

A Dinuclear Phosphidoplatinum(II) Fragment as a Building Block for Tri-, Tetra-, Hexa-, and Octanuclear Complexes^[‡]

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The dinuclear complex $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(NCCH_3)_2]$ (**1**) is described and fully characterised. Complex **1** reacts with 2,2'-bipyrimidine and *cis*- $[M(C_6F_5)_2(THF)_2]$ to form the di-, tri- and tetranuclear complexes **2**, **3** and **4**, respectively, depending on the ratio of reagents and the type of metal (*M* = Pt, Pd). Complex **1** reacts with KCN to form the anionic dinuclear complex $[PPh_3(CH_3)]_2[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(CN)_2]$ (**6**).

Complex **6** acts as a metalloligand towards *cis*- $[M(C_6F_5)_2(THF)_2]$ or **1** to yield the corresponding hexanuclear or octanuclear complexes **7**, **8** and **9**. The structure of $[PPh_3(CH_3)]_4\{[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-CN)_2Pd(C_6F_5)_2]_2\}$ (**8**) has been established by X-ray diffraction.

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Introduction

The use of transition metal centres and coordination chemistry for directing the formation of complex structures has evolved into one of the most widely used strategies for organizing molecular building blocks into supramolecular arrays.^[2–7] The directional-bonding approach, or “molecular library”, involves the assembly of large metal-containing structures wherein the metal centres act as highly directional corner or side units in the resulting geometric shapes or polyhedra. This approach uses a blocking ligand to protect coordination sites at the metal centre, thus controlling the positions available for the binding of bridging ligands and enabling the construction of the desired architecture. This type of research began with the use of mononuclear coordination centres, especially Pd^{II} and Pt^{II} ,^[8–10] but considerable success has since been achieved by using dimetallic entities instead.^[11,12] In the course of our research in phosphido derivatives we have prepared several polynuclear complexes that contain the “ $(C_6F_5)_2Pt(\mu-PPh_2)_2Pt$ ” fragment.^[13–19] In some cases the precursor for this fragment is the complex $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(S)_2]$ ^[20] (*S* = solvent) which has been prepared in situ but never isolated. In this paper we describe the isolation of the dinuclear derivative $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(NCCH_3)_2]$ (**1**) and we study its coordination chemistry towards different ligands with the aim of establishing its synthetic potential as a building block for species with predefined geometric shapes.

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Results and Discussion

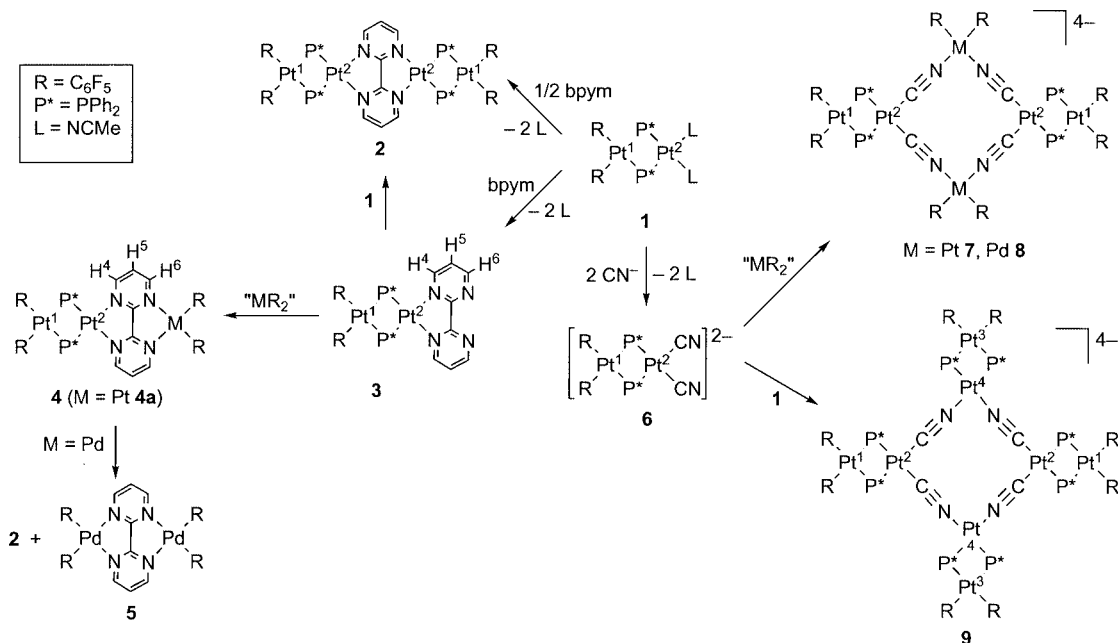
The addition of $AgClO_4$ to an acetone/acetonitrile solution of $[Bu_4N]_2\{[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-Cl)]_2\}$ (molar ratio 2:1) results in the precipitation of silver chloride; $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(NCCH_3)_2]$ (**1**) is isolated as a white, stable solid from the mother liquors. The ^{19}F NMR spectrum shows a signal with platinum satellites for the *o*-F atoms and the resonances due to *m*- and *p*-F atoms (higher field) appear overlapped, with the expected 2:3 intensity ratio confirming the equivalence of both C_6F_5 groups. The ^{31}P NMR spectrum shows a signal ($\delta = -143.8$ ppm) with platinum satellites for the two equivalent P atoms. The chemical shift appears at high field, indicating that both PPh_2 ligands are supporting two metal centres not involved in M–M bonds [3.443(1) Å]. Two values of $^1J_{Pt,P}$ (1927 and 2454 Hz for Pt^I and Pt^2 , respectively) can be calculated from the platinum satellites (see Scheme 1 for atom numbering). The assignment of each value to Pt^I or Pt^2 can be carried out considering the great *trans* influence of the C_6F_5 group and comparing the values with those obtained in other similar pentafluorophenyl derivatives.^[21] The IR spectrum shows, in the 800 cm^{-1} region, two absorptions of similar intensity due to the X-sensitive mode of the C_6F_5 groups, in agreement with the presence of the “*cis*- $Pt(C_6F_5)_2$ ” fragment,^[22,23] and two absorptions in the 2300 cm^{-1} region due to $\nu(CN)$ of the coordinated acetonitrile. All significant spectroscopic data are given in the Exp. Sect.

The crystal structure of complex **1** was determined by X-ray diffraction and is shown in Figure 1. During the resolu-

[‡] Polynuclear Homo- or Heterometallic Palladium(II)-Platinum(II) Pentafluorophenyl Complexes Containing Bridging Diphenylphosphido Ligands, 17. Part 16; Ref.^[1]

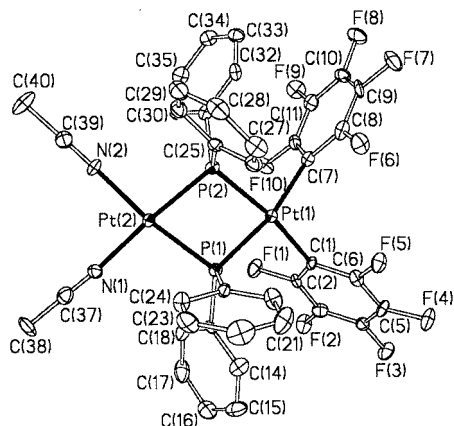
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Scheme 1.

tion of the structure, two essentially identical molecules of **1** were found in the asymmetric part of the unit cell and we will discuss only one of them now. Selected bond lengths and angles are listed in Table 1. Complex **1** is a dinuclear complex (Figure 1) in which the two Pt atoms are bridged by two diphenylphosphido ligands. The square-planar environments of the metal centres are completed by two *cis*-pentafluorophenyl groups in the case of Pt(1), and two *cis*-acetonitrile ligands in the case of Pt(2). The two acetonitrile moieties are practically linear, as expected, and the bond lengths and angles fall in the range usually found for this ligand coordinated to Pt.^[24–28] The molecular skeleton C₂Pt₂PtN₂ is not planar. The angle between the perpendicular lines to the best square planes formed by the Pt atoms and the atoms directly bonded to them is 33.94(4)°.

Figure 1. Structure of the complex [(C₆F₅)₂Pt(μ-PPh₂)₂Pt(NCCH₃)₂] (**1**).Table 1. Selected bond lengths [Å] and angles [°] for [(C₆F₅)₂Pt(μ-PPh₂)₂Pt(NCCH₃)₂]·Me₂CO (**1**·Me₂CO).

Pt(1)–C(1)	2.061(5)	Pt(1)–C(7)	2.065(5)
Pt(1)–P(2)	2.2844(14)	Pt(2)–N(1)	2.068(5)
Pt(2)–P(2)	2.2641(14)	Pt(2)–P(1)	2.2728(14)
Pt(3)–C(47)	2.070(5)	Pt(3)–P(4)	2.2815(14)
Pt(4)–N(4)	2.083(5)	Pt(4)–N(3)	2.087(5)
Pt(4)–P(4)	2.2702(14)	Pt(4)–P(3)	2.2566(14)
Pt(1)–P(1)	2.2820(14)	Pt(2)–N(2)	2.079(4)
Pt(3)–C(41)	2.070(5)	Pt(3)–P(3)	2.2933(14)
C(1)–Pt(1)–C(7)	92.6(2)	C(1)–Pt(1)–P(1)	98.01(15)
C(7)–Pt(1)–P(1)	167.61(15)	C(1)–Pt(1)–P(2)	169.16(15)
C(7)–Pt(1)–P(2)	93.19(15)	P(1)–Pt(1)–P(2)	75.36(5)
N(1)–Pt(2)–N(2)	87.54(18)	N(1)–Pt(2)–P(2)	175.44(13)
N(2)–Pt(2)–P(2)	96.47(13)	N(1)–Pt(2)–P(1)	100.08(13)
N(2)–Pt(2)–P(1)	172.36(13)	P(2)–Pt(2)–P(1)	75.94(5)
Pt(2)–P(1)–Pt(1)	98.22(5)	Pt(2)–P(2)–Pt(1)	98.40(5)
C(41)–Pt(3)–C(47)	92.77(19)	C(41)–Pt(3)–P(4)	167.51(15)
C(47)–Pt(3)–P(4)	97.61(14)	C(41)–Pt(3)–P(3)	94.46(14)
C(47)–Pt(3)–P(3)	172.27(14)	P(4)–Pt(3)–P(3)	74.88(5)
N(4)–Pt(4)–N(3)	88.36(18)	N(4)–Pt(4)–P(3)	172.82(13)
N(3)–Pt(4)–P(3)	98.47(13)	N(4)–Pt(4)–P(4)	97.29(13)
N(3)–Pt(4)–P(4)	174.06(13)	P(3)–Pt(4)–P(4)	75.82(5)
Pt(4)–P(3)–Pt(3)	100.13(6)	Pt(4)–P(4)–Pt(3)	100.07(5)

The well-known stability of Pt–C₆F₅ bonds and the Pt(μ-PPh₂)₂Pt skeleton, and the lability of the Pt–N (acetonitrile) bonds, make complex **1** an excellent dinuclear starting material with a 90° angle between the “open-coordination sites”.

Reaction of **1** with 2,2'-Bipyrimidine

In order to explore the potential of complex **1** as a precursor for self-assembly chemistry, we started the study by

substituting the two acetonitrile ligands in **1** with 2,2'-bipyrimidine (bpym), a ligand with four N donor atoms that can be used as a linker of the building blocks.^[29–32] Addition of bpym to an acetone solution of **1** in a 1:2 molar ratio (see Scheme 1) gave the linear tetranuclear complex $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-bpym)Pt(\mu-PPh_2)_2Pt(C_6F_5)_2]$ (**2**). This process is facilitated by both the sp^2 hybridisation at the N atoms, the chelate effect of the ligand and the high insolubility of **2**. Nevertheless, when the ligand is added in a 1:1 molar ratio the dinuclear complex $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(bpym)]$ (**3**) is obtained. The bpym ligand in **3** is coordinated in a terminal chelating mode, and thus the other two N atoms can be used for further coordination. Complex **2** can be obtained by the addition of **1** to solutions of **3** in acetone (1:1 molar ratio).

With the aim of synthesising asymmetric derivatives we added *cis*- $[M(C_6F_5)_2(THF)_2]$ ($M = Pt, Pd$) to CH_2Cl_2 solutions of **3** (1:1 molar ratio); the results are different for $M = Pt$ or Pd . In the first case the two donor N atoms of **3** coordinate to the added platinum centre and the asymmetric, linear, trinuclear derivative $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-bpym)Pt(C_6F_5)_2]$ (**4a**) crystallises from the solution. However, the reaction of **3** with *cis*- $[Pd(C_6F_5)_2(THF)_2]$ does not yield the heteronuclear complex $[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-bpym)Pd(C_6F_5)_2]$ (**4b**) but rather a mixture of **2** and $[(C_6F_5)_2Pd(\mu-bpym)(C_6F_5)_2]$ (**5**),^[33] which were identified by IR spectroscopy. The two complexes can be easily separated from this solid by dissolving **5** in acetone. The 1H NMR spectra of **3** and **4a** show, in addition to PPh_2 groups, three resonances due to the H^4 , H^5 and H^6 atoms of the bpym ligand, as expected for these asymmetric compounds. The ^{19}F NMR spectra of **3** shows three signals (2 *o*-F, 2 *m*-F, *p*-F) due to the equivalence of both C_6F_5 groups, while complex **4a** shows, as expected, the signals due to both types of inequivalent C_6F_5 groups (see Exp. Sect.). The ^{31}P NMR spectra of **3** and **4a** show the same pattern as **1**.

In the IR spectra of complexes **2** and **3** two absorptions of the same intensity due to the X-sensitive mode of the C_6F_5 groups are observed in the 800 cm^{-1} region, in agreement with the presence of the “*cis*- $M(C_6F_5)_2$ ” fragment.^[22,23] For complex **4a** four absorptions due to the two different “*cis*- $M(C_6F_5)_2$ ” fragments are observed. In addition, two intense sharp peaks of nearly equal intensity at approximately 1580 and 1560 cm^{-1} (ring stretching modes of bpym) characterise the terminal-chelating mode of the bpym ligand in complex **3**. The presence of the bis(chelating) mode (complexes **2**, **4a** and **5**), however, is indicated either by an asymmetric doublet or a single strong broad feature in the same range.^[34]

All our attempts to obtain a single crystal of the tetranuclear complex **2** suitable for X-ray diffraction purposes failed, probably due to its insolubility. Although we obtained single crystals of the asymmetric complex **4a** and collected data for two different crystals, in both cases the value of R was not satisfactory, thus the structure of **4a** cannot be fully described. However, the skeleton of the molecule and the connectivity of the atoms are as expected.

Reaction of **1** with Cyanide

The cyanide ligand can act as a linear linker in polynuclear systems that exhibit fascinating structures and properties.^[35–41] Although the design of molecular entities has produced large rings, stars, boxes, cages and clusters involving cyanide bridging ligands, only a few examples with platinum centres in their structure have been reported.^[42–47] With the aim of synthesising other homo- or heteronuclear square molecules we decided to use the cyanide ligand as: a) it can easily act as a terminal ligand, thus allowing a designed synthesis through a two-pot process; b) although some bent cyanide bridges are known,^[48] this group is usually rigid and linear when acting as a bridging ligand; and c) their anionic nature allows the synthesis of anionic molecular squares. Although we have recently reported some examples of anionic heterometallic squares,^[42] these molecules are usually neutral or cationic with a high charge.

The addition of KCN to acetone solutions of **1** in a 2:1 molar ratio (a methyltriphenylphosphonium salt was also added to facilitate the crystallisation) yielded the dinuclear complex $[PPh_3(CH_3)]_2[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(CN)_2]$ (**6**) in which the cyanide groups act as terminal ligands. The two N atoms of **6** are bonded to other *cis*-blocked metal centres to form the expected squares. The reaction of *cis*- $[M(C_6F_5)_2(THF)_2]$ ($M = Pt, Pd$) with CH_2Cl_2 solutions of the metalloligand **6** (1:1 molar ratio) gave the hexanuclear anionic macrocycles $[PPh_3(CH_3)]_4\{[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-CN)_2M(C_6F_5)_2]_2\}$ ($M = Pt, 7; Pd, 8$). Similarly, the reaction of **6** and **1** (1:1 molar ratio) afforded the octanuclear complex $[PPh_3(CH_3)]_4\{[(C_6F_5)_2Pt(\mu-PPh_2)_2Pt(\mu-CN)Pt(\mu-PPh_2)_2Pt(C_6F_5)_2]_2\}$ (**9**; Scheme 1). The ^{19}F NMR spectrum of **6** shows three signals in a 2:2:1 intensity ratio and the low-field signal, due to the *o*-F atoms, shows platinum satellites. This is the expected pattern for **6** in which both C_6F_5 groups are equivalent. In agreement with the formulation given in Scheme 1, the ^{19}F NMR spectrum of **7** exhibits two signals in the *o*-F region (2:2 intensity ratio), two high-field multiplets for the *m*-F (2:2 intensity ratio) and two different signals for the *p*-F atoms (1:1 intensity ratio), thus confirming the presence of two non-equivalent C_6F_5 rings (C_6F_5 *trans* to CN and C_6F_5 *trans* to P). The spectrum of **8** is analogous, but one *m*-F signal appears overlapped with that of the *p*-F one. Moreover, only one signal, with platinum satellites, is observed for the two types of *o*-F atoms (C_6F_5 bonded to platinum or to palladium), thereby indicating that they are isochronous. This was unambiguously confirmed by considering the intensity ratio of the platinum satellites and the central signal (1:10:1). For complex **9**, the two different *o*-F atoms are isochronous and the signals due to *m*-F atoms are overlapped. Nevertheless, the presence of two inequivalent C_6F_5 groups is unambiguously demonstrated by the two well-separated *p*-F signals (see Exp. Sect.). The ^{31}P NMR spectrum of **6** shows one high-field signal with platinum satellites (1:8:17:8:1 intensity ratio) for the P atoms of the diphenylphosphido groups. The two doublets expected for the two isotopomers in which one platinum centre is ^{195}Pt (22.3% abundance each one) are

overlapped, indicating equal coupling constants between the equivalent P atoms and the inequivalent Pt¹ and Pt² centres. This is in agreement with the easily observed signals due to the isotopomer in which the two metal centres are ¹⁹⁵Pt (11.3% abundance). The same spectral pattern is observed for complexes **7** and **8**, thus indicating that the coordination of the N atoms of the CN ligand in **6** to the metal centre of the “*cis*-M(C₆F₅)₂” fragment (M = Pt, Pd) does not perceptibly change the magnetic environment of the Pt¹ and Pt² centres. The octanuclear macrocycle **9** shows two different types of diphenylphosphido ligands: the PPh₂ groups bridging Pt¹ and Pt² centres, both with two Pt–C bonds (fragment from **6**), and the PPh₂ groups bridging Pt³ and Pt⁴ centres, with two Pt³–C and two Pt⁴–N bonds (fragment from **1**). The ³¹P NMR spectrum of **9** exhibits, in the high-field region, two signals with platinum satellites. The signal at $\delta = -161.0$ ppm shows a pattern similar to the one observed for **6–8** and can be assigned to the P atoms of the “Pt¹(μ -PPh₂)₂Pt²” fragment, while two different values of ¹J_{Pt,P} (1899 and 2400 Hz) can be extracted from the signal

at $\delta = -157.9$ ppm; this signal can be assigned to the P atoms of the “Pt³(μ -PPh₂)₂Pt⁴” fragment. The assignment of both ¹J_{Pt,P} values (see Exp. Sect.) was carried out by comparison with the corresponding values observed in **1**, **3** and **4a**.

The relevant feature of the IR spectra of **6–9** is the presence of two sharp absorptions at 2122 and 2113 cm^{−1} in **6** (terminal cyanide), which are assigned to $\nu(\text{C}\equiv\text{N})$, and their significant shift towards higher frequencies in the squares **7**, **8** and **9** (bridging cyanide).^[49] In all cases the absorptions observed in the 800 cm^{−1} region indicate the presence of “*cis*-M(C₆F₅)₂” fragments.^[22,23]

Figure 2a shows the structure of the anion in complex **8**. Selected bond lengths and angles are given in Table 2. The X-ray structure establishes the presence of the hexanuclear complex anion [$\{(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-CN})_2\text{Pd}(\text{C}_6\text{F}_5)_2\}_2]^{4-}$ and four [PPh₃(CH₃)]⁺ cations along with three molecules of acetone and one molecule of *n*-hexane as lattice solvent. The platinum atoms are bonded to two diphenylphosphido ligands, which act as bridges between both metal centres, and to two C₆F₅ ligands in the case of Pt(2) or to two CN bridging ligands in the case of Pt(1). The N atoms of the cyanide are coordinated to the Pd atoms, which complete their coordination with two C₆F₅ groups in *cis* positions. The distances and angles in each coordination sphere are within the expected values. The maximum deviation of the metal atoms with respect to their best least-squares plane is 0.046 Å in the case of Pt(2). The C₆F₅ rings are essentially perpendicular to their coordination planes, with angles ranging from 77.0 to 91.4°. The coordination planes of Pt(1) and Pd(1) are essentially coplanar (4.8°), while the coordination plane of Pt(2) forms an angle of 22.1° with that of Pt(1). The Pt(1) and Pd(1) atoms form an almost perfect square, with edges of 5.19 and 5.21 Å, in which the CN ligands are located, defining an open cavity which is not large enough to accommodate the bulky cations or solvent molecules (see Figure 2b).

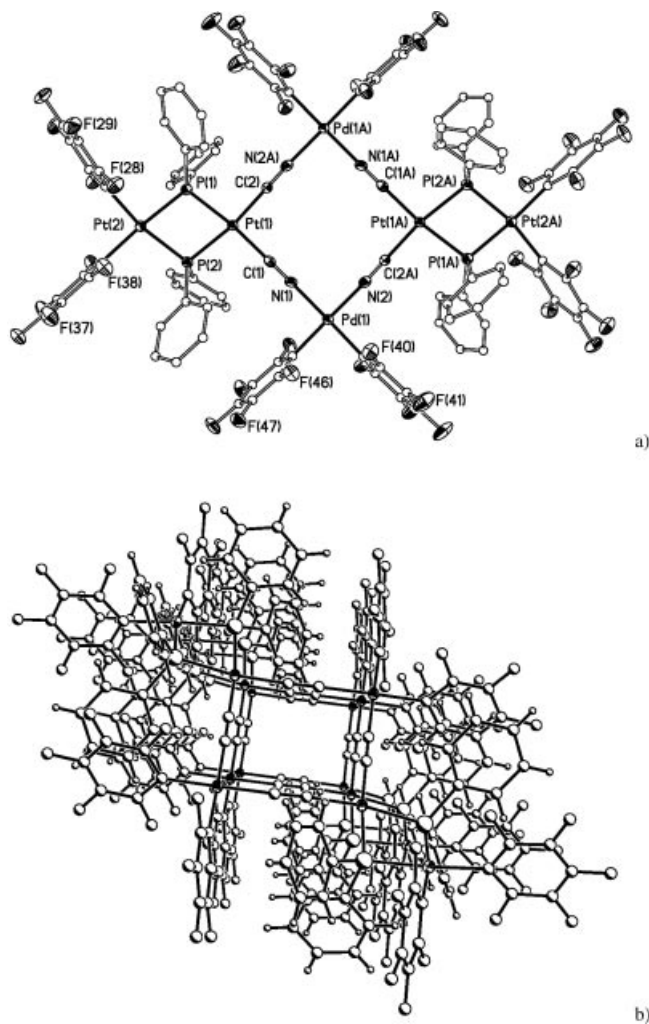


Figure 2. a) Structure of the anion of [PPh₃Me]₄[$\{(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-CN})_2\text{Pd}(\text{C}_6\text{F}_5)_2\}_2]^{4-}$ (**8**). b) Packing diagram of the anions in **8**, showing how the cores of the molecular squares stack to form an infinite tunnel.

Table 2. Selected bond lengths [Å] and angles [°] for [$\{(\text{PPh}_3\text{Me})_2\text{-}[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-CN})_2\text{Pd}(\text{C}_6\text{F}_5)_2]_2\} \cdot 3\text{Me}_2\text{CO} \cdot n\text{-hexane}$ (**8**·3Me₂CO·*n*-hexane)].

Pt(1)–C(2)	1.999(5)	Pt(2)–P(2)	2.3111(14)
Pt(1)–C(1)	2.016(5)	Pd(1)–C(39)	1.990(5)
Pt(1)–P(1)	2.3105(14)	Pd(1)–C(45)	1.993(5)
Pt(1)–P(2)	2.3198(13)	Pd(1)–N(2)	2.045(4)
Pt(2)–C(27)	2.064(5)	Pd(1)–N(1)	2.045(5)
Pt(2)–C(33)	2.069(5)	N(1)–C(1)	1.149(7)
Pt(2)–P(1)	2.2944(13)	N(2)–C(2') ^[a]	1.149(6)
C(2)–Pt(1)–C(1)	91.5(2)	C(33)–Pt(2)–P(2)	99.66(14)
C(2)–Pt(1)–P(1)	95.34(14)	P(1)–Pt(2)–P(2)	76.30(5)
C(1)–Pt(1)–P(1)	172.75(14)	C(39)–Pd(1)–C(45)	88.1(2)
C(2)–Pt(1)–P(2)	171.14(14)	C(39)–Pd(1)–N(2)	91.42(18)
C(1)–Pt(1)–P(2)	97.32(14)	C(45)–Pd(1)–N(2)	177.69(19)
P(1)–Pt(1)–P(2)	75.82(5)	C(39)–Pd(1)–N(1)	177.5(2)
C(27)–Pt(2)–C(33)	90.78(19)	C(45)–Pd(1)–N(1)	90.99(18)
C(27)–Pt(2)–P(1)	93.16(14)	N(2)–Pd(1)–N(1)	89.57(16)
C(33)–Pt(2)–P(1)	175.78(14)	Pt(2)–P(1)–Pt(1)	101.85(5)
C(27)–Pt(2)–P(2)	168.51(14)	Pt(2)–P(2)–Pt(1)	101.06(5)

[a] Symmetry transformation used to generate the equivalent atom C(2'): $-x + 1, -y + 1, -z + 1$.

We also tried to obtain an X-ray structure of complex **9** but unfortunately only poor quality crystals were obtained after many crystallisation attempts. The X-ray data measured with the diffractometer had a very low intensity, which was almost non-existent at 2θ angles $> 40^\circ$. Thus, only a set of poor quality data could be obtained and therefore only the connectivity of the complex was established. The skeleton is rather different to that of **8** since the central core is not planar but angular, as schematized in Figure 3.

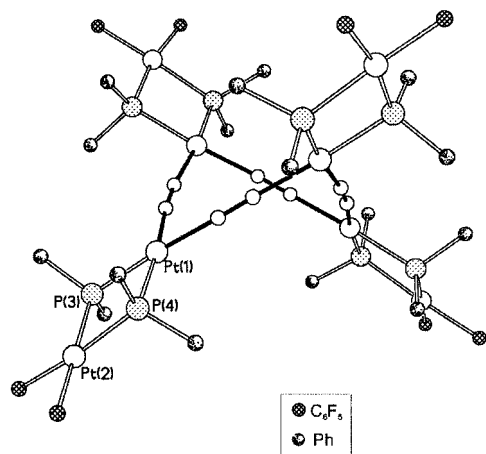


Figure 3. Structure of the anion of $[\text{PPh}_3\text{Me}]_4[\{(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{-Pt}(\mu\text{-CN})_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2\}]$ (**9**).

Conclusion

Complex **1**, in which the two acetonitrile ligands can be easily replaced, can be considered as a neutral dinuclear building block with “open-coordination sites” at 90° . The study involves the design of one-dimensional complexes with both diphenylphosphido and bpym ligands and two-dimensional molecules with diphenylphosphido and cyanide ligands. The anionic dinuclear complex **6** is used as a metalloligand towards neutral mononuclear or dinuclear species. This is a straightforward route for the preparation of homo- or heterometallic species. The choice of neutral entities, “ $(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}$ ” and “ $\text{M}(\text{C}_6\text{F}_5)_2$ ”, and an anionic linker, cyanide, allowed us to synthesize the tetra-anionic squares **7**, **8** and **9**, even though the complexes with this molecular architecture that have been reported so far are usually cationic or neutral species.

Experimental Section

General Procedures: C, H and N analysis was performed with a Perkin–Elmer 240B microanalyser. IR spectra were recorded with a Perkin–Elmer Spectrum One spectrophotometer (Nujol mulls between polyethylene plates in the range $4000\text{--}350\text{ cm}^{-1}$). NMR spectra were recorded with a Varian Unity 300 instrument with SiMe_4 , CFCl_3 and $85\% \text{ H}_3\text{PO}_4$ as external references for ^1H , ^{19}F and ^{31}P , respectively. Conductivities (acetone, $c \approx 5 \times 10^{-4} \text{ M}$) were measured with a Philips PW 9509 conductimeter. Literature methods were

used to prepare the starting materials $[\text{Bu}_4\text{N}][\{(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{-Pt}(\mu\text{-Cl})\}_2]$ ^[21] and *cis*- $[\text{M}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ ($\text{M} = \text{Pt}, \text{Pd}$).^[50]

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparation of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{NCCH}_3)_2]$ (1**):** AgClO_4 (0.150 g, 0.723 mmol) was added to a solution of $[\text{Bu}_4\text{N}][\{(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-Cl})\}_2]$ (1.000 g, 0.364 mmol) in acetone (10 mL) and acetonitrile (10 mL). The mixture was stirred at room temperature for 4 h, filtered, and the resulting solution was concentrated to ca. 5 mL, whereupon **1** crystallised as a white solid. *i*PrOH (5 mL) was added and the mixture was stirred for 1 h. Complex **1** was collected by filtration and washed with 2 mL of *i*PrOH. Yield: 0.651 g (76%). $\text{C}_{40}\text{H}_{26}\text{F}_{10}\text{N}_2\text{P}_2\text{Pt}_2$ (1176.8): calcd. C 40.82, H 2.22, N 2.38; found C 40.98, H 2.03, N 2.59. IR (nujol mull): $\tilde{\nu} = 782$ and 774 (X-sensitive C_6F_5 group),^[22,23] 2323 , 2294 ($\text{N}\equiv\text{C}$) cm^{-1} . ^{19}F NMR (282.4 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -166.0$ (6 *m*- + *p*-F), -114.7 ($^3J_{\text{Pt,F}} = 301 \text{ Hz}$, 4 *o*-F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -143.8$ ($J_{\text{Pt}^1,\text{P}} = 1927$, $J_{\text{Pt}^2,\text{P}} = 2454 \text{ Hz}$) ppm.

Preparation of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-bpym})\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ (2**):** 2,2'-bpym (0.013 g, 0.084 mmol) was added, with stirring, to a colourless solution of **1** (0.200 g, 0.169 mmol) in acetone (15 mL) and **2** began to precipitate as a yellow solid. After 45 min stirring, **2** was filtered off, washed with 1 mL of acetone and vacuum-dried. Yield: 0.161 g (81%). $\text{C}_{80}\text{H}_{46}\text{F}_{20}\text{N}_4\text{P}_4\text{Pt}_4$ (2347.6): calcd. C 41.00, H 1.97, N 2.38; found C 41.49, H 1.84, N 2.17. IR (nujol mull): $\tilde{\nu} = 784$, 776 (X-sensitive C_6F_5 group), 1581 (bpym) cm^{-1} . Complex **2** is not soluble enough in usual organic solvents for NMR studies.

Preparation of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-bpym})]$ (3**):** 2,2'-bpym (0.013 g, 0.084 mmol) was added to a colourless solution of **1** (0.100 g, 0.084 mmol) in acetone (15 mL). After 15 h of stirring at room temperature, the orange solution was concentrated almost to dryness and CHCl_3 (3 mL) was added while stirring. Complex **3** crystallised as a yellow solid, which was filtered off and washed with 1 mL of CHCl_3 . Yield: 0.085 g (81%). $\text{C}_{44}\text{H}_{26}\text{F}_{10}\text{N}_4\text{P}_4\text{Pt}_2$ (1252.9): calcd. C 42.14, H 2.07, N 4.47; found C 41.74, H 1.85, N 4.16. IR (nujol mull): $\tilde{\nu} = 783$, 775 (X-sensitive C_6F_5 group), 1580 , 1556 (bpym) cm^{-1} . ^1H NMR (300 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = 7.68$ (t, $J_{\text{H}^5,\text{H}^4,6} = 5.2 \text{ Hz}$, 2 H^5 -bpym), 8.36 (br. d, 2 H^6 -bpym), 9.32 (br. d, 2 H^4 -bpym) ppm. ^{19}F NMR (282.4 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -166.1$ (2 *p*-F), -165.9 (4 *m*-F), -114.2 ($^3J_{\text{Pt,F}} = 301 \text{ Hz}$, 4 *o*-F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -125.6$ ($J_{\text{Pt}^1,\text{P}} = 1859$, $J_{\text{Pt}^2,\text{P}} = 2390 \text{ Hz}$) ppm.

Preparation of $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-bpym})\text{Pt}(\text{C}_6\text{F}_5)_2]$ (4a**):** *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ (0.053 g, 0.078 mmol) was added to a yellow solution of **3** (0.100 g, 0.079 mmol) in CH_2Cl_2 (10 mL). The colour of the solution changed to brown, while a solid began to crystallise. After 15 min of stirring, the brown solid **4a** was filtered off and washed with 1 mL of CH_2Cl_2 . Yield: 0.071 g (50%). $\text{C}_{56}\text{H}_{26}\text{F}_{20}\text{N}_4\text{P}_3\text{Pt}_3$ (1782.1): calcd. C 37.70, H 1.45, N 3.10; found C 37.90, H 1.47, N 2.74. IR (nujol mull): $\tilde{\nu} = 816$, 808 , 782 , 774 (X-sensitive C_6F_5 group), 1585 (bpym) cm^{-1} . ^1H NMR (300 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = 8.00$ (t, $J_{\text{H}^5,\text{H}^4,6} = 5.4 \text{ Hz}$, 2 H^5 -bpym), 8.58 (br. d, 2 $\text{H}^{6/4}$ -bpym), 9.08 (br. d, 2 $\text{H}^{4/6}$ -bpym) ppm. ^{19}F NMR (282.4 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -168.0$ (6 *m* + *p*-F), -166.0 (4 *m*-F), -163.5 (2 *p*-F), -120.1 ($^3J_{\text{Pt,F}} = 459 \text{ Hz}$, 4 *o*-F), -116.0 ($^3J_{\text{Pt,F}} = 300 \text{ Hz}$, 4 *o*-F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -128.6$ ($J_{\text{Pt}^1,\text{P}} = 1868$, $J_{\text{Pt}^2,\text{P}} = 2414 \text{ Hz}$) ppm.

Preparation of $[\text{PPh}_3(\text{CH}_3)_2][(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{CN})_2]$ (6**):** KCN (0.030 g, 0.460 mmol) was added to a solution of **1** (0.200 g,

0.170 mmol) in acetone (10 mL) and the mixture was stirred at room temperature for 15 h. $[\text{PPh}_3(\text{CH}_3)]\text{ClO}_4$ (0.128 g, 0.339 mmol) was then added and the mixture was concentrated to dryness. CH_2Cl_2 (10 mL) was added to the white residue and then filtered. The solution was concentrated to ca. 1 mL, *i*PrOH (10 mL) was added and **6** crystallised as a white solid which was filtered off, washed with 2 mL of *i*PrOH and vacuum-dried. Yield: 0.211 g (73%). $\text{C}_{76}\text{H}_{56}\text{F}_{10}\text{N}_2\text{P}_4\text{Pt}_2$ (1701.38): calcd. C 53.65, H 3.31, N 1.64; found C 53.80, H 2.98, N 1.60. IR (nujol mull): $\tilde{\nu} = 782, 773$ (X-sensitive C_6F_5 group), 2122, 2113 $\nu(\text{C}\equiv\text{N}) \text{ cm}^{-1}$. $A_M = 91 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^{19}F NMR (282.4 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -166.4$ (2 *p*-F), -164.6 (4 *m*-F), -111.7 ($^3J_{\text{Pt},\text{F}} = 323 \text{ Hz}$, 4 *o*-F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -150.3$ ($J_{\text{Pt}^{1,2},\text{P}} = 1820 \text{ Hz}$, PPh_2), 27.2 (PPh_3CH_3) ppm.

Preparation of $[\text{PPh}_3\text{CH}_3]_4\{(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-CN})_2\text{M}(\text{C}_6\text{F}_5)_2\}_2$. M = Pt (7): *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ (0.060 g, 0.089 mmol) was added to a solution of **6** (0.150 g, 0.088 mmol) in CH_2Cl_2 (10 mL) and the solution was stirred for 1.5 h. The solvent was evaporated to leave 2 mL while a white solid began to crystallise and CHCl_3 (5 mL) was added. Complex **7** was filtered off and washed with 1 mL of cold CHCl_3 . Yield: 0.134 g (68%). $\text{C}_{176}\text{H}_{112}\text{F}_{40}\text{N}_4\text{P}_8\text{Pt}_6$ (4461.2): calcd. C 47.38, H 2.53, N 1.25; found C 47.03, H 2.03, N 1.19. IR (nujol mull): $\tilde{\nu} = 810, 800, 783, 773$ (X-sensitive C_6F_5 group), 2164 br. $\nu(\text{C}\equiv\text{N}) \text{ cm}^{-1}$. $A_M = 106 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^{19}F NMR (282.4 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -166.8$ (4 *p*-F), -166.6 (4 *p*-F), -166.3 (8 *m*-F), -166.1 (8 *m*-F), -117.7 ($^3J_{\text{Pt},\text{F}} = 505 \text{ Hz}$, 8 *o*-F), -114.4 ($^3J_{\text{Pt},\text{F}} = 333 \text{ Hz}$, 8 *o*-F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -157.2$ ($J_{\text{Pt}^{1,2},\text{P}} = 1831 \text{ Hz}$, PPh_2), 23.1 (PPh_3CH_3) ppm. **M = Pd (8):** This complex was obtained [yield: 0.070 g (56%)] according to a similar procedure to that used for **7** from **6** (0.100 g, 0.058 mmol) and *cis*- $[\text{Pd}(\text{C}_6\text{F}_5)_2(\text{THF})_2]$ (0.034 g, 0.058 mmol). $\text{C}_{176}\text{H}_{112}\text{F}_{40}\text{N}_4\text{P}_8\text{Pd}_2\text{Pt}_4$

(4283.8): calcd. C 49.35, H 2.63, N 1.31; found C 49.57, H 2.44, N 1.25. IR (nujol mull): $\tilde{\nu} = 797, 784, 774$ (X-sensitive C_6F_5 group), 2164, 2157 $\nu(\text{C}\equiv\text{N}) \text{ cm}^{-1}$. $A_M = 162 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^{19}F NMR (282.4 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -166.0$ (4 *p*-F), -164.5 (8 *m*-F), -163.1 (12 *m* + *p*-F), -112.2 (8 *o*-F), -112.2 ($^3J_{\text{Pt},\text{F}} = 328 \text{ Hz}$, 8 *o*-F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -154.8$ ($J_{\text{Pt}^{1,2},\text{P}} = 1835 \text{ Hz}$, PPh_2), 26.9 (PPh_3CH_3) ppm.

Preparation of $[\text{PPh}_3\text{CH}_3]_4\{(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-CN})\}_4$ (9): Complex **1** (0.056 g, 0.048 mmol) was added to a solution of **6** (0.080 g, 0.048 mmol) in acetone (10 mL) and the solution was stirred at room temperature for 15 h. The solvent was evaporated to leave ca. 2 mL and CHCl_3 (8 mL) was added and the mixture concentrated to ca. 5 mL. Complex **9** crystallised as a white solid which was filtered off and washed with 1 mL of CHCl_3 . Yield: 0.076 g (57%). $\text{C}_{224}\text{H}_{152}\text{F}_{40}\text{N}_4\text{P}_{12}\text{Pt}_8$ (5592.2): calcd. C 48.12, H 2.70, N 1.00; found C 48.30, H 2.31, N 0.77. IR (nujol mull): $\tilde{\nu} = 781, 771$ (X-sensitive C_6F_5 group), 2152 br. $\nu(\text{C}\equiv\text{N}) \text{ cm}^{-1}$. $A_M = 91 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^{19}F NMR (282.4 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -167.5$ (4 *p*-F), -167.3 (4 *p*-F), -166.2 (12 *m*-F), -165.6 (4 *m*-F), -114.0 ($^3J_{\text{Pt},\text{F}} = 317 \text{ Hz}$, 16 *o*-F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, $[\text{D}_6]\text{acetone}$, 22°C): $\delta = -161.0$ ($J_{\text{Pt}^{1,2},\text{P}} = 1843 \text{ Hz}$, PPh_2), -157.9 ($J_{\text{Pt}^3,\text{P}} = 1899$, $J_{\text{Pt}^4,\text{P}} = 2400 \text{ Hz}$, PPh_2), 23.0 (PPh_3CH_3) ppm.

Structural Analysis of Complexes 1·Me₂CO and 8·3Me₂CO·*n*-hexane: Crystal data and other details of the structure analysis are presented in Table 3. Single crystals were mounted on quartz fibres in a random orientation and held in place with a fluorinated oil. Data collection was performed at 100 K with a Bruker Smart CCD diffractometer using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) with a nominal crystal-to-detector distance of 6.0 cm. Unit-cell dimensions were determined on the basis of the positions of 9622 (**1**) or 7283 (**8**) reflections from the main dataset. For **1**, a hemisphere of data, based on three ω -scans runs (starting $\omega =$

Table 3. Crystal data and structure refinement for $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{NCCH}_3)_2]\cdot\text{Me}_2\text{CO}$ (**1**·Me₂CO) and $\{(\text{PPh}_3\text{Me})_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-CN})_2\text{Pd}(\text{C}_6\text{F}_5)_2]\}_2\cdot 3\text{Me}_2\text{CO}\cdot n\text{-hexane}$ (**8**·3Me₂CO·*n*-hexane).

	1 ·Me ₂ CO	8 ·3Me ₂ CO· <i>n</i> -hexane
Empirical formula	$\text{C}_{40}\text{H}_{26}\text{F}_{10}\text{N}_2\text{P}_2\text{Pt}_2\cdot\text{Me}_2\text{CO}$	$\text{C}_{176}\text{H}_{112}\text{F}_{40}\text{N}_4\text{P}_8\text{PdPt}_2\cdot 3\text{Me}_2\text{CO}\cdot n\text{-hexane}$
Formula mass	1234.83	4544.04
<i>T</i> [K]	100(1)	100(1)
λ [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$\bar{P}$
<i>a</i> [Å]	12.2295(6)	15.0079(6)
<i>b</i> [Å]	39.6985(18)	19.0293(8)
<i>c</i> [Å]	17.1613(8)	19.1387(8)
α [°]	90	83.089(1)
β [°]	100.560(1)	97.706(11)
γ [°]	90	86.530(1)
<i>V</i> [Å ³]	8190.6(7)	4763.2(3)
<i>Z</i>	8	1
<i>D_c</i> [g cm ⁻³]	2.003	1.584
μ (Mo- K_α) [mm ⁻¹]	6.986	3.269
θ range [°]	1.03–25.04	1.73–28.53
Data collected	48272	44051
Independent data (<i>R</i> _{int})	14445 (0.0463)	21666 (0.0306)
Data/restraints/parameters	14445/0/1085	21666/0/1154
Goodness-of-fit on F^2 ^[a]	1.047	0.980
Final <i>R</i> indices [$I > 2\sigma(I)$] ^[b]	$R_1 = 0.0315$ $wR_2 = 0.0697$	$R_1 = 0.0389$ $wR_2 = 0.1001$
<i>R</i> indices (all data)	$R_1 = 0.0409$ $wR_2 = 0.0730$	$R_1 = 0.0551$ $wR_2 = 0.1046$

[a] Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{0.5}$. [b] $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

–28°) at φ values 0, 90, and 180 with the detector at $2\theta = 28^\circ$, was collected. At each of these runs, frames (606, 435 and 230 respectively) were collected at 0.3° intervals and 10 s per frame. For **8**, a complete sphere of data was collected based on three ω -scans runs at φ values of 0, 120 and 240. At each of these runs, 606 frames were collected at 0.3° intervals and 30 s per frame. The diffraction frames were integrated using the SAINT package^[51] and corrected for absorption with SADABS.^[52] Lorentz and polarisation corrections were also applied. The structures were solved by direct methods. All non-hydrogen atoms of the complexes were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement parameters equal to 1.2- or 1.5-times the U_{iso} values of their respective parent atoms. After all atoms of the molecules had been located, there still remained some areas of electron density that were modelled as the lattice solvent. Final difference electron density maps showed, only in the case of **8**, some peaks above $1 \text{ e}\text{\AA}^{-3}$ (max. 2.69, largest diff. hole –1.07), most of them close to the heavy metal atoms and with no chemical meaning, others were located in the solvent area. The crystals lost solvent very rapidly and because of this their quality was not good. The structures were refined using the SHELXL-97 program.^[53] CCDC-268963 (**1**) and -268963 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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