Synthesis and Crystal Structure of $[\{Mn(\eta\text{-}C_5H_4Me)(CO)_2\}_2\{\mu\text{-}(2\text{—}3\text{-}\eta:4\text{—}5\text{-}\eta)\text{-}MeC{\equiv}CC{\equiv}CMe\}]$,† A Manganese-conjugated Diacetylene Complex

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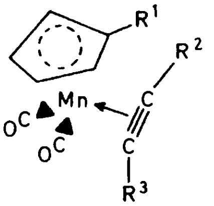
The photochemical reaction of hexa-2,4-diyne and $[Mn(\eta\text{-}C_5H_4Me)(CO)_3]$ gives as the single product the title compound (13), which has been unambiguously identified by *X*-ray crystallography. The compound crystallizes in the monoclinic space group $P2_1/a$ with a = 10.073(4), b = 13.302(7), c = 8.012(3) Å, β = 105.52(4)°, and Z = 2. The structure has been solved by the heavy-atom method and refined by least squares to final agreement indices of R = 0.034 and R' = 0.042 for 944 reflections. Structural and i.r. data suggest that the alkyne ligand in (13) is a good σ donor but a poor π acceptor. This is the first crystallographic study of a $[Mn(\eta\text{-}C_5H_4R)(CO)_2(\text{alkyne})]$ species, even though many such compounds are known.

As part of our continuing interest in interactions of conjugated diynes with transition-metal carbonyls, we have investigated the photochemical reaction between hexa-2,4-diyne and $[Mn(\eta\text{-}C_5H_4Me)(CO)_3]$. The single product of this reaction was subjected to an *X*-ray crystallographic study which, in addition to confirming the identity of the product, revealed several interesting structural features and suggested additional work in the area.

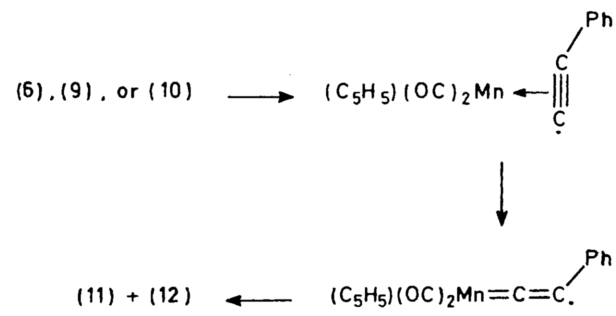
RESULTS AND DISCUSSION

Although several complexes of the type $[Mn(\eta\text{-}C_5H_4R)(CO)_2(\text{alkyne})]$, *viz.* (1)—(10),[1-8] have been reported, little of their chemistry or properties has been investigated. Formation of (1)[1] and (2)[2] is accompanied under some conditions by formation of tetracyclone, C_4Ph_4CO, while (6), (9), and (10) each decomposes to give compounds of formulae $[Mn(C_5H_5)(CO)_2(C_8H_6)]$ (11) and $[Mn_2(C_5H_5)_2(CO)_4(C_{16}H_{10})]$ (12). The mononuclear compound (11) has been shown to have the structure $[Mn(\eta\text{-}C_5H_5)(CO)_2(C{=}CHPh)]$.[9] The structure of (12), which is partially converted into (11) on sublimation,[8] has not been determined. t-Butyl-lithium converts (5) into $[Mn(\eta\text{-}C_5H_5)(CO)_2(C{=}C{=}CBu^t{}_2)]$.[5] No other chemistry of these manganese–alkyne complexes has appeared in the literature, nor has any *X*-ray structural characterization. The dearth of chemical investigation may be due in part to the fact that the compounds are usually produced in rather low yield (≤20%). The absence of *X*-ray work seems quite surprising, however, since several structures of the type $[Mn(\eta\text{-}C_5H_5)(CO)_2(\text{olefin})]$ have been isolated.[10]

In the present study the product was assigned the formula $[Mn_2(C_5H_4Me)_2(CO)_4(C_6H_6)]$ on the basis of its molecular weight (mass spectrum, *m/e* 458). The primary reaction product is expected to be (13). A simple electronic rearrangement, however, would give (14). Since many compounds of the type $[Mn(\eta\text{-}C_4H_4R)(CO)_2(\text{carbene})]$ have been described,[5,9,11] (14) was also considered a plausible structure. It is our view that Scheme 1 represents the most likely pathway for the formation of (11) and (12) and that the correct structure



(1) R^1 = H, R^2 = R^3 = Ph (ref. 1)
(2) R^1 = Me, R^2 = R^3 = Ph (ref. 2)
(3) R^1 = H, R^2 = R^3 = CF_3 (ref. 3)
(4) R^1 = H, R^2 = R^3 = CO_2Et (ref. 4)
(5) R^1 = R^2 = H, R^3 = CO_2Me (ref. 5)
(6) R^1 = R^2 = H, R^3 = Ph (refs. 4,6)
(7) R^1 = H, R^2 = Ph, R^3 = $p\text{-}C_6F_4Cl$ (ref. 7)
(8) R^1 = H, R^2 = Ph, R^3 = $SiPh_3$ (ref. 8)
(9) R^1 = H, R^2 = Ph, R^3 = $GePh_3$ (ref. 8)
(10) R^1 = H, R^2 = Ph, R^3 = $SnPh_3$ (ref. 8)



SCHEME 1

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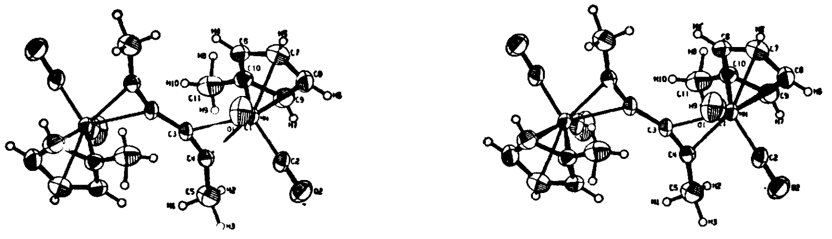
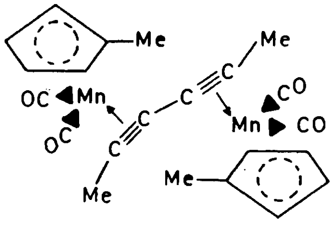
† μ-(2—3-η : 4—5-η)-Hexa-2,4-diyne-bis[dicarbonyl(η-methylcyclopentadienyl)manganese(I)].

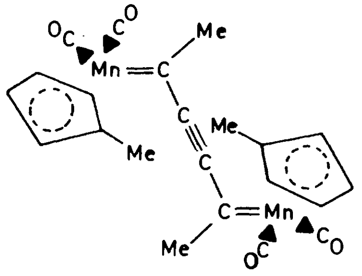


An ORTEP stereodiagram of the title compound. The thermal ellipsoids shown are those of 25% probability

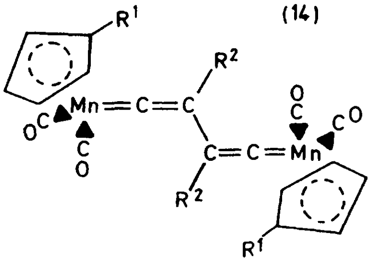
of (12) is (16). We therefore had to consider that (15) might be the correct structure of our product.



(13)



(14)



(15) $R^1 = R^2 = Me$
(16) $R^1 = H, R^2 = Ph$

The Figure presents an ORTEP stereodiagram of the title compound and clearly shows (13) to be the correct structure. The final atomic co-ordinates are given in Table 1, bond distances and angles in Tables 2 and 3, respectively. Final thermal parameters and observed and calculated structure factors are available as Supplementary Publication No. 22560 (7 pp.).‡

The rather short $C\equiv C$ distance (1.240 Å), the large C(3')-C(3)-C(4) angle (158.5°),* and the very low $C\equiv O$ i.r. stretching frequencies (1 934, 1 882 cm^{-1}) all suggest that the alkyne is a poor π acceptor. Indeed, the $C\equiv O$ frequencies are similar to those seen in $[Mn(\eta\text{-}C_5H_5)(CO)_2(amine)]$, where the ligand in question cannot be a π acceptor at all.[12] The only immediately obvious explanation for this is the electron-donating nature of the methyl groups. The approximate relationship between $C\equiv C$ bond length and average ' bend-back ' angle † found for other co-ordinated acetylenes [13] also holds in (13). On the other hand the Mn-C(3) and Mn-C(4) distances (2.136 and 2.109 Å), which are shorter than any corresponding distance reported for $[Mn(\eta\text{-}C_5H_5)(CO)_2(olefin)]$,[10] imply a strong manganese-acetylene σ bond. The rather high $Mn-C(\equiv O)$ stretching frequency (634 cm^{-1}) is also indicative of this.[12,14] (The i.r. band at 649 cm^{-1} is attributable to an Mn ring mode.[15]) If these i.r. data indeed reflect structural information, then certain comparisons can now be drawn. Thus, in (3) [$\nu(C\equiv O)$ at 2 033, 1 969 cm^{-1}; $\nu(Mn-C)$ at 632 cm^{-1}],[3] hexafluorobut-2-yne appears to be about as good a σ donor as hexa-2,4-diyne is in (13), but a much better π acceptor. One would then expect the manganese-alkyne distance in (3) to be slightly shorter than that in (13), but the ' bend-back ' angle in (3) to be significantly greater than that in (13).[13,16] The bond distances in the $Mn(CO)_2$ fragment of (13) are not significantly different from those reported for analogous olefin complexes.[10]

In (13) the manganese atom is not bonded to the cyclopentadienyl ring in a symmetrical way. The order of distance from manganese is $C(7) \approx C(8) > C(6) \approx C(9) > C(10)$. This same phenomenon is seen to a lesser extent in (η-methylcyclopentadienyl)(η-7-*exo*-phenylcyclohepta-1,3,5-triene)manganese.[17] In the present case the inequality may be due to simple steric repulsion between C(3) and H(10) (3.016 Å) and C(4) and H(9) (3.006 Å).

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‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

* Atom C(3') is bonded to atom C(3) and related to C(3) by a centre of symmetry.

† The ' bend-back ' angle is defined as that between the acetylene bond vector and a substituent group-acetylene carbon bond vector.

TABLE 1

Final atomic co-ordinates (× 10^4 for Mn, C, and O; × 10^3 for H)

Atom	*X*	*Y*	*Z*
Mn	2 328(1)	5 292(1)	8 792(1)
C(1)	2 493(5)	5 015(4)	11 014(1)
O(1)	2 567(4)	4 846(4)	12 432(6)
C(2)	1 272(5)	4 224(5)	8 274(7)
O(2)	567(4)	3 527(3)	7 923(6)
C(3)	4 432(4)	4 830(4)	9 359(6)
C(4)	3 772(5)	4 357(4)	8 071(7)
C(5)	3 647(10)	3 628(7)	6 675(10)
C(6)	2 870(7)	6 858(4)	8 712(8)
C(7)	1 614(9)	6 761(5)	9 097(14)
C(8)	712(8)	6 298(6)	7 723(17)
C(9)	1 399(8)	6 106(5)	6 443(11)
C(10)	2 746(5)	6 474(4)	7 063(7)
C(11)	3 848(13)	6 463(7)	6 132(15)
H(1)	447(6)	339(5)	670(7)
H(2)	327(7)	392(5)	571(10)
H(3)	318(12)	289(10)	663(15)
H(4)	367(5)	713(4)	933(7)
H(5)	144(5)	694(4)	1 005(7)
H(6)	−6(9)	599(6)	748(10)
H(7)	108(6)	576(5)	535(8)
H(8)	385(7)	729(6)	556(9)
H(9)	367(7)	597(6)	542(9)
H(10)	468(8)	643(7)	679(11)

TABLE 2

Bond distances (Å)

Mn–C(1)	1.782(7)	C(7)–(8)	1.372(11)
Mn–C(2)	1.758(6)	C(8)–C(9)	1.405(11)
Mn–C(3)	2.136(4)	C(9)–C(10)	1.402(8)
Mn–C(4)	2.109(5)	C(6)–C(10)	1.390(8)
Mn–C(6)	2.158(6)	C(10)–C(11)	1.494(10)
Mn–C(7)	2.119(7)	C(5)–H(1)	0.883(58)
Mn–C(8)	2.104(7)	C(5)–H(2)	0.861(71)
Mn–C(9)	2.155(6)	C(5)–H(3)	1.092(126)
Mn–C(10)	2.208(5)	C(6)–H(4)	0.900(52)
C(1)–O(1)	1.140(6)	C(7)–H(5)	0.859(48)
C(2)–O(2)	1.156(6)	C(8)–H(6)	0.853(81)
C(3)–C(3′)	1.393(10)	C(9)–H(7)	0.967(60)
C(3)–C(4)	1.240(6)	C(11)–H(8)	1.191(78)
C(4)–C(5)	1.459(9)	C(11)–H(9)	0.852(73)
C(6)–C(7)	1.386(9)	C(11)–H(10)	0.863(75)

The distance between manganese atoms in the molecule is 5.268(3) Å.

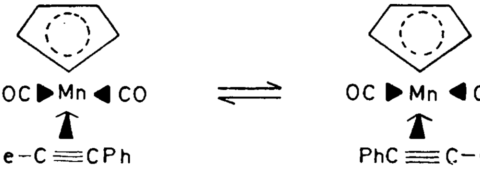
TABLE 3

Selected bond angles (°)

C(1)–Mn–C(2)	87.5(2)	Mn–C(1)–O(1)	178.5(5)
C(1)–Mn–C(3)	84.6(2)	Mn–C(2)–O(2)	179.3(5)
C(1)–Mn–C(4)	105.4(2)	Mn–C(3)–C(3′)	129.5(6)
C(1)–Mn–C(10)	142.3(2)	Mn–C(3)–C(4)	71.9(3)
C(2)–Mn–C(3)	108.7(2)	Mn–C(4)–C(3)	74.2(3)
C(2)–Mn–C(4)	82.9(2)	Mn–C(4)–C(5)	132.6(5)
C(2)–Mn–C(10)	129.2(2)	Mn–C(10)–C(11)	126.7(5)
C(3)–Mn–C(4)	34.0(2)	C(3′)–C(3)–C(4)	158.5(5)
C(3)–Mn–C(10)	89.6(2)	C(3)–C(4)–C(5)	153.2(6)
C(4)–Mn–C(10)	89.3(2)	C(7)–C(6)–C(10)	108.8(6)
C(6)–Mn–C(7)	37.8(2)	C(6)–C(7)–C(8)	108.1(6)
C(7)–Mn–C(8)	37.9(3)	C(7)–C(8)–C(9)	108.5(8)
C(8)–Mn–C(9)	38.5(3)	C(8)–C(9)–C(10)	107.3(7)
C(9)–Mn–C(10)	37.5(2)	C(6)–C(10)–C(9)	107.3(7)
C(6)–Mn–C(10)	37.1(2)	C(6)–C(10)–C(11)	126.0(7)
		C(9)–C(10)–C(11)	126.7(8)

Alternatively, it may be due to the methyl group's destabilizing effect on the resonance contribution in which C(10) bears the negative charge. A third possibility is that, since CO is a very good π acceptor and hexa-2,4-diyne is apparently quite a poor one, a relative *trans* effect may be operative. It would be very interesting in this regard to see the effect of replacing hexa-2,4-diyne by hexafluorobut-2-yne, which from i.r. data appears to have about the same π-acceptor strength as CO.[3,12]

By analogy with [Mn(η-C_5H_5)$(CO)_2$(olefin)] systems,[10] one would expect the triple bond in [Mn(η-C_5H_4R)$(CO)_2$(alkyne)] to be approximately parallel to a line joining the carbonyl carbons. This is in fact the case in (**13**) where the angle between the C(3)–C(4) bond and the C(1)–C(2) vector is 6°. This brings up an interesting point with regard to (**9**). Nesmeyanov *et al.*[8] report that (**9**) crystallizes in two isomers because of hindered rotation about the manganese–alkyne bond. They cite as evidence four C≡O stretching bands of about equal intensity and two ^1H n.m.r. peaks of equal areas for C_5H_5. Clearly these findings are incompatible with the idea that the most stable forms of (**9**) are the ones with the triple bond orientated as in (**17**) and (**18**). One of the isomers may indeed be (**17**) $\rightleftharpoons$ (**18**), but the structural nature of the other one is unclear.



(17) (18)

Hopefully, further structural work will turn some of the foregoing speculations into facts.

EXPERIMENTAL

Hexa-2,4-diyne was purchased from Story Chemical Corporation, [Mn(η-C_5H_4Me)$(CO)_3$] from Ethyl Corporation. These were used without further purification. Infrared spectra were recorded on a Beckman IR-8, mass spectra on a Hewlett-Packard 5980 A quadrupole spectrometer.

Preparation.—All operations involving solutions of the product (**13**) were carried out in an atmosphere of nitrogen. The compound [Mn(η-C_5H_4Me)$(CO)_3$] (7 cm^3, 44 mmol) and hexa-2,4-diyne (1.0 g, 13 mmol) were dissolved in oxygen-free cyclohexane (40 cm^3). This solution was stirred in a Pyrex flask and irradiated with a Hanovia high-pressure mercury lamp for 3.3 h. The resulting red solution was chromatographed on neutral alumina. Elution with light petroleum gave a partial separation of the product (**13**) and unchanged [Mn(η-C_5H_4Me)$(CO)_3$]. The fraction containing the product was evacuated for several days to remove solvent and starting material. The formation of a brown amorphous solid indicated considerable decomposition during this process. The residue was redissolved in isopentane and the solution filtered. Slow evaporation at −20 °C deposited orange crystals of the product [{Mn(η-C_5H_4Me)$(CO)_2$}$_2${μ-(2—3-η:4—5-η)-MeC≡CC≡CMe}] (**13**), m.p. 99 °C. Infrared spectrum (KBr pellet): 3 115w, 2 959w, 2 915w, 1 934s, 1 882s, 1 420mbr, 1 258m, 1 080mbr, 1 064w, 1 015m, 978w, 842s, 831s, 803m, 796m, 649s, and 634s cm^{-1}. Mass spectrum, *m/e* (relative abundance) [assignment]: 458 (3) $[M]^+$, 346 (28) $[M - 4CO]^+$, 268 (12) $[Mn(C_6H_7)(CO)_2(C_6H_6)]^+$, 213 (97) $[Mn(C_6H_7)_2]^+$, 212

(9) $[Mn(C_6H_7)(C_6H_6)]^+$, 134 (100) $[Mn(C_6H_7)]^{2+}$, 79 (48) $[C_6H_7]^+$, 78 (14) $[C_6H_6]^+$, and 55 (46) $[Mn]^+$.

X-*Ray Structural Analysis*.—The title compound (13) solidified as polycrystalline masses. Several of these were broken up, and an irregular block of dimensions *ca.* 0.09 × 0.18 × 0.36 mm which extinguished polarized light uniformly was selected for analysis. The crystal was mounted on a glass fibre with the fibre axis nearly parallel to the longest crystal dimension, later shown to be the *c* axis. Refinement of 2θ values for 32 reflections gave accurate unit-cell dimensions. Systematic absences $0k0$ for $k \neq 2n$ and $h0l$ for $h \neq 2n$ unambiguously identified the space group as $P2_1/a$. Intensities were collected on a four-circle manual General Electric XRD-7 diffractometer equipped with a pulse-height discriminator, NaI scintillation counter, and balanced Zr/Y filters. The take-off angle from the X-ray tube was set at 5.0°. Peak-height counts were recorded for 10 s for each filter. Five strong reflections were measured periodically to monitor crystal alignment and decomposition. The largest decomposition correction applied was 4%. The intensities were converted into structure factors (F_o) after applying corrections for background and linear absorption. The absorption factor was determined as a function of ϕ at $\chi = 90.00°$. The maximum and minimum transmission factors are 0.90 and 0.66, respectively. Of 1 356 independent reflections measured, 944 were deemed significantly above background. The criterion used was $[I_{Zr} - 2\sigma(I_{Zr})] - [I_Y + 2\sigma(I_Y)] > 0$. A weight w was assigned to each reflection where $w = [\sigma^2(F_o) + (5.56 \times 10^{-4})F_o^2]^{-1}$ and $\sigma(F_o) = 0.5 [(LP)^{-1}(I_{Zr} + I_Y)/(I_{Zr} - I_Y)]^{\frac{1}{2}}$. LP is the Lorentz-polarization factor.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations. The function minimized was $\Sigma w(|F_o - |F_c||)^2$, where w is the weight and F_o and F_c the observed and calculated structure factors. All the hydrogen atoms were located on a difference-Fourier map and used in the refinement. Hydrogen atoms were refined isotropically; other atoms were refined anisotropically. The final agreement indices are $R = 0.034$ and $R' = 0.042$, where $R = \Sigma|F_o - |F_c||/\Sigma|F_o|$ and $R' = (\Sigma w|F_o - |F_c||^2/\Sigma w F_o^2)^{\frac{1}{2}}$. If the unobserved reflections are included in the data, the agreement indices are $R = 0.073$ and $R' = 0.054$. All parameters and discussion of the structure except the preceding statement refer to the refinement which excluded unobserved reflections. The largest residual peak was 0.28 e Å^{-3} and was located near the manganese atom. Solution and refinement of the structure were accomplished using the SHELX multi-purpose program of G. M. Sheldrick.

Crystal data. $[\{Mn(\eta\text{-}C_5H_4Me)(CO)_2\}_2\{\mu\text{-}(2\text{—}3\text{-}\eta:4\text{—}5\text{-}\eta)\text{-}MeC{\equiv}CC{\equiv}CMe\}]$, $C_{22}H_{20}Mn_2O_4$, $M = 458.26$, Monoclinic, $a = 10.073(4)$, $b = 13.303(7)$, $c = 8.012(3)$ Å, $\beta = 105.52(4)°$, $U = 1\,034.4(8)$ Å^3, $Z = 2$, $F(000) = 468$, $D_c = 1.47$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 11.67$ cm^{-1}, $P2_1/a$.

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