Tris-μ-[bis(diphenylphosphino)methane]-diplatinum(0)*

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The synthesis of $[Pt_2(\mu\text{-dppm})_3]$ [dppm = bis(diphenylphosphino)methane], either by the reduction of $[PtCl_2(dppm)]$ by $Na[BH_4]$ in aqueous ethanol, in the presence of 2 mol equivalents of dppm, or by a ligand displacement from $[Pt(PPh_3)_4]$ by an excess of dppm, is described, and the complex was shown to have a 'manxane'-type (bicyclo[3.3.3]undecane-type) structure in solution by multinuclear n.m.r. studies. This novel complex forms a bis(benzene) solvate whose crystal structure was determined by *X*-ray diffraction [space group *I*2, a = 22.539(4), b = 16.878(2), c = 20.641(2) Å, β = 109.82(1)°, Z = 4, R = 0.032 for 4 968 independent reflections with $I > 3\sigma(I)$]. The complex $[Pt_2(\mu\text{-dppm})_3]$ has the same C_{3h} structure in the solid state as in solution, and displays a trigonal-planar co-ordination about each of the platinum atoms, which are separated by 3.023(1) Å. Although it contains no formal metal–metal bond, it does exhibit a significant metal–metal interaction. Spectroscopic studies are consistent with the known complex $[Pd_2(\mu\text{-dppm})_3]$ possessing the same structure.

In 1972, Stern and Maples [1,2] reported the catalytic activity of a complex formulated as $[Pd_2(dppm)_3]$ [dppm = bis(diphenylphosphino)methane], prepared by reducing an ethanolic suspension of $[Pd(PPh_3)_2Cl_2]$ and dppm with anhydrous hydrazine and characterised by elemental analysis and spectra (no further details were given). More recently, Balch and co-workers [3,4] reported a fascinating series of reactions of $[Pd_2(dppm)_3]$ with, *inter alia*, halogens and organic halides: in all cases a facile oxidative addition was accompanied by elimination of 1 mol of dppm. Details of the ^{31}P n.m.r. spectrum of $[Pd_2(dppm)_3]$ were also published for the first time [5] in 1980, and the reaction of $[Pd_2(dppm)_3]$ with $[Mn(CO)_5Br]$ to give $[PdMnBr(CO)_3(\mu\text{-dppm})_2]$ illustrated its potential use as a synthetic reagent for the preparation of heterobimetallic complexes.[6] However, heretofore, no structure has been explicitly proposed for $[Pd_2(dppm)_3]$.

In 1978, Vaska and co-workers [7] reported the catalytic activity of a deep red complex, $[Pt_2(dppm)_3]$, towards the reactions shown in equations (1) and (2). The compound

$$2NO + CO \xrightarrow{[Pt_2(dppm)_3]} N_2O + CO_2 \qquad (1)$$

$$O_2 + 2CO \xrightarrow{[Pt_2(dppm)_3]} 2CO_2 \qquad (2)$$

$[Pt_2(dppm)_3]$ was assigned an empirical formula, but no preparative, analytical, structural, or spectroscopic information concerning this novel complex was presented.[7] Although Vaska's report [7] cited a reference to a manuscript submitted for publication containing more details of $[Pt_2(dppm)_3]$, no such article has appeared in the period from 1978 to 1986.

We present here full details of the preparation, analysis, spectroscopic characterisation, and molecular structure of the complex tris-μ-[bis(diphenylphosphino)methane]-diplatinum(0), $[Pt_2(\mu\text{-dppm})_3]$, and discuss its relationship with the known platinum(I) hydride salt $[Pt_2H(dppm\text{-}P)(\mu\text{-dppm})_2][PF_6]$.[8] Some of the results presented here have formed the substance of two preliminary communications.[9,10]

Experimental

Experiments were carried out using standard Schlenk-tube techniques, under dry nitrogen, unless otherwise stated. Platinum complexes used as reagents were prepared according to standard literature methods.[11,12]

N.m.r. spectra were recorded using JEOL FX-90Q [ambient and variable-temperature ^{31}P (36.27 MHz) and ^{195}Pt (19.16 MHz)], Bruker WH-90 [ambient ^{1}H (90.00 MHz) and ^{31}P (36.43 MHz)], Bruker WH-300 [ambient ^{1}H (300.13 MHz) and ^{31}P (121.49 MHz)], and Bruker WH-400 [ambient and variable-temperature ^{1}H (400.13 MHz), ^{31}P (161.96 MHz), and ^{195}Pt (85.62 MHz)] spectrometers. All chemical shifts are defined as positive to low field (high frequency) of the reference compound. Proton chemical shifts were measured relative to tetramethylsilane, phosphorus chemical shifts relative to trimethyl phosphate and solvent corrected, and platinum chemical shifts relative to a frequency of 21.4 MHz on an n.m.r. machine on which tetramethylsilane resonates at exactly 100.00 MHz [see Appendix (iii) of ref. 12]. Electronic absorption spectra were recorded using a Perkin-Elmer PE 330 spectrophotometer.

*Preparation of Tris-*μ*-[bis(diphenylphosphino)methane]-diplatinum*(0).—Four alternative syntheses are described: (*a*) and (*c*) are considered to be the most convenient.

(*a*) *From [bis(diphenylphosphino)methane]dichloroplatinum*(II) *and dppm.* The complex $[PtCl_2(dppm)]$ (0.25 g, 0.40 mmol) was suspended in ethanol (50 cm^3), dppm (0.29 g, 0.8 mmol) was added, and the solution was stirred under dinitrogen for 5 min. Sodium tetrahydroborate (0.5 g, 13.1 mmol) was added to the

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* *Supplementary data available* (No. SUP 56572, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

solution over a period of 1 h. During this time, the initially colourless solution gradually turned through yellow and orange into a deep red suspension. This red suspension was stirred for a further 40 min, until the supernatant liquid was colourless. The red solid was then collected by filtration, washed with hot ethanol (20 cm^3), and dried *in vacuo* for 24 h, affording pure $[Pt_2(\mu\text{-dppm})_3]$ (0.27 g, 93%) (Found: C, 58.95; H, 4.40; Cl, <0.05. Calc. for $C_{75}H_{66}P_6Pt_2$: C, 58.35; H, 4.30; Cl, 0.00%).

(*b*) *From dichloro*(1,5-*cyclo-octadiene*)*platinum*(II) *and dppm.* The complex $[PtCl_2(cod)]$ (cod = 1,5-cyclo-octadiene) (0.1 g, 0.26 mmol) was suspended in ethanol (50 cm^3), dppm (0.3 g, 0.78 mmol) was added, and the solution was stirred under dinitrogen for 5 min. Sodium tetrahydroborate (0.5 g, 13.1 mmol) was added over a period of 20 min, the colourless solution soon turning brown. The brown suspension was stirred under dinitrogen for 2 h and the dark red-brown crystals were collected by filtration and dried *in vacuo* (yield 0.05 g, 25%). The filtrate was red-brown in colour.

(*c*) *From tetrakis*(*triphenylphosphine*)*platinum*(0) *and dppm.* Absolute ethanol (160 cm^3) was added to a mixture of $[Pt(PPh_3)_4]$ (12.40 g, 9.96 mmol) and dppm (7.66 g, 19.93 mmol). The mixture was heated in an oil-bath with stirring and kept at the boiling point for 2.5 h. Deep red crystals slowly formed and the solution became light red. The crystals were recovered by filtration from the hot solution, washed with hot ethanol (30 cm^3), and dried *in vacuo*, affording pure $[Pt_2(\mu\text{-dppm})_3]$ (6.64 g, 86%) (Found: C, 58.65; H, 4.25; P, 12.40. Calc. for $C_{75}H_{66}P_6Pt_2$: C, 58.35; H, 4.30; P, 12.05%). Several other similar experiments gave yields of 84—93%. The complex was stored in sealed tubes under vacuum.

(*d*) *From bis*-μ-[*bis*(*diphenylphosphino*)*methane*]-*dichlorodiplatinum*(I)[11,12] *and dppm.* A solution of potassium hydroxide (0.011 g, 0.20 mmol) in water (2 cm^3) and ethanol (8 cm^3) was added to a mixture of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (0.100 g, 0.081 mmol) and dppm (0.075 g, 0.20 mmol). The mixture was heated under reflux for 1 h, whence the colour changed from yellow to deep red, and red crystals appeared. The crystals were recovered by filtration from the hot solution, washed with warm ethanol (5 cm^3), water (15 cm^3), and finally with cold ethanol (5 cm^3), and were then dried *in vacuo* to afford $[Pt_2(\mu\text{-dppm})_3]$ (0.055 g, 37%).

Preparation of Tris-μ-[*bis*(*diphenylphosphino*)*methane*]-*dipalladium*(0).—The complex $[PdCl_2(dppm)]$ (1.00 g, 1.78 mmol) was suspended in ethanol (100 cm^3), dppm (0.86 g, 2.23 mmol) was added, and the solution stirred under dinitrogen for 5 min. Sodium tetrahydroborate (1.0 g, 26.2 mmol) was then added over a period of 1 h. During this time the initially colourless solution gradually turned yellow, then orange, before darkening into an orange-red suspension. This suspension was stirred for a further 40 min until the supernatant liquid was colourless. The orange solid was collected by filtration, washed with hot ethanol (20 cm^3), and dried *in vacuo* for 24 h to afford $[Pd_2(\mu\text{-dppm})_3]$ (1.08 g, 90%) (Found: C, 67.35; H, 5.00; Cl, <0.05. Calc. for $C_{75}H_{66}P_6Pd_2$: C, 66.05; H, 4.85; Cl, 0.00%).

Protonation of $[Pt_2(\mu\text{-dppm})_3]$ *with Buffer Solution* (pH 6.8).—The buffer solution comprised of potassium dihydrogenphosphate (3.42 g) and disodium hydrogenphosphate (3.55 g) made up to 100 cm^3 with distilled water. Potassium hexafluorophosphate (0.074 g, 0.402 mmol) was dissolved in an aliquot (10 cm^3) of the buffer and the resulting solution added to a solution of $[Pt_2(\mu\text{-dppm})_3]$ (0.200 g, 0.130 mmol) in benzene (5 cm^3). The mixture of the two phases was stirred for 2.5 h, during which time the deep red colour faded and a yellow precipitate separated. This was recovered by filtration, washed with water (10 cm^3), ethanol (5 cm^3), and diethyl ether (5 cm^3), and finally dried *in vacuo* to afford $[Pt_2H(dppm\text{-}P)(\mu\text{-dppm})_2][PF_6]$ (0.206 g, 94%) (Found: C, 53.90; H, 4.05; Cl, 0.00. Calc. for $C_{75}H_{67}F_6P_7Pt_2$: C, 54.50; H, 4.00; Cl, 0.00%). The product was also characterised by its i.r. [ν(PtH) 2 037 cm^{-1}], ^1H and ^{31}P n.m.r. spectra.[8]

Protonation of $[Pt_2(\mu\text{-dppm})_3]$ *prepared* in situ *from Tetrakis*(*triphenylphosphine*)*platinum*(0) *and dppm.*—A similar protonation of the red solution prepared from $[Pt(PPh_3)_4]$ (0.100 g, 0.080 mmol), dppm (0.090 g, 0.23 mmol), and benzene (5 cm^3) also gave $[Pt_2H(dppm\text{-}P)(\mu\text{-dppm})_2][PF_6]$ (0.059 g, 88%).

Determination of the Crystal Structure of $[Pt_2(\mu\text{-dppm})_3]\cdot 2C_6H_6$.—Red, plate-like crystals were isolated from a benzene–propan-1-ol solution under dinitrogen by filtration: they were sufficiently stable to be kept in the air. A crystal of dimensions 0.102 ($001/00\bar{1}$), 0.172 ($011/0\bar{1}\bar{1}$), 0.219 ($0\bar{1}\bar{1}/0\bar{1}1$), and 0.578 ($10\bar{1}/\bar{1}01$) mm was used for all crystallographic measurements. These were made with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å) and an Enraf–Nonius CAD4 diffractometer.

Crystal data. $C_{87}H_{78}P_6Pt_2$, $M = 1\,699.60$, monoclinic, $a = 22.539(4)$, $b = 16.878(2)$, $c = 20.641(2)$ Å, $\beta = 109.82(1)°$, $U = 7\,387$ Å^3 (by least-squares treatment of diffractometer angles of 25 reflections with $14.5 < \theta < 18.2°$), $Z = 4$, $D_c = 1.528$ g cm^{-3}, $F(000) = 3\,384$ e^-, μ(Mo-K_α) = 39.94 cm^{-1}, space group *I*2 (an alternative setting of *C*2, no. 5).

Systematically absent reflections were compatible with space groups *I*2/*m*, *Im*, and *I*2, but the last was indicated by the Patterson function and confirmed by the successful structure analysis.

Data collection and processing. The intensities of 7 044 *hkl* and $hk\bar{l}$ reflections with $2\theta \leq 50°$ were measured by the θ—2θ scan technique. The scans of 0.9° in θ were increased by 25% at each end of the scan range to allow for the background effects; they were taken with speeds of 0.8—6.7° min^{-1}. The intensities of two reflections, which were remeasured every 2 h throughout data collection, displayed a linear decrease of *ca.* 30.4%.

The integrated intensities, *I*, and their variances, σ(*I*), determined as described earlier,[13] were corrected for Lorentz, polarisation, absorption (by Gaussian integration), and crystal-decomposition effects. The transmission factors on F^2 were 0.42—0.71. Rejection of the reflections with $I \leq 3\sigma(I)$ and averaging of 182 0*kl* and $0k\bar{l}$ pairs ($R_F = 0.014$) yielded 4 968 independent structure amplitudes which were used in all subsequent calculations.

Structure solution and refinement. The structure was solved by Patterson and difference-synthesis techniques. It was refined by block-diagonal, and later by large-block, approximation to the normal least-squares matrix. The function minimised was $\Sigma w\Delta^2$, where $w = \sigma^{-2}(|F_o|)$ and $\Delta = |F_o| - |F_c|$.

The phenyl-ring carbon atoms were assigned isotropic, and the remaining non-hydrogen atoms anisotropic, thermal parameters. The hydrogen atoms of the platinum complex (but not those of the solvent molecules) were included in the structural model in idealised positions [r(CH) = 1.08 Å], but their co-ordinates and individual isotropic thermal parameters were not allowed to vary. Complex, neutral-atom scattering factors[14] were used throughout. The refinement converged (shift/e.s.d. < 0.1) to $R = 0.032$ and $R'[= (\Sigma w\Delta^2/\Sigma wF_o^{\,2})^{\frac{1}{2}}] = 0.040$ for 436 structural parameters.

In the final difference synthesis, the four highest peaks (0.65—1.72 e Å^{-3}) were close to the positions of the platinum atoms. An analysis of the average values of $w\Delta^2$ with $(\sin\theta)/\lambda$, $|F_o|$, *h*, *k*, and *l* revealed no unexpected trends. The polarity index,[15] $(1 + |\eta|)/\sigma(\eta) = 69.7$, indicated that the correct enantiomeric structure has been assigned to the crystal actually investigated. The final fractional atomic co-ordinates are shown in Table 1.

Table 1. Fractional atomic co-ordinates with standard deviations in parentheses for [$Pt_2(\mu\text{-dppm})_3$]

Atom	*x*	*y*	*z*
Pt(1)	0.326 41(1)	0	0.013 01(2)
Pt(2)	0.192 10(1)	−0.004 49(4)	0.012 20(2)
P(1)	0.357 9(1)	0.073 6(2)	0.110 7(1)
P(2)	0.222 7(1)	0.050 8(2)	0.118 6(1)
P(3)	0.329 3(1)	−0.134 1(2)	0.016 2(1)
P(4)	0.191 4(1)	−0.138 6(2)	0.011 0(1)
P(5)	0.298 5(1)	0.066 0(2)	−0.088 9(2)
P(6)	0.161 9(1)	0.067 4(2)	−0.085 7(2)
C(1)	0.291 4(5)	0.115 8(6)	0.135 8(6)
C(2)	0.271 4(5)	−0.178 2(6)	0.050 7(5)
C(3)	0.213 5(5)	0.056 4(6)	−0.137 8(5)
C(1A)	0.409 5(6)	0.028 5(7)	0.193 7(6)
C(2A)	0.414 2(7)	−0.050 9(8)	0.197 4(7)
C(3A)	0.449 5(8)	−0.085 7(9)	0.260 6(9)
C(4A)	0.477 5(9)	−0.039 5(10)	0.316 5(10)
C(5A)	0.476(1)	0.040(1)	0.312(1)
C(6A)	0.439 8(8)	0.078 6(9)	0.249 3(10)
C(1B)	0.404 7(5)	0.164 3(7)	0.112 1(6)
C(2B)	0.453 5(7)	0.155 5(8)	0.086 2(7)
C(3B)	0.494 9(8)	0.217 1(10)	0.089 2(8)
C(4B)	0.488 1(8)	0.285 3(10)	0.118 6(9)
C(5B)	0.439 0(9)	0.298 3(11)	0.137 6(10)
C(6B)	0.396 4(7)	0.235 3(8)	0.140 3(8)
C(1C)	0.240 3(4)	−0.008 3(9)	0.196 4(5)
C(2C)	0.194 4(6)	−0.061 3(8)	0.199 1(7)
C(3C)	0.202 3(8)	−0.111 2(10)	0.257 2(9)
C(4C)	0.255 5(9)	−0.112 0(11)	0.308 7(9)
C(5C)	0.303 6(9)	−0.060 1(11)	0.310 5(9)
C(6C)	0.294 7(6)	−0.014 0(9)	0.254 1(6)
C(1D)	0.165 6(5)	0.120 4(7)	0.134 8(6)
C(2D)	0.181 8(8)	0.166 7(10)	0.192 8(8)
C(3D)	0.135 2(9)	0.222 0(11)	0.201 2(10)
C(4D)	0.077 1(8)	0.221 2(10)	0.155 9(9)
C(5D)	0.058(1)	0.175(1)	0.095(1)
C(6D)	0.105 9(7)	0.125 3(9)	0.086 8(8)
C(1E)	0.317 5(6)	−0.194 4(7)	−0.062 0(7)
C(2E)	0.299 9(7)	−0.158 7(8)	−0.121 6(7)
C(3E)	0.293 0(8)	−0.202 9(10)	−0.183 7(9)
C(4E)	0.300 3(7)	−0.281 6(9)	−0.179 4(8)
C(5E)	0.315 4(8)	−0.318 5(10)	−0.120 6(9)
C(6E)	0.326 9(8)	−0.276 0(10)	−0.056 7(9)
C(1F)	0.403 6(6)	−0.181 6(7)	0.071 9(6)
C(2F)	0.408 2(7)	−0.236 2(8)	0.120 2(7)
C(3F)	0.466 9(7)	−0.268 6(8)	0.163 5(8)
C(4F)	0.520 9(7)	−0.239 1(9)	0.153 0(8)
C(5F)	0.515 2(7)	−0.182 5(9)	0.105 4(8)
C(6F)	0.457 8(7)	−0.149 3(8)	0.064 1(7)
C(1G)	0.158 5(6)	−0.196 7(7)	−0.068 6(7)
C(2G)	0.128 2(7)	−0.160 6(8)	−0.128 0(8)
C(3G)	0.095 4(9)	−0.203 7(11)	−0.186 5(10)
C(4G)	0.100 8(8)	−0.281 8(10)	−0.188 1(10)
C(5G)	0.131(1)	−0.320(1)	−0.131(1)
C(6G)	0.164(1)	−0.280(1)	−0.067(1)
C(1H)	0.148 1(6)	−0.186 6(7)	0.062 4(6)
C(2H)	0.090 8(7)	−0.158 9(8)	0.054 7(7)
C(3H)	0.054(1)	−0.191(1)	0.092(1)
C(4H)	0.076 6(7)	−0.252 8(9)	0.134 8(8)
C(5H)	0.133 5(7)	−0.281 6(9)	0.144 5(8)
C(6H)	0.171 8(6)	−0.248 4(8)	0.108 2(7)
C(1I)	0.332 0(5)	0.032 4(6)	−0.154 8(5)
C(2I)	0.296 9(5)	0.017 7(7)	−0.221 7(6)
C(3I)	0.328 6(6)	−0.005 1(13)	−0.268 4(7)
C(4I)	0.391 4(7)	−0.010 8(12)	−0.246 1(7)
C(5I)	0.425 6(6)	0.002 6(13)	−0.180 8(7)
C(6I)	0.395 8(6)	0.026 0(8)	−0.132 2(7)
C(1J)	0.310 7(6)	0.175 1(7)	−0.093 5(8)
C(2J)	0.325 8(7)	0.210 1(8)	−0.147 6(7)
C(3J)	0.333 8(8)	0.293 2(9)	−0.147 4(8)
C(4J)	0.330 1(7)	0.335 2(9)	−0.094 6(8)
C(5J)	0.312 3(8)	0.300 2(10)	−0.042 6(9)
C(6J)	0.307 1(6)	0.218 6(8)	−0.041 1(7)
C(1K)	0.149 5(6)	0.176 4(8)	−0.088 0(7)
C(2K)	0.162 1(6)	0.216 9(8)	−0.030 5(7)
C(3K)	0.154 4(8)	0.300 1(10)	−0.029 5(9)
C(4K)	0.132 7(8)	0.339 4(10)	−0.091 2(9)
C(5K)	0.123(1)	0.300(1)	−0.153(1)
C(6K)	0.130 4(8)	0.217 6(9)	−0.150 4(8)
C(1L)	0.083 8(5)	0.039 3(7)	−0.147 8(6)
C(2L)	0.039 3(7)	0.021 2(9)	−0.122 1(7)
C(3L)	−0.021 8(7)	−0.008 3(14)	−0.165 6(8)
C(4L)	−0.036 0(6)	−0.009 0(12)	−0.234 4(7)
C(5L)	0.010 1(6)	0.005 2(12)	−0.260 3(7)
C(6L)	0.070 5(7)	0.027 7(8)	−0.217 7(7)
C(S1)	0.229(1)	0.006(2)	0.511(1)
C(S2)	0.163(1)	0.023(1)	0.479(1)
C(S3)	0.142(1)	0.050(1)	0.413(1)
C(S4)	0.182(1)	0.071(1)	0.375(1)
C(S5)	0.240(1)	0.059(2)	0.406(2)
C(S6)	0.268(1)	0.032(2)	0.479(1)
C(S7)	1.000	0.116(2)	0.500
C(S8)	0.971(1)	0.081(1)	0.442(1)
C(S9)	0.968 2(9)	−0.007 8(16)	0.438 4(9)
C(S10)	1.000	−0.043(2)	0.500
C(S11)	0	0.425(2)	0
C(S12)	0.058 2(8)	0.477 2(11)	0.014 6(9)
C(S13)	0.050(1)	0.557(1)	0.014(1)
C(S14)	0	0.605(3)	0

All calculations were performed on the local minicomputer SEL 32/27, using the GX crystallographic program package.[16]

Results and Discussion

Preparation and Properties of [$Pt_2(dppm)_3$].—Despite the report by Vaska and co-workers[7] of the existence of a complex described as [$Pt_2(dppm)_3$], there was no indication as to how that compound had been prepared. Our early attempts to prepare this complex focused on routes based upon the observation that [$Pt_2H(dppm\text{-}P)(\mu\text{-dppm})_2$][$PF_6$][8] is formally the protonated analogue of [$Pt_2(dppm)_3$]. However, all attempts to deprotonate the platinum hydride salt were unsuccessful.[8] Similarly unsuccessful were attempts to prepare [$Pt_2(dppm)_3$] by the electrochemical reduction of [$Pt_2Cl_2(\mu\text{-dppm})_2$] or [$Pt_2(PPh_3)_2(\mu\text{-dppm})_2$]$^{2+}$, although a transient red colouration was occasionally observed. The preparation of [$Pt_2(dppm)_3$] was achieved, however, when chemical reducing agents were used in the presence of an excess of dppm. Reduction of [$PtCl_2(dppm)$] by Na[BH_4] in aqueous ethanol, in the presence of an equimolar quantity of dppm, had previously afforded [$Pt_2H(dppm\text{-}P)(\mu\text{-dppm})_2$]$^+$,[8] quantitatively. Repeating this reaction in the presence of 2 mol equivalents of dppm [in the hope that the excess of phosphine would stabilise platinum(0)] produced deep red [$Pt_2(dppm)_3$] in almost quantitative yield (N.B. later studies showed that only 1.25 mol equivalents of dppm are required). Similar logic led to the isolation of the same product from the reduction of ethanolic [$PtCl_2(cod)$] with Na[BH_4] in the presence of an excess of dppm, and from the reduction of [$Pt_2Cl_2(\mu\text{-dppm})_2$] with ethanolic potassium hydroxide in the presence of an excess of dppm, albeit in significantly lower yields. An alternative synthetic strategy, ligand displacement from tetrakis(triphenylphosphine)platinum(0) by an excess of dppm, also produced

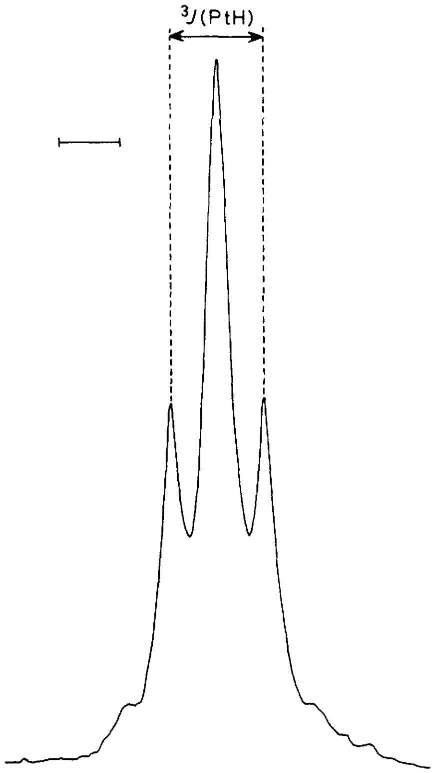


Figure 1. The CH_2 region of the ^1H n.m.r. (300.13 MHz) spectrum of [Pt_2(μ-dppm)$_3$] in C_6D_6 at ambient temperature. The bar represents 20 Hz

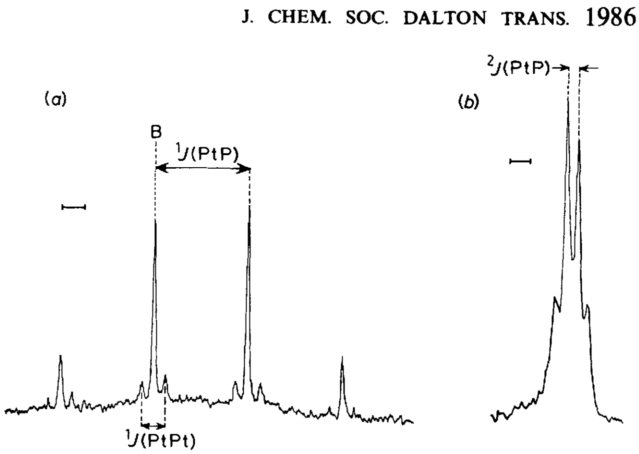
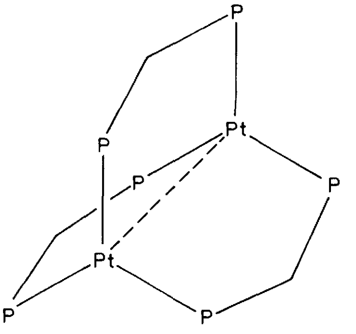


Figure 2. (*a*) The ^{195}Pt n.m.r. (89.56 MHz) spectrum of [Pt_2(μ-dppm)$_3$] in C_6D_6 at ambient temperature. The bar represents 1 000 Hz. (*b*) An expansion of signal B. The bar represents 100 Hz



(1)

[Pt_2(dppm)$_3$] in near quantitative yield. Analysis and spectroscopic characterisation (see below) confirmed that all four routes produced the same product. It was not possible, however, to confirm whether or not this was the same complex reported by Vaska and co-workers,[7] given the total lack of any reported details either of their synthetic methods or of the spectroscopic properties of their complex. However, in the absence of any evidence to the contrary, it is probable that both red complexes are the same.

Solid [Pt_2(dppm)$_3$] is soluble in benzene, toluene, tetrahydrofuran, and dichloromethane. This last solvent was rarely used in our studies, though, since it appeared to react with the complex. In general, degassed, sodium/potassium-dried benzene was used as solvent, unless low-temperature n.m.r. spectroscopic studies were required, when toluene was used instead. Exposure of deep red solutions of [Pt_2(dppm)$_3$] to air results in them rapidly turning yellow, although the solid is appreciably more air stable.

Structure of [Pt_2(dppm)$_3$] *in Solution as determined by N.M.R. Spectroscopy.*—The complex [Pt_2(dppm)$_3$] was studied by ^1H, ^{31}P, and ^{195}Pt n.m.r. spectroscopy, and elementary considerations of the high symmetry revealed by these spectra established that it possessed structure (**1**) in solution. The detailed analysis of these spectra will now be considered.

Proton n.m.r. spectroscopy. The ^1H n.m.r. (300.13 MHz) spectra of [Pt_2(dppm)$_3$] were recorded in dried C_6D_6 and CD_2Cl_2 (N.B. when using the latter solvent, the spectrum had to be rapidly recorded immediately after preparing the solution). In C_6D_6, the CH_2 resonances are all equivalent (see Figure 1), and form a *ca.* 1:8:17:8:1 quintet at $\delta = 3.18$ p.p.m. [^3J(PtH) = 30.9 Hz]: a similar spectral profile was observed in CD_2Cl_2 [$\delta = 3.02$ p.p.m., ^3J(PtH) = 32.8 Hz]. No hydride resonances were observed. The quintet pattern is as expected for the methylene resonances of dppm bridging between two platinum atoms, given the natural isotopomer distribution (the reasons for this pattern are discussed in detail elsewhere[11,12]), and the equivalence of all six bridging-methylene protons is strongly suggestive of a structure of type (**1**). No fine structure was observed due to ^2J(PH) coupling {or, more correctly, the expected heptet splitting upon each of the observed lines of $\frac{1}{2}[^2J(PH) + {}^4J(PH)]$ (= J', the apparent coupling constant) due to virtual coupling with the six phosphorus atoms}, suggesting it has a rather low magnitude for complexes of this type {*cf.* for [Pt_2Cl_2(μ-dppm)$_2$], J' = 3.85 Hz[12]}. It is also worthy of note that the chemical shift of [Pt_2(μ-dppm)$_3$] is almost 1.5 p.p.m. to higher field (lower frequency) than that found for platinum(I) dimers {*e.g.* for [Pt_2Cl_2(μ-dppm)$_2$], $\delta(CH_2)$ = 4.38 p.p.m. in CD_2Cl_2[12]}, consistent with the methylene protons being more shielded in the electron-rich platinum(0) dimer than in comparable platinum(I) complexes. Moreover, in the platinum(0) complex there is no formal metal–metal bond [although there is a metal–metal interaction (see below)], and the dppm ligands are more free to select their 'natural' unstrained geometry [for free dppm, $\delta(CH_2)$ = 2.92 p.p.m.].

Platinum-195 *n.m.r. spectroscopy.* The ^{195}Pt-{^1H} n.m.r. spectrum of [Pt_2(dppm)$_3$] in C_6D_6 (Figure 2) is first order. The basic pattern is a 1:3:3:1 quartet of 1:3:3:1 quartets ($\delta = -47.0$ p.p.m.), the larger quartet separation (4 455 Hz) being attributable to ^1J(PtP) and the smaller (51 Hz) to ^2J(PtP), unambiguously verifying the essential structural features illustrated in (**1**). In addition to these principal features, the weaker satellites are attributable to ^1J(PtPt) coupling (1 130 Hz) in the

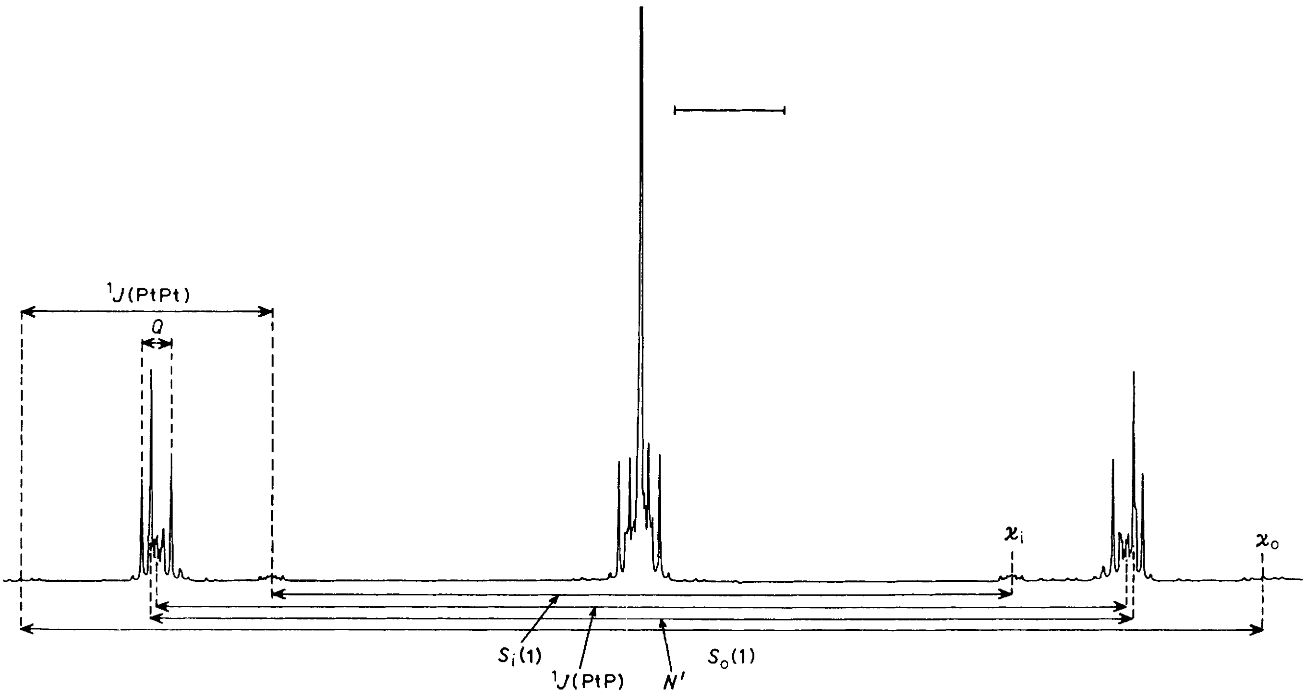


Figure 3. The ^{31}P n.m.r. (121.49 MHz) spectrum of $[Pt_2(\mu\text{-dppm})_3]$ in $C_6D_5CD_3$ at ambient temperature. The bar represents 500 Hz

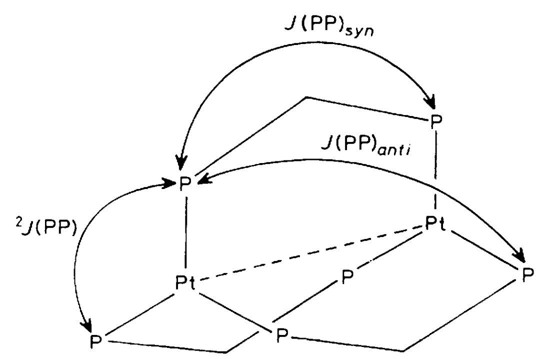


Figure 4. The ^nJ(PP) coupling constants for $[Pt_2(\mu\text{-dppm})_3]$

AA′A″A‴A⁗A‴″XX′ isotopomer, and this assignment was confirmed by computer simulation.*

Phosphorus-31 *n.m.r. spectroscopy.* The $^{31}P\text{-}\{^1H\}$ n.m.r. (121.49 MHz) spectrum of $[Pt_2(dppm)_3]$ in $C_6D_5CD_3$ (Figure 3) shows a strong central peak (δ = 36.8 p.p.m.) with a complex satellite pattern. The spectrum arises from the superposition of the signals arising from three different spin systems: AA′A″A‴A⁗A‴″, AA′A″A‴A⁗A‴″X, and AA′A″A‴A⁗A‴″XX′. The AA′A″A‴A⁗A‴″ spin system (43.8%) yields a sharp singlet. The AA′A″A‴A⁗A‴″XX′ spin system (11.4%) is a particular case of the more general $A_nXX'A'_n$ (n = 1, 2, 3, *etc.*) spin system.[17-19] The important features arising from this spin system are marked on Figure 3, and ^1J(PtPt) is directly measurable as both χ_o and χ_i were observed (see the Appendix of ref. 12). The unambiguous observation of the N' lines also enabled the sign and magnitude of ^2J(PtP) to be calculated (+53.0 Hz). The remaining lines in the observed spectrum are due to the AA′A″A‴A⁗A‴″X spin system (44.8%), for which no specific theoretical treatment has appeared, but from which ^1J(PtP) can readily be measured (4 453 Hz). This sub-spectrum was thus interpreted by an iterative simulation method, accepting the parameters obtained from the AA′A″A‴A⁗A‴″XX′ sub-spectrum and the ^{195}Pt spectrum for ^1J(PtP), ^2J(PtP), and ^1J(PtPt) as invariant starting values. Figure 4 defines the three other important coupling constants in the molecule: ^2J(PP), $J(PP)_{syn}$, and $J(PP)_{anti}$. The through-bond contributions to the synperiplanar and anticlinal coupling constants are given by equations (3) and (4), respectively.

$$J(PP)_{syn} = {}^3J(PPtPtP)_{syn} + {}^2J(PCH_2P) \quad (3)$$

$$J(PP)_{anti} = {}^3J(PPtPtP)_{anti} + {}^4J(PPtPCH_2P) \quad (4)$$

Empirically, the separation, Q, of the strong outer lines of each satellite (see Figure 3) is defined by equation (5). This fixes

$$Q = J(PP)_{syn} + 2J(PP)_{anti} \quad (5)$$

the relationship between $J(PP)_{syn}$ and $J(PP)_{anti}$, and hence reduces the number of independent variables still to be determined to two. Experimentally, Q was determined to be 138.5 Hz. Extensive simulations were performed, allowing the two remaining unknowns, ^2J(PP) and $J(PP)_{syn}$, to vary independently, between 0 and 1 000 and 0 and 138.5 Hz, respectively. The satellite profile (both pattern and relative intensity) proved to be immensely sensitive to the magnitude of ^2J(PP). Only two possible magnitudes of ^2J(PP), 85 or 110 Hz, produced a satellite pattern recognizably similar to the experimental results. The final set of simulations (using a line broadening of 4 Hz) are shown in Figure 5, and these illustrate just how sensitive the spectral profiles are to the selected parameters. The best parameter set was ^1J(PtPt) = 1 130.0, ^1J(PtP) = 4 453.0, ^2J(PtP) = 53.0, ^2J(PP) = 110.0, $J(PP)_{syn}$ = 132.5, and $J(PP)_{anti}$ = 3.0 Hz. Comparison between the best simulation

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* Performed using a modified version of UEAC incorporating a merge facility for up to 50 possible isotopomers. We are indebted to Dr. A. Derome for his invaluable assistance with the modification of this package.

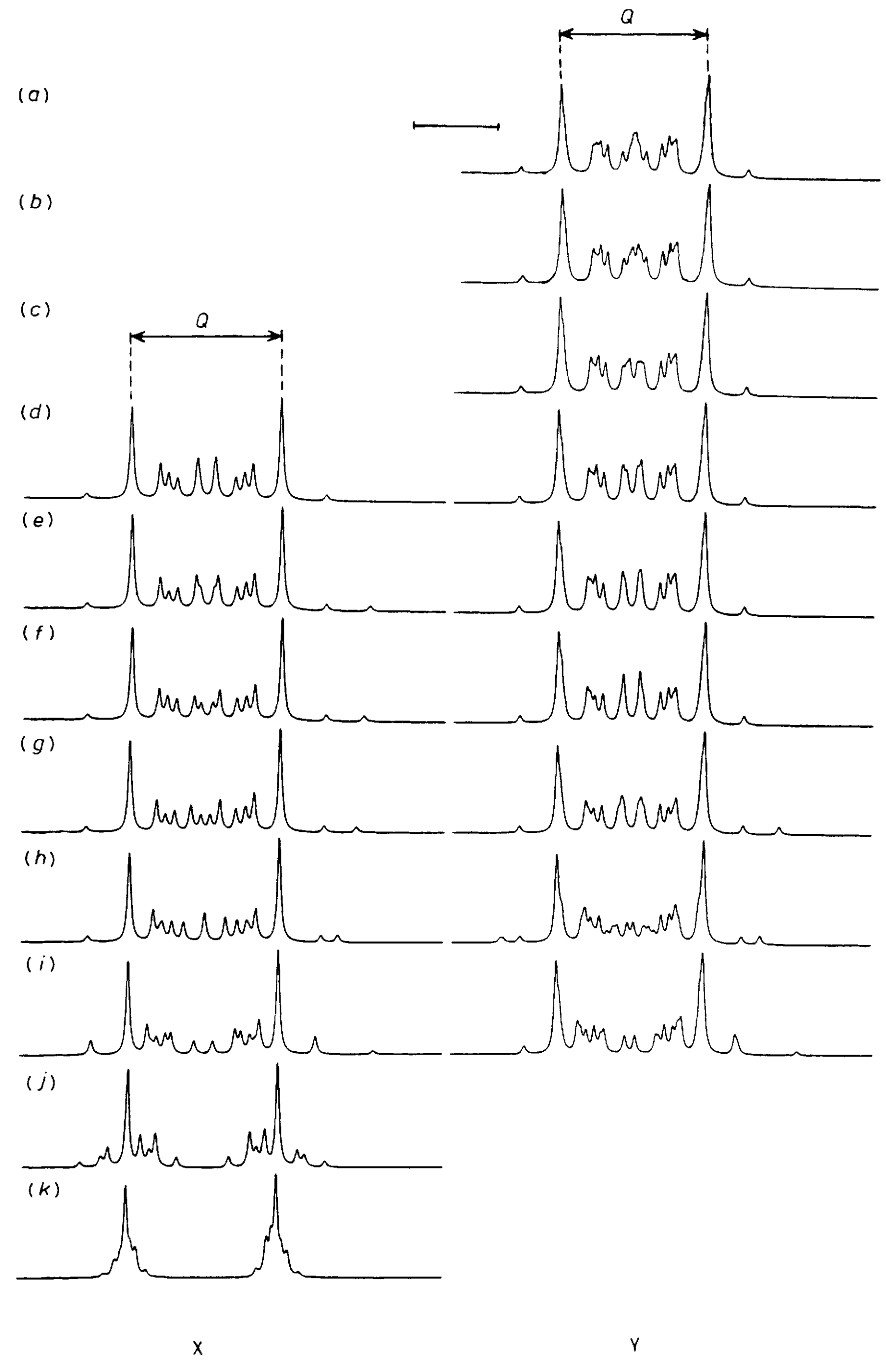

Figure 5. Computer simulations of the low-field satellite of the ^{31}P n.m.r. spectrum of $[Pt_2(\mu\text{-dppm})_3]$, as illustrated in Figure 3. $^2J(PP)$ was varied: (*a*) 115, (*b*) 110, (*c*) 105, (*d*) 100, (*e*) 95, (*f*) 90, (*g*) 85, (*h*) 70, (*i*) 50, (*j*) 30, and (*k*) 10 Hz. Case X corresponds to fixing $J(PP)_{syn}$ = 138.5 Hz and $J(PP)_{anti}$ = 0 Hz, Y to fixing $J(PP)_{syn}$ = 132.5 Hz and $J(PP)_{anti}$ = 3 Hz. The bar represents 80 Hz

and the experimental spectrum (Figure 6) reveals minor differences, but even small changes in the parameters cause a visible deterioration in the quality of the fit. This solution is clearly not unique, as the high symmetry of the complex lends itself to the possibility of a number of degenerate solutions. However, a consideration of the values of $^2J(PP)$, $J(PP)_{syn}$, and $J(PP)_{anti}$ reveals them to be reasonable. For platinum(II) complexes, $^2J(PP)_{cis}$ (*i.e.* angle PPtP 90°) is typically 50 Hz, whereas $^2J(PP)_{trans}$ (*i.e.* angle PPtP 180°) is typically 500 Hz.[20] To the best of our knowledge, no values of $^2J(PP)$ have been determined for trigonal-planar complexes of platinum(0), $[Pt(PR_3)_3]$ (*i.e.* angle PPtP 120°), but a value between 100 and 200 Hz would not be unexpected, and so a value of $^2J(PP)$ of 110.0 Hz for $[Pt_2(\mu\text{-dppm})_3]$ is clearly acceptable. Equation (4) reveals $J(PP)_{anti}$ to be comprised of a $^3J(PPtPtP)_{anti}$ and a $^4J(PPtPCH_2P)$ contribution. The ^4J component should be vanishingly small, and the ^3J component is also expected to be very low in view of the absence of a metal–metal bond (see below) and the anticlinal relationship between the two phosphorus atoms. Thus, a value of $J(PP)_{anti}$ of 3.0 Hz is also reasonable. Finally, according to equation (3), $J(PP)_{syn}$ is comprised of a $^3J(PPtPtP)_{syn}$ and a $^2J(PCH_2P)$ contribution.

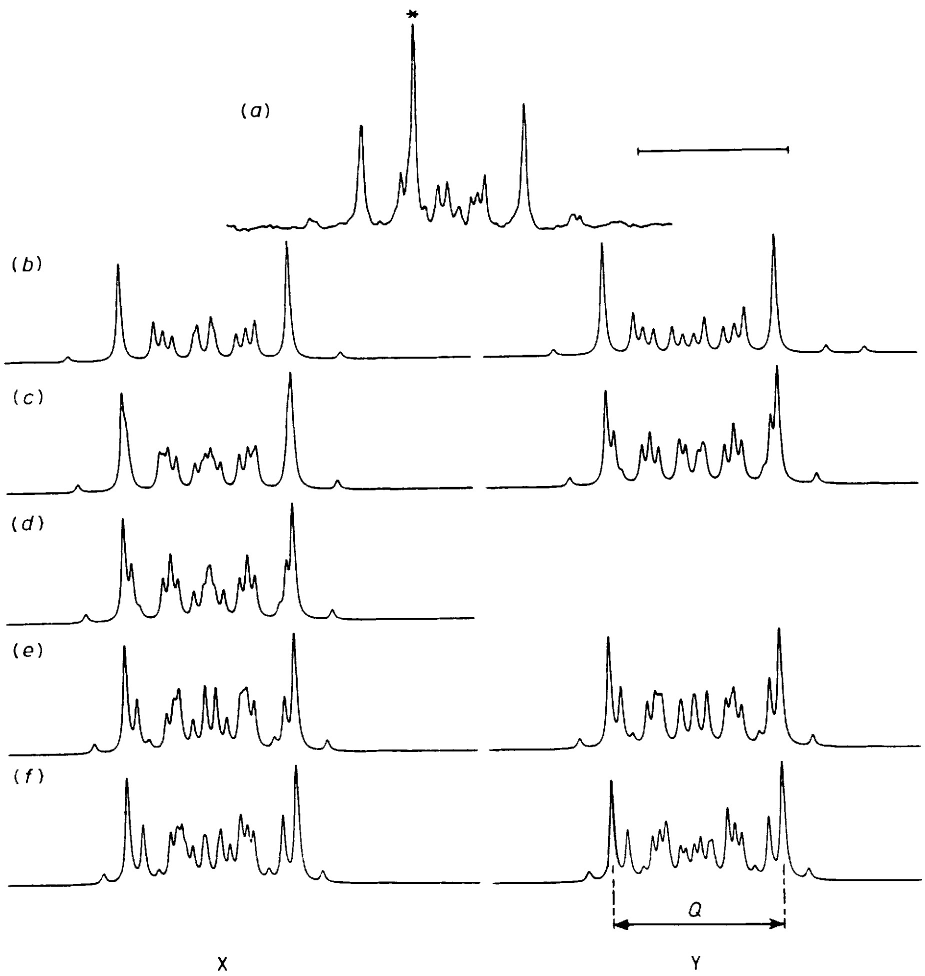

Figure 6. The best computer simulations of the low-field satellite of the ^{31}P n.m.r. spectrum of $[Pt_2(\mu\text{-dppm})_3]$, as illustrated in Figure 3. (*a*) The experimental spectrum, case X corresponds to fixing $^2J(PP)$ = 110 Hz, Y to fixing $^2J(PP)$ = 85 Hz. $J(PP)_{syn}$, $J(PP)_{anti}$ were varied: (*b*) 138.5, 0; (*c*) 132.5, 3; (*d*) 126.5, 6; (*e*) 120.5, 9; and (*f*) 114.5, 12 Hz. The best simulation corresponds to case X(*c*). The bar represents 120 Hz. The asterisk marks the *N'* line, which is *not* simulated

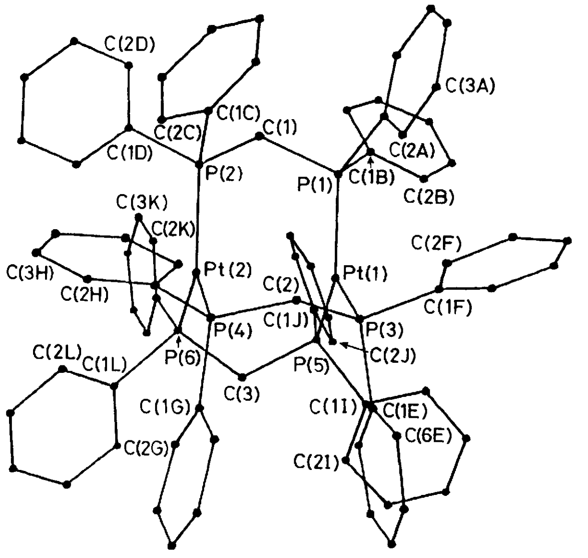

Figure 7. The molecular structure of $[Pt_2(\mu\text{-dppm})_3]$. For clarity, all atoms are represented by spheres of arbitrary size; in each phenyl ring, only two carbon atoms are labelled and they indicate the direction of the progressive sequence C(*n*), C(*n* + 1), ... C(*n* + 5)

Again, the ^3J component should be small, but the ^2J contribution should be significant. For a range of platinum(I) and platinum(II) dppm complexes, $^2J(PP)$ has been found to be typically 60 Hz.[12,21] For the unsymmetrical ligand $Ph_2PCH_2P(Se)Ph_2$, $^2J(PP)$ is 85.1 Hz, and for $[Cr(CO)_4\{Ph_2PCH_2P(Se)Ph_2\}]$ $^2J(PP)$ is 83 Hz.[22] Thus, although higher than these related values, a value of $J(PP)_{syn}$ of 132.5 Hz is also acceptable.

The Crystal Structure of $[Pt_2(\mu\text{-dppm})_3]\cdot 2C_6H_6$.—The molecular structure of $[Pt_2(\mu\text{-dppm})_3]$, illustrated in Figure 7, provides the first example of a new structural type of dppm-bridged bimetallic complexes. It comprises two platinum(0) atoms linked by three bridging dppm ligands to form a manxane-like[23] (bicyclo[3.3.3]undecane-type) molecular frame (Figure 8). The co-ordination geometry around each metal centre is trigonal planar, with the displacements of the Pt(1) and Pt(2) atoms from their local P_3 planes towards each other [0.051(1) and 0.019(1) Å] indicating small pyramidal distortions. The P_3 planes are parallel to one another (with a dihedral angle of 0.46°) and the two PtP_3 fragments adopt a practically eclipsed configuration. Thus, the molecular structure of $[Pt_2(\mu\text{-dppm})_3]$ approximates to C_{3h} symmetry, with the mirror plane passing through the methylenic carbon atoms. Deviations from regular C_{3h} symmetry, which are particularly obvious from the orientations of the phenyl groups (Figure 7)

Table 2. Selected details of the molecular geometry of $[Pt_2(\mu\text{-dppm})_3]$; distances in Å, angles in °

Pt(1)–P(1)	2.268(3)[a]	P(1)–C(1)	1.88(1)
Pt(1)–P(3)	2.264(4)	P(2)–C(1)	1.83(1)
Pt(1)–P(5)	2.272(3)	P(3)–C(2)	1.84(1)
Pt(2)–P(2)	2.268(3)	P(4)–C(2)	1.83(1)
Pt(2)–P(4)	2.263(4)	P(5)–C(3)	1.85(1)
Pt(2)–P(6)	2.255(3)	P(6)–C(3)	1.84(1)
P–C (phenyl)	1.82(1)—1.87(1)		
C–C	1.30(3)—1.46(3)		
Pt(1) ··· Pt(2)	3.022 5(3)	P(1) ··· P(2)	3.130(4)
Pt(1) ··· H(C2A)[b]	3.09	P(3) ··· P(4)	3.075(4)
Pt(1) ··· H(C2E)	3.07	P(5) ··· P(6)	3.103(4)
Pt(2) ··· H(C6D)	2.94	C(1A) ··· C(6C)	3.31(2)
Pt(2) ··· H(C2L)	3.10	C(1B) ··· C(6J)	3.31(2)
P(1)–Pt(1)–P(3)	121.6(2)	Pt(1)–P(5)–C(3)	111.9(4)
P(5)–Pt(1)–P(3)	120.9(2)	Pt(2)–P(2)–C(1)	113.2(4)
P(5)–Pt(1)–P(1)	117.3(2)	Pt(2)–P(4)–C(2)	111.0(4)
P(2)–Pt(2)–P(4)	114.9(2)	Pt(2)–P(6)–C(3)	114.2(4)
P(6)–Pt(2)–P(4)	122.0(2)	P(1)–C(1)–P(2)	114.8(6)
P(6)–Pt(2)–P(2)	123.1(2)	P(3)–C(2)–P(4)	113.4(6)
Pt(1)–P(1)–C(1)	114.4(4)	P(5)–C(3)–P(6)	114.5(6)
Pt(1)–P(3)–C(2)	113.4(4)		
Pt–P–C (phenyl)	114.2(4)—123.6(5)		
C–P–C	97.8(6)—103.9(5)		

[a] Estimated standard deviations are shown in parentheses. [b] Hydrogen atoms are assigned labels of the carbon atoms to which they are bonded.

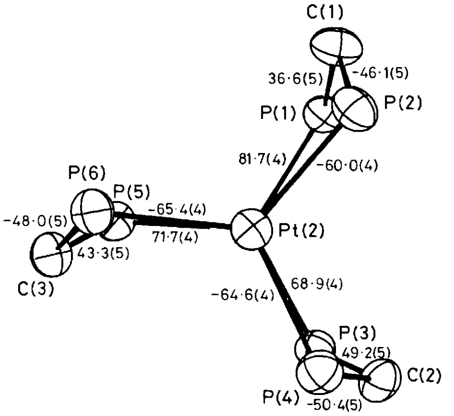

Figure 8. A view of the $Pt_2P_6C_3$ core, illustrating the manxane-type geometry, torsion angles (°), and conformations of the $Pt_2P_4C_2$ metallacycles. The Pt(1) atom is obscured by Pt(2). The atomic vibrational ellipsoids display 50% probability. The C–P(*m*)–Pt–P(*n*) torsion angles are such that a counter-clockwise rotation of the figure by 120° about Pt(1)–Pt(2) takes P(*m*) into P(*n*), *i.e.* C(1)–P(1)–Pt(1)–P(5), C(2)–P(3)–Pt(1)–P(1), *etc.*

and the angular distortions in the co-ordination planes of the metal atoms [angle PPtP 114.9(2)—123.1(2)°], may originate from crystal-packing effects. The co-ordinatively unsaturated metal atoms are each in contact with two phenyl-group hydrogens, at Pt ···. H distances of 2.9—3.1 Å (Table 2).

As is evident from the torsion angles shown in Figure 8, the eight-membered dimetallacycles $Pt_2P_4C_2$ adopt boat–chair conformations of approximate C_s symmetry. The conformations of the dppm ligands are practically the same as in platinum 'A-frame' complexes such as, for example, $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$.[24]

In the dppm ligands, the angles subtended at the methylenic carbon atoms are considerably distorted from the tetrahedral value [angle PCP 113.4(6)—114.8(6)°]. The other bond angles and bond distances are as expected (Table 2). The Pt–P bond lengths [2.255(3)—2.272(3) Å] agree with those of 2.25(1)—2.28(1) Å found in the mononuclear trigonal-planar d^{10} complex $[Pt(PPh_3)_3]$;[25] they are also comparable with Pt–P distances usually found in the d^9 and d^8 $Pt_2(dppm)_2$ complexes [2.248(4)—2.308(5) Å].[24]

The Pt–Pt separation [3.023(1) Å] is too long to be considered indicative of a significant bonding interaction. It lies outside the range of Pt^0–Pt^0 bond distances usually found in clusters (2.61—2.79 Å).[26–28] It is 0.26 Å longer than the distended Pt–Pt bond [2.765(1) Å] in the d^{10}–d^{10} dimer $[Pt_2\{(Me_3C)_2P(CH_2)_3P(CMe_3)_2\}_2]$ where a closer mutual approach of the metal atoms is thought to be precluded by steric requirements of the bulky ligands.[26] Thus the existence of a fully developed metal–metal bond in $[Pt_2(\mu\text{-dppm})_3]$ is neither indicated by the Pt–Pt distance, nor required for the platinum atoms to obtain 16-electron configurations.

The crystal structure is built of the $[Pt_2(\mu\text{-dppm})_3]$ and benzene molecules, separated by van der Waals distances. Each unit cell contains eight benzene solvent molecules, four of which show crystallographically imposed C_2 symmetry.

The Electronic Structure of $[Pt_2(\mu\text{-dppm})_3]$.—The complex $[Pt_2(\mu\text{-dppm})_3]$ shows an intense characteristic visible absorption band at 20 660 cm^{-1} in benzene (see ref. 9, Figure 1) which is associated with the Pt ··· Pt interaction. The origin of this band, and the electronic structure of $[Pt_2(\mu\text{-dppm})_3]$, $[Pd_2(\mu\text{-dppm})_3]$, and their mixed-metal analogue $[PtPd(\mu\text{-dppm})_3]$, will be discussed elsewhere.[29]

Preparation and Structure of $[Pd_2(dppm)_3]$.—Although $[Pd_2(dppm)_3]$ can be satisfactorily prepared by the reduction of $[PdCl_2(PPh_3)_2]$ with hydrazine in the presence of dppm,[1,2] we find that a preparation analogous to that used for $[Pt_2(dppm)_3]$ [see equation (6)] is rather more convenient, and gives the product in >80% yield and high purity.

$$[PdCl_2(dppm)] \xrightarrow[Na[BH_4],\ EtOH]{1.25\ mol\ dppm} [Pd_2(\mu\text{-dppm})_3] \quad (6)$$

The ^1H n.m.r. spectrum of the orange solid in CD_2Cl_2 shows, apart from the phenyl resonances, a clean singlet due to the six equivalent methylene protons at 3.01 p.p.m. {*cf.* 3.02 for $[Pt_2(\mu\text{-dppm})_3]$ in CD_2Cl_2}, with no PH coupling. The ^{31}P n.m.r. spectrum of $[Pd_2(dppm)_3]$ in C_6D_6 shows only a sharp singlet at 10 p.p.m. {*cf.* 36.8 p.p.m. for $[Pt_2(\mu\text{-dppm})_3]$ in C_6D_6}, indicating all six phosphorus atoms are equivalent. Thus, although these data do not establish beyond all question that $[Pd_2(\mu\text{-dppm})_3]$ is isostructural with $[Pt_2(\mu\text{-dppm})_3]$, they are completely compatible with it possessing structure (1). Despite many attempts, we have not yet been able to grow crystals of $[Pd_2(\mu\text{-dppm})_3]$ suitable for an *X*-ray crystallographic study.

Protonation of $[Pt_2(\mu\text{-dppm})_3]$.—Treatment of $[Pt_2(\mu\text{-dppm})_3]$ with an aqueous buffer solution (pH 6.8) in the presence of $K[PF_6]$ gives $[Pt_2H(dppm\text{-}P)(\mu\text{-dppm})_2][PF_6]$[8] in excellent yield. Its ready formation, combined with the difficulty of deprotonating it to reform $[Pt_2(\mu\text{-dppm})_3]$, testifies to the strongly basic nature of $[Pt_2(\mu\text{-dppm})_3]$, resulting from its high axial electron density.[29]

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