Journal of Organometallic Chemistry, 66 (1974) 289—294
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THE CRYSTALLOGRAPHY OF μ-[CARBONYL(TRIPHENYLPHOSPHINE)-PLATINIO] OCTACARBONYLDIIRON (2Pt—Fe, 1Fe—Fe)

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(Received July 6th, 1973)

Summary

Three-dimensional X-ray diffractometer data have defined the structure of the title compound. The crystals are monoclinic, space group $P2_1/c$, with a 11.88, b 14.13, c 17.49 Å, β 106.9°, Z 4. 1626 independent reflexion intensities (Mo-K_α) formed the basis of the analysis and structure refinement (R_1 0.072).

The *closo*-arrangement is based on two Pt—Fe distances of 2.597(5) and 2.530(5) Å and one Fe—Fe bond length of 2.758(8) Å; each iron has four terminal carbonyl ligands, the platinum having terminal carbonyl and triphenylphosphine ligands and a planar stereochemistry.

Introduction

A number of synthetic studies have been described of complexes containing platinum bonded to other Group VIII metals [1 - 4]. A particularly interesting reaction is that of tetrakis(triphenylphosphine)platinum and analogous tertiary phosphine complexes with dodecacarbonyltriiron which provides trinuclear complexes, $PtFe_2(CO)_9L$ (L = tertiary phosphine). The IR data are indicative of terminal carbonyl groups only, in contrast to $Fe_3(CO)_{12}$ [5,6], $OsFe_2(CO)_{12}$ [7], $(MnFe_2(CO)_{12})^-$ [8,9], $(TcFe_2(CO)_{12})^-$ [9] and $(ReFe_2(CO)_{12})^-$ [10] whose stereochemistries are all based on bridging ligands. Our preoccupation with factors influencing cluster geometries and, particularly, the long-standing problem concerned with the decreasing tendency of the late transition elements of the third row to form carbonyl-bridged polynuclear complexes, compared with their first row counter parts, led us to a characterisation of the present complex.

Experimental

Crystal data

$C_{27}H_{15}PtFe_2O_9P$, mol. wt. 820.8, monoclinic, a 11.88(1), b 14.13(2), c

17.49(2) Å, β 106.9(1)°, V 2805.6 Å^3, D_m 1.92(2) g·cm^{-3}, $Z = 4$, $D_c = 1.91$ g·cm^{-3}. Space group $P2_1/c$ from the systematic absences $\{h0l\}$ for $l = 2n + 1$ and $\{0k0\}$ for $k = 2n + 1$. Mo-K_α radiation, λ 0.7107 Å, μ 63.95 cm^{-1}.

A yellow-red crystal of acicular habit and dimensions 0.11 × 0.35 × 0.08 mm. was mounted on the Pailred instrument so that the crystallographic c and instrumental ω axes were coincident; unit cell parameters were established by a least squares analysis of high angle reflexions on precession photographs (Mo-K_α). Integrated reflexion intensities within the layers $hk0$ - 12 were

TABLE 1

ATOMIC POSITIONS, VIBRATIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

(The vibrational coefficients relate to the expression:

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$)

Atom	x/a	y/b	z/c	$10^2 \times U$(Å^2)
Pt	0.2308 (1)	0.2876 (1)	0.3568 (5)	
Fe1	0.3887 (4)	0.1955 (4)	0.4657 (3)	
Fe2	0.4346 (4)	0.3592 (4)	0.3942 (3)	
P	0.1138 (7)	0.3925 (6)	0.2666 (4)	4.4 (0.2)
O1	0.0484 (20)	0.1422 (19)	0.3573 (13)	7.9 (0.7)
O2	0.2909 (27)	0.1942 (26)	0.0750 (17)	12.8 (1.1)
O3	0.2583 (30)	0.4637 (27)	−0.0070 (20)	13.9 (1.2)
O4	0.3882 (34)	−0.1500 (33)	0.4141 (22)	17.0 (1.5)
O5	0.4432 (32)	0.1064 (29)	0.3310 (20)	15.1 (1.3)
O6	0.3051 (21)	0.4707 (20)	0.4808 (14)	9.0 (0.8)
O7	0.5034 (28)	0.0445 (26)	0.1587 (19)	13.3 (1.1)
O8	0.4189 (31)	0.2877 (34)	0.2312 (21)	16.3 (1.3)
O9	0.3209 (27)	−0.1797 (24)	0.0119 (18)	12.6 (1.1)
C1	0.1074 (22)	0.1944 (22)	0.3564 (15)	4.3 (0.7)
C2	0.3377 (34)	0.2581 (31)	0.5320 (23)	9.3 (1.3)
C3	0.3047 (45)	0.0968 (42)	0.4798 (29)	13.5 (1.9)
C4	0.5187 (52)	0.1812 (46)	0.5315 (32)	16.1 (2.2)
C5	0.4222 (40)	0.1419 (38)	0.3894 (26)	11.4 (1.5)
C6	0.3501 (31)	0.4167 (29)	0.4510 (20)	7.6 (1.1)
C7	0.4714 (41)	0.4742 (38)	0.3632 (27)	11.5 (1.6)
C8	0.4158 (41)	0.3016 (43)	0.2959 (27)	12.8 (1.6)
C9	0.5795 (30)	0.3343 (27)	0.4486 (20)	7.2 (1.0)
C10	−0.0119 (23)	0.4187 (22)	0.2965 (15)	4.3 (0.7)
C11	−0.0063 (25)	0.4251 (25)	0.3789 (17)	5.4 (0.8)
C12	−0.1024 (27)	0.4492 (25)	0.4058 (18)	6.2 (0.9)
C13	−0.2053 (29)	0.4743 (27)	0.3505 (19)	6.6 (1.0)
C14	−0.2215 (29)	0.4630 (27)	0.2643 (19)	6.8 (1.0)
C15	−0.1328 (26)	0.4328 (24)	0.2405 (17)	5.3 (0.8)
C16	0.0591 (24)	0.3423 (23)	0.1645 (16)	4.7 (0.8)
C17	0.0033 (30)	0.4042 (28)	0.1040 (19)	7.2 (1.0)
C18	−0.0461 (30)	0.3630 (28)	0.0253 (19)	7.0 (1.0)
C19	−0.0389 (26)	0.2742 (28)	0.0131 (18)	6.5 (0.9)
C20	0.0188 (27)	0.2095 (31)	0.0757 (18)	7.2 (0.9)
C21	0.0676 (24)	0.2507 (21)	0.1524 (16)	4.8 (0.8)
C22	0.1791 (23)	0.5056 (22)	0.2543 (15)	4.2 (0.7)
C23	0.2288 (26)	0.5167 (24)	0.1955 (17)	5.3 (0.8)
C24	0.2758 (32)	0.6090 (30)	0.1873 (21)	8.1 (1.1)
C25	0.2580 (30)	0.6868 (28)	0.2389 (20)	7.4 (1.1)
C26	0.2096 (29)	0.6700 (27)	0.2942 (20)	7.2 (1.1)
C27	0.1629 (32)	0.5790 (29)	0.3030 (21)	7.8 (1.1)

Atom	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	355 (5)	624 (8)	315 (5)	−12 (9)	1 (3)	−3 (8)
Fe1	582 (28)	691 (42)	661 (29)	31 (29)	−103 (23)	78 (28)
Fe2	402 (26)	963 (46)	504 (27)	−123 (27)	−19 (21)	63 (27)

[a] $U_{ij} \times 10^4$.

TABLE 2

SELECTED BOND LENGTHS (Å)[a] AND THEIR ESTIMATED STANDARD DEVIATIONS

Pt—Fe(1)	2.597 (5)	P—C(10)	1.76 (3)
Pt—Fe(2)	2.530 (5)	P—C(16)	1.85 (3)
Pt—P	2.315 (8)	P—C(22)	1.82 (3)
Pt—C(1)	1.97 (3)	C(1)—O(1)	1.20 (4)
Fe(1)—Fe(2)	2.758 (8)	C(2)—O(2)	1.25 (6)
Fe(1)—C(2)	1.70 (4)	C(3)—O(3)	1.08 (7)
Fe(1)—C(3)	1.77 (4)	C(4)—O(4)	1.29 (6)
Fe(1)—C(4)	1.65 (4)	C(5)—O(5)	1.23 (7)
Fe(1)—C(5)	1.68 (4)	C(6)—O(6)	1.14 (4)
Fe(2)—C(6)	1.80 (4)	C(7)—O(7)	1.14 (6)
Fe(2)—C(7)	1.81 (5)	C(8)—O(8)	1.16 (6)
Fe(2)—C(8)	1.86 (4)	C(9)—O(9)	1.20 (4)
Fe(2)—C(9)	1.74 (3)		

[a] The carbon—carbon distances within the phenyl groups of the triphenylphosphido residue vary from 1.30 (4) to 1.50 (4) Å, the average value being 1.40 (4) Å.

obtained by the stationary counter-moving crystal method, all reflexions within the angular range $4^\circ \leqslant 2\theta \leqslant 45^\circ$ being surveyed, the ω scan through these reflexions varied from 1.0° (*hk*0) to 2.6° (*hk*12). The 080, 460 and 600 reflexion intensities served as standards for monitoring crystal and instrumental stabilities. All reflexions whose independent background counts differed significantly (3 σ) were discarded during data processing, the 1626 independent reflexion intensities preserved for the analysis having satisfied the criterion, $F_o^2 \geqslant 3.0\,\sigma\,(F_o^2)$. Lorentz-polarisation and absorption corrections were applied to these data.

An unsharpened Patterson synthesis provided the platinum atomic posi-

TABLE 3

SELECTED BOND ANGLES[a] (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Fe(1)—Pt—Fe(2)	65.1 (2)	Fe(1)—Fe(2)—C(6)	85 (1)
Fe(1)—Pt—P	169.4 (2)	Fe(1)—Fe(2)—C(7)	171 (1)
Fe(1)—Pt—C(1)	92.8 (7)	Fe(1)—Fe(2)—C(8)	94 (2)
Fe(2)—Pt—P	105.0 (3)	Fe(1)—Fe(2)—C(9)	83 (1)
Fe(2)—Pt—C(1)	157.8 (8)	C(6)—Fe(2)—C(7)	89 (2)
P—Pt—C(1)	97.3 (7)	C(6)—Fe(2)—C(8)	141 (2)
Pt—Fe(1)—Fe(2)	56.3 (1)	C(6)—Fe(2)—C(9)	114 (2)
Pt—Fe(1)—C(2)	85 (1)	C(7)—Fe(2)—C(8)	95 (2)
Pt—Fe(1)—C(3)	100 (2)	C(7)—Fe(2)—C(9)	93 (2)
Pt—Fe(1)—C(4)	155 (2)	C(8)—Fe(2)—C(9)	104 (2)
Pt—Fe(1)—C(5)	86 (2)	Pt—C(1)—O(1)	175 (2)
Fe(2)—Fe(1)—C(2)	92 (2)	Fe(1)—C(2)—O(2)	174 (3)
Fe(2)—Fe(1)—C(3)	156 (1)	Fe(1)—C(3)—O(3)	176 (3)
Fe(2)—Fe(1)—C(4)	99 (2)	Fe(1)—C(4)—O(4)	167 (4)
Fe(2)—Fe(1)—C(5)	84 (2)	Fe(1)—C(5)—O(5)	177 (3)
C(2)—Fe(1)—C(3)	89 (2)	Fe(2)—C(6)—O(6)	165 (4)
C(2)—Fe(1)—C(4)	96 (3)	Fe(2)—C(7)—O(7)	177 (3)
C(2)—Fe(1)—C(5)	171 (2)	Fe(2)—C(8)—O(8)	162 (4)
C(3)—Fe(1)—C(4)	105 (3)	Fe(2)—C(9)—O(9)	177 (3)
C(3)—Fe(1)—C(5)	92 (2)	Pt—P—C(10)	109 (1)
C(4)—Fe(1)—C(5)	105 (3)	Pt—P—C(16)	112 (1)
Pt—Fe(2)—Fe(1)	58.7 (2)	Pt—P—C(22)	116.9 (8)
Pt—Fe(2)—C(6)	71 (1)	C(10)—P—C(16)	106 (1)
Pt—Fe(2)—C(7)	126 (1)	C(10)—P—C(22)	106 (1)
Pt—Fe(2)—C(8)	75 (2)	C(16)—P—C(22)	105 (1)
Pt—Fe(2)—C(9)	141 (1)		

[a] Internal phenyl-angles have been omitted. The variation for all C—C—C within the three phenyl groups lies within the limits of 114(3)° and 124(3)°, with an average value of 121(3)°.

tion, the remaining atomic positions being indicated by two successive difference Fourier syntheses with an intervening cycle of block-diagonal least squares refinement. Unit-weights least squares refinement of positions and isotropic thermal parameters converged quickly to R_1 0.098 when block-diagonal least squares refinement of the anisotropic thermal parameters of the platinum and iron atoms was begun. Convergence was now to R_1 0.088 for the non-absorption corrected data which corresponded to 0.074 for the (then available) absorption corrected intensities. Two more cycles of block-diagonal least squares refinement provided terminal values of R_1 0.072 and R_2 0.088. A difference Fourier synthesis at this point revealed no excursions of electron density greater than 0.8 $e \cdot Å^{-3}$; peaks corresponded either to hydrogen atoms attached to the triphenylphosphine ligand or to an obviously inadequate treatment of the thermal vibrations of the platinum atom. Largely on grounds of computer economy, hydrogen atom contributions to the calculated structure factors amplitudes have not been included.

Atomic scattering factors, used in the calculations of $|F_c|$ were those for Pt, Fe, P, O and C [11], that for Pt being corrected for anomalous dispersion.

Table 1 lists final positional and thermal parameters, while Tables 2 and 3 collects together important bond lengths and bond angles. Figure 1 is a perspective view of the complex with atom labelling.

Discussion

The complex is made up of direct metal—metal bonds with, as was suggested by the infrared data, no bridging carbonyl ligands. The two Pt—Fe bond lengths are significantly different in a way which could have been anticipated from the relative *trans*-influence of ligands in mononuclear complexes [12,13]. The average Fe(1)—C(O) and Fe(2)—C(O) bond lengths of 1.70(4) and 1.80(4) Å are not significantly different but again they follow expectations in that the shorter value is essentially *trans* to the triphenylphosphine—platinum fragment. The coordination symmetry around the platinum is planar, the rms atomic deviation from the mean plane defined by Pt, Fe(1), Fe(2), P and C(1) being 0.01 Å. The coplanarity of the ligands with the platinum suggests the complex is usefully regarded as the $[Fe_2(CO)_8]^{2-}$ anion bridged by the $[(Ph_3P)(CO)Pt]^{2+}$ moiety [14]. The cluster is then obviously related to $MFe_2(CO)_{12}^{n-}$ ($n = 0$, M = Ru, Os; $n = 1$, M = Mn, Tc, Re) [5 - 10] which are derived from $Fe_3(CO)_{12}$ through the replacement of the non-bridged iron-carbonyl fragment by the heterometal [15]. As in $Fe_2(CO)_9$ [16], the iron atoms in these mixed metal clusters are assumed to be zerovalent, in obvious contrast to the $Fe_2(CO)_8{}^{2-}$ species which has only terminal carbonyl ligands. The observed structure of $(Ph_3P)(CO)PtFe_2(CO)_8$ implies that the effective electronegativity of the $[(PH_3P)Pt(CO)]^{2+}$ moiety is less than that of the $Fe(CO)_4$ group and that the charge distribution on the iron atoms is closer to that of the octacarbonyldiiron dianion than that which obtains in $Fe_2(CO)_9$.

That there is nothing exceptional in the observed Fe(1)—Fe(2) bond length of 2.758 Å calls for some comment since it bears on our assertion [17] that bridged metal—metal bond lengths depend less on the covalent radius of the bridging atom than upon its donor properties and the number of terminal

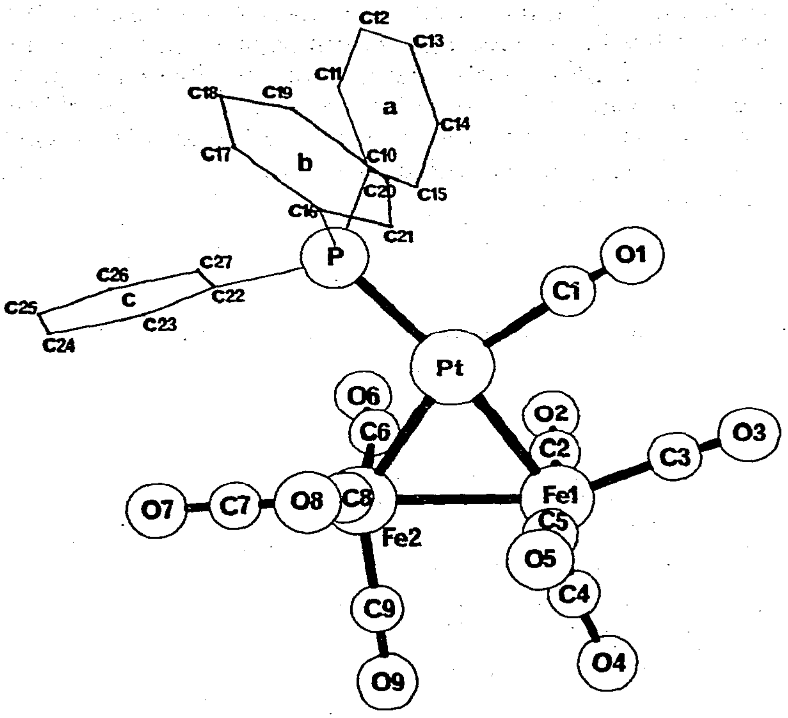

Fig. 1

ligands and non-bonding electrons associated with the metals. In $C_2(C_6H_5)_2$-$Fe_2(CO)_8$ the Fe—Fe bond length is 2.64 Å [18] while in $Fe_2(CO)_8{}^{2-}$ it is 2.88 Å [19]; the overall stereochemistry of the $Fe_2(CO)_8$ fragment in these complexes is very similar and, in turn, essentially equivalent to that observed for the present complex. We have already drawn attention [17] to variations in the Fe—Fe bond lengths in complexes, $Fe_2(CO)_6L_2$, and shown that they relate to the electronegativity of the bridging ligand, L. The trend of the Fe—Fe bond lengths in the octacarbonyldiiron fragments reflect the increasing population of a bridge orbital which is antibonding with respect to the two iron atoms; the Lewis acidity of the μ-diphenylacetylene ligand is demonstrably greater than that of the triphenylphosphineplatinum carbonyl fragment.

The very closely related complex $(OC)_4Fe \cdot Pt_2(P(OPh)_3)_3CO$, has been examined recently by X-ray methods [20]. Two particular points need comment. The average Pt—Fe bond length is very similar in the two clusters: 2.568 Å in the diplatinum complex and 2.564 Å in the diiron species. But the difference between the two Pt—Fe bond lengths is only 0.033 Å in the $FePt_2$ cluster and is 0.067 Å in the $PtFe_2$ complex, this is consistent with the triphenylphosphite ligand, with its increased π-acidity compared with triphenylphosphine, having a much smaller *trans*-influence. The other point is that, as Albano et al. [20] note, both complexes are electron deficient in the sense that unlike, say, the $MFe_2(CO)_{12}^{n-}$ species, they are not 48-valence electron clusters. It is this fact and not multiple bonding per se which is responsible for the relatively short metal—metal bond lengths found in 46-electron-trinuclear clusters compared with their 48-valence electron counterparts— as we have stressed earlier [21], the highest filled molecular orbital in clusters such as $Os_3(CO)_{12}$ is antibonding with respect to the metal—metal bonds. A modification of the donor—acceptor properties of terminal and bridging ligands changes the population of this level and brings about variations of up to 0.15 Å or so in the metal—metal bond lengths.

Acknowledgement

We are grateful to the Science Research Council for support of these studies.

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