

# Synthesis of Neutral and Anionic Tetranuclear Clusters $[\text{Pt}_4(\mu_2\text{-PPh}_2)_3\{\mu_3\text{-PPh}(1,2\text{-}\eta^2\text{-Ph})\text{-}\kappa^3\text{P}\}(\text{C}_6\text{F}_5)_4\text{L}]$ and $[\text{NBu}_4][\text{Pt}_4(\mu_2\text{-PPh}_2)_3\{\mu_3\text{-PPh}(1,2\text{-}\eta^2\text{-Ph})\text{-}\kappa^3\text{P}\}(\text{C}_6\text{F}_5)_5]$ Containing Five Coordinate P Atoms and Two Pt–Pt Bonds<sup>§</sup>

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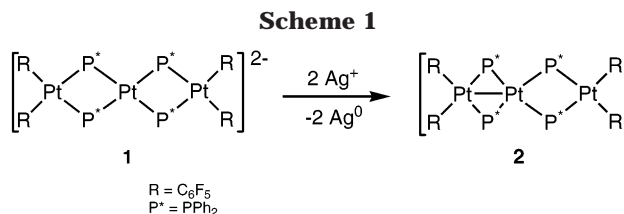
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The reaction of  $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$  with *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$  (molar ratio 1:2) in  $\text{CH}_2\text{Cl}_2$  gives  $[\text{NBu}_4]_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_4]$  and  $[\text{NBu}_4][\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_5]$  (**4**). Its molecular X-ray structure reveals that it is a tetranuclear complex with two Pt–Pt bonds and an unusual  $\mu_3\text{-PPh}_2$  ligand, which has a  $\eta^2\text{-phenyl}$  interaction with one of the platinum centers. Complex **4** reacts with  $\text{HClO}_4$  to form  $[\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_4]$ , **5**, which contains three Pt–Pt bonds and a  $\mu_3\text{-PPh}_2$  bridging ligand. **5** reacts with L (L =  $\text{PPh}_3$ , py) to yield the neutral  $[\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_4\text{L}]$  (**6** and **7**), with structures similar to **4**.

## Introduction

The phosphido ligands are excellent building blocks for the synthesis of polynuclear complexes since they form very stable M–P bonds, and they are also flexible ligands able to bridge metal centers across a wide range of distances.<sup>1–9</sup>

Recently we have reported the synthesis of the trinuclear Pt(II) derivative  $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ , **1**, which with 48 valence electron count does not require and does not display any Pt–Pt bond. Oxidation of **1** with  $\text{Ag}^+$  results in the formation of  $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ , **2**, a novel trinuclear compound in which the Pt centers display an average formal oxidation state of 2.67 and that as expected for a 46 valence electron count has one Pt–Pt bond.<sup>10</sup> Scheme 1 shows the skeleton of both the Pt(II)



and the Pt(III, III, II) complexes.

The formation of M–M bonds in these phosphido complexes is driven by the elimination of skeletal electrons either through oxidation processes,<sup>10,11</sup> as is the case of the transformation of **1** in **2**, or by eliminating ligands.<sup>12</sup>

In previous work we have observed that *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$  is an excellent  $\text{C}_6\text{F}_5$  scavenger, which reacts with  $[\text{NBu}_4]_2[\text{M}(\text{C}_6\text{F}_5)_4]$ , forming the binuclear  $[\text{NBu}_4]_2[\text{M}(\text{Pt}(\mu\text{-C}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_4)]$  (M = Pd, Pt) anions containing unusual bridging  $\text{C}_6\text{F}_5$  ligands<sup>13</sup> (see Scheme 2a). In the same context,  $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$  reacts with *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ , yielding the trinuclear  $[\text{NBu}_4][\text{Pt}_3(\mu\text{-PPh}_2)_2(\text{C}_6\text{F}_5)_5]$ , **3**<sup>14</sup> (see Scheme 2b), which can be considered as being formed by interaction between “ $(\text{C}_6\text{F}_5)\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)$ ” and  $[\text{Pt}(\text{C}_6\text{F}_5)_3]^-$ , this being a way to increase the number of the metal atoms in the cluster and to create metal–metal bonds.

<sup>§</sup> Polynuclear Homo- or Heterometallic Palladium(II)–Platinum(II) Pentafluorophenyl Complexes Containing Bridging Diphenylphosphido Ligands. 12. For part 11 see ref 40.

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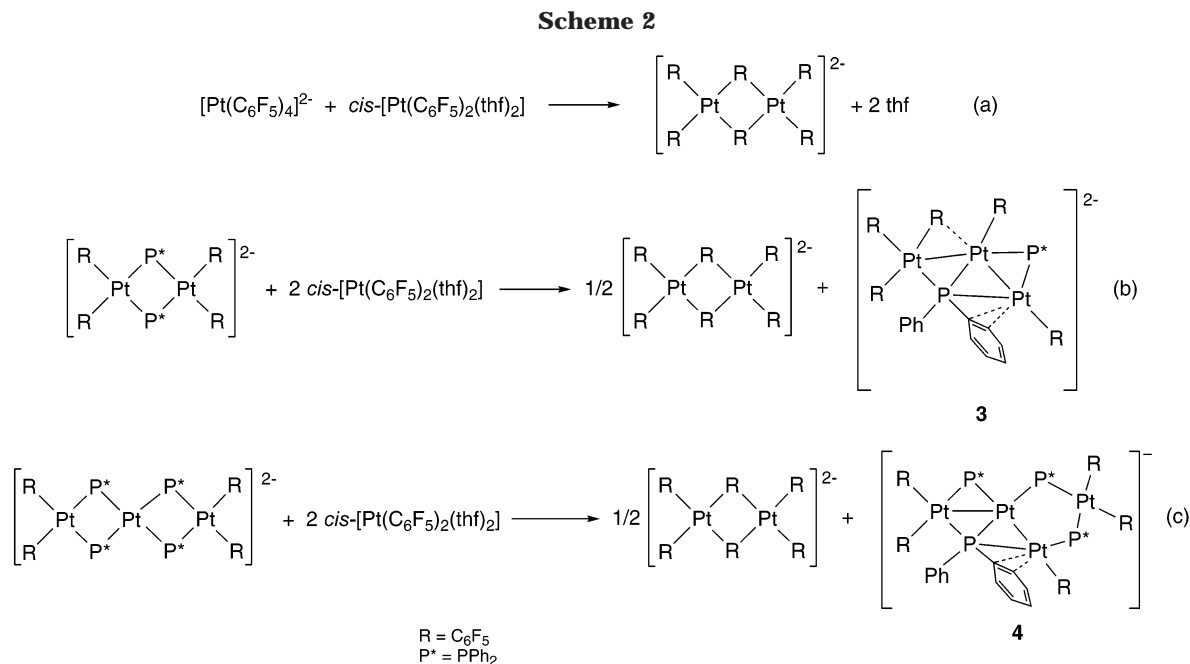
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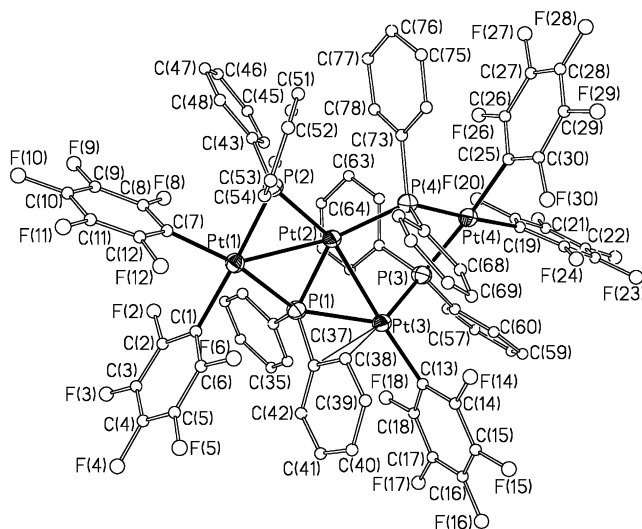


In this paper we report the reaction of  $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$  with  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ , which results in the formation of an unusual tetranuclear Pt<sub>4</sub> cluster with two Pt–Pt bonds and its transformation.

## Results and Discussion

The reaction of a yellow suspension of the symmetric  $[\text{NBu}_4]_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$  in  $\text{CH}_2\text{Cl}_2$  with  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$  in 1:2 molar ratio produces a yellow solution, from which  $[\text{NBu}_4]_2[\text{Pt}_2(\mu\text{-C}_6\text{F}_5)_2(\text{C}_6\text{F}_5)_4]$  and  $[\text{NBu}_4][\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_5]$ , **4**, are isolated. However the low solubility of the starting material in  $\text{CH}_2\text{Cl}_2$  prevents total reaction, and even when using longer reaction times, the yield of **4** is very poor (8%). It can be improved to 40% when  $\text{Li}_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{C}_6\text{F}_5)_2]$ , prepared in situ, is used as starting material, thf is used as solvent, and  $\text{NBu}_4\text{ClO}_4$  is added to the reaction mixture to facilitate crystallization of the resulting product. Scheme 2c summarizes the course of the reaction. The structure of the tetrametallic anion **4** has been established by an X-ray diffraction study.

**Crystal Structure of  $[\text{NBu}_4][\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_5]$  (**4**·2CH<sub>2</sub>Cl<sub>2</sub>).** The structure of the complex anion of **4** along with the atom-labeling scheme is shown in Figure 1. Selected bond distances and angles are listed in Table 1. It contains four platinum atoms joined by diphenylphosphido bridging ligands and two metal–metal bonds. The four platinum atoms lie almost perfectly in a plane, but most of the C and P atoms bonded to the metals are not contained in this plane. The tetranuclear anion can be described as being formed by coupling of two dinuclear fragments: one containing Pt(1) and Pt(2) and the other containing Pt(3) and Pt(4) atoms. Pt(1) and Pt(2) are directly bonded to each other and doubly bridged by two PPh<sub>2</sub> ligands [Pt(1)–Pt(2) distance 2.766(1) Å]. The short Pt(1)–Pt(2) distance requires small Pt(1)–P(1,2)–Pt(2) angles, 72.73(8)° and 74.68(9)°, respectively. The Pt(1) environment



**Figure 1.** Structure of the complex anion of  $[\text{NBu}_4][\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_5]$  (**4**).

is completed by two pentafluorophenyl groups in *cis* positions, giving rise to a “ $(\text{C}_6\text{F}_5)_2\text{Pt}(1)(\mu\text{-PPh}_2)_2\text{Pt}(2)$ ” fragment. This fragment has been frequently found in other clusters of this type such as  $[\text{PtM}(\mu\text{-PPh}_2)_2(\text{C}_6\text{F}_5)_2\text{-PPh}_3]$  (M = Pd, Pt),<sup>12</sup>  $[\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_4(\text{CO})_2]$ ,<sup>15,16</sup>  $[\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_4]$ ,<sup>16</sup> and  $[\text{Pt}_4(\mu\text{-PPh}_2)_4(\text{C}_6\text{F}_5)_4(\text{bipy})]$ .<sup>16</sup> The other part of the anion is formed by Pt(3) and Pt(4), which are held together by a bridging P(3)Ph<sub>2</sub> group which is not supporting a Pt–Pt bond [Pt(3)···Pt(4) distance 3.839(1) Å], and consequently the Pt(3)–P(3)–Pt(4) angle is large, 112.87(12)°. The binuclear fragments are connected in a rather peculiar manner since Pt(4) is bound to Pt(2) only through a bridging P(4)Ph<sub>2</sub> ligand which shows a very large Pt(2)–P(4)–Pt(4) angle (120.45(12)°), corresponding to the long Pt(2)···Pt(4) distance, 4.020(1) Å. Pt(3) is bound to the Pt(1)Pt(2)

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**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex [NBu<sub>4</sub>][Pt<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>5</sub>(μ-PPh<sub>2</sub>)<sub>4</sub>]·2CH<sub>2</sub>Cl<sub>2</sub> (4·2CH<sub>2</sub>Cl<sub>2</sub>)**

Pt(1)–C(7)	2.071(12)	Pt(1)–C(1)	2.141(12)	Pt(1)–P(2)	2.317(3)
Pt(1)–P(1)	2.370(3)	Pt(1)–Pt(2)	2.7660(7)	Pt(2)–P(2)	2.242(3)
Pt(2)–P(1)	2.294(3)	Pt(2)–P(4)	2.313(3)	Pt(2)–Pt(3)	2.8301(7)
Pt(3)–C(13)	2.077(12)	Pt(3)–P(3)	2.279(3)	Pt(3)–P(1)	2.419(3)
Pt(3)–C(37)	2.457(12)	Pt(3)–C(38)	2.574(12)	Pt(4)–C(19)	2.079(14)
Pt(4)–C(25)	2.081(12)	Pt(4)–P(4)	2.318(3)	Pt(4)–P(3)	2.328(3)
P(1)–C(31)	1.833(12)	P(1)–C(37)	1.836(13)		
C(7)–Pt(1)–C(1)	85.8(5)	C(7)–Pt(1)–P(2)	89.2(3)		
C(1)–Pt(1)–P(2)	170.3(3)	C(7)–Pt(1)–P(1)	163.9(3)		
C(1)–Pt(1)–P(1)	83.1(3)	P(2)–Pt(1)–P(1)	103.36(11)		
P(2)–Pt(2)–P(1)	108.31(11)	P(2)–Pt(2)–P(4)	108.50(11)		
P(1)–Pt(2)–P(4)	142.25(11)	P(2)–Pt(2)–Pt(1)	53.89(8)		
P(2)–Pt(2)–Pt(3)	161.90(9)	P(1)–Pt(2)–Pt(3)	55.14(8)		
P(4)–Pt(2)–Pt(3)	87.22(8)	Pt(1)–Pt(2)–Pt(3)	108.50(2)		
C(13)–Pt(3)–P(3)	98.3(4)	C(13)–Pt(3)–P(1)	132.7(3)		
P(3)–Pt(3)–P(1)	117.68(12)	C(13)–Pt(3)–Pt(2)	168.7(4)		
P(3)–Pt(3)–Pt(2)	86.49(8)	P(1)–Pt(3)–Pt(2)	51.10(7)		
C(19)–Pt(4)–C(25)	87.2(5)	C(19)–Pt(4)–P(4)	177.7(4)		
C(25)–Pt(4)–P(4)	90.8(3)	C(19)–Pt(4)–P(3)	91.9(4)		
C(25)–Pt(4)–P(3)	173.9(4)	P(4)–Pt(4)–P(3)	89.98(11)		
C(31)–P(1)–C(37)	112.0(6)	Pt(2)–P(1)–Pt(1)	72.73(8)		
Pt(2)–P(1)–Pt(3)	73.76(9)	Pt(1)–P(1)–Pt(3)	143.06(14)		
Pt(2)–P(2)–Pt(1)	74.68(9)	Pt(3)–P(3)–Pt(4)	112.87(14)		
Pt(2)–P(4)–Pt(4)	120.45(13)				

fragment in a rather more complicated way since it has a Pt(2)–Pt(3) bond (Pt(2)–Pt(3) distance 2.830(1) Å) and the P(1)Ph<sub>2</sub> ligand that bridges Pt(1) and Pt(2) is also bonded to Pt(3). The way in which this phosphido ligand interacts with Pt(3) deserves some comments. An η<sup>2</sup>-interaction between the C<sub>ipso</sub> and C<sub>ortho</sub> atoms of one of the phenyl rings and Pt(3) is formed, the interatomic distances being Pt(3)–C(37) 2.457(12) Å and Pt(3)–C(38) 2.574(12) Å. This interaction does not perceptibly affect the P–C and C–C distances within this group.<sup>17–23</sup> The structural role of the phosphorus atom of this P(1)–Ph<sub>2</sub> ligand is remarkable since it is formally acting as a bridge between three Pt atoms, Pt(1), Pt(2), and Pt(3). The three P(1) distances range from 2.294(3) to 2.419(3) Å, the longest being that to Pt(3). The μ<sub>3</sub>-PPh(1,2-η<sup>2</sup>-Ph)-κ<sup>3</sup>P coordination of the P(1) phosphido anion ligand, which donates six electrons to the metal skeleton through Pt–P bonds and the η<sup>2</sup>-coordination of the phenyl group, is not frequent. Some complexes in which the phosphorus of a phosphido ligand shows similar five coordination are known.<sup>14–16,23–35</sup>

Finally, Pt(4) completes its coordination with two pentafluorophenyl groups and displays a square-planar environment. Pt(3) also carries one C<sub>6</sub>F<sub>5</sub> ligand, although it has a very complicated environment due to the unusual interaction with the P(1)Ph<sub>2</sub> ligand.

In this complex the total valence electron count is 60, which is consistent with the presence of two Pt–Pt bonds.

The <sup>19</sup>F NMR spectra of **4** at room temperature and at 193 K have been recorded. The spectrum at room

temperature is not informative since it shows very broad and overlapped signals (from –106 to –118 ppm for the *o*-F atoms and from –161 to –166 ppm for the *m*- and *p*-F atoms). The spectrum at 193 K has nine signals in the *o*-F region (1:1:1:1:2:1:1:1:1 intensity ratio) with platinum satellites. Some of them appear very close to each other, and the <sup>3</sup>J<sub>Pt–F</sub> cannot be measured in all cases. This part of the spectrum is in agreement with the presence of five inequivalent C<sub>6</sub>F<sub>5</sub> groups. Moreover, in four of the groups the two halves of each ring appear as inequivalent. The *m*- and *p*-F signals are not well resolved, and six broad high-field signals (2:1:4:2:2:4 intensity ratio) are observed, precluding an unambiguous assignment.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows four signals. The signals due to P(2) and P(1) (atom labeling, Scheme 3) appear at 247.1 (d, 71 Hz) and 163.3 (dd, 71 and 114 Hz) ppm, respectively, in the region that indicates the presence of metal–metal bonds supported by μ-phosphido ligands (usually from +300 to +50 ppm).<sup>11,12</sup> The other two PPh<sub>2</sub> groups act as bridging ligands and are supporting nonbonded metal centers, and the signals due to P(4) and P(3) appear at higher field than P(2) and P(1): –11.3 (d, 114 Hz) and –11.7 (s) ppm, respectively. We have previously observed that chemical shifts of single diphenylphosphido bridging ligands that support nonbonded metal centers (“M(μ-PPh<sub>2</sub>)M” fragment) appear at lower field than the signals due to bis-(diphenylphosphido) ligands that doubly bridge nonbonded metal centers (“M(μ-PPh<sub>2</sub>)<sub>2</sub>M” fragment).<sup>16,36</sup> In agreement with this, the δ<sub>P</sub> values for P(3) and P(4) are

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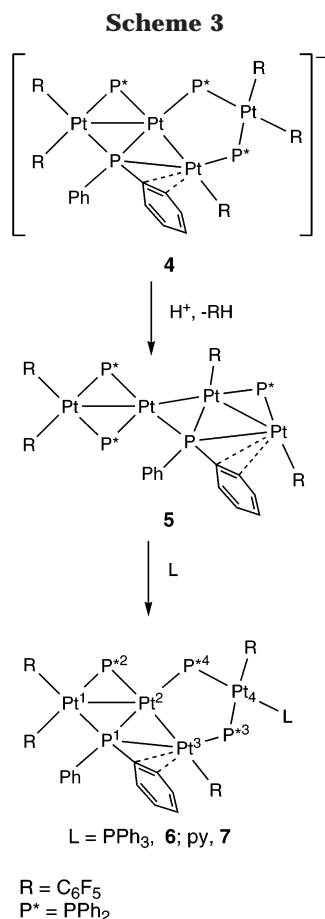
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higher than for the P atoms in the starting material, [NBu<sub>4</sub>]<sub>2</sub>[Pt<sub>3</sub>(μ-PPh<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], -126.4 ppm.<sup>10</sup> All signals show platinum satellites, and in each case two <sup>1</sup>J<sub>Pt-P</sub> values can be calculated (See Experimental Section). From previous work we have observed that <sup>1</sup>J<sub>Pt-P</sub> values are very sensitive to changes in the ligands bonded to Pt.<sup>16</sup> The assignment of each two values cannot be made unambiguously in **4**. The signal due to P(2) shows a pair of closed satellites (<sup>2</sup>J<sub>Pt(3)-P(2)</sub> = 178 Hz) due to the coupling with Pt(3). The platinum satellites of P(1) are more complicated and informative: the signal shows three pairs of satellites, from which three J<sub>Pt-P</sub> values (1229, 1168, and 780 Hz) are obtained. Two of them (1229 and 1168 Hz) are due to the couplings with Pt(1) or Pt(2), and thus the other value has to be due to the coupling with Pt(3). Considering that the P(2)-Pt(2)-Pt(3) angle is 161.90(9)° and <sup>2</sup>J<sub>Pt(3)-P(2)</sub> is 178 Hz, while the P(1)-Pt(2)-Pt(3) angle is much smaller, 55.14(8)°, the 780 Hz value cannot be the result of the coupling between Pt(3) and P(1) through two bonds (<sup>2</sup>J<sub>Pt(3)-P(1) cis</sub>), and it has to be due to <sup>1</sup>J<sub>Pt(3)-P(1)</sub>. This could indicate the existence of a Pt(3)-P(1) bond making P(1) pentacoordinate. However as it is well known the existence

of such couplings is not an irrefutable proof of the presence of a bond but requires only the proximity of Pt and P atoms. As we have stated before in other complexes with an apparently pentacoordinate phosphorus, such as [NBu<sub>4</sub>][Pt<sub>3</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>5</sub>],<sup>14</sup> [Pt<sub>2</sub>Pd<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>3</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(PPh<sub>2</sub>C<sub>6</sub>F<sub>5</sub>)(CO)],<sup>15</sup> and [Pt<sub>4</sub>(μ-PPh<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>],<sup>16</sup> one of the short Pt-P distances could be required by the η<sup>2</sup>-arene-Pt interaction. Complex **4** is the first example containing an apparently pentacoordinate phosphorus in which the three <sup>1</sup>J<sub>Pt-P</sub> values can be evaluated. The three <sup>1</sup>J<sub>Pt-P(1)</sub> values are much smaller than the <sup>1</sup>J<sub>Pt-P</sub> values due to the other P atoms in **4**. In [H<sub>2</sub>Ru<sub>3</sub>Rh(CO)<sub>7</sub>(PPh<sub>3</sub>)<sub>2</sub>(PPh<sub>2</sub>)(PPhC<sub>6</sub>H<sub>4</sub>)] the signal due to the P atom, which is in a similar structural situation, showing a long Rh...P contact (2.840 Å), displays a Rh-P coupling constant of 8 Hz.<sup>37</sup>

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is in agreement with the existence of two Pt-Pt bonds proposed for this tetranuclear cluster of Pt(II) with 60 valence electron count as observed in the X-ray structure. The high values of the chemical shift for P(2) and P(1) are in accord with the Pt(1)-Pt(2) bond and the observed <sup>2</sup>J<sub>Pt(3)-P(2)</sub> with the presence of the Pt(2)-Pt(3) bond.

According to the nature of the products, it can be inferred that in this process the very reactive *cis*-[Pt-(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] plays a double role since it acts as a C<sub>6</sub>F<sub>5</sub> scavenger forming the binuclear [NBu<sub>4</sub>]<sub>2</sub>[Pt<sub>2</sub>(μ-C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and the trinuclear [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-PPh<sub>2</sub>)<sub>2</sub>Pt(μ-PPh<sub>2</sub>)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)]<sup>-</sup>, which reacts immediately with the other equivalent of *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>], forming the tetranuclear derivative **4**. In accord with the total valence electron count of 60 (taking into account the η<sup>2</sup>-coordination of one of the phenyl groups of one PPh<sub>2</sub> bridging ligands) it requires the presence of two Pt-Pt bonds.

This tetranuclear complex of 60 valence electron count displays a structure related to that of the 58-electron species [Pt<sub>4</sub>(μ-PPh<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], **5**, obtained by a totally different route;<sup>16</sup> the only difference in stoichiometry is that **4** contains an additional C<sub>6</sub>F<sub>5</sub> group, which results in an additional pair of skeletal electrons. Complex **4** reacts with HClO<sub>4</sub>, yielding C<sub>6</sub>F<sub>5</sub>H and **5** (see Experimental Section) in good yield. Comparing the two structures, the skeletons of which are presented in Scheme 3, it can be seen that the electronic requirements in **5** (58 e<sup>-</sup>) are fulfilled by formation of a η<sup>2</sup>-phenyl-Pt interaction and three Pt-Pt bonds, while in **4** (60 e<sup>-</sup>) a η<sup>2</sup>-phenyl-Pt interaction and two Pt-Pt bonds are present. It is interesting to note that in **4** the loss of a Pt-Pt bond is preferred to that of the η<sup>2</sup>-phenyl-Pt interaction (see Scheme 3). The flexibility of the phosphido ligand in accommodating the steric requirements of the metal core is remarkable. The formation of **5** from **4** requires not only the formation of an additional Pt-Pt bond but also a change in the structural role of the two phosphido ligands since in **4** the phosphido ligand is bonded to Pt(1) and Pt(2), which forms the η<sup>2</sup>-phenyl interaction with another Pt center, while in **5** it bridges Pt(2) and Pt(3).

The obvious relationship between **4** and **5** is reflected as well by the fact that complex **5** in CH<sub>2</sub>Cl<sub>2</sub> reacts with 1 mol of PPh<sub>3</sub> or py, giving the neutral derivatives [Pt<sub>4</sub>-

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( $\mu$ -PPh<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>L] (L = PPh<sub>3</sub>, **6**; py, **7**). These complexes are structurally analogous to **4** (see Scheme 3). Their structures can be inferred from their NMR spectra. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectra the chemical shifts due to the four signals of the P atoms of the PPh<sub>2</sub> ligands in both complexes (see Experimental Section) are similar to those observed for **4**. This pattern agrees with a structural disposition of both the platinum centers and the PPh<sub>2</sub> bridging ligands as in **4**. Moreover complex **6** shows a doublet (339 Hz) at 22.6 ppm due to the P(5) atom of the PPh<sub>3</sub> ligand. The signals due to the P(2) and P(1) atoms appear as a doublet (64 Hz) and a doublet of doublets (64 and 120 Hz), respectively, as in **4**, while the signal due to P(4) appears in **6** as a doublet of doublets (120 and 339 Hz) and the one due to P(3) is a singlet. This coupling constants unambiguously show that the PPh<sub>3</sub> ligand is coordinated *trans* to the P(4)-Ph<sub>2</sub> ligand (see Scheme 3), the <sup>2</sup>J<sub>P(4)–P(5)</sub>*trans* being 339 Hz. All signals show platinum satellites (see Experimental Section), but those observed for P(1) and P(4) signals appear very overlapped, and unfortunately the J<sub>Pt–P(1 or 4)</sub> values in **6** cannot be calculated. The spectrum of **7** shows a pattern as for **4**. Moreover we have observed in all our complexes that the P signals of the PPh<sub>2</sub> groups *trans* to C<sub>6</sub>F<sub>5</sub> groups are usually broad (due to coupling with *o*-F atoms). The signal due to P(4) in **7** appears as a doublet of doublets (16 and 125 Hz); the large value is due to the coupling with the P(1) atom. Although the 16 Hz value cannot be unambiguously assigned to coupling with P(2) or P(3), the possibility of observation of this small coupling in **7** indicates that the P(4)Ph<sub>2</sub> bridging ligand cannot be *trans* to a C<sub>6</sub>F<sub>5</sub> group; that is, the py ligand has to be *trans* to P(4). As in **4**, the signal due to P(1) displays three pairs of platinum satellites (1289, 1166, and 637 Hz). These values are similar to those obtained for P(1) in **4**, and the 637 Hz value has to be due to <sup>1</sup>J<sub>Pt(3)–P(1)</sub>.

The <sup>19</sup>F NMR spectra of **6** and **7** at room temperature show (see Experimental Section) in the *o*-F atom region eight signals of the same intensity for **6** and seven signals (one of them with double intensity) for **7**, all of them with platinum satellites. Some of them appear very close each other, and the <sup>3</sup>J<sub>Pt–F</sub> cannot be measured in all cases. This part of the spectra is in agreement with the presence of four inequivalent C<sub>6</sub>F<sub>5</sub> groups in **6** and **7**. In the high-field region some of the 12 signals due to *m*- and *p*-F atoms appear overlapped, precluding an unambiguous assignment.

## Experimental Section

**General Data.** C, H, and N analyses, IR and NMR spectra, and conductivity were performed as described elsewhere.<sup>16</sup> Literature methods were used to prepare the starting materials [NBu<sub>4</sub>]<sub>2</sub>[(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>Pt( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>10</sup> and *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>]<sub>2</sub>.<sup>38</sup>

**Preparation of [NBu<sub>4</sub>][Pt<sub>4</sub>( $\mu$ -PPh<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>5</sub>]**4**.** (a) To a yellow suspension of [NBu<sub>4</sub>]<sub>2</sub>[Pt<sub>3</sub>( $\mu$ -PPh<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.300 g, 0.121 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) under N<sub>2</sub> was added a solution of *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] (0.170 g, 0.252 mmol) dissolved in CH<sub>2</sub>-Cl<sub>2</sub> (15 mL), and the mixture was stirred at room temperature for 20 h. After filtration, the resulting red solution was evaporated to dryness. The residue was treated with 5 mL of

Et<sub>2</sub>O, giving rise to an orange solution and red oil. The solution was separated, and CHCl<sub>3</sub> (3 mL) was added with stirring to the oily residue. By keeping in the freezer at –18 °C a deep orange solid formed. It was filtered off, washed with cold CHCl<sub>3</sub> (2 × 0.5 mL), and air-dried (**4**, 0.025 g, 8% yield). From the ether solution a yellow mixture that contains [NBu<sub>4</sub>]<sub>2</sub>[Pt<sub>2</sub>( $\mu$ -C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (<sup>19</sup>F NMR spectroscopy) was obtained.

(b) To a solution of Li<sub>2</sub>[(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>Pt( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (0.111 mmol) prepared in situ at –78 °C in 10 mL of thf<sup>10</sup> was added *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] (0.150 g, 0.222 mmol), and the mixture was stirred at room temperature for 15 min. Then NBu<sub>4</sub>ClO<sub>4</sub> (0.038 g, 0.111 mmol) was added, and the resulting mixture was additionally stirred at room temperature for 6 h. The mixture was filtered off under N<sub>2</sub>, the resulting orange solution was evaporated to dryness, and the residue was treated with CHCl<sub>3</sub> (3 mL). A very small amount of yellow solid was eliminated, and the resulting orange solution was partially evaporated (ca. 2 mL) and kept at –18 °C for 3 days. The crystallized orange solid was filtered off, washed with *n*-hexane (2 × 5 mL), and vacuum-dried. **3**: 0.115 g, 40% yield. Anal. Found (calcd for C<sub>94</sub>F<sub>25</sub>H<sub>76</sub>NP<sub>4</sub>Pt<sub>4</sub>): C, 43.2 (43.4); H, 2.6 (2.9); N, 0.4 (0.5). IR (X-sensitive C<sub>6</sub>F<sub>5</sub>, cm<sup>-1</sup>): 807 (broad), 800 and 787 (shoulder).  $\Lambda_M$  (acetone) = 65  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 193 K, 282.4 MHz):  $\delta$  –107.8 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 254 Hz), –114.6 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 285 Hz), –115.2 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 235 Hz), –116.7 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 354 Hz), –117.1 (2 *o*-F), –117.8 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 239 Hz), –118.9 (1 *o*-F), –119.2 (1 *o*-F), –119.6 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 301 Hz), –161.5 (2 F), –161.7 (1 F), –164.1 (4 F), –165.1 (2 F), –165.4 (2 F), –165.7 (4 F) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 293 K, 121.4 MHz):  $\delta$  247.1 (d, P(2), <sup>2</sup>J<sub>P(1)–P(2)}</sub> = 71, <sup>1</sup>J<sub>Pt(1) or (2)–P(2)}</sub> = 2541 and 1533, <sup>2</sup>J<sub>Pt(3)–P(2)}</sub> = 178 Hz), 163.3 (dd, P(1), <sup>2</sup>J<sub>P(1)–P(2)}</sub> = 71, <sup>2</sup>J<sub>P(1)–P(4)}</sub> = 114, <sup>1</sup>J<sub>Pt(1) or (2)–P(1)}</sub> = 1229 and 1168, <sup>1</sup>J<sub>Pt(3)–P(1)}</sub> = 780 Hz), –11.3 (d, P(4), <sup>2</sup>J<sub>P(1)–P(4)}</sub> = 114, <sup>1</sup>J<sub>Pt(2) or (4)–P(4)}</sub> = 3086 and 2156 Hz), –11.7 (s, P(3), <sup>1</sup>J<sub>Pt(3) or (4)–P(3)}</sub> = 2961 and 2430 Hz) ppm.

**Reaction of **4** with HClO<sub>4</sub>.** To an orange solution of **4** (0.390 g, 0.150 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added 0.150 mmol of aqueous HClO<sub>4</sub> in methanol. The resulting solution was stirred at room temperature for 2 h and then evaporated to dryness. The orange residue was treated with 10 mL of Et<sub>2</sub>O, and the resulting pale orange residue (identified by IR as a mixture of NBu<sub>4</sub>ClO<sub>4</sub> and starting material) was separated by filtration. The ether solution was evaporated to ca. 2 mL, and *n*-hexane (10 mL) was added. Vigorous stirring for 15 min resulted in the formation of a dark orange solid, which was filtered, washed with *n*-hexane (2 × 3 mL), and vacuum-dried. The solid was identified as [Pt<sub>4</sub>( $\mu$ -PPh<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], **5**, 0.229 g, 70% yield.

**Preparation of [Pt<sub>4</sub>( $\mu$ -PPh<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>L] (L = PPh<sub>3</sub>, **6**; py, **7**).** **L = PPh<sub>3</sub>, **6**.** To an orange solution of **5** (0.100 g, 0.046 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added PPh<sub>3</sub> (0.013 g, 0.049 mmol), and the resulting solution was stirred at room temperature for 0.5 h. The orange residue obtained after evaporating to dryness was treated with CHCl<sub>3</sub> (3 mL) and left in the freezer for 3 h. The orange solid was filtered, washed with cold CHCl<sub>3</sub> (2 × 0.5 mL), and air-dried. **6**: 0.052 g, 46% yield. Anal. Found (calcd for C<sub>90</sub>F<sub>20</sub>H<sub>55</sub>P<sub>5</sub>Pt<sub>4</sub>): C, 43.8 (44.1); H, 2.2 (2.3). IR (X-sensitive C<sub>6</sub>F<sub>5</sub>, cm<sup>-1</sup>): 792, 732 (broad). <sup>19</sup>F NMR (CD<sub>2</sub>-Cl<sub>2</sub>, 293 K, 282.4 MHz):  $\delta$  –110.1 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 249 Hz), –114.7 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 336 Hz), –115.9 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 341 Hz), –116.5 (1 *o*-F), –117.2 (1 *o*-F), –118.2 (1 *o*-F, <sup>3</sup>J<sub>Pt–F</sub> = 354 Hz), –118.9 (1 *o*-F), –119.2 (1 *o*-F), –161.2 (2 F), –161.4 (1 *p*-F), –162.0 (1 F), –162.5 (1 F), –163.6 (1 *p*-F), –164.0 (3 F), –164.7 (1 F), –165.1 (1 F), –165.6 (1 F) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 293 K, 121.4 MHz):  $\delta$  254.2 (d, P(2), <sup>2</sup>J<sub>P(1)–P(2)}</sub> = 64, <sup>1</sup>J<sub>Pt(1) or (2)–P(2)}</sub> = 2516 and 1446, <sup>2</sup>J<sub>Pt(3)–P(2)}</sub> = 163 Hz), 172.2 (dd, P(1), <sup>2</sup>J<sub>P(1)–P(2)}</sub> = 64, <sup>2</sup>J<sub>P(1)–P(4)}</sub> = 120 Hz), 22.6 (d, P(5), <sup>2</sup>J<sub>P(4)–P(5)}</sub> = 339, <sup>1</sup>J<sub>Pt(4)–P(5)}</sub> = 2419, <sup>3</sup>J<sub>Pt(2)–P(5)}</sub> = 157 Hz), –10.7 (dd, P(4), <sup>2</sup>J<sub>P(1)–P(4)}</sub> = 120, <sup>2</sup>J<sub>P(4)–P(5)}</sub> = 339 Hz), –25.7 (s, P(3), <sup>1</sup>J<sub>Pt(3) or (4)–P(3)}</sub> = 3113 and 2075 Hz) ppm.

**L = py, **7**.** Complex **7** was prepared similarly from **5** (0.100

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**Table 2. Crystal Data and Structure Refinement for [NBu<sub>4</sub>][Pt<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>5</sub>(μ-PPh<sub>2</sub>)<sub>4</sub>]<sub>2</sub>CH<sub>2</sub>Cl<sub>2</sub> (4·2CH<sub>2</sub>Cl<sub>2</sub>)**

empirical formula	C <sub>94</sub> H <sub>76</sub> F <sub>25</sub> NP <sub>4</sub> Pt <sub>4</sub> ·2CH <sub>2</sub> Cl <sub>2</sub>
fw	2768.65
temperature (K)	173(1)
wavelength (Å)	0.71073
cryst syst	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
unit cell dimens	
<i>a</i> (Å)	14.751(2)
<i>b</i> (Å)	21.760(4)
<i>c</i> (Å)	31.154(6)
β (deg)	101.80(1)
volume (Å <sup>3</sup> )	9788(3)
<i>Z</i>	4
density(calc) (Mg/m <sup>3</sup> )	1.879
abs coeff (mm <sup>-1</sup> )	5.967
<i>F</i> (000)	5312
diffractometer	Siemens SMART
2θ range for data collect. (deg)	2.3–46.6
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
goodness-of-fit on <i>F</i> <sup>2</sup> <i>b</i>	1.669
final <i>R</i> indices ( <i>I</i> > 2σ( <i>I</i> )) <sup>a</sup>	<i>R</i> 1 = 0.0580, <i>wR</i> 2 = 0.1356
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0763, <i>wR</i> 2 = 0.1492

<sup>a</sup>  $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ ;  $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_c^2)^2]^{0.5}$ .  
<sup>b</sup> Goodness-of-fit =  $[\sum w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{0.5}$ .

g, 0.046 mmol) and py (15 μL, 0.182 mmol) as an orange solid. 7: 0.047 g, 45% yield. Anal. Found (calcd for C<sub>77</sub>F<sub>20</sub>H<sub>45</sub>NP<sub>4</sub>Pt<sub>4</sub>): C, 40.8 (40.8); H, 1.95 (2.0); N, 0.7 (0.6). IR (*X*-sensitive C<sub>6</sub>F<sub>5</sub>, cm<sup>-1</sup>): 798 (shoulder), 788 and 782 (shoulder). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 293 K, 282.4 MHz): δ -107.8 (1 *o*-F, <sup>3</sup>*J*<sub>Pt-F</sub> = 226 Hz), -114.4 (1 *o*-F, <sup>3</sup>*J*<sub>Pt-F</sub> = 339 Hz), -117.0 (1 *o*-F, <sup>3</sup>*J*<sub>Pt-F</sub> = 336 Hz), -118.2 (1 *o*-F, <sup>3</sup>*J*<sub>Pt-F</sub> = 356 Hz), -118.9 (1 *o*-F), -119.3 (1 *o*-F, <sup>3</sup>*J*<sub>Pt-F</sub> = 373 Hz), -120.4 (2 *o*-F, <sup>3</sup>*J*<sub>Pt-F</sub> = 288 Hz), -161.4 (1 *p*-F), -161.6 (1 *p*-F), -161.7 (1 *p*-F), -163.1 (1 *p*-F), -163.3 (1 *m*-F), -164.1 (2 *m*-F), -164.5 (3 *m*-F), -165.4 (1 *m*-F), -165.8 (1 *m*-F) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 293 K, 121.4 MHz): δ 253.6 (d, P(2), <sup>2</sup>*J*<sub>P(1)-P(2)}</sub> = 59, <sup>1</sup>*J*<sub>P(1)}</sub> or <sup>(2)-P(2)} = 2474 and 1514, <sup>2</sup>*J*<sub>P(3)-P(2)}</sub> = 97 Hz), 163.5 (dd, P(1), <sup>2</sup>*J*<sub>P(1)-P(2)}</sub> = 59, <sup>2</sup>*J*<sub>P(1)-P(4)}</sub> = 125, <sup>1</sup>*J*<sub>P(1)}</sub> or <sup>(2)-P(1)} = 1289 and 1166, <sup>1</sup>*J*<sub>P(3)-P(1)}</sub> = 637 Hz), -24.2 (s, P(3), <sup>1</sup>*J*<sub>P(3)}</sub> or <sup>(4)-P(3)} = 3235 and 2130 Hz), -25.1 (dd, P(4), <sup>2</sup>*J*<sub>P(2) or (3)-P(4)}</sub> = 16, <sup>2</sup>*J*<sub>P(1)-P(4)}</sub> = 125, <sup>1</sup>*J*<sub>P(2)}</sub> or <sup>(4)-P(4)} = 3600 and 3045 Hz) ppm.</sup></sup></sup></sup>

**X-ray Structure Determination.** Crystal data and other details of the structure analysis are presented in Table 2. Crystals of 4·2CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a solution of 0.020 g of 4 in 4 mL of CH<sub>2</sub>Cl<sub>2</sub>. All diffraction measurements were made at 173 K on a Siemens three-circle SMART area

detector diffractometer using graphite monochromated Mo Kα radiation. Unit cell dimensions were determined from 364 reflections. A full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ 0°, 88°, and 180° with the area detector center held at 2θ = -23°. A total of 40 881 diffracted intensities were measured in a unique hemisphere of reciprocal space, and 13 792 unique observations remained after averaging of duplicate and equivalent measurements (*R*<sub>int</sub> 0.0569) and deletion of the systematic absences, of these 11 309 with *I* > 2σ(*I*). An absorption correction was applied based on 5603 equivalent and identical data (maximum and minimum transmission coefficients were 0.907 and 0.563). Lorentz and polarization corrections were applied.

The structure was solved by Patterson and Fourier methods and refined using the SHELXL-97 program.<sup>39</sup> All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogen atoms were constrained to idealized geometries and their positions refined riding on their parent carbon atoms with a common thermal isotropic parameter. The NBu<sub>4</sub><sup>+</sup> cation shows a severe disorder. After trial of several models, the best one includes some carbon atoms disordered over two sets of positions with 0.5 partial occupancy. The disordered atoms in the same set were refined with the identical thermal parameters. Restraints in the distances for the cation and the two molecules of solvent were applied. Full-matrix least-squares refinement on *F*<sup>2</sup> of this model converged to final residual indices given in Table 2. Final difference electron density maps showed no features outside the range +1.78 to -1.66 e Å<sup>-3</sup>, the biggest being close (less than 1.2 Å) to the Pt atoms and to the cation atoms.

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**Supporting Information Available:** Further details of the structure determination of 4·2CH<sub>2</sub>Cl<sub>2</sub> including atomic coordinates, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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