganese atom. Photolysis of (**1**) with butadiene or allene at room temperature proceeds similarly to give (**2b**)† and (**3b**)† and (**2c**) and (**3c**) respectively; (**3c**)§ is the major product with allene (62% yield) whilst (**2b**) is the major product with butadiene (60% yield). At −20 °C a red complex (**4**)† is the major product (*ca.* 50% yield) from the reaction of (**1**) with butadiene. On the basis of its ^1H n.m.r. spectrum (**4**) is tentatively formulated as an allyl complex, in which the ligand is η^3-bonded to the molybdenum atom. Complex (**4**) is converted slowly into (**2b**) in solution at room temperature under N_2 and is presumably an intermediate in the formation of this latter complex. Under CO (1 atm, room temp.), however, the reaction is reversed and (**4**) is regenerated rapidly and quantitatively from (**2b**).

In contrast to the above reactions of (**1**) with dienes, $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ gives a single type of product, containing an allyl group bonded to only one of the metal atoms.[12]

Reaction of (**1**) with acetylene in hexane under photolysis at −10 °C gives, after 1.5 h, a solution from which a red crystalline complex (**5**)† was isolated by t.l.c. as the major product in *ca.* 30% yield. Complex (**5**) has been characterised by a single crystal *X*-ray analysis.‡ The structure is shown in Figure 3 together with some important bond parameters.

The Mo and Mn atoms are linked by a ligand which has been formed from the Ph_2P bridge and 2 molecules of acetylene. C(1) is bonded to both metal atoms and is also bonded to P(1), H(1), and C(2). The C(1)–Mn bond is bridged by H(1),

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§ Structure confirmed by an *X*-ray study to be reported elsewhere.

although H(1) is further from the Mn atom [2.29(4) Å] than the corresponding bridging H atom in (**2a**). This weaker hydrogen–metal interaction presumably affects the ^{1}H n.m.r. signal ($CDCl_3$ solution) due to the H atom bridge in (**5**) (δ -3.76), since it is not shifted to as high a field as in (**2a**). C(3) and C(4) can be regarded as constituting a bridging vinyl group, being η^2-bonded to the Mn atom and σ-bonded through C(4) to the Mo atom. C(2) forms single C–C bonds to C(1) and C(3) but is not bonded to either metal atom. Overall, the complex is again 2-electrons short of the number required to satisfy the E.A.N. rule but there is no semi-bridging carbonyl group and a weaker $C \cdots H \cdots M$ interaction than in (**2a**). This is compensated for by increased multiple bond character in the Mo–Mn bond, which is 0.12 Å shorter than in (**2a**) and 0.4 Å shorter than in (**1**).

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References

1 J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 1383.
2 J. C. Jeffery, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1581.
3 B. P. Gracey, S. A. R. Knox, K. A. Macpherson, A. G. Orpen, and S. R. Stobart, *J. Organomet. Chem.*, 1984, **272**, C45.
4 R. Regragui, P. H. Dixneuf, N. J. Taylor, and A. J. Carty, *Organometallics,* 1984, **3**, 814.
5 R. P. Rosen, J. B. Hoke, R. R. Whittle, G. L. Geoffroy, J. P. Hutchinson, and J. A. Zubieta, *Organometallics,* 1984, **3**, 846.
6 J. A. Iggo, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1983, 205.
7 D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, 1975, **97**, 4908.
8 C. P. Casey and R. M. Bullock, *Organometallics,* 1984, **3**, 1100.
9 G. M. Dawkins, M. Green, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1982, 41.
10 J. C. Jeffery, A. G. Orpen, W. T. Robinson, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Chem. Commun.*, 1984, 396.
11 M. Green, N. C. Norman, and A. G. Orpen, *J. Am. Chem. Soc.*, 1981, **103**, 1269.
12 J. A. Iggo, Ph.D. Thesis, University of Cambridge, 1983.