Acta Cryst. (1986). C**42**, 975–977

Structure of a Copper(I) Chloride Adduct of a Manganese(I) Complex

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(*Received* 4 *October* 1985; *accepted* 21 *February* 1986)

Abstract. *fac*-Tricarbonyl{σ-[chloro(1–2-η-phenylethynyl)copper(I)][ethylenebis(diphenylphosphine)]-manganese(I), $C_{37}H_{29}ClCuMnO_3P_2$, $M_r = 737{\cdot}52$, monoclinic, $P2_1/n$, $a = 11{\cdot}293$ (2), $b = 15{\cdot}250$ (4), $c = 19{\cdot}104$ (4) Å, $\beta = 94{\cdot}36$ (2)°, $V = 3280{\cdot}5$ (12) Å^3, $Z = 4$, $D_x = 1{\cdot}49$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1290$ m^{-1}, $F(000) = 1504$, 293 K, $R = 0{\cdot}040$ ($wR = 0{\cdot}044$) for 4377 observed reflections. The structure consists of discrete monomeric molecules of {*fac*-[Mn(CO)$_3$(dppe)(C≡CPh)].CuCl}, where the carbon–carbon triple bond of the phenylethynyl moiety acts as a η^2-acetylene ligand coordinated to the Cu$^{\rm I}$ atom, which is thereby in a formally two-coordinated complex. The Mn ion displays a distorted octahedral coordination with the two P atoms of the dppe ligand and the two carbonyl groups in the equatorial plane. The steric hindrance produces an enlargement of the equatorial P—Mn—C angles and a reduction of the apical P—Mn—C angles.

Introduction. Some complexes of the type (L_nM—C≡CR)CuCl are known in which a σ-alkynyl compound is coordinated to a copper atom in a η^2 (dihapto) fashion (Abu-Salah & Bruce, 1974, 1975). Only two such compounds, (η^5-C_5H_5)Fe(CO)$_2$-(C≡CPh).(CuCl)$_2$ (Bruce, Clark, Howard & Woodward, 1972) and (η^5-C_5H_5)Ru(PPh$_3$)$_2$-(C≡CPh).CuCl (Bruce, Abu-Salah, Davis & Raghavan, 1974), have been subjects of X-ray structure determinations, the former being a dimer with bridging chlorine atoms between the two coppers, and the latter a monomer with a terminal chlorocopper unit. We have recently found (Miguel, 1984) that σ-alkynyl compounds of manganese(I) like *fac*-Mn(CO)$_3$(dppe)-(C≡CR) [where dppe = ethylenebis(diphenylphosphine; R = Ph or *tert*-butyl)] react very readily with CuCl in dichloromethane solution, affording crystalline compounds with the formula *fac*-Mn(CO)$_3$(dppe)-(C≡CR).CuCl. It was of interest to undertake an X-ray structure determination of one of these manganese compounds since the two compounds previously reported showed different structures (dimer in the case of Fe, monomer in that of Ru), and the reasons could involve not only steric but also electronic effects. Moreover, the structural information can be valuable in the study of the bonding in such η^2-acetylene molecules.

Experimental. Equidimensional crystal (0·1 × 0·1 × 0·1 mm) obtained from dichloromethane/ethanol mixture. Enraf–Nonius CAD-4; cell parameters from 25 reflections ($4 \leq \theta \leq 15°$); graphite-monochromatized Mo $K\alpha$ radiation, $\theta/2\theta$ scan. Three reflections every two hours as orientation and intensity control; no significant intensity decay. 9519 data in the range $2 \leq \theta \leq 30°$; range of hkl: −15 to 15; 0 to 21; 0 to 22; 4377 with $I \geq 2{\cdot}5\sigma(I)$. Lorentz–polarization correction, absorption ignored. Mn and Cu atoms located by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and remaining non-hydrogen atoms from *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). Isotropic and anisotropic full-matrix least-squares refinement (*SHELX*76; Sheldrick, 1976). Function minimized $\sum w \| F_o | - | F_c \|^2$, $w = [\sigma^2(F_o) + 0{\cdot}0176 | F_o |^2]^{-1}$. f, f' and f'' from *International Tables for X-ray Crystallography* (1974). All hydrogen atoms from $\Delta\rho$ map, refined with overall isotropic temperature factor. Final R 0·040 ($wR = 0{\cdot}044$) for all observed reflections; max. shift/e.s.d. 0·6 in y of C(212); max. and min. $\Delta\rho = 0{\cdot}3$ [1·6 Å from O(7)] and −0·3 e Å^{-3}, respectively. IBM-4341 computer.*

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42837 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/86/080975-03$01.50

Discussion. The final atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2.

Table 1. *Final atomic coordinates* ($\times 10^4$; $\times 10^5$ *for* Cu, Mn) *and equivalent isotropic thermal parameters for non-hydrogen atoms*

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

	x	y	z	B_{eq}(Å^2)
Cu	23466 (5)	29332 (4)	21950 (3)	3·70 (6)
Mn	46296 (5)	38909 (4)	13736 (3)	2·47 (8)
Cl	558 (1)	2558 (1)	1940 (1)	5·27 (14)
P(1)	6405 (1)	3982 (1)	2058 (1)	2·64 (14)
P(2)	5176 (1)	2476 (1)	1128 (1)	2·62 (14)
C(12)	6988 (4)	2857 (3)	2163 (2)	3·2 (5)
C(21)	6718 (4)	2333 (3)	1486 (2)	3·7 (6)
C(3)	4028 (3)	3424 (2)	2272 (2)	2·8 (5)
C(4)	3826 (3)	3130 (3)	2848 (2)	2·9 (5)
C(5)	4189 (4)	5009 (3)	1551 (2)	3·4 (5)
O(5)	3897 (3)	5715 (2)	1628 (2)	5·5 (6)
C(6)	5445 (3)	4253 (2)	649 (2)	2·9 (6)
O(6)	6028 (3)	4478 (2)	216 (2)	4·1 (6)
C(7)	3235 (4)	3758 (3)	845 (2)	3·6 (6)
O(7)	2352 (3)	3706 (3)	509 (2)	5·8 (6)
C(101)	6499 (3)	4432 (3)	2952 (2)	3·2 (6)
C(102)	7361 (4)	4129 (3)	3454 (2)	4·5 (5)
C(103)	7471 (5)	4480 (4)	4115 (3)	4·9 (5)
C(104)	6740 (4)	5147 (4)	4287 (2)	4·6 (6)
C(105)	5926 (4)	5496 (3)	3796 (3)	4·6 (6)
C(106)	5791 (4)	5119 (3)	3121 (2)	3·7 (6)
C(111)	7538 (3)	4634 (3)	1675 (2)	3·2 (5)
C(112)	8544 (4)	4287 (4)	1419 (3)	4·6 (6)
C(113)	9323 (5)	4821 (5)	1089 (3)	6·3 (5)
C(114)	9105 (5)	5714 (4)	1005 (3)	5·9 (6)
C(115)	8121 (5)	6071 (4)	1267 (3)	5·3 (6)
C(116)	7330 (4)	5546 (3)	1588 (3)	4·4 (5)
C(201)	4302 (4)	1592 (2)	1464 (2)	3·2 (6)
C(202)	3203 (4)	1423 (3)	1133 (3)	4·5 (5)
C(203)	2478 (5)	770 (4)	1365 (4)	5·9 (5)
C(204)	2823 (6)	282 (4)	1927 (4)	6·3 (6)
C(205)	3915 (7)	440 (4)	2272 (3)	7·1 (6)
C(206)	4675 (6)	1080 (3)	2047 (3)	5·8 (5)
C(211)	5221 (4)	2126 (3)	209 (2)	3·0 (5)
C(212)	4811 (4)	2647 (3)	−358 (2)	3·6 (6)
C(213)	4903 (4)	2347 (3)	−1041 (2)	4·0 (5)
C(214)	5385 (4)	1547 (3)	−1161 (2)	4·2 (5)
C(215)	5761 (5)	1022 (3)	−603 (3)	5·0 (6)
C(216)	5656 (5)	1298 (3)	78 (2)	4·2 (6)
C(41)	3887 (4)	2856 (3)	3582 (2)	3·1 (5)
C(42)	3117 (4)	2224 (3)	3813 (3)	4·4 (6)
C(43)	3218 (5)	1970 (4)	4515 (3)	5·6 (5)
C(44)	4087 (5)	2336 (4)	4980 (3)	5·1 (5)
C(45)	4813 (6)	2945 (4)	4763 (3)	5·9 (5)
C(46)	4723 (5)	3217 (4)	4067 (2)	5·0 (6)

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

Mn—Cu	3·443 (1)	C(12)—P(1)	1·843 (4)
Cl—Cu	2·120 (1)	C(101)—P(1)	1·838 (4)
C(3)—Cu	2·036 (4)	C(111)—P(1)	1·818 (4)
C(4)—Cu	2·030 (4)	C(21)—P(2)	1·835 (4)
P(1)—Mn	2·313 (1)	C(201)—P(2)	1·816 (4)
P(2)—Mn	2·303 (1)	C(211)—P(2)	1·841 (4)
C(3)—Mn	2·023 (4)	C(21)—C(12)	1·531 (6)
C(5)—Mn	1·816 (4)	C(4)—C(3)	1·226 (5)
C(6)—Mn	1·806 (4)	C(41)—C(4)	1·458 (5)
C(7)—Mn	1·817 (4)	O(5)—C(5)	1·138 (5)
		O(6)—C(6)	1·149 (5)
		O(7)—C(7)	1·146 (5)
C(3)—Cu—Cl	169·4 (1)	C(6)—Mn—P(2)	88·3 (1)
C(4)—Cu—Cl	155·0 (1)	C(6)—Mn—C(3)	168·9 (2)
C(4)—Cu—C(3)	35·1 (2)	C(6)—Mn—C(5)	91·1 (2)
P(2)—Mn—P(1)	86·4 (1)	C(7)—Mn—P(1)	177·0 (1)
C(3)—Mn—P(1)	82·8 (1)	C(7)—Mn—P(2)	91·0 (1)
C(3)—Mn—P(2)	87·4 (1)	C(7)—Mn—C(3)	95·7 (2)
C(5)—Mn—P(1)	94·4 (1)	C(7)—Mn—C(5)	88·3 (2)
C(5)—Mn—P(2)	178·9 (1)	C(7)—Mn—C(6)	94·5 (2)
C(5)—Mn—C(3)	93·4 (2)	C(41)—C(4)—C(3)	165·6 (4)
C(6)—Mn—P(1)	86·8 (1)	C(4)—C(3)—Mn	171·1 (3)

The structure consists of discrete monomeric molecules (Fig. 1) linked by van der Waals forces. The shortest intermolecular distance is 3·32 (1) Å [Cu···H(C214$^{\text{i}}$); (i) = $x-\frac{1}{2}$, $\frac{1}{2}-y$, $z+\frac{1}{2}$]. The Cu ion is coordinated to C(3), C(4) and Cl atoms. These four atoms are nearly planar [largest deviation from atom to mean plane −0·036 (1) Å for Cu]; the Mn atom deviates from this plane by 0·076 (1) Å. The angles C(41)—C(4)—C(3) [165·6 (4)°] and C(4)—C(3)—Mn [171·1 (3)°] are very close to linearity. This, together with the short acetylenic distance [C(3)≡C(4) 1·226 (5) Å] has been attributed in other η^2-acetylene complexes to a significant π-donor interaction and poor π back donation between the metal atom and the acetylene moiety (Otsuka & Nakamura, 1976). Poor π back donation is in agreement with the value of the C≡C stretching wave number (1989 cm^{-1}), which is somewhat high compared with other η^2-acetylene complexes.

The Cu—C(acetylene) bond lengths [average value: 2·034 (3) Å] are similar to those observed in (η^5-C_5H_5)Ru(PPh_3)$_2$(C≡CPh).CuCl (Bruce, Abu-Salah, Davis & Raghavan, 1974) [2·02 (1) Å], but a stronger π acceptor (CO) linked to the Mn ion *trans* to the phenylacetylene ligand reduces the π back donation of acetylene. This produces a longer Mn—C compared to Ru—C observed in the preceding compound and a shorter C≡C bond length [1·226 (5) Å in the Mn complex compared to 1·25 (1) Å in the Ru complex].

The Mn ion displays a distorted octahedral coordination, with the P atoms of dppe and two carbonyl ligands in the equatorial plane, and the remaining carbonyl and the alkynyl ligand in the apical positions. The Mn—P bond distance [average value: 2·308 (5) Å] and the Mn—CO bond length with a P atom *trans*

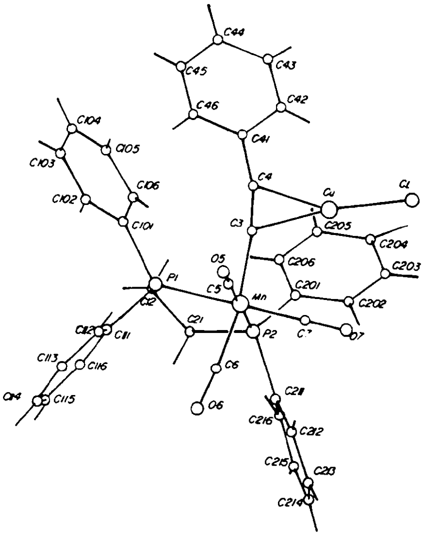

Fig. 1. Computer drawing of a discrete molecule.

[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.

We thank the spanish CAICYT (project 1184/81) for financial support and the CSIC for a grant.

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Acta Cryst. (1986). C**42**, 977–979

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

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(*Received* 28 *October* 1985; *accepted* 28 *February* 1986)

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

0108-2701/86/080977-03$01.50