

Figure 1. View of the cation of **6a**, showing the atom-labeling scheme. Thermal ellipsoids are scaled to 30% probability level. H atoms are of an arbitrary size. The complex lies on an inversion center with the geometry around the Fe atoms being distorted octahedral. The average Fe–N(tertiary amine) bond lengths (2.268 (3) Å) are slightly longer than the average Fe–N(secondary amine) bond lengths (2.126 (2) Å). The average Fe–acetate bond lengths are 1.979 (2) Å, while the oxo-bridge bond lengths are asymmetric with Fe(1)–O(1) = 1.793 (3) Å and Fe(2)–O(1) = 1.761 (3) Å.

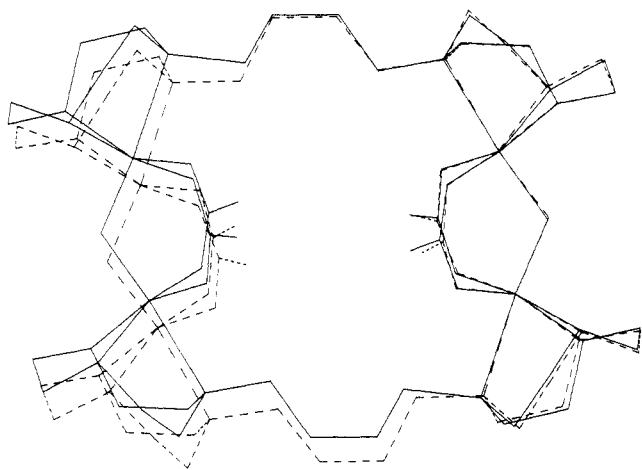


Figure 2. Comparison of the cations of **6a** and **6b**. The coordination sphere of oxo-bridged dimer in **6a** (shown by dotted line) is fitted by least-squares to the equivalent atoms in **6b** (solid lines), highlighting the nearly identical geometry around the Fe atoms.

in the (μ -oxo)bis(μ -acetato)diiron(III) core of **6a** (and **6b**) are quite similar to those reported for complexes **7** and **8** and also, to a lesser extent, azidomethemerythrin itself. In particular, the Fe–Fe distance (3.076 (1) Å) in the diiron core of **6** lies somewhat between that formed in complexes **7** (3.063 (2) Å) and **8** (3.12 (4) Å). Notably, however, unlike those of the simple dimers, the diiron cores in **6a** (and **6b**) are asymmetrical (Fe(1)–O(1) = 1.793 (3) Å; Fe(2)–O(1) = 1.761 (3) Å). We attribute this to constraints placed on the diiron core by the tetramethylene bridge.

Structural and spectroscopic data for Toftlund's related tetranuclear complex, derived from ligand **L₂** (**9**),^{10d} are also reported in Table II for comparison with **6**. Both complexes **6** and **9** contain a tertiary nitrogen trans to the μ -oxo bridge; as a result, the bridging acetates from each diiron core are directed toward the center of the molecule. The preference for this structure over dimer formation has been attributed to the *trans* disposition of the tertiary nitrogen atom and the μ -oxo ligand in each diiron core unit.^{10d} In fact, in **6** the acetate methyl groups on opposite diiron cores are an approximate van der Waals radius apart. The Fe–Fe

distances between core units in **6** (7.604 (1) and 7.933 (9) Å for **6a** and **6b**, respectively) are, therefore, considerably larger than the comparable Fe–Fe distance in **9** (7.469 (2) Å). These minor differences aside, it is worth noting that both ligands **L₂** and **L₃** contain two distinct binding sites separated by a four-carbon chain and they both stabilize similar tetrameric iron(III) cores, *rather than the corresponding dimeric iron(III) complexes*. This finding, in our opinion, serves not only to suggest further^{10d} that the iron(III) complex formed from **L₁**¹³ might well be tetrameric in nature but also to underscore the difficulty inherent in preparing viable hemerythrin models by using loosely linked alkyl-bridged ligand systems. As such, the present results may have important implications in terms of preparing improved model systems.

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Supplementary Material Available: Figures showing the structure of cation **6b**, giving atom-labeling schemes, and unit cell packing diagrams for cations **6a** and **6b** (Figures S1–S3), tables listing positional and isotropic or equivalent isotropic thermal parameters for the non-hydrogen atoms of **6a** and **6b** (Tables S1 and S6, respectively), positional and isotropic thermal parameters for the hydrogen atoms of **6a** and **6b** (Tables S2 and S7, respectively), anisotropic thermal parameters for the non-hydrogen atoms of **6a** and **6b** (Tables S3 and S8, respectively), bond lengths and angles for the non-hydrogen atoms of **6a** and **6b** (Tables S4 and S9, respectively), bond lengths and angles for the hydrogen atoms of **6a** (Tables S5 and S10, respectively), and complete crystallographic summaries for systems **6a** and **6b** (Table S11), and text describing experimental X-ray details for **6a** and **6b** (42 pages); tables of observed and calculated structure factor amplitudes (Tables S12 and S13) (72 pages). Ordering information is given on any current masthead page.

Contribution from the School of Chemistry
and Molecular Sciences, University of Sussex,
Falmer, Brighton BN1 9QJ, U.K.

Crystal and Molecular Structure of Bis[1,3-bis(diphenylphosphino)propane]platinum(0): A Reevaluation

Kahtan A. Asker, Peter B. Hitchcock, Roger P. Moulding,
and Kenneth R. Seddon*

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Despite a current active interest in the catalytic, electronic, and luminescent properties of homoleptic platinum(0) phosphine derivatives,^{1,2} there have been remarkably few of these complexes crystallographically characterized. The reported structures include [Pt(PPh₃)₃],³ [Pt(triphos)₂] [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; (Ph₂PCH₂)₃CCH₃],⁴ [Pt(μ -dppm)₃] [dppm = bis(diphenylphosphino)methane; Ph₂PCH₂PPh₂],⁵ and [(dbpp)Pt=Pt(dbpp)] [dbpp = 1,3-bis(di-*tert*-butylphosphino)propane; (Me₃C)₂PCH₂CH₂CH₂P(CMe₃)₂].⁶ Of these, only [Pt(triphos)₂] contains a {Pt⁰P₄} geometry, and the unsymmetrical

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Table I. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($10^3 U_{eq}$) for $[\text{Pt}(\text{dppp})_2]$, with Estimated Standard Deviations in Parentheses

	x	y	z	$10^3 U_{eq}/\text{\AA}^2$
Pt	0	32.2 (2)	2500	23 (1)
P(1)	-918.7 (6)	877.8 (9)	2826.9 (6)	29 (1)
P(2)	442.5 (6)	-989.7 (9)	3467.7 (6)	27 (1)
C(1)	-1829 (2)	1299 (4)	2163 (2)	38 (2)
C(2)	-2379 (3)	592 (4)	1818 (3)	46 (2)
C(3)	-3056 (3)	891 (5)	1291 (3)	63 (3)
C(4)	-3181 (3)	1869 (5)	1098 (3)	66 (3)
C(5)	-2633 (3)	2578 (5)	1422 (3)	62 (3)
C(6)	-1964 (3)	2293 (4)	1954 (3)	47 (2)
C(7)	1282 (2)	-589 (4)	4217 (2)	33 (2)
C(8)	1766 (3)	-1253 (4)	4694 (3)	49 (2)
C(9)	2394 (3)	-905 (5)	5250 (3)	60 (3)
C(10)	2527 (4)	109 (4)	5336 (3)	56 (3)
C(11)	2047 (3)	775 (4)	4876 (3)	51 (3)
C(12)	1432 (3)	437 (4)	4314 (2)	38 (2)
C(13)	744 (3)	-2270 (3)	3326 (2)	33 (2)
C(14)	1313 (3)	-2347 (4)	3006 (3)	41 (2)
C(15)	1550 (3)	-3289 (4)	2854 (3)	51 (3)
C(16)	1218 (3)	-4142 (4)	3004 (3)	57 (3)
C(17)	663 (3)	-4074 (4)	3317 (3)	56 (3)
C(18)	425 (3)	-3141 (4)	3483 (3)	43 (2)
C(19)	-643 (3)	2011 (4)	3385 (2)	39 (2)
C(20)	72 (3)	2454 (4)	3492 (3)	50 (2)
C(21)	319 (4)	3251 (5)	3956 (4)	76 (3)
C(22)	-136 (5)	3622 (5)	4310 (4)	89 (4)
C(23)	-858 (4)	3206 (5)	4204 (4)	87 (3)
C(24)	-1109 (3)	2425 (5)	3744 (3)	63 (3)
C(25)	-1302 (3)	105 (3)	3399 (3)	37 (2)
C(26)	-663 (3)	-285 (4)	4061 (2)	38 (2)
C(27)	-254 (3)	-1226 (4)	3930 (2)	36 (2)

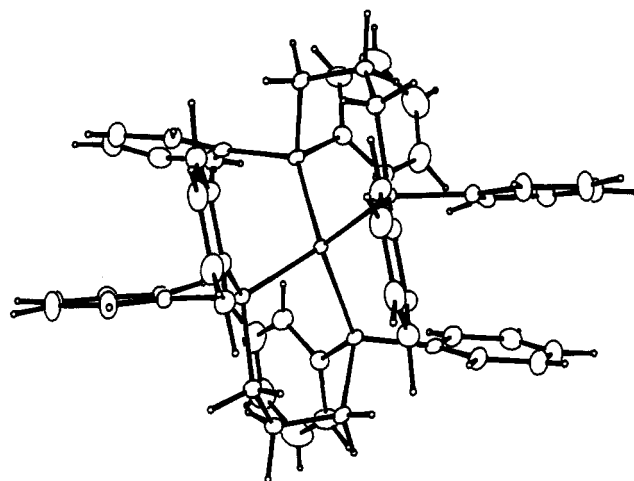
^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

nature of the η^2 -bonded ligand leads to a distortion of the idealized geometry. It was thus of some importance when the structure of $[\text{Pt}(\text{dppp})_2]$ [dppp = 1,3-bis(diphenylphosphino)propane; $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$] was recently published,² with the surprising result that the Pt-P bond lengths within the complex differed by 0.0049 nm. In our own work⁷ upon the platinum complexes of bis(diphenylphosphinomethyl)phenylphosphine (dpmp; $\text{Ph}_2\text{PCH}_2\text{PPhCH}_2\text{PPh}_2$), we had noticed the structural relationship between $[\text{Pt}(\text{dpmp})_2]$ ⁸ and $[\text{Pt}(\text{dppp})_2]$, a $\{\text{Pt}_2\text{P}_3\text{C}_2\}$ chelating ring as opposed to a $\{\text{Pt}_2\text{P}_2\text{C}_3\}$ ring, and had independently crystallographically characterized $[\text{Pt}(\text{dppp})_2]$, prior to its publication by Gray and co-workers.² We report here the results of our own structural analysis and demonstrate that the distortions detected in the coordination sphere in the earlier paper² arise because the diffraction data were incorrectly indexed and the structure was refined in an incorrect space group.

Experimental Section

Synthesis of Bis[1,3-bis(diphenylphosphino)propane]platinum(0). The complex $[\text{PtCl}_2(\text{cod})]_2$ ⁹ (1.0 g, 2.67 mmol; cod = cycloocta-1,5-diene) was dissolved in dichloromethane (30 cm³), and dppp (1.10 g, 2.67 mmol) was added. Upon standing overnight, the solution deposited white crystals of $[\text{PtCl}_2(\text{dppp})]$, and these were collected by filtration (1.65 g, 91%). The product was placed in aqueous ethanol (100 cm³; 96%), dppp (0.95 g) was added, and the resulting suspension was stirred under an atmosphere of dinitrogen; the solids slowly dissolve to form $[\text{Pt}(\text{dppp})_2]^{2+}$, whence solid $\text{Na}[\text{BH}_4]$ (0.4 g) was added over a period of 15 min. Vigorous effervescence occurred, the solution turned yellow, and a yellow solid separated; stirring was continued for 1 h. The yellow solid was collected by filtration, washed with ethanol (5 cm³), and dried in vacuo. ³¹P{¹H} NMR (C_6D_6 ; 36.43 MHz; 303 K, δ/ppm):¹⁰ -12.5, ¹J(PtP) = 3644 Hz.

An identical complex was also formed as one of the products from the reaction of equimolar quantities of $[\text{PtCl}_2(\text{dppf})]$ [dppf = 1,1'-bis(di-

**Figure 1.** Molecular structure of $[\text{Pt}(\text{dppp})_2]$.**Table II.** Selected Distances (nm) and Angles (deg) in $[\text{Pt}(\text{dppp})_2]$

	this work	Gray and co-workers ²	Δ^a
Pt-P(1)	0.2286 (1)	0.2268 (1)	0.0018
Pt-P(2)	0.2286 (1)	0.2317 (1)	-0.0031
P(1)-C(1)	0.1839 (4)	0.1832	0.0007
P(1)-C(19)	0.1843 (5)	0.1847 (5)	-0.0004
P(1)-C(25)	0.1840 (6)	0.1856 (7)	-0.0016
P(2)-C(7)	0.1835 (4)	0.1854 (5)	-0.0019
P(2)-C(13)	0.1838 (5)	0.1845 (6)	-0.0007
P(2)-C(27)	0.1830 (6)	0.1835 (5)	-0.0005
P(1)-Pt-P(1')	121.16 (4)	119.3 (1)	1.86
P(1)-Pt-P(2)	97.76 (4)	97.9 (1)	-0.14
P(1)-Pt-P(2')	116.62 (4)	116.8 (1)	-0.18
P(2)-Pt-P(2')	107.18 (4)	108.9 (1)	-1.72
dihedral angle ^b	87.20 (2)	102.9 (1)	-15.7

^a Δ = the difference between the parameters determined in this work and those determined by Gray and co-workers.² ^b The angle between the $\{\text{PtP}(1)\text{P}(2)\}$ and $\{\text{PtP}(1')\text{P}(2')\}$ planes.

phenylphosphinocyclopentadienyl)iron(II)] with dppp in the presence of $\text{Li}[\text{BHEt}_3]$.¹¹

Determination of the Crystal Structure of $[\text{Pt}(\text{dppp})_2]$. Orange crystals were isolated from tetrahydrofuran solution by filtration: they were stable in air.

Crystal data are as follows: $\text{C}_{54}\text{H}_{52}\text{P}_4\text{Pt}$, $M_r = 1020.09$, monoclinic, space group $C2/c$, $a = 1.8243$ (3) nm, $b = 1.3277$ (3) nm, $c = 2.0053$ (4) nm, $\beta = 109.27$ (2)°, $V = 4.585$ nm³, $Z = 4$, $D_{\text{calc}} = 1.48$ g cm⁻³, $F(000) = 2056$, monochromated Mo K α radiation, $\lambda = 0.071069$ nm, $\mu = 32.6$ cm⁻¹.

Data Collection and Processing. Data were collected by using a crystal ca. $0.3 \times 0.3 \times 0.15$ mm on an Enraf-Nonius CAD4 diffractometer in the θ - 2θ mode with $\Delta\theta = (0.8 + 0.35 \tan \theta)^\circ$ and a maximum scan time of 1 min. A total of 4048 unique reflections was measured for $2 < \theta < 25^\circ$ and $+h, +k, \pm l$, and 2977 with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$. There was no crystal decay and no absorption correction was applied.

Structure Solution and Refinement. The structure was solved by routine heavy-atom methods and refined by full-matrix least squares with non-hydrogen atoms anisotropic. Hydrogen atoms were located on a difference map and refined isotropically. The weighting scheme was $w = \sigma^{-2}(F)$, and the final residuals were $R = 0.030$ and $R' = 0.037$. A final difference map was featureless. Programs from the Enraf-Nonius SDP-Plus package were run on a MicroVax Computer. The final fractional atomic coordinates are listed in Table I.

Results and Discussion

The synthesis of $[\text{Pt}(\text{dppp})_2]$ reported here is based on that of Clark et al.,¹² the products are spectroscopically identical, but we find preparations starting with $[\text{PtCl}_2(\text{cod})]$ rather more convenient.

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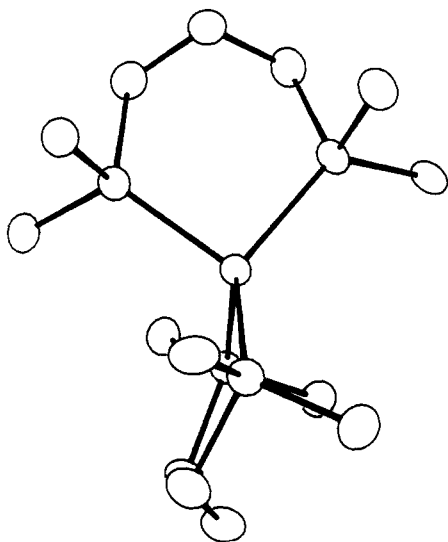


Figure 2. View of the conformation of the $\{PtP_2C_3\}$ chelate rings in $[Pt(dppp)_2]$, with the phenyl rings removed for clarity.

Table III. Crystal Data for $[Pt(dppp)_2]$

	this work	Gray and co-workers ²
a/nm	1.8245 (3)	1.8306 (3)
b/nm	1.3277 (3)	1.3322 (2)
c/nm	2.0053 (4)	1.0067 (3)
α/deg	90	90
β/deg	109.27 (2)	109.28 (2)
γ/deg	90	90
Z	4	2
U/nm^3	4.585	2.317
space group	$C2/c$	$C2/m$

The molecular structure of the complex $[Pt(dppp)_2]$ is shown in Figure 1. The molecule lies on a crystallographic 2-fold rotation axis. The bond lengths and angles in the complex appear normal (Table II). The Pt-P bond lengths (0.2286 nm) are similar to those observed for four-coordinate platinum(0) in $[Pt(trippos)_2]$ ⁴ (0.2275–0.2295 nm) but longer than those found for three-coordinate platinum(0) in $[Pt(PPh_3)_3]$ ³ (0.2262–0.2271 nm), $[(dbpp)Pt=Pt(dbpp)]$ ⁶ (0.2268–0.2272 nm), and $[Pt_2(dppm)_3]$ ⁵ (0.2255–0.2272 nm) and for two-coordinate platinum(0) in $[Pt(PPh(CMe_3)_2)_2]$ ¹³ (0.2252 nm) and $[Pt(P(Cy)_3)_2]$ ¹⁴ (0.2231 nm). This is as expected since, all other factors being equal, $r(ML)$ should decrease in the order $ML_4 > ML_3 > ML_2$. The $\{PtP_2C_3\}$ chelate rings (see Figure 2) display a chair conformation. The dihedral angle between the $\{PtP(1)P(2)\}$ and $\{PtP(1')P(2')\}$ planes is 87.20 (2)°, close to the ideal value of 90°.

After the determination of this structure was complete, Gray and co-workers² independently published the crystal structure of $[Pt(dppp)_2]$. Their results suggested that the complex had a distorted tetrahedral coordination about the platinum atom with Pt-P bond lengths of 0.2267 (1) and 0.2317 (1) nm. The longer Pt-P bond length was attributed to the internal strain imposed by the ring system. A comparison of their crystal data with ours (Table III) shows that their results are based on an incorrect unit cell and space group. Our results show space group $C2/c$, with the platinum atom close to $y = 0$: this means that all reflections with l odd tend to be weak. It appears that Gray and co-workers² missed the weak reflections entirely, thus producing a unit cell of half the c -axis length. This results in overlapping images of the two c glide related molecules, to give an apparently disordered structure of mirror symmetry, which was refined in space group $C2/m$, although it was clear that the authors² were not happy with their assignment, which involved a mirror disorder for 29 out of

its 30 heavy atoms. The demonstrable improvement of the geometry of the $\{PtP_4\}$ core in the present study (see Table III) is convincing evidence that the larger unit cell and space group $C2/c$ are correct.¹⁵ Moreover, the published interpretation of the luminescent properties of $[Pt(dppp)_2]$ ² assume a tetrahedral $\{PtP_4\}$ coordination sphere, which is more in accord with the true C_{2v} structure.

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Supplementary Material Available: Tables listing hydrogen positions, thermal parameters, complete intramolecular bond distances and angles, and torsional angles (8 pages); a table of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

(15) In separate private communications, Profs. H. B. Gray and W. P. Schaefer have each generously acknowledged the error in the space group assignment in ref. 2.

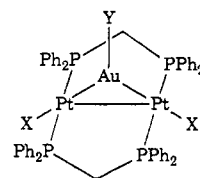
Contribution from the Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia, and Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Formation of Trinuclear Clusters by Addition of $[Au(PPh_3)]^+$ to Dinuclear Platinum(I) Complexes Containing Bridging Cyclometalated Arylphosphines. X-ray Structure of $[(Ph_3P)AuPt_2(C_6H_4P(Ph)CH_2CH_2CH_2PPh_2)_2]BF_4$

Martin A. Bennett,[†] David E. Berry,^{*,†} and Kathryn A. Beveridge[‡]

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A variety of platinum-gold clusters have been made by addition of gold(I) complexes to mononuclear or polynuclear platinum compounds.¹⁻⁶ The A-frame complex **1** containing a Pt_2Au triangle has been isolated from the reaction of $[Au(PPh_3)]^+$ with $Pt_2Cl_2(\mu-dppm)_2$, and the similar complexes **2** and **3** have been made from the reaction of $AuC\equiv C-t-Bu$ with $Pt_2(\mu-dppm)_3$ ⁴ [$dppm$ = bis(diphenylphosphino)methane].



(1) $X = Cl$; $Y = PPh_3$ (mono-cation)

(2) $X = Y = C_2-t-Bu$

(3) $X = C_2-t-Bu$; $Y = I$

The platinum(I)-platinum(I) dimers **4-6** containing two bridging ortho-metalated phenylphosphine ligands^{7,8} react with electrophiles, such as iodine,⁸ methyl iodide,⁹ and acids containing poorly coordinating anions,¹⁰ to give cationic platinum(II) A-frame adducts in which the ligand I, CH_3 , or H bridges the two platinum

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^{*} To whom correspondence should be addressed.

[†] Australian National University.

[‡] University of Victoria.