Synthesis of platinum-mercury clusters and the molecular structure of $Pt_4(HgBr)_2(\mu\text{-}CO)_4(PPh_3)_4$

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New platinum-mercury clusters, $Pt_4(HgX)_2(\mu\text{-}CO)_4(PR_3)_4$ (X = Cl, Br, I, CF_3, or CCl_3; R = Ph or Et), were synthesized. The molecular and crystal structure of the $Pt_4(HgBr)_2(\mu\text{-}CO)_4(PPh_3)_4$ cluster was established by X-ray structural analysis.

Key words: platinum, mercury, carbon monoxide, tertiary phosphines, clusters; molecular and crystal structure, X-ray structural analysis.

Reactions of complexes of metals in normal oxidation states with clusters containing, generally, metals in low oxidation states often produce products considered as complexes in mixed oxidation states. These compounds are known for both platinum and palladium.[1–3] Reactions of carbonylphosphine clusters of platinum and palladium with organomercury compounds were studied, and hexanuclear heterometal $M_4(HgX)_2(CO)_4(PPh_3)_4$ clusters were isolated.[4,5] In this work, we describe the reactions of carbonylphosphine clusters of platinum with mercury(II) halides. The molecular and crystal structure of one of the compounds obtained was established by X-ray structural analysis.

Experimental

Syntheses were carried out under an atmosphere of argon or nitrogen. The solvents used were purified according to standard procedures. The starting platinum clusters were prepared according to the procedures reported previously.[6] Weighed samples were mineralized in a mixture of sulfuric and hydrochloric acids, and the platinum and phosphorus contents of the samples were determined spectrophotometrically in the form of the bromide complex[7] and phosphomolybdate blue,[8] respectively.

Clusters $Pt_4(\mu\text{-}HgX)_2(\mu\text{-}CO)_4(PR_3)_4$ (1–6). Solutions of the starting $Pt_3(\mu\text{-}CO)_3(PPh_3)_4$ complex and HgX_2 in THF were mixed in a molar ratio of 5 : 6. The mixture was stirred for 1 h, and the inert gas was replaced by carbon monoxide. Then the reaction mixture was stirred for 2 h. The solvent was distilled off *in vacuo*. The dry residue was dissolved in benzene, and the solution was applied to a short column packed with Silica gel (Silica gel L 40/100; *d* = 50 mm, *l* = 30 mm). The product was eluted with ethyl acetate and recrystallized from benzene—hexane solution (hexane was added to a solution of the cluster in benzene until crystallization started). The cluster with R = Ph and X = CCl_3 (**4**) was eluted with benzene—diethyl ether mixture (3 : 1). When the cluster with R = Et and X = Cl (**6**) was synthesized, the $Pt_4(\mu\text{-}CO)_5(PEt_3)_4$ complex was used as the starting compound; the molar ratio of the reagents was 1 : 1; chloroform was used as the eluent; the product was recrystllized from chloroform—hexane mixture (hexane was added to a solution of the cluster in $CHCl_3$ until crystallization started).

The data of elemental analysis, the CO stretching frequencies in the IR spectra, and the yields of the compounds are given in Table 1.

X-ray structural study of cluster 1. Single crystals suitable for X-ray structural analysis were grown from a solution of $Pt_4(HgBr)_2(\mu\text{-}CO)_4(PPh_3)_4$ (**1**) in benzene by slow diffusion with hexane as the precipitant. Crystals of **1** are monoclinic, a = 20.32(3) Å, b = 20.549(6) Å, c = 17.932(4) Å, β = 90.50(2)°, V = 7490 Å^3, space group $P2_1/c$, Z = 4. The unit cell parameters and intensities of 9456 reflections were measured on an automated Nonius CAD-4 diffractometer (Mo-Kα radiation, graphite monochromator, $3\omega/5\theta$-scanning technique, $2\theta < 44°$) at -20 °C within the total sphere of the reciprocal space. 4489 independent observed reflections with $I > 3\sigma(I)$ were used in the calculations. The structure of **1** was solved by the direct method and refined anisotropically by the block-diagonal least-squares method to R = 0.042 and R_w = 0.056 (an absorption correction was applied using the DIFABS program[9]). The atomic coordinates of the structure of **1** and a complete list of the bond lengths were deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1W, England. All calculations were carried out on a PDP 11/23+ computer using the SDP PLUS program package.

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Table 1. Yields and principal characteristics of $Pt_4(HgX)_2(CO)_4(PR_3)_4$ clusters

Compound	R	X	Yield (%)	$\frac{\text{Found}}{\text{Calculated}}$ (%) C	H	Pt	P	ν(CO)/cm^{-1}
1	Ph	Br	50	—	—	32.2 31.9	5.24 5.07	—
2	Ph	Cl	64	37.85 37.66	3.38 2.56	32.9 33.1	5.28 5.26	1878 m, 1849 s, 1827 s, 1802 s
3	Ph	I	63	—	—	29.8 30.7	4.92 4.88	—
4	Ph	CCl_3	66	—	—	30.5 30.3	4.83 4.80	—
5	Ph	CF_3[a]	56	38.59 38.61	2.60 2.52	30.4 31.4	4.93 4.90	1870, 1843, 1820 s, 1795
6	Et	Cl[b]	50	—	—	43.3 42.5	7.11 6.75	1854 m, 1818 sh, 1810 s

[a] CF_3HgBr is the starting compound; solvate with 0.5 C_6H_6. For F, found: 4.51%; calculated: 4.52%.
[b] Cluster with PEt_3.

Results and Discussion

The yields of the compounds (determined for Pt) were no more than 66% (see Table 1). Successive elution of the products of reactions of triphenylphosphine clusters of platinum with $HgCl_2$ on a column packed with Silica gel gave a pale-yellow compound $PtCl_2(PPh_3)_2$, which was described previously and whose IR spectrum does not contain C=O stretching bands, in addition to the major reaction product. Under the action of an obvious excess of $HgCl_2$ on the platinum cluster, the solution was decolorized, and $PtCl_2(PPh_3)_2$ was isolated from this solution in a high yield.

$$5\ Pt_3(\mu\text{-}CO)_3(PPh_3)_4 + 6\ HgX_2 =$$
$$3\ Pt_4(\mu\text{-}HgX)_2(\mu\text{-}CO)_4(PPh_3)_4 + 3\ PtX_2(PPh_3)_2$$
1—4

The molecular structure of **1** (according to the X-ray structural data) is shown in Fig. 1. The principal geometric parameters of molecule **1** are given in Tables 2 and 3. Heteronuclear cluster **1** forms when the known "butterfly" cluster $Pt_4(CO)_5L_4$ (L is tertiary phosphine) is completed with two HgBr fragments, which replace formally isoelectronically the μ-CO ligand at the central Pt—Pt bond in the Pt_4 "butterfly". Therefore, as in the case of the known $Pt_4(\mu\text{-}CO)_5L_4$ cluster, the Pt_4 skeleton in molecule **1** contains 58 valence electrons and consists of two central Pt(1) and Pt(2) atoms with 18-electron shells of an inert gas and two atoms of the "wings", Pt(3) and Pt(4), with 16-electron configurations. Previously, analogous clusters of palladium[4] and platinum,[5] $Pd_4(HgBr)_2(CO)_4(PEt_3)_4$ (**7**) and $Pt_4(HgCF_3)_2(CO)_4(PPh_3)_4$ (**5**), were studied. The principal geometric parameters of these molecules and the molecules of the related carbonylphosphine clusters of Pd

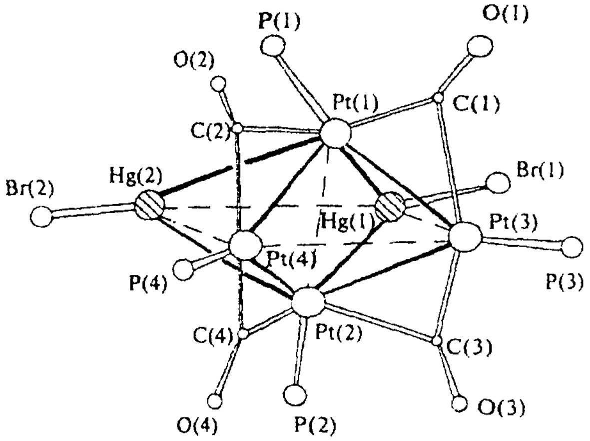

Fig. 1. Structure of molecule **1** (Ph substituents are omitted).

Table 2. Principal interatomic distances (*d*) in structure **1**

Distance	*d*/Å	Distance	*d*/Å
Hg(1)—Pt(1)	2.753(1)	Pt(1)—P(1)	2.271(5)
Hg(1)—Pt(2)	2.736(1)	Pt(2)—P(2)	2.276(6)
Hg(2)—Pt(1)	2.747(1)	Pt(3)—P(3)	2.265(5)
Hg(2)—Pt(2)	2.777(1)	Pt(4)—P(4)	2.253(6)
Pt(1)—Pt(3)	2.751(1)	Pt(1)—C(2)	2.060(2)
Pt(1)—Pt(4)	2.722(1)	Pt(2)—C(3)	2.160(1)
Pt(2)—Pt(3)	2.751(1)	Pt(2)—C(4)	1.990(2)
Pt(2)—Pt(4)	2.727(1)	Pt(3)—C(1)	2.070(2)
Pt(1)...Pt(2)	3.008(1)	Pt(3)—C(3)	2.060(2)
Pt(3)...Pt(4)	3.211(1)	Pt(4)—C(2)	2.030(2)
Hg(1)...Pt(3)	3.113(1)	Pt(4)—C(4)	2.030(3)
Hg(2)...Pt(4)	3.021(1)	C(1)—O(1)	1.150(2)
Hg(1)...Hg(2)	3.617(1)	C(2)—O(2)	1.210(2)
Hg(1)—Br(1)	2.523(3)	C(3)—O(3)	1.130(2)
Hg(2)—Br(2)	2.508(3)	C(4)—O(4)	1.260(3)

Table 3. Bond angles (ω) in structure **1**

Angle	ω/deg	Angle	ω/deg
Pt(1)—Hg(1)—Pt(2)	66.48(1)	Pt(1)—Pt(2)—P(2)	141.90(2)
Pt(1)—Hg(1)—Br(1)	144.97(8)	Hg(1)—Pt(2)—P(2)	91.80(2)
Pt(2)—Hg(1)—Br(1)	147.06(8)	Hg(2)—Pt(2)—P(2)	101.90(2)
Pt(1)—Hg(2)—Br(2)	64.99(1)	Pt(3)—Pt(2)—P(2)	136.60(2)
Pt(1)—Hg(2)—Br(2)	152.83(8)	Pt(4)—Pt(2)—P(2)	149.40(2)
Pt(2)—Hg(2)—Br(2)	140.44(8)	Pt(1)—Pt(3)—Pt(2)	66.30(4)
Hg(1)—Pt(1)—P(1)	95.80(1)	Pt(1)—Pt(3)—P(3)	144.40(1)
Hg(2)—Pt(1)—P(1)	98.80(2)	Pt(2)—Pt(3)—P(3)	149.30(1)
Pt(3)—Pt(1)—P(1)	140.70(2)	Pt(1)—Pt(4)—Pt(2)	67.04(3)
Pt(4)—Pt(1)—P(1)	144.80(2)	Pt(1)—Pt(4)—P(4)	152.70(2)
Pt(2)—Pt(1)—P(1)	143.30(1)	Pt(2)—Pt(4)—P(4)	139.70(2)

and Pt with a 58-electron M_4 "butterfly" are compared in Table 4. As in the case of the carbonylphosphine analogs, the coordinations around the 16-electron atoms of the "wings" in structures **1**, **5**, and **7** are close to planar-trigonal: the sum of the Pt—Pt—Pt and Pt—Pt—P bond angles at the Pt(3) and Pt(4) atoms in molecule **1** are 359.4° and 360°, respectively; in **5**, these angles are 359° and 360°, respectively. Almost identical coordinations (but without the bridging ligands) were observed around the Hg(1) atom (the sums of the bond angles are 358.5° and 357.8° in molecules **1** and **5**, respectively) and Hg(2) atom (359.3° and 357.6° in molecules **1** and **5**, respectively). The central Pt(1)—Pt(2) edges in structures **1** and **5** are lengthened by approximately 0.2 Å compared to the analogous edges linked by bridging CO groups in related homonuclear carbonylphosphine clusters.

The length of the nonbonding Pt—Pt edge in the Pt_4 "butterfly" correlates essentially with Tolman cone angle θ, which is a semiquantitative measure of the van der Waals volume of the ligand L (see Ref. 10). Except for the $Pt_4(\mu\text{-}CO)_5(PEt_3)_4$ cluster with a shortened Pt...Pt contact (3.190 and 3.263 Å in two independent molecules),[11] the bulkier phosphine ligands L generally tend to be arranged at the vertices of a regular tetrahedron, which results in the fact that the "wings" of the butterfly are put together. The shortest contact between the 16-electron atoms of the "wings" (3.074 Å) was observed in the sterically more crowded $Pt_4(\mu\text{-}CO)_2(dppm)_3[Ph_2PCH_2P(O)Ph_2]$ cluster.[12] However, the above-mentioned unusual situation observed for the $Pt_4(\mu\text{-}CO)_5(PEt_3)_4$ cluster and the substantial variation in the lengths of nonbonding Pt...Pt contacts in the crystallographically independent molecules and polymorphs of $M_4(\mu\text{-}CO)_5L_4$ clusters indicate that the "butterfly" conformation can be substantially changed under the effect of the crystal packing.

Interestingly, the individual metal—metal distances in molecule **1** and related clusters also show slight but statistically significant nonequivalence (see Tables 2—4). Because of this nonequivalence, C_{2v} symmetry, which is the maximum possible for this type of clusters, is lowered to C_s in structure **1**. However, the scattering of the individual P—C and C—O distances in molecule **1** analogous to that described previously[11] as asymmetry of the coordination environment in the $Pt_4(\mu\text{-}CO)_5(PEt_3)_4$ cluster, is not statistically significant and, apparently, is caused by the fact that the absorption correction was not adequate (such discrepancies were not observed in the structures of Pd analog **7** and compound **5**, which were determined more precisely).

The similar structures of clusters **1**, **5**, and **7** differ most substantially in the lengths of the nonbonding intramolecular metal—metal contacts (see Table 2). The dihedral angle of "opening" of the Pt_4 "butterfly" in structure **1** is 97.7°, which is near the mean value observed for the analogous angles in clusters **7** and **5** (100.2° and 89.2°, respectively). The Pt(3)...Pt(4) distance in structure **1** is somewhat shorter than the corresponding distance in molecule **3**, whereas the Pt(1)—Pt(2) bond is longer (see Table 4), though the Hg...Hg distance in structure **1** is somewhat smaller than in molecule **5**. This comparison of the bond angles and distances in clusters **1**, **5**, and **7** suggests that the M_3 and HgM_2 fragments rotate rather freely around the central pair of the atoms, Pt(1)—Pt(2), in a joint fashion, which allows substantial changes in the lengths of the equatorial and axial contacts as the ligand environment and the crystal packing change.

Table 4. Geometric parameters of Pd and Pt "butterfly" clusters and their Hg-containing analogs

Cluster	L	θ/deg[10]	d/Å						Reference
			M(3)...M(4)	M(1)—M(2)	(M—M)$_b$	Hg...Hg	M—P	M—C	
$Pt_4(CO)_5L_4$	PEt_3[a]	132	3.190, 3.263	2.737	2.728		2.25	2.05	11
	PMe_2Ph	122	3.543	2.790	2.752		2.28	—	21
$Pt_4(CO)(dppm)_2L$	$Ph_2PCH_2P(O)Ph_2$	—	3.074	2.700	2.659		2.24—2.34	1.99—2.17	12
$Pd_4(CO)_5L_4$	$PMePh_2$	136	3.365	2.750	2.750		2.32		22
	PPh_3[b]	145	3.188—3.324	2.767	2.750		—	—	23, 24
$Pd_4(HgBr)_2(CO)_4L_4$	PEt_3	132	3.428	3.015	2.694	3.251	2.31	2.05	4
$Pt_4(HgBr)_2(CO)_4L_4$	PPh_3	145	3.211	3.008	2.738	3.617	2.26	2.05	[c]
$Pt_4(HgCF_3)_2(CO)_4L_4$	PPh_3	145	3.230	2.949	2.730	3.640	2.26	2.06	5

[a] Two independent molecules. [b] Three crystal modifications. [c] This work.

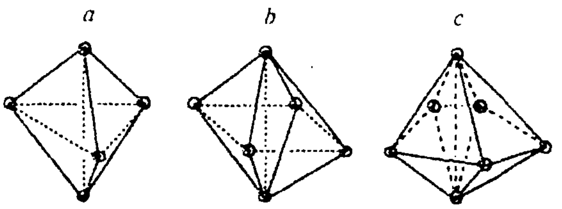

Fig. 2. Structures of bipyramidal clusters with an intrapolyhedral metal—metal contact: *a*, $[Cu_5(\mu\text{-}Ph)_6]^-$ and $[Cu_2Au_3(\mu\text{-}C_2Ph)_6]^-$ (see Refs. 13 and 17); *b*, $(B_{10}H_{12})_2Au_6L_4$ and $Cp_2Ni_2Zn_4$ (see Refs. 16 and 18); *c*, $[Au_7L_7]^+$ and $Cp_2Mo_2As_5$ (see Refs. 14 and 15).

The structural characteristics of clusters **1**, **5**, and **7** make it possible to consider their structures not only as M_4 "butterflies" completed with HgX fragments but also as heteronuclear M_4Hg_2 octahedra distorted in a specific fashion. Distortion of the octahedral metal skeleton of these clusters consists in the contraction of the diagonal of the octahedron, which leads to an axial intrapolyhedral metal—metal contact, and in the expansion of four equatorial edges (see dashed lines in Fig. 1). In this case, structures **1**, **5**, and **7** can be assigned to the family of distorted bipyramids with the inner edge between axial vertices (Fig. 2). In addition to the distorted octahedral clusters, the trigonal-bipyramidal pentanuclear clusters (Cu_5Ph_6 and its substituted heterometal analogs[13]) and the pentagonal-bipyramidal heptanuclear $[Au_7(PPh_3)_7]^+$ and $Cp_2Mo_2As_5$ clusters (see Refs. 14 and 15, respectively) belong to this family. The $(B_{10}H_{12})Au_6(PEt_3)_4$ cluster[16] and the heteronuclear $Cp_6Ni_2Zn_4$ cluster[17] with the apical Ni—Ni bond (2.57 Å), short apical-equatorial Ni—Zn edges (2.40 Å), and elongated equatorial Zn—Zn contacts (2.86 Å, aver.) are structurally closely related to cluster **1**.

The length of the axial inner edge in the bipyramidal clusters, which are shown in Fig. 2, decreases as the number of atoms in the equatorial plane increases. In trigonal-bipyramidal clusters, the inner axial distance is close to the lengths of the equatorial M...M contacts.[18] In the distorted octahedral and pentagonal-bipyramidal clusters, the inner axial distances correspond to the elongated weak bond[19] and short strong metal—metal bond,[14,20] respectively. In agreement with this tendency, the length of the inner Pt(1)—Pt(2) edge is the lower limit of the range of the nonbonding intramolecular metal—metal contacts (3.0—3.6 Å). The scattering of the values of these contacts in clusters **1**, **5**, and **7** is also caused by the *cis* arrangement of Hg heteroatoms in the metal polyhedron, which lowers its symmetry. The latter fact also leads to deviations of the phosphine ligands at the central metal atoms from the axial orientation.

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