[1·816 (1) Å] are similar to those observed in *fac*-tricarbonyl(*tert*-butylisocycanide)(dppe)manganese(I) (Solans, Valin, Moreiras & Riera, 1986). The steric hindrance between the phenyl groups of the dppe ligand and the carbonyls produces an enlargement of the equatorial P—Mn—C angles and a decrease in the apical P—Mn—C angles.

The dihedral angle between the equatorial coordination plane of Mn and that defined by C(3), C(4), Cu and Cl is 84·4 (2)°, while it is 21·1 (3)° between the Cu coordination plane and the C(4*x*) phenyl ring.

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Structure of *fac*-Tricarbonyl(*tert*-butylethynyl)[ethylenebis(diphenylphosphine)]-manganese(I)

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Abstract. $C_{35}H_{33}MnO_3P_2$, $M_r = 618·5$, monoclinic, $P2_1/c$, $a = 19·158$ (3), $b = 11·492$ (2), $c = 15·763$ (3) Å, $\beta = 110·59$ (2)°, $V = 3249$ (2) Å^3, $Z = 4$, $D_x = 1·264$ g cm^{-3}, D_m not measured, $F(000) = 1288$, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 5·59 cm^{-1}, room temperature, $R = 0·054$ for 2938 observed reflections. The ligands display a distorted octahedral arrangement surrounding the Mn atom [angles at Mn deviate from 90 or 180° by ≤8·2 (2)°]. The alkynyl ligand is essentially linear.

Introduction. A number of σ-alkynyl carbonyl complexes of manganese(I) have been recently prepared (Miguel & Riera, 1985) and are now being used as starting materials for the preparation of compounds where the σ-alkynyl complex acts as an η^2-acetylene ligand coordinated to other metals such as Co (Carriedo, Riera, Miguel, Manotti Lanfredi & Tiripicchio, 1984), Cu, Ag, or Au (Carriedo, Miguel, Riera, Solans, Font-Altaba, & Coll, 1986).

Very few X-ray structure determinations have been carried out on octahedral σ-alkynyl complexes, and to date no X-ray structure has been determined of a σ-alkynyl complex of manganese(I), although a closely related species, *cis*-[Mn(CO)$_4$(C≡CPPh$_3$)Br], containing the neutral, two-electron ligand C≡CPPh$_3$ has

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been the subject of an X-ray study (Goldberg, Duesler & Raymond, 1972).

It is of interest to obtain structural information about these σ-alkynyl complexes of manganese(I), $Mn(CO)_{5-n}L_n(C{\equiv}CR)$ [L = P-donor ligands (phosphines, diphosphines, phosphites), N-donor ligands (bipyridine, 1,10-phenanthroline, isocyanides); R = Ph, Bu^t, H], for comparison with the structural parameters of the η^2-$Mn(CO)_{5-n}L_n(C{\equiv}CR)$ moiety in more complex species. Variations in the C≡C length and deviation from linearity of the R—C≡C—R unit have been extensively used as a measure of the nature of the bonding between the metal atom and the η^2-acetylene ligand (Otsuka & Nakamura, 1976).

Table 1. *Fractional atomic coordinates* (×10^4; Mn *and* P×10^5) *and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Mn	69342 (5)	5644 (8)	5558 (5)	2·98 (4)
P(1)	69414 (9)	5555 (14)	20283 (10)	3·28 (7)
C(1)	7575 (4)	1715 (6)	2708 (4)	4·29 (32)
C(2)	8054 (4)	2233 (6)	2218 (4)	3·89 (31)
P(2)	75307 (9)	23218 (14)	9871 (10)	3·10 (7)
C(101)	7210 (4)	−725 (5)	2766 (4)	3·74 (29)
C(102)	7484 (4)	−1748 (6)	2514 (5)	5·02 (36)
C(103)	7688 (5)	−2676 (6)	3120 (6)	6·40 (44)
C(104)	7628 (4)	−2604 (7)	3975 (5)	5·78 (41)
C(105)	7347 (5)	−1619 (7)	4204 (5)	5·57 (41)
C(106)	7133 (4)	−667 (6)	3617 (4)	4·76 (34)
C(111)	6039 (4)	922 (6)	2111 (4)	3·88 (31)
C(112)	5537 (4)	28 (7)	2080 (5)	5·29 (37)
C(113)	4818 (4)	318 (9)	2043 (6)	6·83 (49)
C(114)	4587 (5)	1420 (10)	2033 (6)	6·77 (52)
C(115)	5065 (6)	2261 (9)	2018 (8)	8·60 (65)
C(116)	5776 (5)	2024 (7)	2048 (7)	6·82 (52)
C(201)	6930 (3)	3600 (5)	834 (4)	3·23 (28)
C(202)	6957 (4)	4365 (6)	1518 (5)	4·51 (33)
C(203)	6475 (5)	5326 (6)	1335 (6)	5·42 (44)
C(204)	5969 (5)	5482 (6)	483 (8)	6·35 (49)
C(205)	5927 (4)	4722 (7)	−218 (6)	5·42 (41)
C(206)	6405 (4)	3779 (6)	−30 (5)	4·32 (33)
C(211)	8227 (3)	2847 (6)	515 (4)	3·49 (29)
C(212)	8628 (4)	2071 (7)	211 (5)	5·00 (37)
C(213)	9175 (4)	2480 (8)	−130 (6)	6·25 (46)
C(214)	9287 (4)	3663 (8)	−186 (5)	5·74 (44)
C(215)	8865 (4)	4437 (7)	95 (5)	5·41 (38)
C(216)	8349 (4)	4032 (6)	450 (5)	4·43 (34)
C(11)	7952 (3)	−130 (5)	1071 (4)	3·40 (26)
C(12)	8567 (4)	−566 (6)	1373 (4)	4·57 (29)
C(13)	9338 (5)	−1109 (10)	1787 (6)	6·71 (50)
C(14)	9318 (7)	−2359 (9)	1383 (10)	11·92 (79)
C(15)*	9921 (26)	−353 (45)	1348 (42)	9·77 (235)
C(16)*	9545 (28)	−836 (67)	2823 (43)	10·83 (288)
C(15)′*	9881 (20)	−258 (50)	1697 (37)	11·87 (268)
C(16)′*	9543 (41)	−1445 (70)	2795 (52)	15·49 (394)
C(21)	6001 (4)	1162 (6)	118 (4)	4·06 (31)
O(21)	5393 (3)	1497 (5)	−176 (4)	5·54 (26)
C(22)	7025 (4)	615 (6)	−552 (4)	4·10 (30)
O(22)	7097 (3)	663 (5)	−1248 (3)	6·11 (28)
C(23)	6562 (4)	−915 (6)	359 (4)	3·80 (30)
O(23)	6329 (3)	−1821 (4)	228 (4)	6·26 (28)

* Occupancy 0·5.

Table 2. *Selected bond distances* (Å) *and angles* (°)

C(11)—Mn	1·996 (0·006)	C(12)—C(11)	1·214 (0·008)
P(1)—Mn	2·316 (0·002)	C(13)—C(12)	1·522 (0·010)
P(2)—Mn	2·302 (0·002)	O(21)—C(21)	1·157 (0·008)
C(21)—Mn	1·811 (0·007)	O(22)—C(22)	1·155 (0·009)
C(22)—Mn	1·815 (0·007)	O(23)—C(23)	1·124 (0·008)
C(23)—Mn	1·827 (0·007)		
C(12)—C(11)—Mn	179·0 (0·5)	C(23)—Mn—P(1)	91·8 (0·2)
C(13)—C(12)—C(11)	178·0 (0·8)	C(21)—Mn—C(11)	177·9 (0·3)
C(22)—Mn—P(2)	92·9 (0·2)	P(2)—Mn—P(1)	83·1 (0·1)
C(23)—Mn—C(22)	91·7 (0·3)		

Here we report the X-ray crystal structure of the title compound, *fac*-$[Mn(CO)_3(dppe)(C{\equiv}CBu^t)]$, the preparation of which has been previously described (Miguel & Riera, 1985).

Experimental. Colorless acicular crystals obtained on cooling a hot solution of the compound in a CH_2Cl_2/EtOH (1:1) mixture; crystal (0·08 × 0·08 × 0·15 mm) selected; Philips PW-1100 diffractometer; unit cell from 25 reflections ($4 \leq \theta \leq 9°$), graphite-monochromated Mo $K\alpha$ radiation, ω-scan technique, scan width 0·8°, scan speed 0·03° s^{-1}. Three reflections measured every two hours as orientation and intensity control, no significant intensity decay; 3111 reflections in the range $2 \leq \theta \leq 25°$, *hkl* range: −21 to 21; 0 to 13; 0 to 18; 2972 independent, R_{int}, 0·015; 2938 with $I \geq 2{\cdot}5\sigma(I)$ used in analysis; Lorentz-polarization corrections, no absorption correction; Mn and P atoms located by direct methods with *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); remaining non-hydrogen atoms by use of *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981); anisotropic full-matrix least-squares refinement with *SHELX*76 (Sheldrick, 1976); function minimized $\sum w\|F_o\| - \|F_c\|^2$, $w = [\sigma^2(F_o) - 0{\cdot}22\,|F_o|^2]^{-1}$; f, f' and f'' from *International Tables for X-ray Crystallography* (1974).

After three isotropic refinement cycles disorder in the *tert*-butylethynyl ligand involving atoms C(15) and C(16) was indicated by a difference synthesis. An occupancy factor of 0·5 was assigned to the disordered atoms, according to the heights of the peaks in the Fourier synthesis; 22 H atoms located from difference synthesis; refined with an overall isotropic temperature factor. Final R 0·054 (wR = 0·061) for all observed reflections. Max shift/e.s.d. = −0·50 in U_{22} of C(13), max. and min. electron density in final $\Delta\rho$ map 0·3 to −0·2 e Å^{-3}.

Discussion. Final atomic parameters are listed in Table 1* and selected bond lengths and angles in Table 2. The Mn atom displays a distorted octahedral coordination (Figs. 1 and 2) with the two P atoms of the 1,2-bis(diphenylphosphino)ethane ligand and two carbonyl ligands in the equatorial plane, and the *tert*-butylethynyl ligand and the remaining CO in the apical positions.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete bond length and angle data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42886 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Mn—P(dppe) bond distances [average 2·309 (6) Å] are similar to those observed in {[*fac*-Mn$(CO)_3$(dppe)(C≡CPh)]CuCl} [average value 2·308 (5) Å] (Solans, Solans, Miratvilles, Miguel, Riera & Rubio-Gonzalez, 1986). Similarly the Mn—CO (*trans* to P) bond lengths [average value 1·821 (3) Å] are close to the corresponding lengths in {[*fac*-Mn$(CO)_3$(dppe)(C≡CPh)]CuCl} [average value 1·816 (4) Å] and in {*fac*-Mn(NCS)$(CO)_3$(dppm)}* [average value 1·823 (5) Å] (Carriedo, Crespo, Riera, Sanchez, Valin, Moreiras & Solans, 1986).

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* dppm = bis(diphenylphosphino)methane.

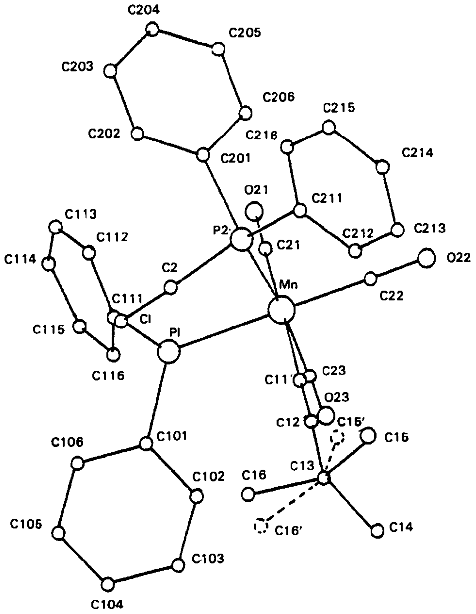

Fig. 1. Drawing of a discrete molecule showing the atom numbering scheme.

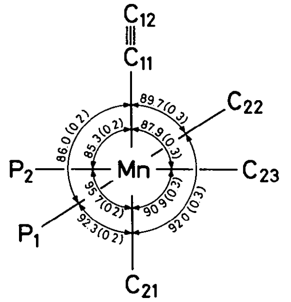

Fig. 2. Schematic drawing showing the angles (°) around the Mn atom.

The alkynyl moiety is essentially linear with angles C(13)—C(12)—C(11) = 178·0 (6)° and Mn—C(11)—C(12) = 179·0 (5)°. The C(11)—C(12) bond length is 1·214 (8) Å, very close to that expected for a C≡C triple bond. The C(acetylene)—Mn—P angles are smaller than the C(acetylene)—Mn—C(equatorial carbonyl) (see Fig. 2) and all of them are smaller than 90°. In contrast, the angles between C(carbonyl apical), Mn and the equatorial atoms P(1), P(2), C(22) and C(23) are larger than 90°. This type of distortion is not unexpected since the C(carbonyl)—Mn bond distances are shorter than the P—Mn and C(acetylene)—Mn bond distances, and therefore the carbonyl groups have greater steric requirements around the Mn atom. Thus, it is significant that all of the C(carbonyl)—Mn—C(carbonyl) angles are larger than 90° and the same occurs in the structure of the related *cis*-[Mn$(CO)_4$(C≡$CPPh_3$)Br] (Goldberg *et al.*, 1972).

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