Acetylene Linkage at a Di-metal Centre: *X*-Ray Crystal Structures of $[Cr_2(CO)(\eta\text{-}C_5H_5)_2(PhC_2Ph)_2]$ and $[Mo_2(\eta\text{-}C_5H_5)_2\{(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}]$

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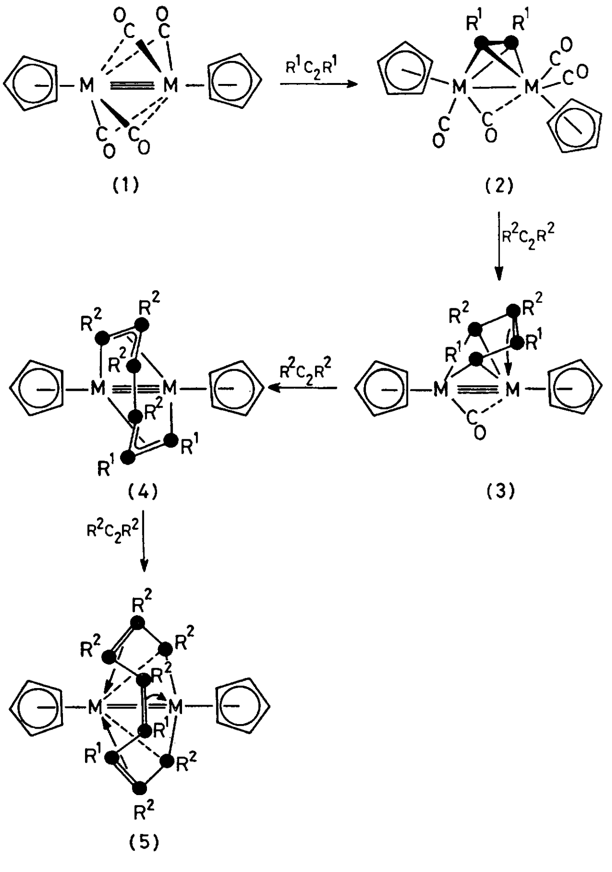
Summary A sequence of acetylene linking at a di-metal centre has been identified; *X*-ray diffraction studies have established the structures of di-chromium and di-molybdenum complexes containing two and four acetylene molecules, respectively.

In the 30 years since Reppe *et al.*[1,2] reported the nickel(II)-catalysed cyclisation of acetylene to form cyclo-octatetraene and benzene, numerous mono-, di-, or tri-metal complexes have been shown to cyclotrimerise acetylenes.[3] It is generally assumed[2,4] that cyclotetramerisation proceeds *via* insertion reactions at a single metal centre, but although metallacycloheptatriene complexes are known no metallacyclononatetraene species has been identified. Neither, to our knowledge, has a complex of any type been isolated which contains an unbranched carbon chain derived from four acetylene molecules. We now describe results of experiments which suggest that di-metal complexes may play a crucial role in the linking together of more than three acetylene molecules.

The formation[5] of complexes (**2**; M = Mo or W), and the structures[6] of two of the molybdenum derivatives are well established. However, we find that the compounds (**2**) represent only the first stage in a series of insertion reactions which proceed at heptane or octane reflux temperatures. Thus although (**1**; M = Cr) reacts under u.v. irradiation with diphenylacetylene to give a low yield of brown-black crystalline (**2**; M = Cr, R^1 = Ph) [ν_{CO}(hexane): 1 983m, 1 928s, and 1 863m cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): τ, 2·81 (m, 10H) and 5·20 (s, 10H)]; upon brief heating of (**1**; M = Cr) with $R^1C_2R^1$ (R^1 = H, CO_2Me, or Ph) in heptane, black crystalline (**3**; M = Cr) is produced (74%) directly [for (**3**; M = Cr, R^1 = R^2 = Ph) ν_{CO}(hexane): 1 814 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$): τ, 3·06 (m, 12H), 3·21 (m, 4H), 3·80 (m, 4H), 4·61 (s, 5H), and 5·47 (s, 5H)].



Scheme

In contrast, complex (**1**; M = Mo) when treated with acetylenes [*e.g.* C_2H_2, C_2Ph_2, C_2Me_2, $C_2(CO_2Me)_2$, MeC_2H, or PhC_2H] at room temperature affords in good yield (50—80%) complexes of type (**2**; M = Mo). The latter react further with acetylenes in refluxing octane, the course of reaction depending on the nature of the acetylene substituents. Treatment of (**2**; M = Mo, R^1 = Ph) with additional PhC_2Ph thus gives (**3**; M = Mo, $R^1 = R^2$ = Ph) exclusively (70%), whereas similar reaction of (**2**; M = Mo, R^1 = H) with acetylenes progresses to (**4**) or (**5**). For example, diphenylacetylene and (**2**; M = Mo, R^1 = H) give (65%) dark green crystals of (**4**; M = Mo, R^1 = H, R^2 = Ph) [^{1}H n.m.r. ($CDCl_3$): τ, 2·6—3·0 (m, 20H), 3·06 (d, 1H, *J* 6 Hz), 3·99 (d, 1H, *J* 6 Hz), 5·19 (s, 5H), and 5·44 (s, 5H)] while $C_2(CO_2Me)_2$ and (**2**; M = Mo, R^1 = H) give (50%) purple crystals of (**5**; M = Mo, R^1 = H, R^2 = CO_2Me) [^{1}H n.m.r. ($CDCl_3$): τ, 4·62 (d, 1H, *J* 2 Hz), 4·74 (s, 4H) (2 CH_2Cl_2 of crystallisation), 4·84 (s, 5H), 5·08 (s, 5H), 5·94 (s, 3H), 6·04 (s, 3H), 6·17 (s, 3H), 6·28 (s, 6H), and 7·44 (d, 1H, *J* 2 Hz)].

X-Ray diffraction studies have been performed on complexes (**3**; M = Cr, $R^1 = R^2$ = Ph) and (**5**; M = Mo, R^1 = H, R^2 = CO_2Me), each of which crystallises from dichloromethane–hexane solvent with dichloromethane incorporated into the crystal.

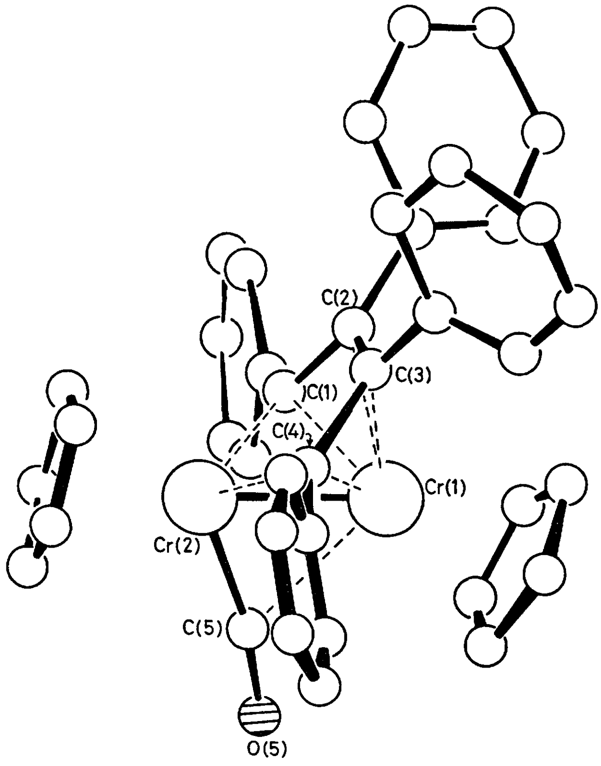


FIGURE 1. Molecular structure of $[Cr_2(CO)(\eta\text{-}C_5H_5)_2(PhC_2Ph)_2]$. Bond lengths: Cr(1)–Cr(2), 2·337(2); Cr(2)–C(1), 2·024(7); Cr(2)–C(4), 2·020(7); Cr(1)–C(1), 2·032(7); Cr(1)–C(4), 2·023(7); Cr(1)–C(2), 2·229(7); Cr(1)–C(3), 2·232(8); C(1)–C(2), 1·422(10); C(4)–C(3), 1·419(11); C(2)–C(3), 1·428(11) Å.

Crystals of $[Cr_2(CO)(\eta\text{-}C_5H_5)_2(PhC_2Ph)_2]\cdot(\frac{1}{2}CH_2Cl_2)$ are orthorhombic, *a* = 19·569(4), *b* = 19·731(5), *c* = 16·637(2) Å, space group *Pbcn*, *Z* = 8, *U* = 6424(2) Å^3, *F*(000) = 2644, μ(Mo-K_α) = 6·9 cm^{-1}. For the 3166 independent reflections [$I \geqslant 3{\cdot}0\ \sigma(I)$], *R* = 0·066.

Crystals of $[Mo_2(\eta\text{-}C_5H_5)_2\{(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}]\cdot(2CH_2Cl_2)$ are triclinic, *a* = 11·519(7), *b* = 18·602(9), *c* = 8·709(3) Å, α = 86·65(4), β = 100·99(4), γ = 97·54(5)°, space group $P\bar{1}$, *Z* = 2, *U* = 1815(2) Å^3, *F*(000) = 948, μ(Mo-K_α) = 9·4 cm^{-1}. For the 3450 independent reflections [$I \geqslant 3{\cdot}0\ \sigma(I)$], *R* = 0·054.

Both structures were solved by conventional heavy-atom methods from data collected on a Syntex $P2_1$ four-circle diffractometer to $2\theta_{max}$ = 60°.†

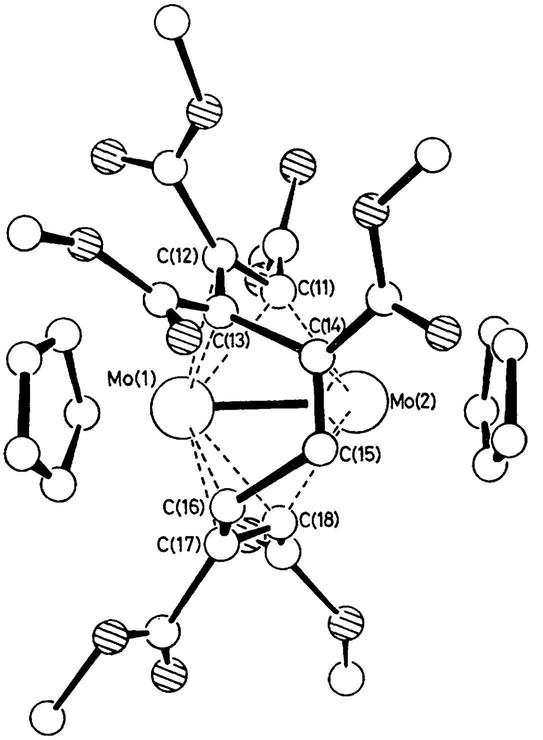


FIGURE 2. Molecular structure of $[Mo_2(\eta\text{-}C_5H_5)_2\{(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}]$. Bond lengths: Mo(1)–Mo(2), 2·618(1); Mo(1)–C(11), 2·225(10); Mo(2)–C(11), 2·082(8); Mo(1)–C(12), 2·339(9); Mo(1)–C(13), 2·335(8); Mo(2)–C(14), 2·227(9); Mo(2)–C(15), 2·211(10); Mo(1)–C(16), 2·330(8); Mo(1)–C(17), 2·327(8); Mo(1)–C(18), 2·243(9); Mo(2)–C(18), 2·088(8); C(11)–C(12), 1·403(13); C(12)–C(13), 1·434(13); C(13)–C(14), 1·507(11); C(14)–C(15), 1·414(12); C(15)–C(16), 1·505(13); C(16)–C(17), 1·442(12); C(17)–C(18), 1·429(14) Å.

In $[Cr_2(CO)(\eta\text{-}C_5H_5)_2(PhC_2Ph)_2]$ (**3**; M = Cr, $R^1 = R^2$ = Ph) (Figure 1) two acetylene molecules are linked by a direct C(2)-C(3) bond which makes an effectively η^2-olefinic interaction with Cr(1). The remaining acetylenic carbon atoms C(1) and C(4) symmetrically bridge the chromium atoms, whose close proximity [2·377(2) Å] indicates triple metal–metal bonding, as does the 18-electron rule. Description of the carbon atoms C(1) and C(4) as 'bridging carbenes'

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† 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.

appears justified by their very low field ^{13}C n.m.r. shift (310 p.p.m. downfield of Me_4Si). Also notable is the 'semi-bridging' character of the lone carbonyl ligand [Cr(2)–C(5) = 1·849(8), Cr(1)–C(5) = 2·365(8) Å, ∠Cr(2)–C(5)–O(5) = 165·1(7)°].

In $[Mo_2(\eta\text{-}C_5H_5)_2\{(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}]$ (Figure 2) the four acetylene molecules have linked to form an unbranched eight-carbon chain (**5**) comprising atoms C(11)—C(18). Of these, C(15) and C(16) carry the single hydrogen atoms which identify them as derived from the initially co-ordinated acetylene. Once again the terminal carbon atoms of the chain bridge the two metal atoms, but do so asymmetrically such that C(11) and C(18) are 0·15 Å nearer to Mo(2) than Mo(1). The remainder of the chain is bonded to the two Mo atoms in alternate pairs [C(12) and C(13) to Mo(1), C(14) and C(15) to Mo(2), C(16) and C(17) to Mo(1)]. The Mo-Mo distance of 2·618(1) Å is consistent with metal–metal double bonding. The consequent representation of the molecular structure as (**5**; M = Mo, R^1 = H, R^2 = CO_2Me) clearly indicates that the bridging carbons should interact unequally with the molybdenum atoms if each metal is to achieve an 18-electron valence shell.

No precedent for structure (**5**) exists, but complexes akin to (**3**) and (**4**) have been previously described, namely $[Fe_2(CO)_6(RC_2R)_2]$[7] and $[Co_2(CO)_4(RC_2R)_3]$,[3,8] respectively. These differ, however, from (**3**) and (**4**) in having only a single metal–metal bond. We believe that the presence of structures (**2**)—(**5**) in a unified reaction sequence (Scheme) reflects the facility for transfer of the M · · · M interaction between single, double, and triple bonding in accommodating extension of the hydrocarbon chain. Experiments are continuing to determine whether the new complexes can generate unco-ordinated hydrocarbons and also whether (**1**; M = W) is active in the sense described here. Preliminary results of experiments with the latter indicate the formation of complexes containing *five* linked acetylene molecules.

We are grateful to the S.R.C. for support and the award of a Research Studentship (to M.J.W.).

(*Received, 5th December* 1977; *Com.* 1241.)

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