

Pt(1)—Pt—P(2)	94.9 (1)	Pt—P(2)—C(5)	112.6 (4)
P(1)—Pt—O(1)	170.6 (2)	Pt—P(2)—C(6)	110.7 (4)
P(1)—Pt—O(4)	92.9 (2)	C(4)—P(2)—C(5)	101.7 (6)
P(2)—Pt—O(1)	91.2 (2)	C(4)—P(2)—C(6)	106.8 (5)
P(2)—Pt—O(4)	167.5 (2)	C(5)—P(2)—C(6)	104.5 (6)
O(1)—Pt—O(4)	82.3 (3)	Pt—O(1)—N(1)	118.3 (7)
Pt—P(1)—C(1)	113.1 (4)	Pt—O(4)—N(2)	117.8 (7)
Pt—P(1)—C(2)	112.3 (4)	O(1)—N(1)—O(2)	119 (1)
Pt—P(1)—C(3)	117.9 (4)	O(1)—N(1)—O(3)	117 (1)
C(1)—P(1)—C(2)	103.5 (6)	O(2)—N(1)—O(3)	124 (1)
C(1)—P(1)—C(3)	106.3 (5)	O(4)—N(2)—O(5)	118 (1)
C(2)—P(1)—C(3)	102.3 (5)	O(4)—N(2)—O(6)	118.7 (9)
Pt—P(2)—C(4)	119.3 (4)	O(5)—N(2)—O(6)	123 (1)
Pt—O(1)—N(1)—O(2)	0 (1)	O(1)—Pt—P(1)—C(1)	48 (1)
Pt—O(1)—N(1)—O(3)	179.8 (7)	O(1)—Pt—P(1)—C(2)	-69 (1)
Pt—O(4)—N(2)—O(5)	-170.4 (8)	O(1)—Pt—P(1)—C(3)	173 (1)
Pt—O(4)—N(2)—O(6)	12 (1)	O(1)—Pt—P(2)—C(4)	-128.8 (5)
P(1)—Pt—P(2)—C(4)	44.1 (5)	O(1)—Pt—P(2)—C(5)	-9.9 (5)
P(1)—Pt—P(2)—C(5)	163.1 (5)	O(1)—Pt—P(2)—C(6)	106.8 (5)
P(1)—Pt—P(2)—C(6)	-80.3 (4)	O(1)—Pt—O(4)—N(2)	91.3 (8)
P(1)—Pt—O(1)—N(1)	153 (1)	O(4)—Pt—P(1)—C(1)	106.7 (5)
P(1)—Pt—O(4)—N(2)	-80.6 (8)	O(4)—Pt—P(1)—C(2)	-10.1 (5)
P(2)—Pt—P(1)—C(1)	-83.1 (4)	O(4)—Pt—P(1)—C(3)	-128.6 (5)
P(2)—Pt—P(1)—C(2)	160.2 (5)	O(4)—Pt—P(2)—C(4)	173 (1)
P(2)—Pt—P(1)—C(3)	41.6 (4)	O(4)—Pt—P(2)—C(5)	-68 (1)
P(2)—Pt—O(1)—N(1)	-75.7 (7)	O(4)—Pt—P(2)—C(6)	48 (1)
P(2)—Pt—O(4)—N(2)	150.7 (8)	O(4)—Pt—O(1)—N(1)	93.6 (7)

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μ -Hydroxo Diplatinum(II) Complex Containing Bridging Cyclometallated 1,3-Bis(diphenylphosphino)propane as the Tetrafluoroborate Salt

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Abstract

The structure of the title compound bis- μ -(2-[(diphenylphosphino)propyl](phenyl)phosphino)phenyl-1 κ C¹:2 κ^2 P,P';1 κ^2 P,P':2 κ C¹- μ -hydroxo-diplatinum(II) tetrafluoroborate bis(dichloromethane) solvate is reported as one of the few examples of a derivative of the parent dimers [Pt-*o*-C₆H₄(Ph)P(CH₂)_nPPh₂]₂ where *n* = 2 or 3. Such dimers are linked by two bridging *ortho*-metallated phenyls attached to a coordinated P atom. The hydroxo group symmetrically bridges the two Pt atoms increasing their separation to 2.867 Å.

Comment

The title complex was isolated as the result of an *in situ* hydrolysis of the product of reaction of the dimer [Pt- μ -(*o*-C₆H₄(Ph)PCH₂CH₂CH₂PPh₂)]₂ with silver tetrafluoroborate. NMR evidence of the mixture suggested that a silver-platinum complex was initially formed (Dekker, Elsevier, Poelsma, Vrieze, van Leeuwen, Smeets & Spek, 1992), which slowly changed to the bridging hydroxo species.

Few examples containing these *ortho*-metallated complexes have been characterized crystallographically – particularly in the series where the chelating phosphine has a propane backbone. The framework of the parent dimer is retained, although the changes in the P—Pt—Pt angles reflect the orientation demands of the bridging hydroxo

Colorless prism crystals were obtained by slow evaporation of a dichloromethane solution of the title compound. The density was measured by flotation in a diiodomethane/1,2-dibromoethane/hexane mixture.

The X-ray diffraction intensities were collected at the Research Center for Spectrochemistry, Faculty of Science, The University of Tokyo. The data were collected with a scan speed of 8.0° min⁻¹ (in ω). Decay correction was applied. The structure was solved using the Patterson heavy-atom method which revealed the position of the Pt atom. The remaining non-H atoms were subsequently located in successive difference Fourier maps. All non-H atoms were refined anisotropically. The positions of H atoms were calculated geometrically. All calculations were performed using the TEXSAN (Molecular Structure Corporation, 1985) crystallographic software package and carried out on a DEC MicroVAX II computer at the Research Center for Spectrochemistry. Molecular graphics: ORTEPII (Johnson, 1976).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55983 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1039]

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moiety. This is particularly true for the diphenylphosphino groups lying approximately along the Pt–Pt axis. The P–Pt distance for these groups is also shortened relative to the P–Pt distance of the phosphino group *trans* to the *ortho*-metallated ring (Bennett, Berry, Bhargava, Ditzel, Robertson & Willis, 1987).

The hydroxo group was found to have increased the Pt··Pt distance to 2.867 Å compared to that of 2.628 Å found in the analogous parent dimer containing the ethane backbone (Arnold, Bennett, Bilton & Robertson, 1982). The Pt–Pt–O triangle was found to be reasonably symmetrical with O–Pt··Pt angles of 48.3 and 47.8°.

These head-to-toe dimers can show isomerism when a bridging group has been introduced. The orientation shown in the present example is also found in the μ -iodo species (Bennett, Berry, Bhargava, Ditzel, Robertson & Willis, 1987), whereas the enantiomeric orientation is found for both the μ -methylene derivative (Arnold, Bennett, McLaughlin & Robertson, 1983) and a bridging gold moiety (Bennett, Berry & Beveridge, 1990).

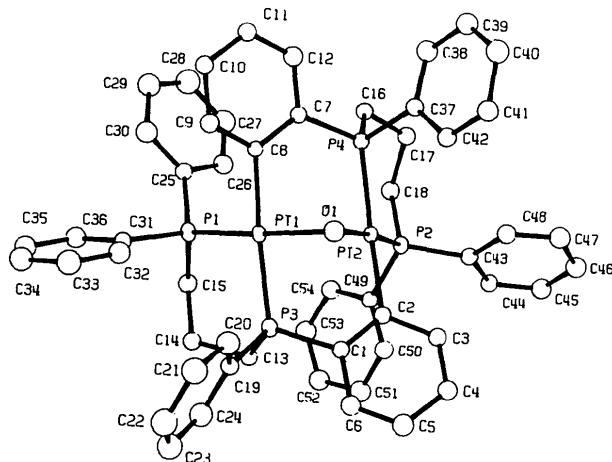


Fig. 1. View of the complex cation showing the atomic numbering scheme.

Experimental

Crystal data

$[\text{Pt}_2(\text{C}_{27}\text{H}_{25}\text{P}_2)_2(\text{OH})] \cdot$
 $\text{BF}_4 \cdot 2(\text{CH}_2\text{Cl}_2)$

$M_r = 1486.74$

Monoclinic

$P2_1/a$

$a = 25.008$ (4) Å

$b = 14.045$ (2) Å

$c = 17.378$ (3) Å

$\beta = 112.39$ (1)°

$V = 5643.6$ Å³

$Z = 4$

$D_x = 1.75$ Mg m⁻³

$D_m = 1.74$ Mg m⁻³

Density measured by flotation

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 24 reflections

$\theta = 12$ – 24°

$\mu = 5.357$ mm⁻¹

$T = 293$ K

Block

$1.02 \times 0.67 \times 0.65$ mm

Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

EMPABS (North, Phillips & Mathews, 1968)

$T_{\min} = 0.48$, $T_{\max} = 1.0$

9461 measured reflections

9193 independent reflections

6803 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 25^\circ$

$h = -29 \rightarrow 29$

$k = 0 \rightarrow 16$

$l = 0 \rightarrow 19$

3 standard reflections

frequency: 60 min

intensity variation: none

Refinement

Refinement on F

Final $R = 0.0597$

$wR = 0.0619$

$S = 1.8532$

6803 reflections

320 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.001F^2]$

The BF_4^- anion was constrained by both B–F bond distance and F–B–F angle.

$(\Delta/\sigma)_{\max} = 0.027$

$\Delta\rho_{\max} = 2.79$ e Å⁻³

$\Delta\rho_{\min} = -1.82$ e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Data collection: Nonius. Cell refinement: Nonius. Data reduction: *NEWCRYS2* (Bushnell, 1988). Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976). Program(s) used to refine structure: *SHELX76*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å²)

U_{iso} for C, B and F atoms; for Pt, P and O $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Pt1	0.42714 (2)	0.30169 (4)	0.27884 (3)	0.0285 (2)
Pt2	0.39028 (2)	0.10719 (4)	0.26896 (3)	0.0285 (2)
P1	0.4091 (2)	0.4062 (3)	0.1767 (2)	0.034 (1)
P2	0.3268 (2)	0.0328 (3)	0.1608 (2)	0.035 (1)
P3	0.3413 (2)	0.3299 (3)	0.2961 (2)	0.033 (1)
P4	0.4707 (2)	0.0755 (3)	0.2374 (2)	0.033 (1)
O1	0.4448 (4)	0.1932 (6)	0.3715 (6)	0.032 (4)
C1	0.3164 (5)	0.2263 (10)	0.3370 (9)	0.035 (3)
C2	0.3301 (5)	0.1362 (9)	0.3205 (8)	0.033 (3)
C3	0.3073 (6)	0.0586 (10)	0.3524 (9)	0.040 (3)
C4	0.2713 (6)	0.0756 (11)	0.3965 (10)	0.046 (4)
C5	0.2588 (6)	0.1697 (11)	0.4114 (10)	0.047 (4)
C6	0.2799 (7)	0.2446 (11)	0.3814 (10)	0.049 (4)
C7	0.5202 (6)	0.1766 (10)	0.2540 (9)	0.036 (3)
C8	0.5060 (5)	0.2669 (10)	0.2742 (8)	0.034 (3)
C9	0.5490 (6)	0.3396 (11)	0.2890 (10)	0.043 (4)
C10	0.6034 (6)	0.3197 (10)	0.2883 (10)	0.042 (3)
C11	0.6152 (6)	0.2295 (11)	0.2632 (10)	0.045 (4)
C12	0.5738 (6)	0.1566 (11)	0.2474 (10)	0.045 (4)
C13	0.2803 (6)	0.3602 (10)	0.2026 (9)	0.037 (3)
C14	0.2931 (6)	0.4463 (11)	0.1542 (10)	0.049 (4)
C15	0.3314 (6)	0.4198 (11)	0.1080 (9)	0.042 (3)
C16	0.4596 (6)	0.0337 (10)	0.1339 (9)	0.042 (3)
C17	0.4099 (6)	−0.0446 (11)	0.1015 (10)	0.049 (4)
C18	0.3503 (7)	0.0049 (11)	0.0732 (10)	0.050 (4)
C19	0.3485 (6)	0.4277 (10)	0.3704 (9)	0.039 (3)
C20	0.4007 (7)	0.4307 (12)	0.4392 (11)	0.057 (4)
C21	0.4081 (9)	0.5045 (16)	0.5008 (14)	0.083 (6)
C22	0.3623 (9)	0.5724 (15)	0.4862 (14)	0.077 (6)
C23	0.3113 (8)	0.5641 (15)	0.4204 (13)	0.073 (5)
C24	0.3051 (7)	0.4911 (13)	0.3590 (11)	0.059 (4)
C25	0.4412 (6)	0.3732 (10)	0.1028 (9)	0.040 (3)
C26	0.4173 (7)	0.2934 (12)	0.0526 (12)	0.059 (4)

C27	0.4422 (9)	0.2589 (15)	-0.0049 (14)	0.078 (6)
C28	0.4902 (9)	0.3070 (15)	-0.0068 (14)	0.080 (6)
C29	0.5156 (8)	0.3845 (14)	0.0422 (12)	0.068 (5)
C30	0.4906 (7)	0.4194 (12)	0.0980 (11)	0.055 (4)
C31	0.4332 (5)	0.5275 (10)	0.2125 (9)	0.035 (3)
C32	0.4551 (7)	0.5472 (11)	0.2969 (10)	0.050 (4)
C33	0.4737 (8)	0.6400 (14)	0.3308 (13)	0.069 (5)
C34	0.4686 (7)	0.7119 (13)	0.2688 (12)	0.062 (5)
C35	0.4446 (8)	0.6941 (13)	0.1822 (12)	0.064 (5)
C36	0.4267 (7)	0.5981 (12)	0.1536 (11)	0.058 (4)
C37	0.5143 (5)	-0.0167 (10)	0.3088 (9)	0.036 (3)
C38	0.5579 (6)	-0.0638 (11)	0.2946 (10)	0.048 (4)
C39	0.5950 (7)	-0.1231 (12)	0.3567 (11)	0.057 (4)
C40	0.5862 (8)	-0.1431 (14)	0.4287 (12)	0.065 (5)
C41	0.5418 (7)	-0.1010 (12)	0.4411 (11)	0.057 (4)
C42	0.5039 (6)	-0.0340 (11)	0.3808 (10)	0.044 (4)
C43	0.3037 (6)	-0.0822 (11)	0.1834 (10)	0.043 (3)
C44	0.2477 (7)	-0.1175 (11)	0.1334 (10)	0.046 (4)
C45	0.2315 (7)	-0.2101 (11)	0.1471 (11)	0.052 (4)
C46	0.2715 (7)	-0.2654 (12)	0.2111 (11)	0.053 (4)
C47	0.3252 (8)	-0.2306 (13)	0.2622 (12)	0.061 (5)
C48	0.3408 (7)	-0.1391 (11)	0.2458 (10)	0.050 (4)
C49	0.2602 (6)	0.1017 (10)	0.1085 (10)	0.043 (3)
C50	0.2195 (7)	0.1078 (11)	0.1464 (10)	0.049 (4)
C51	0.1700 (8)	0.1653 (13)	0.1121 (12)	0.062 (5)
C52	0.1619 (7)	0.2188 (13)	0.0400 (11)	0.059 (4)
C53	0.2031 (7)	0.2144 (12)	-0.0010 (11)	0.058 (4)
C54	0.2526 (7)	0.1527 (11)	0.0347 (10)	0.049 (4)
C11	0.4174 (3)	-0.1682 (5)	0.4840 (5)	0.111 (2)
C12	0.3015 (3)	-0.1663 (5)	0.4767 (5)	0.108 (2)
C13	0.1217 (4)	-0.0654 (7)	0.1935 (7)	0.163 (3)
C14	0.1438 (4)	-0.1164 (7)	0.3629 (7)	0.165 (4)
C55	0.3740 (11)	-0.1209 (18)	0.5321 (16)	0.103 (8)
C56	0.1513 (20)	-0.1556 (33)	0.2788 (32)	0.225 (20)
B1	0.3608 (4)	0.0656 (7)	0.8486 (6)	0.153 (3)
F1	0.3348 (6)	0.0867 (10)	0.9031 (8)	0.153 (3)
F2	0.4172 (4)	0.0400 (10)	0.8923 (8)	0.153 (3)
F3	0.3321 (6)	-0.0082 (8)	0.7982 (8)	0.153 (3)
F4	0.3592 (6)	0.1439 (8)	0.8007 (8)	0.153 (3)

Table 2. Geometric parameters (Å, °)

Pt2—Pt1	2.867 (1)	C31—P1	1.835 (14)
P1—Pt1	2.211 (4)	C18—P2	1.870 (16)
P3—Pt1	2.312 (4)	C43—P2	1.808 (15)
O1—Pt1	2.137 (8)	C49—P2	1.840 (15)
C8—Pt1	2.063 (13)	C1—P3	1.830 (14)
P2—Pt2	2.206 (4)	C13—P3	1.805 (14)
P4—Pt2	2.318 (3)	C19—P3	1.845 (15)
O1—Pt2	2.153 (9)	C7—P4	1.833 (14)
C2—Pt2	2.062 (13)	C16—P4	1.809 (15)
C15—P1	1.862 (15)	C37—P4	1.837 (14)
C25—P1	1.814 (15)		
P1—Pt1—Pt2	128.4 (1)	O1—Pt2—Pt1	47.8 (2)
P3—Pt1—Pt2	83.0 (1)	O1—Pt2—P2	173.2 (2)
P3—Pt1—P1	94.3 (1)	O1—Pt2—P4	88.3 (2)
O1—Pt1—Pt2	48.3 (2)	C2—Pt2—Pt1	93.2 (4)
O1—Pt1—P1	176.0 (2)	C2—Pt2—P2	93.2 (4)
O1—Pt1—P3	87.7 (2)	C2—Pt2—P4	168.9 (4)
C8—Pt1—Pt2	93.6 (4)	C2—Pt2—O1	82.4 (4)
C8—Pt1—P1	91.8 (4)	C1—P3—Pt1	112.6 (4)
C8—Pt1—P3	173.9 (4)	C7—P4—Pt2	114.2 (5)
C8—Pt1—O1	86.2 (4)	Pt2—O1—Pt1	83.9 (3)
P2—Pt2—Pt1	127.8 (1)	C2—C1—P3	120.2 (10)
P4—Pt2—Pt1	84.8 (1)	C8—C7—P4	121.4 (10)
P4—Pt2—P2	96.7 (1)		

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55990 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1032]

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Structure of the Trigonal Phase of Bis(methynyltricobalteneacarbonyl), [CCo₃(CO)₉]₂

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Abstract

A second, trigonal, phase of [CCo₃(CO)₉]₂, μ_6 -dicarbide-1:2:3 κ^3 C¹:4:5:6 κ^3 C²-hexakis(tricarbonylcobalt)-(6 Co—Co), has been found, in addition to the monoclinic one reported earlier [Brice & Penfold (1972). *Inorg. Chem.* **11**, 1381–1384]. The intermolecular geometry of the molecule in the two crystallographic modifications is virtually the same. The two Co₃ triangles are twisted by *ca* 28° with respect to each other, indicating a conformation between staggered and eclipsed. Optically active crystals of the trigonal phase form by spontaneous resolution of the enantiomorphic conformers.

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