The Sequential Linking of Alkynes at Dichromium and Dimolybdenum Centres; *X*-Ray Crystal Structure of $[Cr_2(CO)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ *

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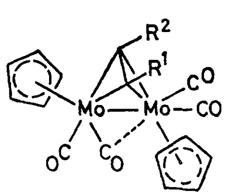
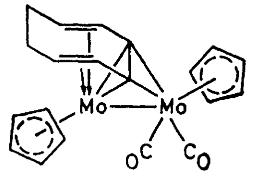
In heptane at reflux, the alkynes RC≡CR (R = Ph, H, or CO_2Me) react with $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ to give complexes $[Cr_2(CO)(\mu\text{-}C_4R_4)(\eta\text{-}C_5H_5)_2]$. An *X*-ray diffraction study on the product from PhC≡CPh shows that the crystals of $[Cr_2(CO)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ when grown from dichloromethane–hexane incorporate $\frac{1}{4}CH_2Cl_2$ per molecule of complex and are orthorhombic, with $Z = 8$ in a unit cell of dimensions $a = 19.569(4)$, $b = 19.731(5)$, $c = 16.637(2)$ Å, and space group *Pbcn* (no. 60). The structure has been solved by heavy-atom methods from 3 166 data for which $I \geqslant 3.0\sigma(I)$, collected on a four-circle diffractometer, and refined to *R* 0.066. The axis of the molecule comprises a $(\eta\text{-}C_5H_5)Cr{\equiv}Cr(\eta\text{-}C_5H_5)$ moiety which is non-linear, with the cyclopentadienyl rings in an unsymmetrical *trans* relationship to one another, and with a carbonyl ligand semi-bridging in a plane which is effectively a mirror plane for the whole molecule. Two PhC≡CPh molecules have joined to form a four-carbon chain, of which the two terminal atoms form a quasi-tetrahedral group with the two chromium atoms [Cr≡Cr 2.337(2), Cr–C 2.025(7) mean, C ··· C(non-bonded) *ca.* 2.7 Å], and the two central atoms are π-bonded to that Cr atom which does not carry the carbonyl ligand. The two metal atoms lie on opposite sides of the plane through the four-carbon portion of the CrC_4Ph_4 ring. The alkynes RC≡CH (R = Ph or Me) react with $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ to yield as major products the complexes $[Cr_2(CO)(\mu\text{-}C_4H_2R_2)(\eta\text{-}C_5H_5)_2]$ in which there is a head-to-tail arrangement of the Ph or Me groups in the C_4Cr rings. However, with phenylacetylene the isomer containing the ring system $\overline{\text{CrC(Ph)CH=CHC}}\text{Ph}$ was also detected. The compounds $[Mo_2(CO)_n(\eta\text{-}C_5H_5)_2]$ (n = 4 or 6) react with PhC≡CPh in octane at reflux to give $[Mo_2(CO)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$, and similarly $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ affords $[Mo_2(HC_2H)(PhC_2Ph)_2(\eta\text{-}C_5H_5)_2]$, a 'fly-over' complex containing a six-carbon chain bridging a Mo≡Mo bond. Reaction of $[Mo_2(CO)_4(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2]$ with RC≡CR (R = CO_2Me) yields the complexes $[Mo_2(CO)_2(\mu\text{-}C_6H_2R_4)(\eta\text{-}C_5H_5)_2]$ (two isomers) and $[Mo_2(\mu\text{-}C_8H_2R_6)(\eta\text{-}C_5H_5)_2]$ (two isomers) in which C_6 and C_8 chains bridge Mo–Mo and Mo=Mo bonds respectively. The structures of these species were deduced from ^1H and ^{13}C n.m.r. spectra. Reaction of $[Mo_2(CO)_4(\mu\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$ with RC≡CR (R = CO_2Me) gives $[Mo_2(CO)_2(\mu\text{-}C_6R_6)(\eta\text{-}C_5H_5)_2]$ and $[Mo_2(\mu\text{-}C_8R_8)(\eta\text{-}C_5H_5)_2]$ (two isomers), characterised *inter alia* by their ^1H and ^{13}C n.m.r. spectra. Treatment of $[Mo_2(HC_2H)(PhC_2Ph)_2(\eta\text{-}C_5H_5)_2]$ with $MeO_2CC{\equiv}CCO_2Me$ gives two isomers of composition $[Mo_2(HC_2H)(PhC_2Ph)_2(MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)_2]$, thereby establishing that the complexes with four linearly linked alkynes are formed from the species with three such linked groups. Possible mechanisms for carbon-chain growth on the dichromium and dimolybdenum centres are discussed and are related to the changes in multiplicities of the metal–metal bonds.

THE first alkyne-bridged dimolybdenum complexes of type (1) to be reported were obtained by treating $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ or $[MoH(CO)_3(\eta\text{-}C_5H_5)]$ with alkynes.[1] Following discovery [2] of the molybdenum–molybdenum triple-bonded species $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ it was found [2-4] that alkynes readily react at room temperature with this compound to give complexes with the dimetallatetrahedrane structure (1). The favourability of this $\overline{\text{Mo}(\mu\text{-}C_2)\text{Mo}}$ unit is illustrated in the reaction of cyclo-octatetraene with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, when the olefin undergoes an unprecedented rearrangement to afford the μ-cyclo-octadienyne complex $[Mo_2(CO)_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]$ (2).[5] A related $\overline{\text{Co}(\mu\text{-}C_2)\text{Co}}$ unit is present in the long-established cobalt complexes $[Co_2(CO)_6(\mu\text{-}RC_2R)]$, derived by reaction of alkynes with dicobalt octacarbonyl.[6] At elevated temperatures, these species react further with alkynes to produce so-called ' fly-over ' bridge complexes $[Co_2(CO)_4(\mu\text{-}C_6R_6)]$ (3), in which three alkynes are linked in a six-carbon chain. This prompted us to investigate reactions of alkynes with $[Mo_2(CO)_4(\mu\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$ (1) and with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ under more vigorous conditions than those employed previously,[2-4] in anticipation of discovering alkyne-linking processes. We have also made a study of similar reactions of $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [7] in order to compare the behaviour of the dichromium and dimolybdenum systems. A preliminary account of this work has been given.[8]



(1)



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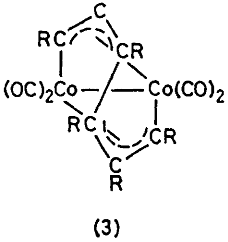

(3)

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* *a*-Carbonyl-*bd*-bis(η-cyclopentadienyl)-μ-[2—3-η-tetraphenyl but-2-ene-1,1,4,4-tetrayl-C^1C^4(Cr^1),$C^1C^{2-3}C^4$(Cr^2)]-dichromium (3*Cr*–*Cr*).

RESULTS AND DISCUSSION

Dichromium Compounds.—The compound $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ reacts rapidly with $PhC\equiv CPh$ in heptane at reflux, affording in 75% yield a black crystalline complex (4) which was characterised by elemental analysis, i.r., mass, and n.m.r. spectroscopy (Tables 1 and 2). The i.r. spectrum has a single peak in the CO stretching region at 1 814 cm^{-1} indicative of a semi-bridging carbonyl. The mass spectrum showed a molecular ion, albeit of low intensity, and a major ion corresponding to the loss of one CO group. The ^1H and ^{13}C n.m.r. spectra of (4) revealed different environments for the two C_5H_5 ligands and that the four Ph groups were pairwise equivalent, as expected for the structure proposed.

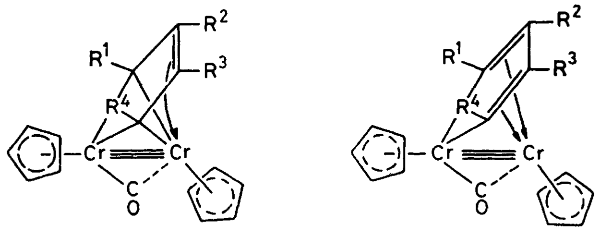
TABLE 1

Analytical[a] and other data for the dichromium complexes

Complex[b]	$\tilde{\nu}_{max.}(CO)$[c]/ cm^{-1}	Yield (%)	Analysis (%) C	Analysis (%) H	M[d]
(4)	1 814	75	71.3 (73.7)[e]	4.7 (4.8)[e]	618 (618)
(5)	1 779	40			314 (314)
(6)	1 852[f]	65	50.4 (50.5)	4.1 (4.0)	546 (546)
(9)	1 801	70	68.6 (69.5)	4.9 (4.7)	466 (466)
(11)[g]	1 794				342 (342)
(12)	1 983m, 1 928s, 1 863m	13	63.8 (64.1)	3.8 (3.8)	524 (524)

[a] Calculated values are given in parentheses. [b] All complexes are maroon to black in colour, except (12) which is brown. [c] In hexane. [d] From parent ion in mass spectrum. [e] Crystallises with dichloromethane. [f] Bands due to CO_2Me groups at 1 733 and 1 694 cm^{-1}. [g] Yield not recorded due to difficulty in crystallising compound (see text).

Under reflux in heptane, the alkynes $HC\equiv CH$ and $MeO_2CC\equiv CCO_2Me$ also reacted with $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$, affording compounds (5) and (6) respectively. The black crystalline complex (5) was very air-sensitive, and it was not possible to obtain satisfactory elemental analyses, although the mass spectrum showed the expected molecular ion, and it was possible to record the ^1H and the ^{13}C n.m.r. spectra of a pure sample (Table 2).



(a) (b)

	R^1	R^2	R^3	R^4
(4)	Ph	Ph	Ph	Ph
(5)	H	H	H	H
(6)	CO_2Me	CO_2Me	CO_2Me	CO_2Me
(9)	Ph	H	Ph	H
(10)	Ph	H	H	Ph
(11)	Me	H	Me	H

In order to establish firmly the structure of complexes (4)—(6), a single-crystal *X*-ray diffraction study was carried out on (4). The results are summarised in Tables 3 and 4, and the molecular structure is illustrated in Figure 1, which also shows the atomic numbering scheme.

It is evident that two $PhC\equiv CPh$ molecules have linked together and are bridging the two chromium atoms, which are separated by 2.337(2) Å. This distance may be compared with those of 2.225(3) and 2.280(3) Å in the complexes $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [9] and $[Cr_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ [10] respectively, species which undoubtedly contain $Cr\equiv Cr$ bonds.

TABLE 2

Hydrogen-1 and ^{13}C n.m.r. data for the dichromium complexes[a]

Complex	^1H (τ)	^{13}C (δ)[b]
(4)	3.06 (m, 12 H, Ph), 3.21 (m, 4 H, Ph), 3.80 (m, 4 H, Ph), 4.61 (s, 5 H, C_5H_5), 5.47 (s, 5 H, C_5H_5)	310.0 (CO), 212.6 (*C*Ph), 149.2, 138.3, 131.7, 127.5, 126.7, 126.5, 125.9, 123.6 (Ph), 110.3 (*C*Ph), 100.7 (C_5H_5), 98.8 (C_5H_5)
(5)	2.12 [d of d, 2 H, CH, *J*(HH) 5, 3], 4.20 [d of d, 2 H, CH, *J*(HH) 5, 3], 4.80 (s, 5 H, C_5H_5), 4.98 (s, 5 H, C_5H_5)	[c] 196.5 (CH), 96.5 (C_5H_5), 96.0 (C_5H_5), 94.8 (CH)
(6)	4.53 (s, 5 H, C_5H_5), 4.62 (s, 5 H, C_5H_5), 6.21 (s, 6 H, Me), 6.57 (s, 6 H, Me)	293.1 (CO), 184.9, 172.9, 166.7 (*C*CO_2Me or *C*O_2Me), 103.8 (C_5H_5), 101.6 (*C*CO_2Me), 99.3 (C_5H_5), 52.7 (Me), 51.4 (Me)
(9)	1.43 [d, 1 H, CH, *J*(HH) 3], 2.82 (m, 8 H, Ph), 3.49 (m, 2 H, Ph), 3.70 [d, 1 H, CH, *J*(HH) 3], 4.85 (s, 5 H, C_5H_5), 5.25 (s, 5 H, C_5H_5)	316.3 (CO), 208.3 (*C*Ph), 194.5 (CH), 151.9, 139.2, 128.3, 127.3, 127.1, 126.3, 125.6 (Ph), 107.8 (*C*Ph), 98.9 (C_5H_5), 97.1 (C_5H_5), 86.2 (CH)
(10)	3.00 (m, 6 H, Ph), 3.47 (m, 4 H, Ph), 4.12 (s, 2 H, CH), 5.15 (s, 5 H, C_5H_5), 5.25 (s, 5 H, C_5H_5)	[d] 208.7 (*C*Ph), 151.6, 127.4, 125.8, 125.1 (Ph), 97.8 (C_5H_5), 97.6 (C_5H_5), 87.4 (CH)
(11)	2.14 [d, 1 H, CH, *J*(HH) 2.5], 4.59 [d, 1 H, CH, *J*(HH) 2.5], 4.87 (s, 5 H, C_5H_5), 5.12 (s, 5 H, C_5H_5), 8.06 (s, 3 H, Me), 8.33 (s, 3 H, Me)	
(12)	2.81 (m, 10 H, Ph), 5.20 (s, 10 H, C_5H_5)	221.7 (CO), 146.6, 128.8, 128.1, 125.7 (Ph), 91.8 (C_5H_5)

[a] Measured in $CDCl_3$ at ambient temperatures, unless otherwise stated. Coupling constants in Hz. [b] Hydrogen-1 decoupled, chemical shifts in p.p.m. relative to $SiMe_4$ with positive values to high frequency. [c] Measured at −28 °C. [d] Measured at −60 °C.

Interest centres on the four-atom carbon chain C(1)—C(4). The two terminal carbon atoms [C(1) and C(4)] are separated by a non-bonding distance of 2.70 Å, and are symmetrically related to the two chromium atoms with which they form a quasi-tetrahedral core [mean Cr-μ-C 2.025(7) Å]. The C–C distances within the four-carbon chain (Table 4) are approximately equal [mean 1.423(11) Å], implying delocalised bonding in the ring. Atoms C(2) and C(3) lie 2.230(8) Å from Cr(1). This distance is, within experimental error, the same as that found [mean 2.221(3) Å] between chromium and the η^2-bonded C atoms of the CH=CH$_2$ group in the complex [Cr(CO)$_2${C$_6$H$_3$(CH$_2$OCH$_2$CH=CH$_2$-1)Me$_2$-3,5}].[11] The atoms of the four-carbon chain, C(1)—C(4), are coplanar, but it is interesting to note that Cr(2), with which these atoms form a five-membered ring, lies 0.51 Å away from this plane, on the opposite side to Cr(1), which lies 1.50 Å from this plane (see below).

TABLE 3

Atomic positional co-ordinates (fractional cell co-ordinates) for (4), [Cr$_2$(CO)(μ-C$_4$Ph$_4$)(η-C$_5$H$_5$)$_2$]·0.25CH$_2$Cl$_2$, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	0.366 8(4)	0.173 8(4)	−0.029 6(4)
C(2)	0.430 0(4)	0.206 4(4)	−0.012 8(4)
C(3)	0.427 0(4)	0.267 7(4)	0.032 8(4)
C(4)	0.360 9(4)	0.289 3(4)	0.056 7(4)
C(5)	0.239 5(4)	0.197 0(4)	0.072 0(5)
C(6)	0.356 4(4)	0.110 2(4)	−0.073 9(4)
C(7)	0.394 4(5)	0.088 7(5)	−0.139 3(5)
C(8)	0.381 8(6)	0.026 0(6)	−0.177 3(6)
C(9)	0.330 3(7)	−0.013 1(5)	−0.151 6(7)
C(10)	0.289 2(6)	0.007 5(5)	−0.092 0(6)
C(11)	0.302 5(5)	0.068 2(4)	−0.053 2(5)
C(12)	0.498 1(4)	0.175 2(5)	−0.037 2(5)
C(13)	0.530 2(5)	0.203 8(6)	−0.105 9(6)
C(14)	0.590 6(6)	0.169 4(8)	−0.134 7(8)
C(15)	0.614 3(6)	0.110 2(7)	−0.099 6(8)
C(16)	0.582 5(5)	0.086 5(6)	−0.034 4(7)
C(17)	0.525 0(4)	0.117 3(5)	−0.003 2(6)
C(18)	0.489 5(4)	0.307 0(4)	0.058 8(5)
C(19)	0.526 1(6)	0.342 7(6)	0.001 2(7)
C(20)	0.577 9(7)	0.386 5(7)	0.023 7(7)
C(21)	0.595 1(6)	0.395 6(6)	0.104 2(7)
C(22)	0.560 2(5)	0.360 0(6)	0.159 8(6)
C(23)	0.507 8(4)	0.314 8(4)	0.137 1(5)
C(24)	0.344 3(4)	0.352 4(4)	0.101 8(5)
C(25)	0.370 0(6)	0.415 9(5)	0.079 7(6)
C(26)	0.353 2(7)	0.475 6(5)	0.125 5(7)
C(27)	0.309 4(6)	0.469 2(5)	0.190 3(6)
C(28)	0.283 4(5)	0.408 7(5)	0.210 5(5)
C(29)	0.299 7(4)	0.351 3(5)	0.167 7(5)
C(30)	0.390 8(4)	0.188 7(4)	0.218 9(4)
C(31)	0.436 6(5)	0.148 3(4)	0.175 5(5)
C(32)	0.398 5(5)	0.095 2(4)	0.142 0(5)
C(33)	0.330 8(5)	0.102 6(4)	0.163 7(5)
C(34)	0.324 7(5)	0.161 5(4)	0.212 4(5)
C(35)	0.227 9(5)	0.227 9(5)	−0.119 4(5)
C(36)	0.190 6(5)	0.270 8(5)	−0.067 7(5)
C(37)	0.230 5(5)	0.328 2(5)	−0.052 9(5)
C(38)	0.290 9(5)	0.323 1(5)	−0.096 8(5)
C(39)	0.289 5(5)	0.261 2(6)	−0.138 6(5)
C(40) [a]	0.000 0	0.059 9(17)	0.250 0
Cr(1)	0.359 2(1)	0.190 8(1)	0.090 5(1)
Cr(2)	0.289 4(1)	0.239 4(1)	−0.007 9(1)
O(5)	0.195 8(3)	0.175 4(4)	0.112 3(4)
Cl(1) [b]	0.061 8(8)	0.084 2(9)	0.300 7(11)
Cl(2) [b]	0.066 8(7)	0.122 8(8)	0.254 9(10)

[a] The site occupancy of C(40) is 0.5. [b] The site occupancy of each Cl is 0.25.

TABLE 4

Bond distances and angles for [Cr$_2$(CO)(μ-C$_4$Ph$_4$)(η-C$_5$H$_5$)$_2$]·0.25CH$_2$Cl$_2$ (4), with estimated standard deviations in parentheses

(*a*) Distances (Å)

Cr(1)–Cr(2)	2.337(2)	Cr(2)–C(5)	1.849(8)
Cr(1)–C(5)	2.365(8)	C(5)–O(5)	1.174(10)
Cr(2)–C(1)	2.024(7)	Cr(1)–C(1)	2.032(7)
Cr(2)–C(4)	2.020(7)	Cr(1)–C(4)	2.023(7)
C(1)–C(2)	1.422(10)	Cr(1)–C(2)	2.229(7)
C(2)–C(3)	1.428(11)	Cr(1)–C(3)	2.232(8)
C(3)–C(4)	1.419(11)		
C(1)–C(6)	1.470(11)	C(2)–C(12)	1.522(11)
C(3)–C(18)	1.513(11)	C(4)–C(24)	1.489(10)
C–C (phenyl) mean 1.38_4			
Cr(1)–C(30)	2.224(7)	Cr(2)–C(35)	2.223(9)
Cr(1)–C(31)	2.236(9)	Cr(2)–C(36)	2.261(10)
Cr(1)–C(32)	2.210(9)	Cr(2)–C(37)	2.227(9)
Cr(1)–C(33)	2.196(9)	Cr(2)–C(38)	2.218(9)
Cr(1)–C(34)	2.215(8)	Cr(2)–C(39)	2.216(8)
C–C (cyclopentadienyl) mean 1.40_3			
C(40)–Cl(1)	1.55(2)	C(40)–Cl(2)	1.81(3)

(*b*) Angles (°)

Cr(1)–Cr(2)–C(5)	67.6(3)	C(4)–Cr(1)–C(1)	83.3(3)
Cr(2)–Cr(1)–C(5)	46.3(2)	C(4)–Cr(2)–C(1)	83.6(3)
Cr(2)–Cr(1)–C(2,3) [a]	75.7(3)	Cr(2)–C(5)–O(5)	165.1(7)
Cr(2)–C(1)–C(2)	109.1(5)	Cr(2)–C(4)–C(3)	109.6(5)
Cr(2)–C(1)–C(6)	122.1(5)	Cr(2)–C(4)–C(24)	121.6(5)
C(6)–C(1)–C(2)	127.2(7)	C(24)–C(4)–C(3)	126.3(7)
Cr(1)–C(1)–C(2)	78.2(4)	Cr(1)–C(4)–C(3)	78.7(4)
Cr(1)–C(1)–C(6)	128.6(5)	Cr(1)–C(4)–C(24)	131.2(5)
Cr(1)–C(1)–Cr(2)	70.4(2)	Cr(1)–C(4)–Cr(2)	70.6(2)
C(1)–C(2)–C(3)	116.8(7)	C(4)–C(3)–C(2)	116.2(7)
C(3)–C(2)–C(12)	121.4(7)	C(2)–C(3)–C(18)	123.5(7)
C(1)–C(2)–C(12)	121.7(7)	C(4)–C(3)–C(18)	120.2(7)
Cl(1)–C(40)–Cl(1′) [b]	144(3)	Cl(2)–C(40)–Cl(2′)	93(2)
Cl(1)–C(40)–Cl(2′)	110(3)		

[a] C(2,3) is the midpoint of the line joining C(2) to C(3). [b] Primed atoms are related to the others by the C_2 axis.

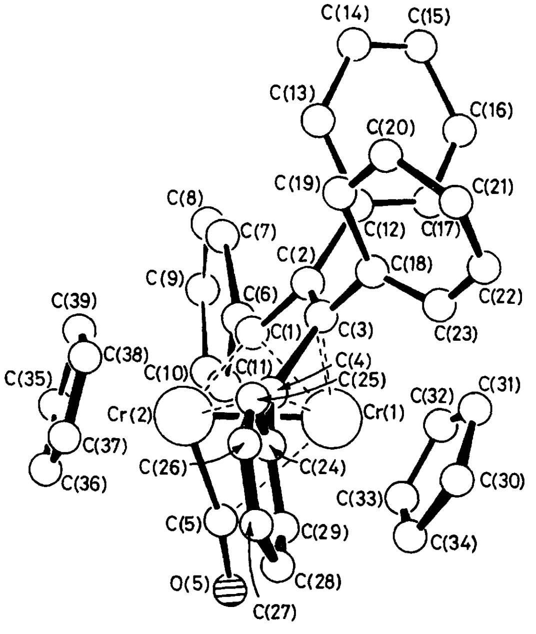
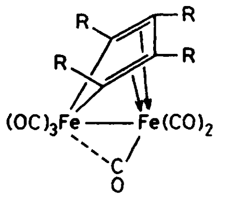


FIGURE 1 Molecular structure of [Cr$_2$(CO)(μ-C$_4$Ph$_4$)(η-C$_5$H$_5$)$_2$] (4), showing the crystallographic numbering

The CO ligand attached to Cr(2) is semi-bridging to Cr(1) [Cr(2)–C(5) 1.85 and Cr(1)–C(5) 2.37 Å; Cr(2)–C(5)–O(5) 165°], in accordance with the relatively low-frequency CO stretch observed in the i.r. spectrum, mentioned above. The plane defined by the two chromium atoms and the carbon and oxygen atoms of this semi-bridging carbonyl ligand is indeed an approximate mirror plane (not required crystallographically) for the molecule as a whole. This mirror passes through atoms C(31) and C(36) of the cyclopentadienyl ligands, and the symmetry is almost exact in relation to the core of the molecule. Only the phenyl rings transgress the symmetry by having somewhat different twists in relation, for example, to the C(1)—C(4) plane [C(6)—C(10) 32.6, C(24)—C(29) 48.7, C(12)—C(17) 74.8, and C(18)—C(23) 67.1°]. The two cyclopentadienyl rings lie off the metal–metal axis but astride the mirror plane, and are inclined *trans* to one another (Figure 1) although at unequal angles to the Cr–Cr bond direction [C(35)—C(39) 10.0 and C(30)—C(34) 26.7°]. These stereochemical relationships can best be appreciated from the stereopair drawing given in Figure 2. The packing of the molecules of (4) in the orthorhombic unit cell is shown in Figure 3.

The bridge system is probably best considered as a resonance hybrid of the bis(μ-alkylidene) formulation (4a) and the chromole structure (4b). During the course of our work Bradley[12] reported preliminary *X*-ray diffraction results on (4), and interpreted the results in terms of structure (4b), drawing analogy with the well established ferrole structures (7) and (8).[13,14] However, both the n.m.r. data and our *X*-ray diffraction data suggest that for (4) the more important canonical form is (4a).



R
(7) H
(8) Ph

The ^{13}C n.m.r. spectrum of (4) shows two peaks at δ 212.6 and 310.0 p.p.m. Initially we considered the latter signal to be due to the C(1) and C(4) nuclei of the CrC_4 ring and the former resonance to the CO ligand.[8] Studies using ^{13}CO, however, established that the reverse assignment was true, in agreement with the conclusion of Bradley.[12] The resonances at 212.6 p.p.m. in the spectrum of (4) and at 196.5 p.p.m. in the spectrum of (5) have chemical shifts in the region where signals are observed for the bridging carbon atoms in alkylidene dimetal compounds. Thus the μ-C atom in $[(OC)_5Cr\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}Pt(PMe_3)_2]$ resonates at 203 p.p.m.[15] In the ^{13}C n.m.r. spectra of the ferroles (7) and (8) the resonances for the bridging carbon atoms are more shielded at δ 156.6 and 173.8 p.p.m. respectively.[16]

There are also interesting differences between the molecular structure of (4) and that of the ferrole complex (8),[14] which suggest that the nature of the organo-bridge bonding is different in the two species. In the ferrole (8) the C_4Fe ring is nearly planar (mean deviation *ca.* 0.05 Å), with the second iron atom at a distance of 1.69 Å from this plane. In (4), in contrast, the C_4Cr ring has a marked 'envelope' conformation, with the Cr atom 0.51 Å away from the plane defined by the C_4 chain, and with the other Cr atom on the *opposite* side of this plane. Moreover, whereas in (4) the CO ligand is terminally bound to Cr(2) and semi-bridging to Cr(1), the reverse situation occurs with (7) and (8), where two CO groups are terminally bonded to the iron atom which is σ,η^4-bonded to the FeC_4 ring and one is semi-bridged to the other atom.[13,14] This suggests that the charge distribution between the two metal atoms of (4) and those of (7) or (8) is reversed.[17]

Reactions between the alkynes RC≡CH (R = Me or Ph) and $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ were studied with a view to investigating possible stereospecificity of alkyne linkage. Phenylacetylene reacted smoothly to give the black crystalline complex (9) in 70% yield. The residue, following crystallisation, was shown by ^{1}H and ^{13}C n.m.r. spectroscopy to contain a small quantity of an isomeric complex (10). The head-to-tail arrangement of the PhCCH groups in (9) is indicated by the observation of two different environments for the CH groups of the C_4Cr ring, the low-field signal at τ 1.43 (Table 2) being

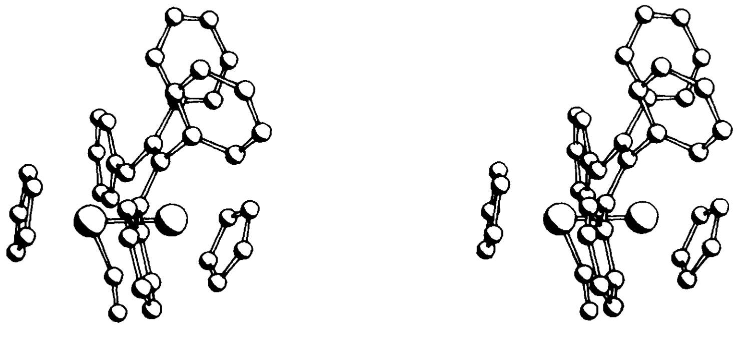


FIGURE 2 Stereoscopic view of the molecular structure of complex (4)

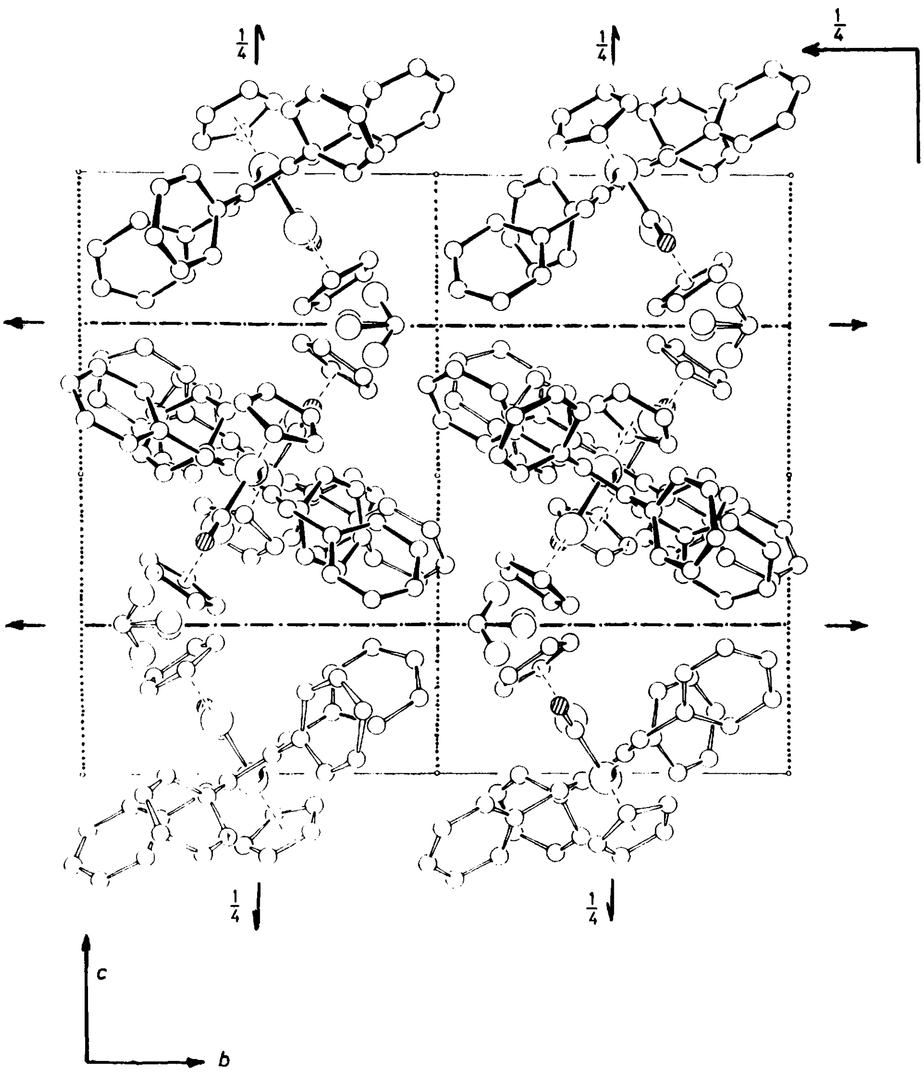


FIGURE 3 Packing of the molecules of complex (4) in the orthorhombic unit cell, seen in projection down *a* looking towards the origin. The disordered incorporation of molecules of CH_2Cl_2 is also shown

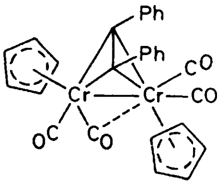
assigned to the $\overline{\mathrm{Cr}(\mu\text{-CH})\mathrm{Cr}}$ group. Confirmation of the structure came from the ^{13}C n.m.r. spectrum which showed four resonances for the C_4Cr group in the expected intensity ratios for two carbon atoms bearing hydrogen atoms and two devoid of them.

The ^1H n.m.r. spectrum of the residue remaining after removal of (9) by crystallisation indicated that only one organometallic species was present, and this was assigned structure (10) on the basis of a single CH signal at τ 4.12, and a single C_6H_5 environment in the C_4Cr ring. The ^{13}C n.m.r. spectrum was in accord with the proposed structure, showing two pairwise equivalent carbon environments in the C_4Cr ring, a strong peak at δ 87.4 p.p.m. (CH), and a low-intensity signal at 208.7 p.p.m. (CC_6H_5). Bradley[12] has also prepared compound (9), but did not detect the presence of (10).

The reaction between MeC≡CH and $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ afforded compound (11), isolated in low yield owing to its reluctance to crystallise. Failure to detect isomers of (11) does not therefore necessarily mean that they were not formed in the reaction. The ^1H n.m.r. spectrum of (11) showed two C_5H_5 environments, two singlets for the Me groups, and two doublets integrating to one proton each, as expected for the assigned geometry.

The prevalence of the asymmetric complexes (9) and (11) as products of the reaction with monosubstituted alkynes contrasts with the general formation of symmetrical ferroles in the reaction of these alkynes with iron carbonyls.[18,19] The reason for the difference in stereochemistry of the products from the chromium and the iron systems probably lies in differences between the mechanisms of the two reactions, discussed below. A random process in the reaction of $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with PhC≡CH or MeC≡CH would produce a 50% yield of the asymmetric isomer and 25% yields of each of the two possible symmetric products.

In view of the existence of the compounds (1), it is reasonable to assume that the complexes (4)—(6) and (9)—(11) form *via* dichromium species $[Cr_2(CO)_4(\mu\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$. With the object of isolating a chromium compound of this type a mixture of $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and diphenylacetylene was refluxed in pentane. Reaction proceeded slowly but only i.r. bands due to (4) and to starting material were observed after 3 weeks. However, treatment of a toluene solution of $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and PhC≡CPh with u.v. light for 4 days afforded the desired complex (12) (Tables 1 and 2).



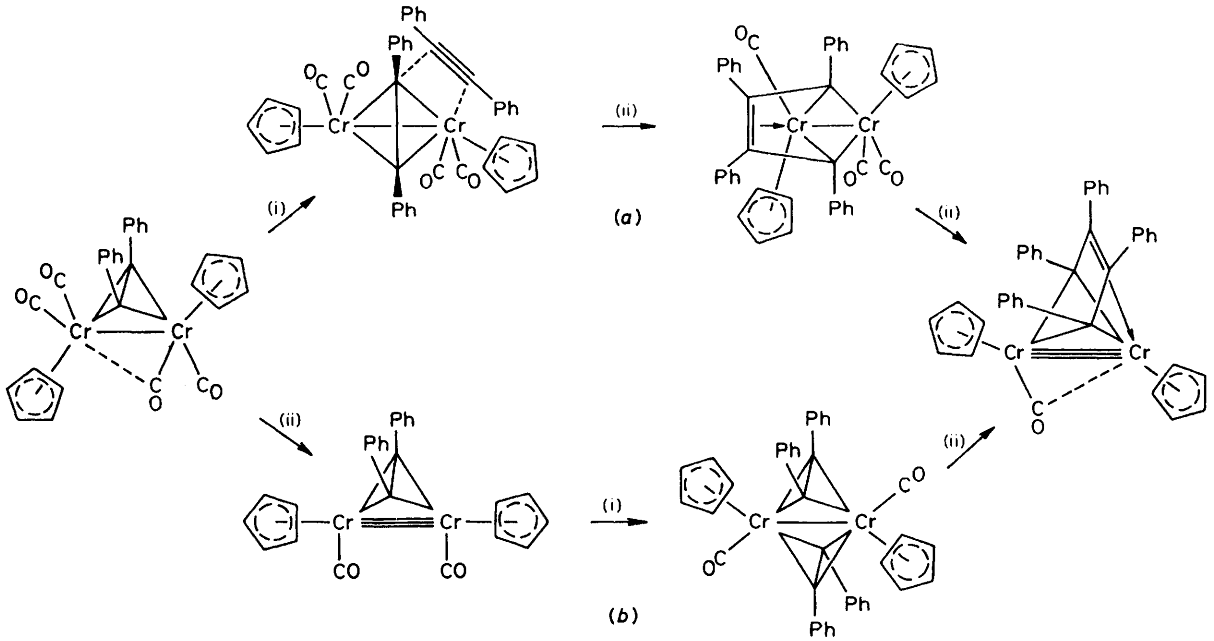
(12)

Refluxing a mixture of (12) and PhC≡CPh in hexane yielded complex (4); i.r. monitoring showed the three CO stretching bands of (12) decreasing in intensity as the single band due to (4) grew in magnitude.

In Scheme 1 two possible routes for the generation of (4) from (12) are depicted. Pathway (*a*), with ' side-on ' attack of the alkyne in the first step, follows the proposal [20] for the mechanism of formation of ferroles (7) or (8), while (*b*) involves initial loss of two molecules of CO from (12) to give a Cr≡Cr species to which a second molecule of alkyne adds, giving a bis(μ-alkyne) intermediate. Further loss of CO and linkage of the two alkynes affords the observed product (4). Strong evidence in favour of pathway (*b*) has recently been obtained by Davidson *et al.*,[21] who observed that the bis(μ-alkyne) complexes $[(\eta\text{-}C_5H_5)(OC)M(\mu\text{-}CF_3C_2CF_3)_2Co(CO)_2]$ (M = Mo or W) undergo alkyne linking under mild conditions to afford compounds $[(\eta\text{-}C_5H_5)(OC)_2M\{\mu\text{-}C_4(CF_3)_4\}Co(CO)_2]$, with a $M(\mu\text{-}C_4R_4)Co$ unit like those in (4)—(11). The existence of such a bis(μ-alkyne) complex as an intermediate in the dichromium system could explain the preference for head-to-tail linking of monosubstituted alkynes; clearly, steric factors would favour a ' trans ' orientation of the two molecules of alkyne when bridging the Cr_2 unit, so that the substituents were furthest apart. This would lead to head-to-tail linking upon carbon–carbon bond formation.

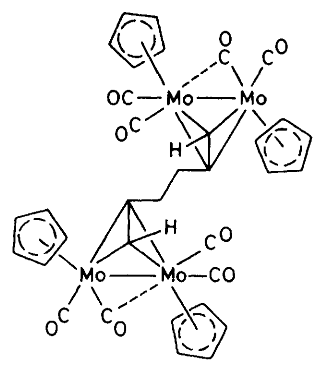
Dimolybdenum Compounds.—As mentioned in the introduction, by treating $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with alkynes at room temperature previous workers [1-4] have prepared several complexes of type (1; $R^1 = R^2$ = H, Me, Et, Ph, or CO_2Me; R^1 = H, R^2 = Ph, CF_3, or CH_2CH_2OH; R^1 = Ph, $R^2 = CH_2OH$). We have extended the series by synthesising the compounds [1; $R^1 = R^2 = C_6H_4Me\text{-}4$; R^1 = H, R^2 = Me or $(CH_2)_2C{\equiv}CH$]. The reaction of hexa-1,5-diyne with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ also afforded the tetramolybdenum complex (13).

Of primary interest was whether any of the complexes (1) could be converted by reaction with excess of alkyne into molybdenum analogues of the chromium compounds (4)—(6), or (9)—(11). Accordingly, compound (1; $R^1 = R^2$ = Ph) was treated with PhC≡CPh in octane at reflux, thereby affording an emerald green complex (14) (Table 5) in 75% yield. The complex was also produced directly from $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ by refluxing the latter in octane with diphenylacetylene. The extreme air sensitivity of (14) prevented satisfactory elemental analysis. However, the mass spectrum showed the

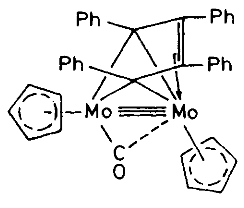


SCHEME 1 Possible routes for the conversion of complex (12) into (4): (i) +PhC≡CPh, (ii) −CO

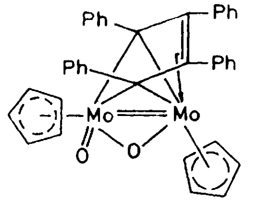
expected molecular ion, and a peak corresponding to the loss of one CO group. The latter showed itself in the i.r. spectrum with a band at 1 755 cm^{-1}. The appearance of the ^{1}H and ^{13}C n.m.r. spectra of (14) (Table 6) were qualitatively very similar to those of the chromium analogue (4), as would be expected for similar structures. Thus the ^{13}C spectrum, measured in the presence of $[Cr(acac)_3]$ (acac = acetylacetonate), revealed the resonance for the CO ligand at δ 300.6 p.p.m., and signals for the pairwise equivalent *C*Ph atoms at 199.7 and 106.7 p.p.m., the former being assigned to the two carbon atoms bonded to both molybdenum atoms. It is noteworthy that all three resonances occur slightly to lower field than the corresponding signals in the spectrum of (4).



(13)



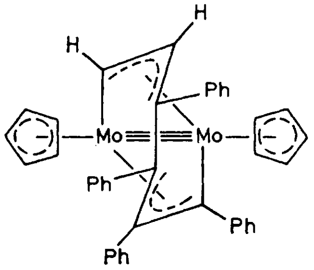
(14)



(15)

The green dichloromethane solution of (14) turns brown within a few minutes on exposure to air. The i.r. spectrum of the brown crystalline product showed that no CO ligand was present. The mass spectrum and elemental analysis of the compound were in accord with the formulation $[Mo_2O_2(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$. From the mass spectrum, following the parent ion, peaks were observed corresponding to the successive loss of two oxygen atoms. The ^{13}C n.m.r. spectrum (Table 6) established that the compound had a more asymmetric structure than (14). The *C*Ph nuclei gave rise to four separate signals instead of the two observed in the spectrum of (14), and there were more signals for the phenyl-ring carbon atoms. From the analytical and spectroscopic data structure (15) is proposed for this oxidation product.

Since compound (1; R^1 = R^2 = Ph) reacts with diphenylacetylene to give (14), it was useful to extend this result by investigating similar reactions of other compounds of type (1). Accordingly, (1; R^1 = R^2 = H) was refluxed in octane with diphenylacetylene, whereupon within 2 h the CO stretch in the i.r. spectrum of the starting complex disappeared and a black solid $[Mo_2(HC_2H)(PhC_2Ph)_2(\eta\text{-}C_5H_5)_2]$ (16) was isolated. Although the air sensitivity of this product led to erratic microanalytical results, the mass spectrum which gave a molecular ion and the ^{1}H and ^{13}C n.m.r. spectra (Table 6) were in complete accord with the ' fly-over ' structure for (16) shown, analogous to that of (3). The ^{1}H spectrum, in addition to two resonances for non-equivalent C_5H_5 ligands, showed two HC signals of relative intensity 1 : 10 with respect to the Ph groups. There were difficulties associated with recording the ^{13}C n.m.r. spectrum due to the relative insolubility of the compound, and to its partial decomposition over the period required for measurement. However, it was readily apparent that (16) contains two inequivalent C_5H_5 ligands and four inequivalent phenyl environments. Identification of the six signals expected for the carbon atoms of the chain, resulting from linkage of three alkyne molecules, was hampered by their long relaxation times, and the appearance of peaks due to decomposition products. Nevertheless, by inspection of several spectra the six peaks were identified, with the two of higher intensity being attributed to the CH groups.



(16)

The analogous reactions of alkynes with $[Co_2(CO)_6(RC_2R)]$ to afford ' fly-over ' bridge complexes (3) are often accompanied by formation of arenes, cyclopentadienones, and polymers,[6] but such products were not observed in the present study, probably due to the enhanced stability of carbon–molybdenum σ bonds relative to those of cobalt, so that the organomolybdenum species do not decompose to organic species as readily.

Formation of (16) probably proceeds *via* an intermediate with a structure similar to (14). Although no such intermediate was isolated, sampling of the reaction mixture in its early stages showed, in addition to CO bands due to (1; R^1 = R^2 = H), a carbonyl-stretching band at 1 746 cm^{-1}, which compares well in frequency with that of 1 755 cm^{-1} in the spectrum of (14). While the intermediate evidently reacts with excess of PhC≡CPh to give (16), it is not obvious why insertion occurs at the Mo–C(Ph) rather than the Mo–C(H) end of the chain. Nor is it apparent why (14) did not react with more

TABLE 5

Analytical[a] and other data for the dimolybdenum compounds

Complex	Colour	$\tilde{\nu}_{max.}$(CO) [b]/cm^{-1}	Yield (%)	Analysis (%) C	Analysis (%) H	*M*
(14)	Green	1 755br	70			706 (706)
(15)	Brown			64.0 (64.2)	4.8 (4.2)	710 (710)
(16)	Green		65			704 (704)
(17)	Brown	1 948s, 1 699m	23	44.7 (45.3)	3.7 (3.5)	688 (688)
(18)	Brown	1 973m, 1 933s, 1 697m	1	45.4 (45.3)	3.7 (3.5)	688 (688)
(19) [c]	Violet	1 691br	44	40.8 (40.7)	3.7 (3.6)	774 (774)
(20)	Blue	1 692br	1	46.4 (46.5)	3.7 (3.9)	774 (774)
(21)	Violet	1 721s, 1 698m	24	45.4 (45.8)	3.8 (3.8)	890 (890)
(22)	Pink	1 722s, 1 691m	2	45.8 (45.8)	4.2 (3.8)	890 (890)
(23)	Orange-yellow	2 006s, 1 961w, 1 729m, 1 694m	9	44.8 (43.8)	3.7 (3.5)	804 (804)
(24)	Black	1 710s, 1 689m	18	64.4 (65.2)	4.9 (4.5)	846 (846)
(25)	Black	1 710s, 1 689m	23	64.2 (65.2)	5.2 (4.5)	846 (846)

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2. [c] Crystallised with two molecules of CH_2Cl_2, see text.

TABLE 6

Hydrogen-1 and ^{13}C n.m.r. data for the dimolybdenum complexes[a]

Complex	^1H (τ)	^{13}C (δ) [b]
(14)	3.1 (m, 16 H, Ph), 3.53 (m, 4 H, Ph), 4.33 (s, 5 H, C_5H_5), 4.93 (s, 5 H, C_5H_5)	300.6 (CO), 200 (*C*Ph), 151.9, 138.7, 132.7, 128.8, 128.3, 126.6, 125.8, 124.0 (Ph), 106.7 (*C*Ph), 99.2 (C_5H_5), 98.8 (C_5H_5)
(15)	2.35 (m, 3 H, Ph), 2.68 (m, 8 H, Ph), 3.00 (m, 8 H, Ph), 3.84 (m, 1 H, Ph), 4.29 (s, 5 H, C_5H_5), 4.78 (s, 5 H, C_5H_5)	242.8 (*C*Ph), 197.9 (*C*Ph), 150.9, 145.0, 144.6, 137.6, 130.5, 129.8, 128.2, 127.4, 127.2, 126.9, 126.0, 125.6, 125.1 (Ph), 106.6 (C_5H_5), 99.4 (C_5H_5), 90.9 (*C*Ph), 84.7 (*C*Ph)
(16)	2.6—3.0 (m, 20 H, Ph), 3.06 [d, 1 H, CH, *J*(HH) 6], 3.99 [d, 1 H, CH, *J*(HH) 6], 5.19 (s, 5 H, C_5H_5), 5.44 (s, 5 H, C_5H_5)	191.9 (*C*Ph), 158.8 (*C*H), 152.4, 146.6, 145.9, 139.5 (Ph), 133.2 (*C*Ph), 129.5, 129.0, 128.0, 127.7, 126.6, 126.0, 124.4, 123.5 (Ph), 102.1 (*C*Ph), 96.9 (CH), 96.2 (C_5H_5), 91.4 (C_5H_5), 86.8 (*C*Ph)
(17)	4.90 (s, 5 H, C_5H_5), 6.07 (s, 2 H, CH), 6.13 (s, 6 H, Me), 6.37 (s, 6 H, Me)	226.8 (CO), 188.4 (*C*CO$_2$Me or C*C*O$_2$Me), 178.2 (*C*CO$_2$Me or C*C*O$_2$Me), 93.3 (C_5H_5), 73.5 (CH), 52.5 (Me), 51.8 (Me)
(18)	4.86 (s, 5 H, C_5H_5), 5.12 (s, 5 H, C_5H_5), 5.86 [d, 1 H, CH, *J*(HH) 3], 6.08 [d, 1 H, CH, *J*(HH) 3], 6.10 (s, 3 H, Me), 6.13 (s, 3 H, Me), 6.33 (s, 3 H, Me), 6.37 (s, 3 H, Me)	
(19)	4.62 [d, 1 H, *J*(HH) 2], 4.74 (s, 4 H, CH_2Cl_2), 4.84 (s, 5 H, C_5H_5), 4.88 (s, 5 H, C_5H_5), 5.94 (s, 3 H, Me), 6.04 (s, 3 H, Me), 6.16 (s, 3 H, Me), 6.28 (s, 6 H, Me), 6.59 (s, 3 H, Me), 7.44 [d, 1 H, CH, *J*(HH) 2]	178.3 (*C*CO$_2$Me), 176.7 (*C*O$_2$Me), 175.1 (*C*O$_2$Me), 174.8 (*C*O$_2$Me), 173.7 (*C*O$_2$Me), 167.4 (*C*CO$_2$Me + *C*O$_2$Me), 167.2 (*C*O$_2$Me), 120.8 (*C*CO$_2$Me), 101.8 (*C*O$_2$Me), 100.3 (C_5H_5), 96.0 (C_5H_5), 65.1 (CH), 63.4 (*C*CO$_2$Me), 60.7 (CH), 57.1 (*C*CO$_2$Me), 53.4 (Me), 52.8 (Me), 52.1 (Me), 50.8 (Me)
(20)	2.66 [d, 1 H, CH, *J*(HH) 3], 4.60 (s, 5 H, C_5H_5), 5.11 (s, 5 H, C_5H_5), 5.19 [d, 1 H, CH, *J*(HH) 3], 5.83 (s, 3 H, Me), 6.23 (s, 3 H, Me), 6.25 (s, 3 H, Me), 6.28 (s, 3 H, Me), 6.48 (s, 6 H, Me)	
(21)	4.70 (s, 5 H, C_5H_5), 4.76 (s, 5 H, C_5H_5), 5.92 (s, 6 H, Me), 6.18 (s, 6 H, Me), 6.33 (s, 6 H, Me), 6.41 (s, 6 H, Me)	176.0 (*C*CO$_2$Me), 174.9 (*C*O$_2$Me), 172.4 (*C*O$_2$Me), 171.1 (*C*O$_2$Me), 167.0 (*C*O$_2$Me), 116.0 (*C*CO$_2$Me), 103.7 (C_5H_5), 99.6 (C_5H_5), 67.1 (*C*CO$_2$Me), 62.9 (*C*CO$_2$Me), 53.8 (Me), 52.7 (Me), 52.4 (Me), 51.6 (Me)
(22)	4.60 (s, 10 H, C_5H_5), 6.08 (s, 6 H, Me), 6.10 (s, 6 H, Me), 6.27 (s, 6 H, Me), 6.50 (s, 6 H, Me)	
(23)	4.98 (s, 10 H, C_5H_5), 6.17 (s, 6 H, Me), 6.24 (s, 6 H, Me), 6.63 (s, 6 H, Me)	219.0 (CO), 175.2 (*C*CO$_2$Me or *C*O$_2$Me), 173.2 (*C*CO$_2$Me or *C*O$_2$Me), 169.0 (*C*CO$_2$Me or *C*O$_2$Me), 153.9 (*C*CO$_2$Me), 95.3 (*C*CO$_2$Me), 92.9 (C_5H_5), 52.7 (Me), 52.2 (Me), 51.8 (Me)
(24)	2.10—3.50 (m, 20 H, Ph), 5.50 (s, 5 H, C_5H_5), 5.60 (s, 5 H, C_6H_5), 5.72 [d, 1 H, CH, *J*(HH) 2], 6.05 (s, 3 H, Me), 6.06 (s, 3 H, Me), 7.27 [d, 1 H, CH, *J*(HH) 2]	
(25)	2.10—3.70 (m, 20 H, Ph), 5.30 (br, 1 H, CH), 5.50 (s, 5 H, C_5H_5), 5.61 (s, 5 H, C_5H_5), 5.87 (s, 3 H, Me), 6.07 (s, 3 H, Me), 6.92 (br, 1 H, CH)	

[a] Measured in $CDCl_3$ at ambient temperatures; coupling constants in Hz. [b] Hydrogen-1 decoupled chemical shifts in p.p.m. relative to $SiMe_4$, with positive values to high frequency.

diphenylacetylene under reflux in octane for several days to give a ' fly-over ' complex similar to (16).

Reaction of (1; $R^1 = R^2 = H$) with $MeO_2CC{\equiv}CCO_2Me$ in refluxing octane afforded an indigo-coloured mixture which, after chromatography, yielded four compounds. The first two compounds to be eluted were evidently isomers of composition $[Mo_2(CO)_2(HC_2H)(MeO_2CC_2CO_2Me)_2(\eta\text{-}C_5H_5)_2]$. Mass spectra of both species showed molecular ions, with further ions corresponding to successive loss of two CO groups.

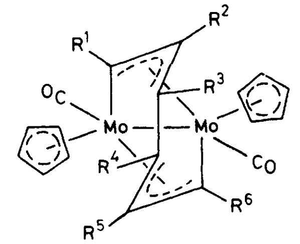
The ^1H n.m.r. spectrum of the first complex indicated that it had a symmetrical structure. There was only one resonance for the C_5H_5 ligands, one for the HC groups, and two signals for the CO_2Me substituents. The ^{13}C n.m.r. spectrum also supported the structure (17) proposed, although one of the expected signals (Table 6) was absent, but it is not clear whether the missing resonance is a CO ligand signal or one of the carbon-chain signals. The former seems more likely in view of the difficulties encountered in observing such resonances at 25.15 MHz in non-enriched ^{13}CO samples.

The second complex had a less symmetrical structure, as evidenced by the observation in the ^1H n.m.r. spectrum of two C_5H_5 resonances, four Me signals, and a doublet assigned to a proton from the originally co-ordinated ethyne. The second proton resonance expected for the latter was partially obscured by the two Me peaks at lowest field (Table 6). Insufficient compound was available for measurement of a ^{13}C n.m.r. spectrum, but on the basis of the data available, a structure (18) for this product seems very probable. Preparation of the two isomers (17) and (18) by treating (1; $R^1 = R^2 = H$) with $MeO_2CC{\equiv}CCO_2Me$ implies that a probable intermediate with a structure analogous to (14) can undergo insertion of the second alkyne molecule at either the Mo–C(H) or the Mo–$C(CO_2Me)$ end of the chain.

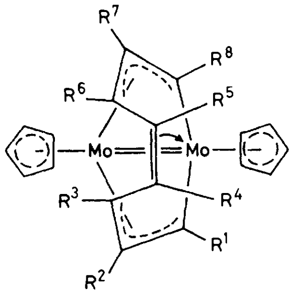
The third product obtained by chromatographing the reaction mixture was isolated as black crystals. From elemental analysis and the ^1H n.m.r. spectrum it became apparent that this complex crystallised with two molecules of CH_2Cl_2 per molecule of compound. The n.m.r. data did not allow unambiguous assignment of the structure and consequently a single-crystal *X*-ray diffraction study was carried out.[22] This established that the compound (19) had a molybdenum–molybdenum double bond bridged by an eight-carbon chain, formed by linkage of four alkyne groups in the manner shown.

In the eight-carbon chain the substituents R^5 and R^6 are the hydrogen atoms of the original $\overline{Mo(\mu\text{-}HC_2H)Mo}$ system of (1). The two terminal carbon atoms bridge the two molybdenum atoms in a slightly asymmetric manner, contrasting with the symmetric bridging structure observed for (4). This asymmetry takes the form of both terminal carbon atoms being *ca.* 0.15 Å closer to that molybdenum atom which is η^2 co-ordinated by the $R^4C{=}CR^5$ group.

The fourth reaction product was obtained in low yield (*ca.* 1%) also in the form of black crystals; it proved to be an isomer of (19) to which structure (20) is assigned. Although insufficient material was available for measurement of the ^{13}C n.m.r. spectrum, the ^1H spectrum showed a doublet resonance at τ 2.66 (Table 6), this chemical shift being near that for the corresponding $\overline{Mo(\mu\text{-}CH)Mo}$ signal in (16).



	R¹	R²	R³	R⁴	R⁵	R⁶
(17)	CO_2Me	CO_2Me	H	H	CO_2Me	CO_2Me
(18)	H	H	CO_2Me	CO_2Me	CO_2Me	CO_2Me
(23)	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me

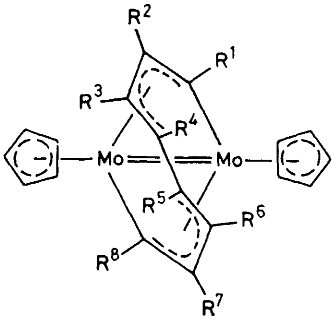


	R¹	R²	R³	R⁴	R⁵	R⁶	R⁷	R⁸
(19)	CO_2Me	CO_2Me	CO_2Me	CO_2Me	H	H	CO_2Me	CO_2Me
(20)	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	H	H
(21)	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me
(24)	Ph	Ph	Ph	Ph	H	H	CO_2Me	CO_2Me
(25)	H	H	Ph	Ph	Ph	Ph	CO_2Me	CO_2Me

The two major products of the reaction of (1; $R^1 = R^2 = H$) with $MeO_2CC{\equiv}CCO_2Me$ were compounds (17) and (19), and the proportions varied according to the reaction conditions. With a low concentration of the alkyne, yields of (17) and (19) were *ca.* 6 and 50% respectively, but at high alkyne concentration the yields were *ca.* 25 and 45% respectively. The increase in yield of the three-alkyne complex (17) relative to the four-alkyne complex (19) when higher concentrations of alkyne reagent are employed is at first sight surprising. We conclude that (17) is not an intermediate in the formation of (19), and is formed by reaction of alkyne with a transient di- or tri-carbonyl species of the type illustrated in Scheme 1.

The reaction between (1; $R^1 = R^2 = CO_2Me$) and $MeO_2CC{\equiv}CCO_2Me$ was next investigated, in the expectation of obtaining an oligomerisation product $[Mo_2(MeO_2CC_2CO_2Me)_4(\eta\text{-}C_5H_5)_2]$ with a structure related to that of (19). Reaction occurred readily in refluxing octane to give, after chromatographic separation, four products including a trace amount of a green substance which was not identified. Three dimolybdenum complexes were characterised, two of these (in 24 and 2% yield) being isomers of $[\mathrm{Mo_2(MeO_2CC_2CO_2Me)_4(\eta\text{-}C_5H_5)_2}]$, and the third (9%) having the composition $[\mathrm{Mo_2(CO)_2(MeO_2CC_2CO_2Me)_3(\eta\text{-}C_5H_5)_2}]$.

The isomers of $[\mathrm{Mo_2(MeO_2CC_2CO_2Me)_4(\eta\text{-}C_5H_5)_2}]$ have n.m.r. spectra which show pairwise equivalence of $\mathrm{CO_2Me}$ groups, but one of them (the minor product) has equivalent cyclopentadienyl ligand environments while for the major violet crystalline isomer they are inequivalent. This immediately characterises the latter as having structure (21), *i.e.* as being an analogue of structurally established (19). The minor pink crystalline isomer was shown by an *X*-ray diffraction study to have structure (22),[22] with the expected C_2 axis passing through the Mo=Mo and $\mathrm{R^4C\stackrel{...}{=}CR^5}$ bonds, as reflected in the ^{1}H n.m.r. spectrum. The ^{13}C n.m.r. signals (Table 6) in the spectrum of (21) are assignable when taken together with the data for (19). There are two $\mathrm{C_5H_5}$ resonances and four peaks assigned to Me groups. Four resonances of approximately equal intensity in the range 167—175 p.p.m. are assigned to the eight $\mathrm{CO_2Me}$ atoms, indicating pairwise equivalence. The eight carbon atoms of the chain, also in pairwise environments, appear as four signals of lower intensity than the $\mathrm{CO_2Me}$ resonances owing to their longer relaxation times. A low-field signal of this set at 176.0 p.p.m. is assigned to the two terminal bridging ' alkylidene ' carbon atoms.



(22) R = $\mathrm{CO_2Me}$

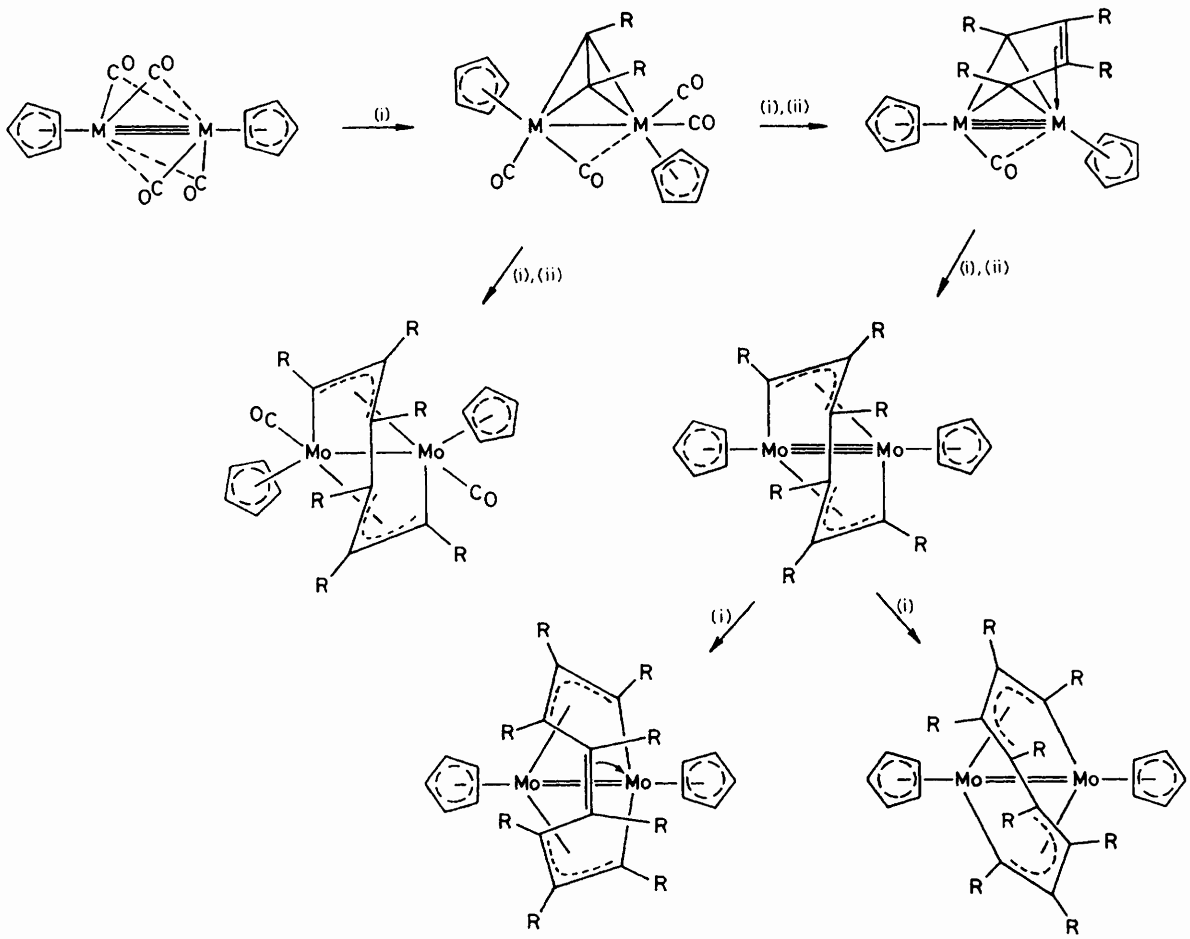
The yellow air-stable compound $[\mathrm{Mo_2(CO)_2(MeO_2CC_2CO_2Me)_3(\eta\text{-}C_5H_5)_2}]$ was identified by microanalysis, mass spectrometry, and its ^{1}H and ^{13}C n.m.r. spectra as being of structure (23), analogous to complexes (17) and (18). Only one $\mathrm{C_5H_5}$ ligand resonance and three Me signals are visible in both the ^{1}H and ^{13}C n.m.r. spectra of (23), as expected for such a symmetrical structure.

A reaction between (16) and $\mathrm{MeO_2CC{\equiv}CCO_2Me}$ was studied in order to establish that compounds containing four linearly linked alkynes could be formed from molecules having a bridge system with six carbon atoms. From the reaction, two green isomeric complexes of composition $[\mathrm{Mo_2(HC_2H)(PhC_2Ph)_2(MeO_2CC_2CO_2Me)(\eta\text{-}C_5H_5)_2}]$ were obtained, confirming this point. However, the asymmetry of substitution on the $\mathrm{C_8}$ chains does not allow us to draw a clear distinction between structural types (19) and (22) for these products. Nevertheless, in view of their formation in fair yields, and the very low yield of (22) obtained, structures (24) and (25) seem most likely. It thus appears that $\mathrm{MeO_2CC{\equiv}CCO_2Me}$ has added to each end of the $\mathrm{C_6}$ chain in (16). On the basis that μ-CH groups at the end of carbon chains tend to occur at relatively low field, *e.g.* at τ 3.06 in (16), the isomer with the $\mathrm{HC_2H}$ unit resonances at lowest field was assigned structure (25).

At the time of our original work,[5] structures such as those of compounds (19)—(22), (24), and (25), involving the linkage of four alkynes, were unprecedented. Recently it has been found [23] that the mononuclear molybdenum salt $[\mathrm{Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$, when reduced with $[\mathrm{Fe(CO)_2(\eta\text{-}C_5H_5)}]^-$, affords a complex $[\mathrm{Mo_2(\mu\text{-}C_8Me_8)(\eta\text{-}C_5H_5)_2}]$ with a molecular structure similar to that established for (19) by *X*-ray crystallography [22] and deduced for (20), (21), (24), and (25). In all these species the $\mathrm{C_8}$ chain begins and ends with σ bonds to the same molybdenum atom which also has an η^2 interaction with the two C(4)–C(5) carbon atoms of the molybdenacyclononatetraene ring. The latter is also attached to the second molybdenum atom *via* two η^3-allylic interactions. This mode of bonding of the $\mathrm{C_8}$ chain contrasts with that established for (22),[22] where the chain begins and ends with σ bonds to different molybdenum atoms, *i.e.* an eight-carbon ' fly-over '. In (22) the carbon chain is bonded through an η^4-diene interaction to each of the molybdenum atoms, which are also formally double-bonded. This mode of bridge bonding of a $\mathrm{C_8}$ chain between two metal centres has also been found in the compound $[\mathrm{Cr_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2}]$, prepared by treating $[\mathrm{Cr(\eta\text{-}C_5H_5)_2}]$ with $\mathrm{Na_2[C_8H_8]}$ (ref. 24), in a process involving $\mathrm{C_8}$ ring opening.

Our observations of stepwise $\mathrm{C_8}$ chain growth are summarised in Scheme 2. Surprisingly, in view of the existence of $[\mathrm{Cr_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2}]$, no complexes with three or four linked alkynes were observed with dichromium compounds and insertion to give an isolable complex ceased at the $\overline{\mathrm{Cr{-}C_4{-}Cr}}$ stage. With molybdenum, species with three and four linked alkynes were formed readily and, moreover, two different arrangements of the $\mathrm{C_8}$ chain about the dimolybdenum unit were discovered. Clearly the nature of the metal is an important determining factor in carbon-chain growth. So also is the nature of the alkyne, with $\mathrm{C_6}$ and $\mathrm{C_8}$ chains being commonly observed with electronegative substituents such as $\mathrm{CO_2Me}$ and Ph.

Two routes from the complexes (1) to the $\overline{\mathrm{M{-}C_4{-}M}}$ system have been discussed (Scheme 1), and there is evidence, as discussed earlier (see also ref. 21), that the one actually followed involves simultaneous bridging of the $\mathrm{M_2}$ unit by two alkynes prior to C–C bond formation. In progressing from $\overline{\mathrm{M{-}C_4{-}M}}$ through $\overline{\mathrm{M{-}C_6{-}M}}$ to the $\overline{\mathrm{M{-}C_8{-}M}}$ chain it is possible that at each stage an incoming



SCHEME 2 Acetylene linkage at a dimetal centre: (i) $+\mathrm{RC_2R}$, (ii) $-\mathrm{CO}$

molecule of alkyne also first co-ordinates to the M_2 unit as a bridging ligand, and that rearrangement to give an extended chain follows. In both the $\overline{\mathrm{M{-}C_4{-}M}}$ and $\overline{\mathrm{M{-}C_6{-}M}}$ systems there is, formally,[25] a triple bond between the metal atoms and pre-co-ordination at this site is to be expected in view of the reactivity of $[\mathrm{Mo_2(CO)_4(\eta\text{-}C_5H_5)_2}]$ towards alkynes. An important feature of Scheme 2 is, in fact, the demonstration that stepwise formation of C–C bonds is accompanied by changes in multiplicity of metal–metal bonding in the dimetal unit. Such versatility may well be crucial in any catalytic activity of future systems based on dimetal species.

The discovery[24] of $[\mathrm{Cr_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2}]$, and our own observations, led to the proposal[5,26] that dimetal centres could be involved in some metal-catalysed cyclisation reactions of alkynes, including the nickel-catalysed Reppe synthesis of cyclo-octatetraene. This was reinforced by the liberation of cyclo-octatetraene from $[\mathrm{Cr_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2}]$ upon treatment with CO.[24] In the present work, however, no cyclo-octatetraenes were observed as products; although, if formed in small quantity, their isolation would not be easy and we cannot rule out the possibility that some are formed. Attempts to degrade (19) by the action of $\mathrm{Me_3NO}$ were unsuccessful, and although a rapid reaction was observed with cerium(IV) ion in acetone, no organic compound was isolated from the mixture. Heating (19) in air to *ca.* 250 °C led to recovery of the complex unchanged. Moreover, heating (21) in octane for several days failed to produce its isomer (22), and these two structural types do not appear to be readily interconvertible. The formation of hexakis(methoxycarbonyl)benzene was observed in the reaction which produced (19). Interestingly, this benzene derivative was quantitatively produced by treating (6) with $\mathrm{MeO_2CC{\equiv}CCO_2Me}$, but the reaction is not catalytic, compound (6) being consumed in the reaction.

EXPERIMENTAL

All reactions were carried out under an atmosphere of oxygen-free nitrogen, using conventional techniques. Solvents were dried and distilled prior to use. Products, analytical data for which are given in Tables 1 and 5, were in general separated by chromatography on alumina (Brockman activity II). Mass spectra were recorded on an AEI MS902 spectrometer operating at 70 eV,* and n.m.r. spectra measured with JEOL PS-100 and PFT-100 instruments. Infrared spectra were measured in hexane solutions unless otherwise stated. The complex $[\mathrm{Mo_2(CO)_4(\eta\text{-}C_5H_5)_2}]$ was

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

prepared as described previously,[2] as were various compounds of type (1).[3]

Preparations.—[Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$]. The complex [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] can be obtained from [Cr$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$].[4,7] An alternative synthesis which avoids the necessity to prepare first the hexacarbonyl species is as follows. Chromium hexacarbonyl (10 g, 45.5 mmol) was refluxed in acetonitrile (200 cm^3) for 3 d, after which i.r. bands due to [Cr(CO)$_4$(NCMe)$_2$] were observed. The solvent was removed *in vacuo* and toluene (200 cm^3) and freshly distilled cyclopentadiene (6 g, 92 mmol) were added. The mixture was heated to reflux (2 h), filtered through Kieselguhr, and volatiles removed *in vacuo*, affording a green residue. Sublimation removed small quantities of [Cr(CO)$_5$(NCMe)], and the remaining solid was crystallised from toluene–hexane to give dark green needles of [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (5.5 g, 70%).[7]

[Mo$_2$(CO)$_4$(μ-alkyne)(η-C$_5$H$_5$)$_2$]. (*i*) Maroon *crystals* of [Mo$_2$(CO)$_4$(μ-MeC$_2$H)(η-C$_5$H$_5$)$_2$] (1; R^1 = H, R^2 = Me) were obtained in 75% yield by passing MeC≡CH through a toluene solution of [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] at ambient temperatures. Removal of solvent followed by chromatography, eluting with dichloromethane–hexane (3 : 7), afforded (1; R^1 = H, R^2 = Me).

(*ii*) A mixture of [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (4 mmol) and 4,4′-MeC$_6$H$_4$C≡CC$_6$H$_4$Me (5 mmol) was refluxed (2.5 h) in octane. Chromatography, eluting with dichloromethane–hexane (4 : 6), afforded a maroon-coloured solution from which was obtained *crystals* of [Mo$_2$(CO)$_4$(μ-4,4′-MeC$_6$H$_4$C$_2$C$_6$H$_4$Me)(η-C$_5$H$_5$)$_2$] (1; R^1 = R^2 = C$_6$H$_4$Me-4) (58%).

(*iii*) A toluene solution of [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (2 mmol) was treated with hexa-1,5-diyne (4.5 mmol) and the mixture stirred for 15 min. Chromatography separated two bands. The first, eluted with dichloromethane–hexane (4 : 6), afforded maroon *crystals* of [Mo$_2$(CO)$_4${μ-HC$_2$(CH$_2$)$_2$C$_2$H}(η-C$_5$H$_5$)$_2$] [1; R^1 = H, R^2 = (CH$_2$)$_2$C$_2$H] (0.66 g, 63%), m.p. 129—131 °C (Found: C, 46.7; H, 3.1%; *M*, 512. C$_{22}$H$_{16}$Mo$_2$O$_4$ requires C, 46.9; H, 3.1%; *M*, 512); $\nu_{max.}$ (CO) at 1 995s, 1 932s, 1 920s, 1 915s, and 1 848s cm^{-1}; n.m.r. (CDCl$_3$), ^{1}H, τ 3.96 (s, 1 H, CH), 4.71 (s, 10 H, C$_5$H$_5$), 7.25 (m, 2 H, CH$_2$), and 8.00 (m, 3 H, CH$_2$ and CH); ^{13}C, δ 91.2 (C$_5$H$_5$), 86.1 (CH), 84.2 (≡*C*CH$_2$), 68.9 (CH), 56.5 (≡C*C*H$_2$), 34.6 and 21.5 p.p.m. (CH$_2$). The second band, eluted with dichloromethane, gave maroon *crystals* of [Mo$_4$(CO)$_8${μ-HC$_2$(CH$_2$)$_2$C$_2$H}(η-C$_5$H$_5$)$_4$] (13) (93 mg, 10%), m.p. >190 °C (Found: C, 42.8; H, 2.8%; *M*, 946. C$_{36}$H$_{26}$Mo$_4$O$_8$ requires C, 43.1; H, 2.7%; *M*, 946); $\nu_{max.}$ (CO) in CH$_2$Cl$_2$ at 1 984m, 1 908s, and 1 831s cm^{-1}; n.m.r. (CDCl$_3$), ^{1}H, τ 4.02 (s, 2 H, CH), 4.70 (s, 20 H, C$_5$H$_5$), and 7.58 (s, 4 H, CH$_2$).

Dichromium compounds. (*i*) A mixture of [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (500 mg, 1.45 mmol) and PhC≡CPh (280 mg, 1.57 mmol) was refluxed in hexane (200 cm^3) for 35 min, giving a brown-maroon solution. After removal of solvent *in vacuo* the black residue was washed with hexane, dissolved in dichloromethane–hexane, and cooled to −30 °C to give maroon *crystals* of [Cr$_2$(CO)(μ-C$_4$Ph$_4$)(η-C$_5$H$_5$)$_2$]·0.25CH$_2$Cl$_2$ (4) (720 mg).

A mixture of [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (600 mg, 1.74 mmol) and PhC≡CPh (1 g, 5.61 mmol) was irradiated with u.v. light in toluene (50 cm^3) for 4 d. Chromatography afforded, on elution with hexane and after crystallisation, brown crystals of [Cr$_2$(CO)$_4$(μ-PhC$_2$Ph)(η-C$_5$H$_5$)$_2$] (12) (101 mg, 13%).

(*ii*) Ethyne was bubbled slowly through a solution of [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (400 mg, 1.16 mmol) in refluxing heptane (40 cm^3). After 20 min, the very air-sensitive mixture was cooled to room temperature, filtered through Kieselguhr, and cooled to −78 °C affording black *crystals* of [Cr$_2$(CO)(μ-C$_4$H$_4$)(η-C$_5$H$_5$)$_2$] (5) (144 mg).

(*iii*) A mixture of [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (500 mg, 1.45 mmol) and MeO$_2$CC≡CCO$_2$Me (500 mg, 3.52 mmol) was refluxed in heptane (50 cm^3) for 25 min. Filtration of the cooled mixture through Kieselguhr followed by crystallisation at −30 °C gave *crystals* of [Cr$_2$(CO){μ-C$_4$(CO$_2$Me)$_4$}(η-C$_5$H$_5$)$_2$] (6) (390 mg).

(*iv*) A solution of PhC≡CH in heptane was added to a refluxing heptane solution of [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (300 mg, 0.87 mmol) until the i.r. spectrum showed the absence of the latter compound. Filtration through Kieselguhr, followed by reduction in volume *in vacuo* and cooling to −30 °C gave black *crystals* of [Cr$_2$(CO)(μ-C$_4$H$_2$Ph$_2$)(η-C$_5$H$_5$)$_2$] (9) (280 mg). The maroon residue did not yield further crystals but was shown by n.m.r. to contain the isomeric complex (10) (see Discussion).

(*v*) As in the preparation of (5), a heptane (40 cm^3) solution of [Cr$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (300 mg, 0.87 mmol) was treated with MeC≡CH. Crystallisation of the product from heptane at −30 °C afforded a small quantity of maroon *crystals* of [Cr$_2$(CO)(μ-C$_4$H$_2$Me$_2$)(η-C$_5$H$_5$)$_2$] (11).

Dimolybdenum compounds. (*i*) A mixture of (1; R^1 = R^2 = Ph) (1.60 g, 2.61 mmol) and PhC≡CPh (1.40 g, 7.87 mmol) was refluxed in octane (80 cm^3) for 19 h. Chromatography of the green mixture, eluting with dichloromethane–hexane (3 : 7), gave a small amount of (1). Elution with dichloromethane–hexane (1 : 1) gave a green solution from which *crystals* of [Mo$_2$(CO)(μ-C$_4$Ph$_4$)(η-C$_5$H$_5$)$_2$] (14) (1.29 g) were obtained.

(*ii*) A mixture of (1; R^1 = R^2 = H) (930 mg, 2.02 mmol) and PhC≡CPh (900 mg, 5.06 mmol) was refluxed in octane (80 cm^3) for 2.5 h. Chromatography of the mixture, eluting with dichloromethane–hexane (3 : 7), gave a green solution from which dark green *crystals* of [Mo$_2${μ-C$_6$H$_2$Ph$_4$}(η-C$_5$H$_5$)$_2$] (16) (930 mg) were isolated.

(*iii*) A mixture of (1; R^1 = R^2 = H) (2 g, 4.35 mmol) and MeO$_2$CC≡CCO$_2$Me (5 g, 35.2 mmol) was refluxed in octane (60 cm^3) for 19 h to give a purple-black mixture. Chromatography, eluting with dichloromethane, afforded four products, crystallised at −30 °C: brown *crystals* of [Mo$_2$(CO)$_2${μ-C$_6$H$_2$(CO$_2$Me)$_4$}(η-C$_5$H$_5$)$_2$] (17) (682 mg), brown *crystals* of [Mo$_2$(CO)$_2${μ-C$_6$H$_2$(CO$_2$Me)$_4$}(η-C$_5$H$_5$)$_2$] (18) (20 mg), violet *crystals* of [Mo$_2${μ-C$_8$H$_2$(CO$_2$Me)$_6$}(η-C$_5$H$_5$)$_2$]·2CH$_2$Cl$_2$ (19) (1.78 g), and Prussian blue *crystals* of [Mo$_2${μ-C$_8$H$_2$(CO$_2$Me)$_6$}(η-C$_5$H$_5$)$_2$] (20) (20 mg).

In a different experiment, (1; R^1 = R^2 = H) (0.46 g, 10.0 mmol) and MeO$_2$CC≡CCO$_2$Me (1.2 g, 8.45 mmol) in refluxing octane (60 cm^3) for 19 h, gave (17) (6%), (18) (0.5%), and (19) (51%). Complex (20) was not detected.

(*iv*) A mixture of (1; R^1 = R^2 = CO$_2$Me) (500 mg, 0.87 mmol) and MeO$_2$CC≡CCO$_2$Me (1.2 g, 8.45 mmol) was refluxed in octane (60 cm^3) for 2 h. Chromatography of the mixture, eluting with dichloromethane, afforded the following products, crystallised at −30 °C from dichloromethane–hexane: pink *crystals* of [Mo$_2${μ-C$_8$(CO$_2$Me)$_8$}(η-C$_5$H$_5$)$_2$] (22) (18 mg), purple-black *crystals* of [Mo$_2${μ-C$_8$(CO$_2$Me)$_8$}(η-C$_5$H$_5$)$_2$] (21) (182 mg), and yellow *crystals* of [Mo$_2$(CO)$_2${μ-C$_6$(CO$_2$Me)$_6$}(η-C$_5$H$_5$)$_2$] (23) (65 mg).

(*v*) A mixture of (16) (400 mg, 0.57 mmol) and MeO$_2$CC≡CCO$_2$Me (2.4 g, 16.9 mmol) was refluxed in octane (60 cm^3) for 4 d. Chromatography of the products, eluting with dichloromethane, afforded solutions from which black *microcrystals* of [$Mo_2\{\mu$-$C_8H_2(CO_2Me)_2Ph_4\}(\eta$-$C_5H_5)_2$] (24) (85 mg) and of [$Mo_2\{\mu$-$C_8H_2(CO_2Me)_2Ph_4\}(\eta$-$C_5H_5)_2$] (25) (110 mg) were obtained.

Crystal-structure Determination of [$Cr_2(CO)(\mu$-$C_4Ph_4)(\eta$-$C_5H_5)_2$].—Crystals of (4) grow as maroon (nearly black) prisms from dichloromethane–hexane solution with incorporation of CH_2Cl_2 into the structure. Diffracted intensities were collected from a non-ideal crystal of approximate dimensions 0.10 × 0.20 × 0.35 mm on a Nicolet $P2_1$ four-circle diffractometer at room temperature. The scan rate varied between 0.488 and 0.048 8° s^{-1} according to the magnitude of a 2-s pre-scan, for limiting counts of 1 500 and 150 respectively. Of the total 6 809 independent observations, 3 166 satisfied the criterion $I \geqslant 3.0\sigma(I)$; only these were used in the refinement of the structure. Three standard reflections which were monitored throughout the 206 h of data collection indicated a mean decrease in intensity over that period of 15%. A correction, assuming exponential decay, was applied for this and for Lorentz and polarisation effects, but not for the effects of *X*-ray absorption [μ(Mo-K_α) = 6.94 cm^{-1}]. The high proportion of weak reflections is indicative of poor crystal quality and has resulted in a relatively poor refinement.

Crystal data. $C_{39}H_{30}Cr_2O\cdot0.25CH_2Cl_2$, $M = 639.9$, Orthorhombic, $a = 19.569(4)$, $b = 19.731(5)$, $c = 16.637(2)$ Å, $U = 6\,424(2)$ Å^3, $D_m = 1.36$, $Z = 8$, $D_c = 1.32$ g cm^{-3}, $F(000) = 2\,644$, space group *Pbcn* (no. 60), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 6.94 cm^{-1}.

Structure solution and refinement. The structure was solved by heavy-atom methods which allowed location of all non-hydrogen atoms. Refinement, by blocked-matrix least squares, allowed anisotropic thermal parameters for all these atoms. Hydrogen atoms were incorporated at calculated positions with a fixed isotropic thermal parameter $U_{iso.}(H) = 0.05$ Å^2. After location of all the atoms of the [$Cr_2(CO)(\mu$-$C_4Ph_4)(\eta$-$C_5H_5)_2$] molecule, residual peaks were found on an electron-density difference synthesis which could be interpreted as dichloromethane showing two-fold disorder around a crystallographic two-fold axis with the carbon atoms occupying the same site. The total solvent incorporation is equivalent to one-quarter of a molecule for every molecule of the complex, so that the site occupancy factor for the C atom is 0.5 and 0.25 for each of the two Cl atoms. No attempt was made to account for the H atoms of the solvent.* The disordered positions for the solvent can be seen in Figure 3.

In the final stages of refinement weights were applied according to the scheme $w = 1.251[\sigma^2|F_o| + 0.001|F_o|^2]^{-1}$, and convergence was obtained at R 0.066 (R' 0.067). Scattering factors were from ref. 27 for hydrogen and from ref. 28 for all other atoms. All computational work was carried out on the South Western Universities' Computer Network with the SHELX system of programs.[29] The results are summarised in Tables 3 and 4. Observed and calculated structure factors, all thermal parameters, and hydrogen-atom co-ordinates are listed in Supplementary Publication No. SUP 23162 (23 pp.).†

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* It is interesting that the crystals of the same complex studied by Bradley [12] were obtained from hexane and contained no solvent. The molecules crystallise in the same space group but are slightly less densely packed: $a = 19.545(4)$, $b = 20.323(3)$, $c = 16.663(3)$ Å, $U = 5\,519$ Å^3.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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