# Unsymmetrical Bridging of an Acetylide Ligand in the Cation $[Pt_2(C{\equiv}CBu^t)_3(\mu\text{-dppm})_2]^+$ (dppm = $Ph_2PCH_2PPh_2$): *X*-Ray Structure Determination of the Tetraphenylborate Salt *

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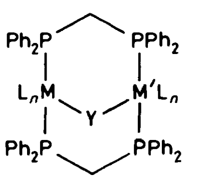
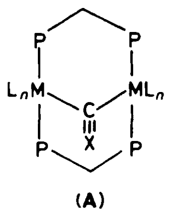
Treatment of $[PtCl_2(\text{dppm-}PP')]$ (dppm = $Ph_2PCH_2PPh_2$) with $LiC{\equiv}CBu^t$ in tetrahydrofuran gives $[Pt_2(C{\equiv}CBu^t)_3(\mu\text{-dppm})_2]Cl$ in 59% yield. The *X*-ray crystal structure of the $BPh_4$ salt shows that the cation has an unsymmetrically bridged ($\sigma,\pi$ bonded) acetylide ligand in the solid state; in solution, fluxional behaviour is indicated by the time averaging of the $^{31}P$ and $^1H$ n.m.r. spectra.

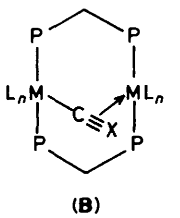
Molecules of typical structure (**1**), first prepared by Kubiak and Eisenberg[1] and designated 'A-frame' systems, have attracted great interest as potential bimetallic activators for small molecules or ions, Y, as reviewed by Puddephatt.[2] In most cases M and M′ are the same but heterometallic systems are known, *e.g.* M = Pt, M′ = Rh.[3] The orbitals utilised in molecular A-frames have been analysed in detail[4] and the point which has aroused most interest is the nature of the binding of Y when this is a member of the isoelectronic series CO, $CN^-$, CNR, or $CCR^-$ (R = alkyl or aryl): this can take two forms, (**A**) or (**B**). Examples of the $\sigma$-symmetric structure (**A**) and the $\sigma,\pi$-asymmetric structure (**B**) are known[2,5] for each example of Y but the factors determining which is adopted are not yet fully understood.



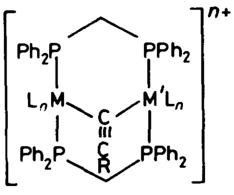
(**1**)



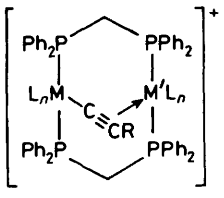
(**A**)



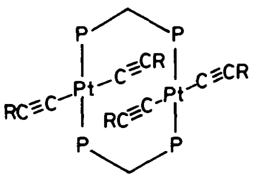
(**B**)



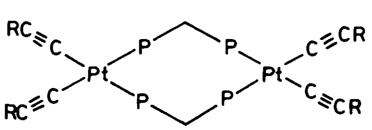
(**2a**) $ML_n = M'L_n = PtMe$; R = Me; $n = 1$
(**2b**) $ML_n = Pt(C{\equiv}C_6H_4Me\text{-}p)$; $M'L_n = W(CO)_3$; $R = C_6H_4Me\text{-}p$; $n = 0$



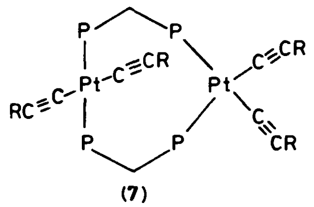
(**3a**) $ML_n = M'L_n = Rh(CO)$; $R = Bu^t$
(**3b**) $ML_n = Pt(C{\equiv}CMe)$; $M'L_n = Rh(CO)$; R = Me
(**3c**) $ML_n = PtCl$; $M'L_n = Rh(CO)$; R = Me



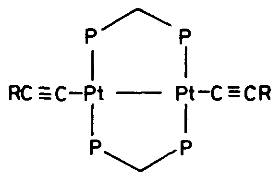
(**5**)



(**6**)



(**7**)



(**8**)

The crystal structures of many A-frames (**1**) where Y = CO have been determined [2,5] and all but one adopt the symmetric (**A**) structure; the one exception being $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-dppm})_2]$ (dppm = $Ph_2PCH_2PPh_2$).[6] Structural studies of (**1**) where Y = $\mu$-C≡CR have only recently been reported, but both alternatives (**A**) and (**B**) have been characterised. Structure (**A**) is found for the diplatinum complex (**2a**)[7] and the platinum–tungsten complex (**2b**)[8] while structure (**B**) is found for the dirhodium complex (**3a**)[9] and the platinum–rhodium complexes (**3b**) and (**3c**);[3] a $\sigma,\pi$-acetylide is also present[10] in $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)]$. Molecules that have structure (**B**) show fluxionality in solution, the $\sigma,\pi$-mode of bonding alternating between two metals by the so-called 'windscreen-wiper' action

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* Di-μ-[bis(diphenylphosphino)methane]-μ-(σ,η-3,3-dimethylbutynyl)-bis[(3,3-dimethylbutynyl)platinum(II)] tetraphenylborate.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xix.

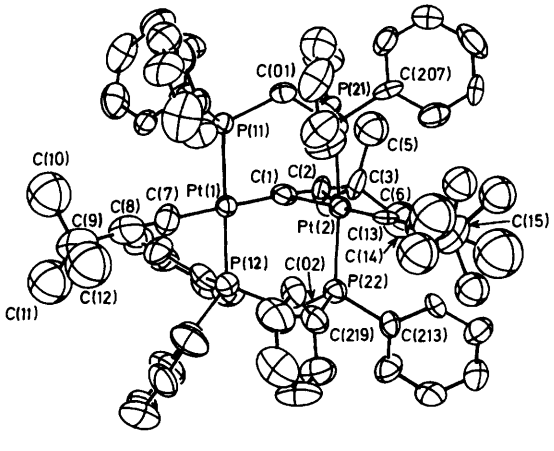


**Figure 1.** View of the $[\mathrm{Pt_2(C{\equiv}CBu^t)_3(\mu\text{-}dppm)_2}]^+$ cation, showing the numbering of the principal atoms. H atoms are omitted for clarity, but both sets of disordered methyl groups on C(15) are included

at a rate giving an averaged environment on the n.m.r. time-scale.[10,11]

In this paper we describe the synthesis and structural characterisation, both in solution and in the solid state, of the cationic complex $[\mathrm{Pt_2(C{\equiv}CBu^t)_3(\mu\text{-}dppm)_2}]^+$ (**4**) and discuss its structure in relation to the complexes described above.

## Results

A range of diplatinum acetylide compexes of types (**5**)—(**8**) are now known.[12–15] Complexes of type (**5**) are formed by treating the chelate $[\mathrm{PtCl_2(dppm\text{-}}PP')]$ with LiC≡CR (R = Ph or $\mathrm{C_6H_4Me\text{-}}p$) in boiling tetrahydrofuran (thf). Under similar conditions, using LiC≡CMe, complex (**5**; R = Me) was not isolated.[13] We now find that treatment of $[\mathrm{PtCl_2(dppm\text{-}}PP')]$ with $\mathrm{LiC{\equiv}CBu^t}$ in boiling thf gives the new complex $[\mathrm{Pt_2(C{\equiv}CBu^t)_3(\mu\text{-}dppm)_2}]\mathrm{Cl}$ (**4a**). Using a large excess of $\mathrm{LiC{\equiv}CBu^t}$ in this reaction leads to decreased yields of (**4a**) but no evidence (*e.g.* from solution $^{31}$P n.m.r. studies) for the formation of (**5**; $\mathrm{R = Bu^t}$).

The chloride anion in (**4a**) is readily exchanged for $\mathrm{BPh_4}^-$ to give (**4b**). Complexes (**4a**) and (**4b**) were characterised by elemental analysis and had almost identical spectroscopic (i.r., $^1$H and $^{31}$P n.m.r.) properties except for signals associated with the $\mathrm{BPh_4}^-$ anion, hence the formulation of (**4a**) as a cationic complex (see later).

The i.r. spectra of (**4a,b**) (KBr disc or saturated $\mathrm{CH_2Cl_2}$ solution) showed very weak bands at 2 140 and 2 040 cm$^{-1}$ assigned to ν(C≡C). There were no bands in the range 200—400 cm$^{-1}$ which may have been attributed to Pt–Cl stretches; this is consistent with the ionic formulation of (**4a**). The $^{31}$P-{$^1$H} n.m.r. spectrum of (**4a,b**) was a singlet at δ 2.65 p.p.m. with complex AA′A″A‴X satellites [$^1J$(PtP) 2 477 Hz], typical of a $\mathrm{Pt_2(\mu\text{-}dppm)_2}$ framework.[16] The $^1$H n.m.r. spectrum showed two multiplets for the inequivalent $\mathrm{PCH_2P}$ protons typical of an 'A-frame'.[17] These n.m.r. spectroscopic properties did not alter at −60 °C in $\mathrm{CDCl_3}$ and are consistent with a symmetric type (**A**) structure or a fluxional type (**B**) structure.

In view of these ambiguous conclusions from the n.m.r. spectroscopic results, we determined the solid-state structure of (**4b**) by *X*-ray crystallography. The crystal structure (Figure 1) shows asymmetric bridging of type (**B**). The terminal carbon atom of the bridging $\mathrm{C{\equiv}CBu^t}$ group is slightly nearer Pt(1) [1.99(1) Å; 2.25(1) Å to Pt(2)]. The C(2)–Pt(2) distance is slightly longer still [2.52(1) Å]. The terminal C(acetylide)–Pt distances are 1.91(1) and 2.00(1) Å. Thus, the complex can best be regarded as having Pt(1) forming single bonds to two acetylides which are almost *trans* [C(7)–Pt(1)–C(1) 174.6(5)°], while Pt(2) has a σ bond to C(13), and a π bond to C≡C [C(1)–C(2)]. The Pt–C(13) bond is however asymmetric with respect to this π bond, being almost aligned with Pt–C(1) [C(13)–Pt(2)–C(1) 177.9(5)°]. The terminal groups are essentially linear at both carbon atoms, but the bridging group is significantly bent at C(2) [168(1)°].

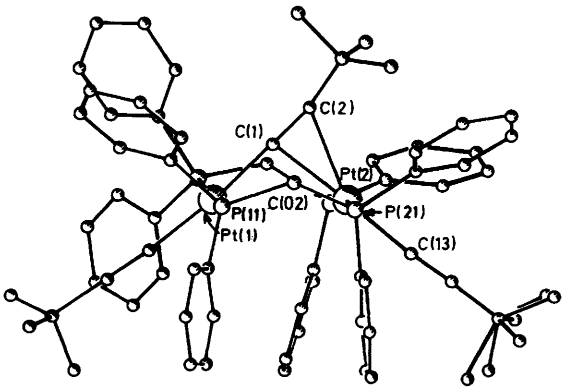
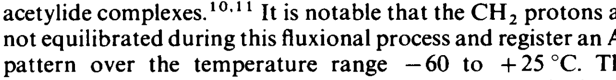


**Figure 2.** Sideways view of the cation, with some atom numbers included for identification

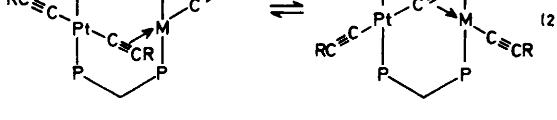
Other dimensions of the molecule are standard. The molecules show no abnormally short intermolecular contacts. It is possible that asymmetrical bridging acetylide would be distorted by intermolecular interactions, but it is more likely that the distortion arises from intramolecular contacts. A side-on view of the molecule (Figure 2) shows that the phenyl groups attached to P(12) and P(22) are oriented to avoid the bridging acetylide.

## Discussion

The structure of (**4b**) in the solid state is therefore of the σ,π-type (**B**), similar to the dirhodium complex (**3a**). If it has the same structure in solution as in the solid state, then rapid oscillation of the bridging $\mathrm{C{\equiv}CBu^t}$ group [equation (1)] must be taking place rendering both the $^{31}$P and $^{195}$Pt nuclei equivalent on the n.m.r. time-scale. A similar 'windscreen wiper' action has been used to explain the equivalence of the $^{31}$P nuclei in related μ-acetylide complexes.[10,11] It is notable that the $\mathrm{CH_2}$ protons are not equilibrated during this fluxional process and register an AB pattern over the temperature range −60 to +25 °C. This eliminates fluxionality due to interchanging terminal and bridging acetylide ligands [equation (2)] as observed in other μ-acetylide complexes of both types (**A**) and (**B**); for example,



(**4a**) X = Cl$^-$
(**4b**) X = $\mathrm{BPh_4^-}$



complexes (**2b**)[7] and (**3b**)[4] both show this type of fluxionality. The slower interchange observed in (**4a,b**) may be due to the steric effect of the bulky Bu$^t$ groups. This may also explain why a complex of type (**5**; R = Bu$^t$) was not formed in the reaction of [PtCl$_2$(dppm-*PP'*)] with LiC≡CBu$^t$ (see above).

It is not obvious why the σ-C≡CR structure should be assumed by the diplatinum complex (**2a**) whereas the σ,π-C≡CR structure is preferred by the ostensibly closely related diplatinum complex (**4b**). It has been suggested that the *trans* influence of the Me groups in (**2a**) destabilises a π interaction with the Pt. This effect may be very subtle, since the difference in *trans* influence of Me and C≡CR is probably quite small. The similarity of the solution and solid-state i.r. spectra in the range 2 000—2 200 cm$^{-1}$ indicates that the structure is essentially the same in both phases. However, the ν(C≡C) bands in this region are very weak (lower intensity than the aromatic overtone bands) and we cannot exclude the possibility that linkage isomers exist in solution: the mechanism of interchange of the μ-C≡CBu$^t$ ligand [equation (1)] must involve the σ-C≡CBu$^t$ structure either as a transition state or an intermediate.

## Experimental

*General.*—All reactions were carried out in a dry nitrogen atmosphere, although products were handled in air. The tetrahydrofuran (thf) was dried by distillation from sodium–benzophenone under nitrogen. The complex [PtCl$_2$(dppm-*PP'*)] was prepared by a literature method.[18] Bu$^t$C≡CH and

**Table 1.** Atomic co-ordinates ( × 10$^4$) for [Pt$_2$(C≡CBu$^t$)$_3$(μ-dppm)$_2$]BPh$_4$ (**4b**)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pt(1) | 78(1) | 5 000 | 2 984(1) |
| Pt(2) | 1 332(1) | 4 101(1) | 1 980(1) |
| P(11) | 1 440(3) | 5 630(2) | 3 542(2) |
| P(12) | −1 387(3) | 4 531(2) | 2 233(3) |
| P(21) | 2 719(3) | 4 716(2) | 2 602(3) |
| P(22) | −78(3) | 3 467(2) | 1 598(3) |
| C(01) | 2 407(10) | 5 546(6) | 2 834(10) |
| C(02) | −1 233(9) | 3 924(7) | 1 318(10) |
| C(1) | 410(8) | 4 999(7) | 1 706(9) |
| C(2) | 562(8) | 4 989(7) | 878(9) |
| C(3) | 571(11) | 5 068(8) | −131(9) |
| C(4) | −389(12) | 5 469(8) | −623(12) |
| C(5) | 1 507(13) | 5 488(9) | −208(13) |
| C(6) | 582(14) | 4 402(9) | −589(13) |
| C(7) | −351(10) | 5 045(8) | 4 157(9) |
| C(8) | −685(12) | 5 096(9) | 4 878(11) |
| C(9) | −1 168(17) | 5 137(12) | 5 767(12) |
| C(10) | −570(20) | 5 673(14) | 6 427(20) |
| C(11) | −2 262(19) | 5 193(14) | 5 502(18) |
| C(12) | −871(22) | 4 531(15) | 6 342(22) |
| C(13) | 2 143(9) | 3 306(6) | 2 273(10) |
| C(14) | 2 622(11) | 2 824(7) | 2 382(12) |
| C(15) | 3 224(15) | 2 246(8) | 2 573(14) |
| C(16)* | 3 767(42) | 2 188(31) | 3 600(42) |
| C(17)* | 2 527(27) | 1 648(19) | 2 097(27) |
| C(18)* | 3 193(48) | 1 877(35) | 1 709(47) |
| C(19)* | 4 317(28) | 2 423(19) | 3 108(27) |
| C(20)* | 4 145(33) | 2 329(22) | 2 062(32) |
| C(21)* | 3 065(42) | 1 962(29) | 3 649(38) |
| C(102) | 2 682(8) | 6 088(5) | 5 204(7) |
| C(103) | 3 203 | 6 041 | 6 149 |
| C(104) | 3 132 | 5 487 | 6 671 |
| C(105) | 2 539 | 4 979 | 6 248 |
| C(106) | 2 017 | 5 026 | 5 304 |
| C(101) | 2 088 | 5 580 | 4 781 |
| C(108) | 1 745(5) | 6 941(5) | 3 259(7) |
| C(109) | 1 432 | 7 577 | 3 138 |
| C(110) | 452 | 7 735 | 3 136 |
| C(111) | −216 | 7 258 | 3 256 |
| C(112) | 96 | 6 622 | 3 377 |
| C(107) | 1 077 | 6 464 | 3 379 |
| C(114) | −3 258(7) | 4 256(6) | 2 553(7) |
| C(115) | −3 909 | 3 946 | 3 019 |
| C(116) | −3 539 | 3 550 | 3 797 |
| C(117) | −2 518 | 3 464 | 4 108 |
| C(118) | −1 867 | 3 774 | 3 642 |
| C(113) | −2 237 | 4 170 | 2 864 |
| C(120) | −2 154(7) | 5 744(5) | 2 086(5) |
| C(121) | −2 646 | 6 279 | 1 628 |
| C(122) | −3 078 | 6 254 | 657 |
| C(123) | −3 017 | 5 694 | 143 |
| C(124) | −2 526 | 5 159 | 601 |
| C(119) | −2 094 | 5 184 | 1 573 |
| C(202) | 4 315(8) | 4 851(5) | 4 114(7) |
| C(203) | 4 939 | 4 682 | 4 979 |
| C(204) | 4 741 | 4 134 | 5 461 |
| C(205) | 3 920 | 3 755 | 5 076 |
| C(206) | 3 296 | 3 923 | 4 211 |
| C(201) | 3 494 | 4 471 | 3 729 |
| C(208) | 4 114(8) | 5 348(4) | 1 777(6) |
| C(209) | 4 728 | 5 398 | 1 131 |
| C(210) | 4 752 | 4 905 | 482 |
| C(211) | 4 163 | 4 363 | 479 |
| C(212) | 3 549 | 4 313 | 1 126 |
| C(207) | 3 524 | 4 806 | 1 775 |
| C(214) | 635(5) | 2 670(5) | 381(6) |
| C(215) | 570 | 2 218 | −344 |
| C(216) | −356 | 2 016 | −857 |
| C(217) | −1 218 | 2 265 | −644 |
| C(218) | −1 154 | 2 717 | 81 |
| C(213) | −227 | 2 920 | 593 |
| C(220) | −870(7) | 2 480(5) | 2 460(6) |
| C(221) | −993 | 2 111 | 3 234 |
| C(222) | −420 | 2 238 | 4 142 |
| C(223) | 275 | 2 733 | 4 275 |
| C(224) | 397 | 3 102 | 3 500 |
| C(219) | −175 | 2 975 | 2 592 |
| B(1) | 5 305(13) | 2 939(9) | 8 380(12) |
| C(302) | 5 361(5) | 4 233(5) | 8 082(7) |
| C(303) | 5 882 | 4 784 | 7 941 |
| C(304) | 6 903 | 4 753 | 8 005 |
| C(305) | 7 402 | 4 172 | 8 210 |
| C(306) | 6 881 | 3 621 | 8 351 |
| C(301) | 5 860 | 3 652 | 8 287 |
| C(312) | 3 445(8) | 3 262(5) | 7 594(7) |
| C(313) | 2 443 | 3 352 | 7 585 |
| C(314) | 2 093 | 3 240 | 8 408 |
| C(315) | 2 744 | 3 038 | 9 240 |
| C(316) | 3 746 | 2 949 | 9 249 |
| C(311) | 4 097 | 3 060 | 8 426 |
| C(322) | 5 774(7) | 2 654(4) | 6 700(8) |
| C(323) | 5 672 | 2 259 | 5 902 |
| C(324) | 5 095 | 1 706 | 5 833 |
| C(325) | 4 619 | 1 547 | 6 561 |
| C(326) | 4 721 | 1 942 | 7 360 |
| C(321) | 5 299 | 2 495 | 7 429 |
| C(322) | 6 063(8) | 2 991(4) | 10 232(8) |
| C(333) | 6 461 | 2 714 | 11 115 |
| C(334) | 6 694 | 2 063 | 11 176 |
| C(335) | 6 528 | 1 688 | 10 353 |
| C(336) | 6 129 | 1 965 | 9 469 |
| C(331) | 5 897 | 2 616 | 9 408 |

* Disordered, included with 0.5 occupancy.

$LiBu^n$ (1.5 mol dm$^{-3}$ in hexane) were purchased from Aldrich Chemical Co. N.m.r. spectra were recorded on Bruker WH90 and WH400 spectrometers using deuterium as internal lock. $^1H$ N.m.r. shifts are to high frequency of $SiMe_4$ and $^{31}P$ n.m.r. shifts are to high frequency of 85% $H_3PO_4$.

*Preparation of* $[Pt_2(C{\equiv}CBu^t)_3(\mu\text{-dppm})_2]Cl{\cdot}CH_2Cl_2$ (**4a**).—A solution of $LiBu^n$ in hexane (1.6 mol dm$^{-3}$, 0.625 cm$^3$, 1.0 mmol) was added dropwise to a solution of $Bu^tC{\equiv}CH$ (0.133 g, 1.62 mmol) in dry thf (10 cm$^3$) at 0 °C over 5 min. After 30 min $[PtCl_2(\text{dppm-}PP')]$ (0.324 g, 0.5 mmol) and dry benzene (25 cm$^3$) were added. The mixture was then stirred at 0 °C for 1 h and then heated under reflux for 14 h. The yellow product was then filtered off, washed successively with benzene (10 cm$^3$), water (10 cm$^3$), and diethyl ether (20 cm$^3$), and dried *in vacuo*. Yield: 0.213 g (59%), m.p. 325—330 °C (decomp.) (Found: C, 54.65; H, 4.80; Cl, 7.5. Calc. for $C_{69}H_{73}Cl_3P_4Pt_2$: C, 54.45; H, 4.85; Cl, 7.00%). $^1H$ N.m.r. ($CDCl_3$): δ 8.0—7.1 (m, 20 H, $C_6H_5$); 4.42, 4.18 (m, 4 H, $CH_2$), 0.60 [s, 9 H, $\mu\text{-}C{\equiv}CC(CH_3)_3$], 0.54 [s, 18 H, terminal $C{\equiv}CC(CH_3)_3$]; $^{31}P$ n.m.r. ($CDCl_3$): δ 2.65 p.p.m., $^1J(PtP)$ = 2 477, $^3J(PtP)$ *ca.* 30, $[^2J(PP) + {}^4J(PP)]$ = 59 Hz; u.v.–visible ($CH_3CN$): $\lambda_{max.}(\varepsilon_{max.})$ 343 (7 250), 376 (sh) (8 660), 388 (8 750), and 413 nm (sh) (72 230 dm$^3$ mol$^{-1}$ cm$^{-1}$).

*Preparation of* $[Pt_2(C{\equiv}CBu^t)_3(\mu\text{-dppm})_2]BPh_4$ (**4b**).—A solution of $NaBPh_4$ (0.10 g, 0.29 mmol) in methanol (5 cm$^3$) was added to a solution of (**4a**)$\cdot CH_2Cl_2$ (0.10 g, 0.066 mmol) in methanol (10 cm$^3$). A precipitate formed immediately, which was filtered off, washed with methanol (2 cm$^3$), and dried *in vacuo*. Yield: 0.11 g (96%) (Found: C, 64.75; H, 5.55. Calc. for $C_{92}H_{91}BP_4Pt_2$: C, 64.40; H, 5.35%). Spectroscopic data for (**4b**) were very similar to (**4a**).

*Crystal-structure Analysis of* (**4b**).—*Crystal data.* $C_{92}H_{91}BP_4Pt_2$, $M$ = 1 721.7, monoclinic, space group $P2_1$, $a$ = 13.825(3), $b$ = 20.874(6), $c$ = 14.392(4) Å, β = 102.74(2)°, $U$ = 4 051(2) Å$^3$, $Z$ = 2, $D_c$ = 1.41 g cm$^{-3}$, Mo-$K_\alpha$ radiation, $T$ = 290 K, λ = 0.710 69 Å, μ(Mo-$K_\alpha$) = 36.05 cm$^{-1}$, $F(000)$ = 1 728; $R$ = 0.042 for 5 154 unique observed $[I/\sigma(I) \geqslant 3.0]$ reflections. [An unstable second modification was also obtained: orthorhombic, space group $Pn..$ ($n$ glide ⊥ to $a$, undetermined symmetry elements ⊥ to $b$ and $c$), $a$ = 12.39, $b$ = 19.65, $c$ = 18.08 Å, $U$ = 4 402 Å$^3$; this decomposed in 12 h.]

Crystal character: yellow laths from $CH_2Cl_2$–diethyl ether. Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ 48°, with scan range ±0.9° (2θ) around the $K_{\alpha 1} - K_{\alpha 2}$ angles, scan speed 2.5—29° min$^{-1}$, depending on the intensity of a 2 s pre-scan; backgrounds measured at each end of the scan for 0.25 of the scan time; $hkl$ ranges were 0—16, 0—23, and −16 to 16.

Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection: the data were rescaled to correct for this. The density was measured by flotation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections (20 < 2θ < 25°). Reflections were processed using profile analysis to give 7 303 unique reflections ($R_{int}$ = 0.027); 5 154 were considered to be observed $[I/\sigma(I) \geqslant 3.0]$ and used in the refinement; these were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method;[19] maximum and minimum transmission factors were 0.79 and 0.44. Crystal dimensions were 0.30 × 0.50 × 0.10 mm, with bonding faces: $\{001\}$, $10\bar{1}$; $\bar{1}01$; $11\bar{1}$; $\bar{1}11$; $\{010\}$.

**Table 2.** Principal bond lengths (Å) and angles (°) for $[Pt_2(C{\equiv}CBu^t)_3(\mu\text{-dppm})_2]BPh_4$ (**4b**)

| | | | |
|---|---|---|---|
| Pt(1)–Pt(2) | 3.117(1) | Pt(1)–P(11) | 2.292(3) |
| Pt(1)–P(12) | 2.297(4) | Pt(1)–C(1) | 1.991(13) |
| Pt(1)–C(7) | 1.911(14) | Pt(2)–P(21) | 2.317(3) |
| Pt(2)–P(22) | 2.319(3) | Pt(2)–C(1) | 2.252(14) |
| Pt(2)–C(2) | 2.517(13) | Pt(2)–C(13) | 1.995(13) |
| P(11)–C(01) | 1.859(15) | P(11)–C(101) | 1.814(10) |
| P(11)–C(107) | 1.812(10) | P(12)–C(02) | 1.862(15) |
| P(12)–C(113) | 1.811(12) | P(12)–C(119) | 1.812(10) |
| P(21)–C(01) | 1.834(13) | P(21)–C(201) | 1.809(10) |
| P(21)–C(207) | 1.810(12) | P(22)–C(02) | 1.827(13) |
| P(22)–C(213) | 1.818(10) | P(22)–C(219) | 1.791(11) |
| C(1)–C(2) | 1.255(19) | C(2)–C(3) | 1.465(19) |
| C(8)–C(9) | 1.570(28) | C(7)–C(8) | 1.231(23) |
| C(13)–C(14) | 1.195(20) | C(14)–C(15) | 1.457(23) |

| | | | |
|---|---|---|---|
| Pt(2)–Pt(1)–P(11) | 90.5(1) | Pt(2)–Pt(1)–P(12) | 92.6(1) |
| P(11)–Pt(1)–P(12) | 168.8(1) | Pt(2)–Pt(1)–C(1) | 46.1(4) |
| P(11)–Pt(1)–C(1) | 89.1(4) | P(12)–Pt(1)–C(1) | 85.3(3) |
| Pt(2)–Pt(1)–C(7) | 138.7(5) | P(11)–Pt(1)–C(7) | 93.1(4) |
| P(12)–Pt(1)–C(7) | 91.7(4) | C(1)–Pt(1)–C(7) | 174.6(5) |
| Pt(1)–Pt(2)–P(21) | 89.2(1) | Pt(1)–Pt(2)–P(22) | 86.0(1) |
| P(21)–Pt(2)–P(22) | 171.2(1) | Pt(1)–Pt(2)–C(1) | 39.6(3) |
| P(21)–Pt(2)–C(1) | 89.7(3) | P(22)–Pt(2)–C(1) | 91.2(3) |
| Pt(1)–Pt(2)–C(2) | 69.4(3) | P(21)–Pt(2)–C(2) | 92.0(3) |
| P(22)–Pt(2)–C(2) | 93.1(3) | C(1)–Pt(2)–C(2) | 29.9(5) |
| Pt(1)–Pt(2)–C(13) | 138.3(4) | P(21)–Pt(2)–C(13) | 90.0(4) |
| P(22)–Pt(2)–C(13) | 88.8(4) | C(1)–Pt(2)–C(13) | 177.9(5) |
| C(2)–Pt(2)–C(13) | 152.2(5) | Pt(1)–P(11)–C(01) | 112.9(4) |
| Pt(1)–P(11)–C(101) | 120.1(4) | C(01)–P(11)–C(101) | 105.9(6) |
| Pt(1)–P(11)–C(107) | 108.8(3) | C(01)–P(11)–C(107) | 103.4(5) |
| Pt(1)–P(12)–C(02) | 113.5(4) | Pt(1)–P(12)–C(113) | 122.5(4) |
| C(02)–P(12)–C(113) | 105.0(6) | Pt(1)–P(12)–C(119) | 104.2(4) |
| C(02)–P(12)–C(119) | 106.4(5) | Pt(2)–P(21)–C(01) | 112.7(4) |
| Pt(2)–P(21)–C(201) | 117.8(4) | C(01)–P(21)–C(201) | 102.7(5) |
| Pt(2)–P(21)–C(207) | 112.3(3) | C(01)–P(21)–C(207) | 103.0(6) |
| Pt(2)–P(22)–C(02) | 113.7(4) | Pt(2)–P(22)–C(213) | 119.3(3) |
| C(02)–P(22)–C(213) | 102.3(5) | Pt(2)–P(22)–C(219) | 110.2(3) |
| C(02)–P(22)–C(219) | 105.0(6) | P(11)–C(01)–P(21) | 114.5(7) |
| P(12)–C(02)–P(22) | 115.5(7) | Pt(1)–C(1)–Pt(2) | 94.3(5) |
| Pt(1)–C(1)–C(2) | 176.2(9) | Pt(2)–C(1)–C(2) | 86.8(10) |
| Pt(2)–C(2)–C(1) | 63.3(8) | Pt(2)–C(2)–C(3) | 127.8(10) |
| C(1)–C(2)–C(3) | 168.4(14) | Pt(1)–C(7)–C(8) | 175.4(13) |
| C(7)–C(8)–C(9) | 176.5(15) | Pt(2)–C(13)–C(14) | 175.5(13) |
| C(13)–C(14)–C(15) | 176.7(17) | | |

Systematic absences $0k0$, $k \neq 2n$ indicated either space group $P2_1/m$ or $P2_1$. Examination of the Patterson interpretation showed no consistent Pt–P vectors in the former. The latter was therefore chosen initially, and shown to be correct by the successful refinement. Heavy atoms were located by the Patterson interpretation section of SHELXTL[19] and the light atoms then found on successive Fourier syntheses; the methyl groups attached to C(15) were disordered between two positions, and the phenyl rings were treated as regular hexagons (C–C 1.395 Å). Anisotropic thermal parameters were used for all non-H atoms except terminal $CH_3$ groups. Hydrogen atoms were given fixed isotropic thermal parameters, $U$ = 0.07 Å$^2$. Those defined by the molecular geometry were inserted at calculated positions and not refined; H atoms of methyl groups were not included. The hand of the individual chiral crystal chosen was checked by refinement of a $\delta f''$ multiplier (and following refinement to −1 the hand was reversed). The $y$ co-ordinate of Pt(1) was fixed to define the origin. Final refinement was on $F$ by cascaded least-squares methods. Largest positive and negative peaks on a final difference Fourier synthesis were of heights 0.9 and −1.1 e Å$^{-3}$.

A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g$ = 0.0008 was used and shown to be satisfactory by a weight analysis. Final $R$ = 0.042, $R'$ = 0.041. Maximum shift to error action in the final cycle was 0.3. Computing was with SHELXTL[19] on a Data General DG30 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from International Tables.[20] Final atomic co-ordinates are given in Table 1, and bond lengths and angles in Table 2.

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