

## Metallation of Unactivated Methyl Groups – Platinum(II) Derivatives with 6-Alkyl-2,2'-bipyridines

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The reaction of  $K_2[PtCl_4]$  with three 6-alkyl-2,2'-bipyridines HL, ( $N_2C_{10}H_7R$ ;  $R = CH_2Me$ ,  $HL^{et}$ ;  $CHMe_2$ ,  $HL^{ip}$ ;  $CH_2CMe_3$ ,  $HL^{np}$ ) affords five- and six-membered cyclometallated complexes  $[Pt(L)Cl]$  where L is a terdentate *N,N,C* anionic ligand which originates from HL through direct activation of a  $C(sp^3)-H$  bond. In the case of  $HL^{ip}$ , metallation generates a stereogenic carbon atom  $\beta$  to the metal. Complex **5**,  $[Pt(L^{np})Cl]$ , having an uncommon six-membered ring containing a  $Pt-C(sp^3)$  bond, was studied in depth in solution, by means of 1- and 2- dimensional NMR spectroscopy, and in the solid state by X-ray diffraction. Differences are observed in the behaviour of these ligands: thus with  $HL^{et}$  an adduct,  $[Pt(HL^{et})Cl_2]$ , was also isolated and its structure was determi-

ned by X-ray diffraction. In the metallated species, the fourth ligand, Cl, can easily be substituted by neutral or anionic ligands (CO,  $PPh_3$ ,  $CN^-$ ). The metallated species react with potentially bidentate ligands  $L'-L''$  [ $Ph_2PCH_2PPh_2$  (dppm),  $Ph_2P(CH_2)_2PPh_2$  (dppe),  $Ph_2P(CH_2)_2AsPh_2$  (dppae)] to give, with different Pt:L ratios, mononuclear  $[Pt(L)(L'-L'')]^+$  or dinuclear  $[(L)Pt(\mu-L'-L'')Pt(L)]^{++}$  cationic species. In the second case an uncommon unsupported  $L'-L''$  bridge is present. The cyclometallated species are stable in air and moisture, and the *N,N,C* system is rather robust.

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### Introduction

Cyclometallated compounds, in particular those derived from nitrogen ligands, have attracted considerable interest as a consequence of the wide range of their potential applications in many areas including organic synthesis,<sup>[1]</sup> homogeneous catalysis<sup>[2]</sup> (even asymmetric), photochemistry<sup>[3]</sup>, and the design of new metallomesogens<sup>[4]</sup>, sensors<sup>[5]</sup> and antitumour drugs.<sup>[6]</sup>

In recent years, in addition to the classical bidentate *N,C* systems, attention has also been devoted towards potentially terdentate-bound anionic ligands able to coordinate through different sets of donor atoms (e.g. *N,N,C*,<sup>[7]</sup> *N,C,N*,<sup>[8]</sup> *C,N,C*<sup>[9]</sup>). The sequence of coordinating atoms, the size of the metallacycles and the type of metallated carbon atom can be tuned to obtain complexes with different properties.

Although cyclometallation reactions, especially those concerning metals of the platinum group, have been extensively studied, the factors that control the process are not completely understood. Whereas for  $Pd^{II}$  the most common

mechanism is electrophilic, in the case of  $Pt^{II}$  both electrophilic and nucleophilic behaviour has been ascertained.<sup>[10]</sup> The reaction, besides the obvious electronic and steric factors, seems to be affected by a number of factors: we have shown in previous papers that even subtle differences in the substituents of the ligands can drive the cyclometallation reactions towards unpredictable results.<sup>[7a]</sup>

In general, nitrogen donor ligands show a strong tendency to form five-membered rings, although a few six-membered rings are known. The great majority of papers in this field concern  $C(sp^2)-H$  bond activation, in spite of the present interest in activation of alkyl groups. Only few cyclometallated species containing nitrogen ligands and  $C(sp^3)-Pt$  bonds are known and, to the best of our knowledge, only two six-membered cyclometallated species with a  $Pt-C(sp^3)$  bond have been described,<sup>[11]</sup> but none of them derives from a true  $C-H$  activation.

Here we describe a series of platinum(II) complexes containing terdentate bound anionic ligands with an *N,N,C*( $sp^3$ ) sequence of donor atoms obtained by the direct activation of a methyl group of 6-alkyl-2,2'-bipyridines. The substituents on the bipyridines have been chosen in order to compare five and six-membered rings. In addition, one of the ligands ( $HL^{ip}$ ,  $N_2C_{10}H_7CHMe_2-6$ ), is potentially able to give a stereogenic carbon atom directly by metallation.

Depending on the ligand and the reaction conditions both adducts  $[Pt(HL)Cl_2]$  and five- or six-membered cyclo-

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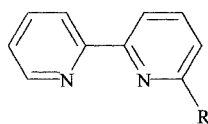
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metallated species,  $[\text{Pt}(\text{L})\text{Cl}]$ , can be obtained from  $\text{K}_2[\text{PtCl}_4]$ . The chloride ligand in the metallated species has been found to be rather substitution labile, so that its replacement by anionic or neutral ligands as  $\text{CN}^-$ ,  $\text{CO}$  or  $\text{PPh}_3$  has been studied. We also report on the reaction with the potentially chelating ligands  $\text{L}'\text{--L}''$  [ $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm),  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$  (dppe),  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$  (dppae)] with 1:1 and 2:1  $\text{Pt/L}'\text{--L}''$  molar ratios.

The behaviour of  $[\text{PtCl}_4]^{2-}$  is compared with that of  $[\text{PdCl}_4]^{2-}$ , which is previously described.<sup>[7a]</sup>

## Results and Discussion

The ligands 6-ethyl-2,2'-bipyridine ( $\text{HL}^{\text{et}}$ ), 6-isopropyl-2,2'-bipyridine ( $\text{HL}^{\text{ip}}$ ) and 6-neopentyl-2,2'-bipyridine ( $\text{HL}^{\text{np}}$ ) were obtained as previously described.<sup>[12]</sup>



| R                                    |                         |
|--------------------------------------|-------------------------|
| $\text{CH}_2\text{CH}_3$             | $\text{HL}^{\text{et}}$ |
| $\text{CH}(\text{CH}_3)_2$           | $\text{HL}^{\text{ip}}$ |
| $\text{CH}_2\text{C}(\text{CH}_3)_3$ | $\text{HL}^{\text{np}}$ |

The activation of one  $\text{C}(\text{sp}^3)\text{--H}$  bond was achieved with  $\text{HL}^{\text{ip}}$  and  $\text{HL}^{\text{np}}$ , in high yields (ca. 90%), by reacting the ligand with  $\text{K}_2[\text{PtCl}_4]$  in aqueous  $\text{HCl}$  under refluxing conditions. In the case of  $\text{HL}^{\text{et}}$  the metallation, possibly owing to the presence of only one methyl group, is more difficult and a mixture of the metallated complex  $[\text{Pt}(\text{L}^{\text{et}})\text{Cl}]$  (**2**) and the adduct  $[\text{Pt}(\text{HL}^{\text{et}})\text{Cl}_2]$  (**1**), is obtained. We recently reported<sup>[7a]</sup> that the analogous reactions of these ligands with  $\text{Na}_2[\text{PdCl}_4]$  give only the adducts  $[\text{Pd}(\text{HL})\text{Cl}_2]$ :  $\text{C--H}$  activation however can be easily obtained from  $[\text{Pd}(\text{OAc})_2]$ . A peculiar behaviour is observed with a forth ligand  $\text{HL}^{\text{tb}}$  ( $\text{R} = \text{C}(\text{CH}_3)_3$ ): activation of a methyl group by reaction with  $[\text{PdCl}_4]^{2-}$  occurs even at room temperature, whereas refluxing conditions are needed with  $[\text{PtCl}_4]^{2-}$ .

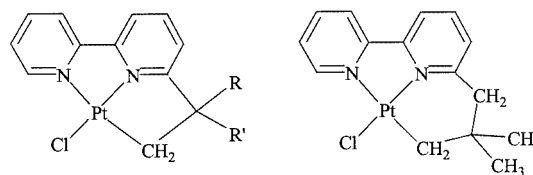
The adduct  $[\text{Pt}(\text{HL}^{\text{et}})\text{Cl}_2]$ , **1**, can also be synthesised from *cis*- $[\text{Pt}(\text{DMSO})_2\text{Cl}_2]$  (see the Exp. Sect.) in fairly good yields. The  $^1\text{H}$  NMR spectrum (see Table 1) shows all the expected resonances: in particular the 6'-H and the  $\text{CH}_2$  protons are strongly deshielded with respect to the free ligand ( $\Delta\delta = 0.95$  and  $0.83$  ppm, respectively) as is often observed when a chlorine atom is coordinated in their proximity. In addition the 6'-H is strongly coupled to platinum ( $^3J_{\text{Pt--H}} = 40$  Hz), providing evidence for the coordination of the nitrogen atom of the unsubstituted pyridine ring. Complex **1** was characterised in the solid state by X-ray diffraction.

The structure consists of the packing of  $[\text{Pt}(\text{HL}^{\text{et}})\text{Cl}_2]$  molecules with no unusual van der Waals contacts. There are two crystallographically independent molecules, A and B, in the asymmetric unit. Selected bond lengths and angles for the two molecules are reported in Table 4. An ORTEP

view of molecule A is shown in Figure 1. The platinum atom displays a square-planar coordination with a slight square-pyramidal distortion. The displacement of the metal atom from the best plane of atoms  $\text{Cl}(1)$ ,  $\text{Cl}(2)$ ,  $\text{N}(1)$ , and  $\text{N}(2)$  is  $0.090(1)$  Å in molecule A and  $0.111(1)$  Å in molecule B. Corresponding bond lengths and angles in the two molecules are all very similar (see Table 4). The  $\text{Pt--Cl}(1)$  and  $\text{Pt--Cl}(2)$  distances, (average  $2.298$  and  $2.284$  Å, respectively) are both in good agreement with the  $\text{Pt--Cl}$  bond length,  $2.299(2)$  Å, found in  $[\text{PtCl}(\text{Me})(\text{HL}^{\text{et}})]_2$  compound **19**.<sup>[13]</sup> The  $\text{Pt--N}(2)$  distance, average  $2.050$  Å, is longer than the  $\text{Pt--N}(1)$  one, average  $1.996$  Å, and the  $\text{Cl}(1)\text{--Pt--N}(2)$  angle, average  $100.5^\circ$ , is much larger than the  $\text{Cl}(2)\text{--Pt--N}(1)$  angle, average  $92.7^\circ$ . Both effects are probably due to the steric hindrance of the ethyl substituent on atom  $\text{C}(10)$ . An even larger  $\text{Cl--Pt--N}(2)$  angle,  $103.1(1)^\circ$ , had been found in **19**. It must be observed that in compound **19** a clear intramolecular hydrogen bond was found between a  $\text{CH}_2$  hydrogen atom and the Cl ligand ( $\text{Cl}\cdots\text{H}$   $2.28$  Å,  $\text{C}(11)\text{--H}\cdots\text{Cl}$  angle  $160.4^\circ$ , see ref.<sup>[13]</sup>). There is no such hydrogen bond in either of the two present independent molecules, which exhibit different conformations of the ethyl substituent, with a shortest  $\text{Cl}(1)\cdots\text{H}$  distance of  $2.52$  Å and a  $\text{C}(11)\text{--H}\cdots\text{Cl}(1)$  angle of  $126.6^\circ$  in molecule B.

## Metallated Compounds

From  $\text{K}_2[\text{PtCl}_4]$  the metallated compounds  $[\text{Pt}(\text{L}^{\text{ip}})\text{Cl}]$  (**3**) and  $[\text{Pt}(\text{L}^{\text{np}})\text{Cl}]$  (**5**) have been obtained in pure form, whereas isolation of complex **2** requires separation from adduct **1** by column chromatography. The synthesis of complex **4** has been previously reported.<sup>[7b]</sup>



**2**  $\text{R} = \text{R}' = \text{H}$

**3**  $\text{R} = \text{H}, \text{R}' = \text{CH}_3$

**4**  $\text{R} = \text{R}' = \text{CH}_3$

**5**

Metallation entails a  $\text{C}(\text{sp}^3)\text{--H}$  activation to give a five-membered cycle in the case of compounds **2**, **3** and **4**, and a less common six-membered ring in the case of complex **5**. To the best of our knowledge this is the first six-membered cyclometallated species of platinum(II) with nitrogen donors originating directly from an unactivated  $\text{C}(\text{sp}^3)\text{--H}$  bond: two precedent reports involved a benzylic  $\text{C--H}$  bond<sup>[11a]</sup> and an acidic  $\text{C--H}$  group in the presence of alkali.<sup>[11b]</sup>

The metallated species were fully characterised by analytical and spectroscopic methods. In particular NMR spectroscopy ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ) gives evidence for a methylenic

Table 1. Proton NMR spectroscopic data<sup>[a]</sup>

|                                                                                            |                          | CH <sub>3</sub>                | CH <sub>2</sub> –Pt                                                                    | CH <sub>2</sub> –C, CH <sub>2</sub> –P/As                              | CH               | H(6')                           | other aromatics     |
|--------------------------------------------------------------------------------------------|--------------------------|--------------------------------|----------------------------------------------------------------------------------------|------------------------------------------------------------------------|------------------|---------------------------------|---------------------|
| Pt(HL <sup>et</sup> )Cl <sub>2</sub>                                                       | <b>1</b>                 | 1.43 (t, 3 H)<br>(7.5)         |                                                                                        | 3.73 (q, 2 H) (7.5)                                                    |                  | 9.65<br>(dd, 1 H) [40]          | 7.4–8.2 (m, 6 H)    |
| Pt(L <sup>et</sup> )Cl                                                                     | <b>2</b>                 |                                | 2.96 (t, 2 H)<br>(6.4)[85]                                                             | 3.92 (t, 2 H) (6.4) [31]                                               |                  | 9.23<br>(ddd, 1 H) [10]         | 7.4–8.35 (m, 6 H)   |
| Pt(L <sup>ip</sup> )Cl                                                                     | <b>3</b>                 | 1.46 (d, 3 H)<br>(7.2)         | 2.66 (dd 1 H)<br>(12.0, 5.6) [89]<br>3.07 (dd 1 H)<br>(12.0, 7.5) [79]                 |                                                                        | 3.45<br>(m, 1 H) | 9.21<br>(ddd, 1 H) [12]         | 7.25–8.25 (m, 6 H)  |
| Pt(L <sup>np</sup> )Cl                                                                     | <b>5</b>                 | 1.09 (s, 6 H)                  | 2.43 (s, 2 H) [87]                                                                     | 2.82 (s, 2 H)                                                          |                  | 9.56<br>(ddd, 1 H) [10]         | 7.28–8.10 (m, 6 H)  |
| [Pt(L <sup>ip</sup> )(CN)]                                                                 | <b>6</b>                 | 1.42 (d, 3 H)<br>(7.1)         | 2.57 (dd, 1 H)<br>(12.9, 5.5) [78]<br>3.01 (dd, 1 H)<br>(12.9, 7.2) [64]               |                                                                        | 3.54<br>(m, 1 H) | 9.08<br>(dd, 1 H) [15]          | 7.40–8.18 (m, 6 H)  |
| [Pt(L <sup>ip</sup> )(CO)][BF <sub>4</sub> ]                                               | <b>7</b>                 | 1.54 (d, 3 H)<br>(7.0)         | 2.83 (dd, 1 H)<br>(12.2, 5.6) [66]<br>3.25 (dd, 1 H)<br>(12.2, 6.6) [52]               |                                                                        | 3.88<br>(m, 1 H) | 8.85<br>(ddd, 1 H) [15]         | 7.68–8.55 (m, 6 H)  |
| [Pt(L <sup>np</sup> )(CO)][BF <sub>4</sub> ]                                               | <b>8</b>                 | 1.17 (s, 6 H)                  | 2.50 (s, 2 H) [52]                                                                     | 3.14 (s, 2 H)                                                          |                  | 8.76<br>(dd, 1 H) [n.r.]<br>[c] | 7.58–8.82 (m, 6 H)  |
| [Pt(L <sup>et</sup> )(PPh <sub>3</sub> )][BF <sub>4</sub> ]                                | <b>9</b>                 |                                | 2.21 (td, 2 H)<br>(6.2) [71]{2.7}                                                      | 3.97 (t, 2 H) (6.2) [35]                                               |                  |                                 | 7.14–8.71 (m, 7 H)  |
| [Pt(L <sup>ip</sup> )(PPh <sub>3</sub> )][BF <sub>4</sub> ]                                | <b>10</b>                | 1.43 (d, 3 H)<br>(7.1)         | 2.08 (ddd, 1 H)<br>(12.4, 6.8){3.4}[n.r.]<br>2.24 (ddd, 1 H)<br>(12.4, 5.6){2.2}[n.r.] |                                                                        | 3.52<br>(m, 1 H) |                                 | 7.14–8.69 (m, 22 H) |
| [Pt(L <sup>np</sup> )(PPh <sub>3</sub> )][BF <sub>4</sub> ]                                | <b>11</b>                | 0.86 (s, 6 H)                  | 1.60 (d, 2 H)<br>{7.1} [67]                                                            | 2.91 (s, 2 H)                                                          |                  | [c]                             | 6.94–8.72 (m, 22 H) |
| [Pt <sub>2</sub> (L <sup>np</sup> ) <sub>2</sub> (μ-dppm)][BF <sub>4</sub> ] <sub>2</sub>  | <b>12</b>                | 0.93 (s, 12 H)                 | 1.52 (d, 4 H)<br>{6.5} [60]                                                            | 2.65 (s, 4 H) (bipy)<br>3.71 (t, 2 H)<br>{12.2} (dppm)                 |                  | [c]                             | 6.97–8.35 (m, 34 H) |
| [Pt <sub>2</sub> (L <sup>ip</sup> ) <sub>2</sub> (μ-dppe)][BF <sub>4</sub> ] <sub>2</sub>  | <b>13</b>                | 1.33 (d, 6 H)<br>(7.2)         | 2.12 (m, 2 H)<br>2.28 (m, 2 H)                                                         | 2.81 (m, 4 H)                                                          | 3.53<br>(m, 2 H) | [c]                             | 7.24–8.42 (m, 34 H) |
| [Pt <sub>2</sub> (L <sup>np</sup> ) <sub>2</sub> (μ-dppe)][BF <sub>4</sub> ] <sub>2</sub>  | <b>14</b>                | 0.81 (s, 12 H)                 | 1.61 (d, H)<br>[60] {ca 5.0}                                                           | 2.94 (s, 4 H) (bipy)<br>2.72 (m, 4 H) (dppe)                           |                  | [c]                             | 6.94–8.42 (m, 34 H) |
| [Pt <sub>2</sub> (L <sup>np</sup> ) <sub>2</sub> (μ-dppae)][BF <sub>4</sub> ] <sub>2</sub> | <b>15</b> <sup>[b]</sup> | 0.87 (s, 6 H)<br>0.88 (s, 6 H) | 1.73 (d, 2 H)<br>{6.9} [ca 65]<br>1.84 (s, 2 H)<br>[ca 65] <sup>[d]</sup>              | 2.97 (s, 2 H) (bipy)<br>2.99 (s, 2 H) (bipy)<br>2.73 (m, 4 H) (dppae)  |                  | [c]                             | 6.96–8.42 (m, 34 H) |
| [Pt(L <sup>np</sup> )(dppm)][BF <sub>4</sub> ]                                             | <b>16</b>                | 0.85 s, 6H                     | 1.69 (d, 2 H)<br>{7.3} [65]                                                            | 2.84 (s, 2 H) (bipy)<br>3.43 d {10.5} [49]<br>2H (dppm)                |                  | [c]                             | 6.97–8.56 (m, 27 H) |
| [Pt(L <sup>np</sup> )(dppe)][BF <sub>4</sub> ]                                             | <b>17</b>                | 0.31 (s, 3 H)<br>0.76 (s, 3 H) | 1.18–2.84<br>(m, 8 H) <sup>[d]</sup>                                                   |                                                                        |                  | [c]                             | 6.43–8.19 (m, 27 H) |
| [Pt(L <sup>np</sup> )(dppae)][BF <sub>4</sub> ]                                            | <b>18</b>                | 0.91 (s 6 H)                   | 1.79 (d, 2 H)<br>{6.8} [62]                                                            | 2.96 (s, 2 H) (bipy)<br>2.25 (m, 2 H) (dppae)<br>2.42 (m, 2 H) (dppae) |                  | [c]                             | 6.92–8.64 (m, 27 H) |

<sup>[a]</sup> Room temperature, solvent CDCl<sub>3</sub>, chemical shifts in ppm from internal SiMe<sub>4</sub>, coupling constants in,  $J_{\text{Pt,H}}$  in square brackets,  $J_{\text{P,H}}$  in braces; n.r. = not resolved. <sup>[b]</sup> Solvent: CD<sub>2</sub>Cl<sub>2</sub>. <sup>[c]</sup> In all the phosphane complexes the 6'-H is strongly shielded. <sup>[d]</sup> Complex pattern from  $\delta$  = 1.18 to 2.84 ppm, due CH<sub>2</sub>–Pt, CH<sub>2</sub> (dppe), CH<sub>2</sub>(bipy), 8 H.

group strongly coupled to the metal ( $^2J_{\text{Pt,H}}$  = 80–90,  $^1J_{\text{Pt,C}}$  = 668–743 Hz, see Table 1 and 2).

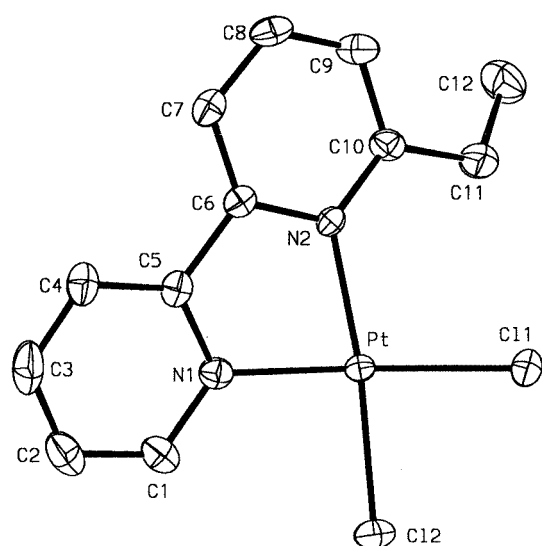
In complexes **2–5** the signals of the 6'-H protons are strongly deshielded and coupled to the metal ( $^3J_{\text{Pt,H}}$  = ca. 10 Hz). In the series of palladium(II) and platinum(II) *N,N,C* cyclometallated compounds derived from 6-substituted 2,2'-bipyridines<sup>[7a–7g]</sup> (see Scheme 1) the chemical shifts of 6'-H appear to be strongly dependent on the nature of the metal and of the fourth ligand as well as on the size of the metallated cycle.

Coordinated halides exert a strong deshielding effect. At variance, the chemical shifts are not remarkably affected by the nature of the carbon atom, C(sp<sup>3</sup>) or C(sp<sup>2</sup>), bonded to the metal.

For platinum(II) compounds, in the case of 5,5 fused rings, values of ca.  $\delta$  = 9.20 ppm are typical, whereas for 5,6 fused rings more deshielded resonances (ca. 9.60 ppm) are usually observed. In the analogous palladium species the same trend is observed, but all the signals are less deshielded (ca. 0.4 ppm) than in the corresponding platinum

Table 2.  $^{13}\text{C}$  NMR spectroscopic data (room temperature,  $\text{CDCl}_3$ , chemical shifts in ppm from TMS, coupling constants in Hz,  $J_{\text{Pt,C}}$  in square brackets)

|                          | $[\text{Pt}(\text{L}^{\text{et}})\text{Cl}]$ , <b>2</b> | $[\text{Pt}(\text{L}^{\text{ip}})\text{Cl}]$ , <b>3</b> | $[\text{Pt}(\text{L}^{\text{np}})\text{Cl}]$ , <b>5</b> | $[\text{Pt}(\text{L}^{\text{ip}})(\text{CO})][\text{BF}_4]$ , <b>7</b> |
|--------------------------|---------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|------------------------------------------------------------------------|
| $\text{CH}_2\text{--Pt}$ | - 1.2 [743]                                             | 10.1 [736]                                              | 18.2 [668]                                              | 16.2 [567]                                                             |
| $\text{CH}_3$            |                                                         | 21.8 [44]                                               | 29.6 [28]                                               | 22.4 [39]                                                              |
| $\text{CH}_2$            | 44.0                                                    |                                                         | 55.5 [68]                                               |                                                                        |
| $\text{CH}$              |                                                         | 49.3 [10]                                               |                                                         | 49.4 [5]                                                               |
| $\text{C}$               |                                                         |                                                         | 32.2 [28]                                               |                                                                        |
| $\text{C3, C3}'$         | 127.7, 124.1 [51]                                       | 127.3, 124.2 [59]                                       | 120.2 [33], 121.3                                       | 129.8 [15], 125.3 [14]                                                 |
| $\text{C5, C5}'$         | 123.4 [11], 119.8 [35]                                  | 121.8 [12], 119.7 [36]                                  | 128.7 [45], 126.8                                       | 125.1 [47], 122.1 [25]                                                 |
| $\text{C4, C4}'$         | 138.5, 135.6                                            | 138.1, 135.4                                            | 136.6 (C4)<br>137.8 (C4')                               | 143.5, 142.3                                                           |
| $\text{C2, C2}'$         |                                                         | 156.2, 152.6                                            | 157.6, 154.6                                            |                                                                        |
| $\text{C6}$              |                                                         | 172.5                                                   | 164.2                                                   |                                                                        |
| $\text{C6}'$             | 147.9 [19]                                              | 147.8 [19]                                              | 148.0 [25]                                              | 152.3 [30]                                                             |

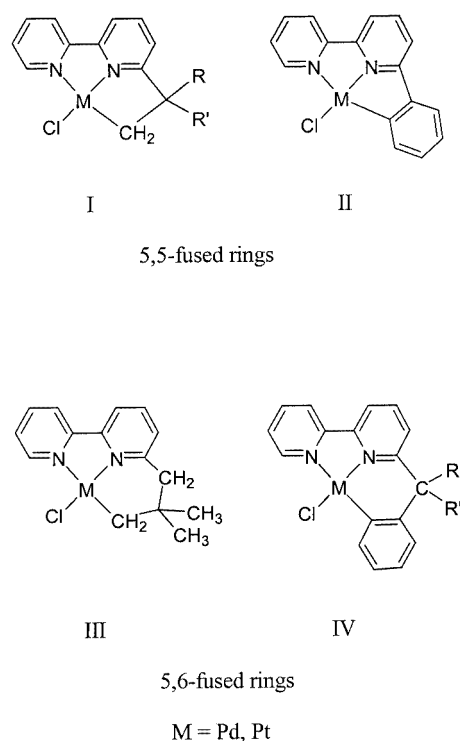
Figure 1. ORTEP view of molecule A in compound **1**; thermal ellipsoids are drawn at the 30% probability level

complexes. Similar trends have also been recently observed for analogous gold(III) cationic species  $[\text{Au}(\text{N},\text{N},\text{C})\text{Cl}]^+$  [7g] for which, however, less experimental data are available.

The  $^{13}\text{C}\{^1\text{H}\}$  spectra of **2–5** deserve comments: the chemical shifts of the  $\text{CH}_2\text{--Pt}$  resonances depend mainly on the degree of substitution on the carbon  $\beta$  to the metal, irrespective of the cycle [e.g.  $\text{Pt--CH}_2\text{--C}(\text{CH}_3)_2\text{--}$ , ca. 18–19 ppm (**4** and **5**),  $\text{Pt--CH}_2\text{--CH}(\text{CH}_3)\text{--}$ , ca.  $\delta$  = 10 ppm (**3**), and  $\text{Pt--CH}_2\text{--CH}_2\text{--}$ , -1.2 ppm (**2**)] reflecting only electronic effects. At variance, the  $^1J_{\text{Pt,C}}$  values are higher for the five-membered rings (ca 740 Hz, **2–4**) than for the six-membered one (668 Hz in **5**).

In the analogous palladium compounds the  $\text{CH}_2\text{--Pd}$  resonances are shifted downfield (e.g.  $\text{Pd}(\text{L}^{\text{ib}})\text{Cl}$ ,  $\delta$  = 32.8 ppm;  $\text{Pd}(\text{L}^{\text{np}})\text{Cl}$ ,  $\delta$  = 34.9 ppm). [7a]

In the case of compound **5**, taking into account the rarity of six-membered cyclometallated rings containing  $\text{C}(\text{sp}^3)\text{--Pt}$  bonds, complete assignment of  $^1\text{H}$  and  $^{13}\text{C}$  signals was accomplished by 2D NMR studies (COSY and HETCOR experiments, see experimental). The coupling



Scheme 1

constants  $J_{\text{Pt,C}}$  in the inner pyridine ring are much larger than those of the outer one [e.g.:  $^3J(\text{Pt--C}(3)) = 33$  Hz,  $^3J(\text{Pt--C}(3'))$  not observed,  $^4J(\text{Pt--C}(4)) = 45$  Hz,  $^4J(\text{Pt--C}(4'))$  not observed] indicating that the pyridine involved in the cyclometallation is more tightly bonded than the other one, in agreement with the X-ray data.

The crystal structure of  $\mathbf{5}\cdot\text{CHCl}_3$  consists of the packing of  $[\text{Pt}(\text{L}^{\text{np}})\text{Cl}]$  and  $\text{CHCl}_3$  molecules in a 1:1 molar ratio with no unusual van der Waals contacts. Selected bond parameters are listed in Table 5. An ORTEP view of **5** is shown in Figure 2. The Pt atom is in a square-planar coordination with a very slight square-pyramidal distortion. It is displaced by only 0.026(1) Å from the best plane of atoms Cl(1), N(1), N(2), and C(13). A comparison can be made between compound **5** and the corresponding Pd derivative,

Table 3.  $^{31}\text{P}$  NMR spectroscopic data (room temperature, solvent  $\text{CDCl}_3$ , chemical shifts in ppm downfield from external 85%  $\text{H}_3\text{PO}_4$ )

|                                                                          |           | solvent                  | $\delta$ | $^1J_{\text{Pt,P}}/\text{Hz}$ | $J_{\text{P,P}}/\text{Hz}$ | $^3J_{\text{Pt,P}}/\text{Hz}$ |
|--------------------------------------------------------------------------|-----------|--------------------------|----------|-------------------------------|----------------------------|-------------------------------|
| $[\text{Pt}(\text{L}^{\text{et}})(\text{PPh}_3)][\text{BF}_4]$           | <b>9</b>  |                          | 20.27    | 4038                          |                            |                               |
| $[\text{Pt}(\text{L}^{\text{ip}})(\text{PPh}_3)][\text{BF}_4]$           | <b>10</b> |                          | 20.36    | 4066                          |                            |                               |
| $[\text{Pt}(\text{L}^{\text{np}})(\text{PPh}_3)][\text{BF}_4]$           | <b>11</b> |                          | 22.59    | 4453                          |                            |                               |
| $[\text{Pt}_2(\text{L}^{\text{np}})_2(\mu\text{-dppm})][\text{BF}_4]_2$  | <b>12</b> | $\text{CD}_2\text{Cl}_2$ | 8.86     | 4581                          |                            | 32                            |
| $[\text{Pt}_2(\text{L}^{\text{ip}})_2(\mu\text{-dppe})][\text{BF}_4]_2$  | <b>13</b> | $\text{CD}_2\text{Cl}_2$ | 14.49    | 4020                          | 52                         |                               |
| $[\text{Pt}_2(\text{L}^{\text{np}})_2(\mu\text{-dppe})][\text{BF}_4]_2$  | <b>14</b> | $\text{CD}_2\text{Cl}_2$ | 15.28    | 4412                          | 52                         |                               |
| $[\text{Pt}_2(\text{L}^{\text{np}})_2(\mu\text{-dppae})][\text{BF}_4]_2$ | <b>15</b> | $\text{CD}_2\text{Cl}_2$ | 15.14    | 4414                          |                            |                               |
| $[\text{Pt}(\text{L}^{\text{np}})(\text{dppm})][\text{BF}_4]$            | <b>16</b> |                          | 7.69     | 4421                          | 83                         |                               |
|                                                                          |           |                          | −25.09   |                               |                            | 94                            |
| $[\text{Pt}(\text{L}^{\text{np}})(\text{dppe})][\text{BF}_4]$            | <b>17</b> |                          | 44.84    | 1912                          |                            |                               |
|                                                                          |           |                          | 32.37    | 4138                          |                            |                               |
| $[\text{Pt}(\text{L}^{\text{np}})(\text{dppae})][\text{BF}_4]$           | <b>18</b> |                          | 15.22    | 4382                          |                            |                               |

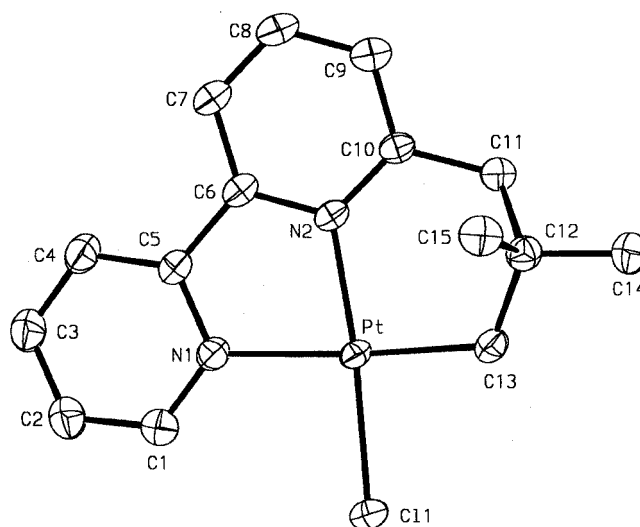
Table 4. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound **1**

|                | molecule A | molecule B |
|----------------|------------|------------|
| Pt–Cl(1)       | 2.295(2)   | 2.300(2)   |
| Pt–Cl(2)       | 2.286(2)   | 2.282(2)   |
| Pt–N(1)        | 1.998(6)   | 1.994(5)   |
| Pt–N(2)        | 2.045(5)   | 2.054(5)   |
| Cl(1)–Pt–Cl(2) | 84.9(1)    | 87.1(2)    |
| Cl(1)–Pt–N(1)  | 170.8(2)   | 170.9(2)   |
| Cl(1)–Pt–N(2)  | 101.3(2)   | 99.7(2)    |
| Cl(2)–Pt–N(1)  | 93.0(2)    | 92.4(2)    |
| Cl(2)–Pt–N(2)  | 173.6(2)   | 172.5(2)   |
| N(1)–Pt–N(2)   | 80.6(2)    | 80.3(2)    |

Table 5. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound **5**

|                |          |               |          |
|----------------|----------|---------------|----------|
| Pt–Cl(1)       | 2.309(1) | Pt–N(1)       | 2.116(3) |
| Pt–N(2)        | 2.020(3) | Pt–C(13)      | 2.040(4) |
| Cl(1)–Pt–N(1)  | 95.5(1)  | Cl(1)–Pt–N(2) | 175.0(1) |
| Cl(1)–Pt–C(13) | 88.1(1)  | N(1)–Pt–N(2)  | 79.8(1)  |
| N(1)–Pt–C(13)  | 176.1(1) | N(2)–Pt–C(13) | 96.7(1)  |

$[\text{PdL}^{\text{np}}\text{Cl}]$ , compound **20**.<sup>[7a]</sup> The Pt–Cl, Pt–N(1), and Pt–N(2) distances, 2.309(1), 2.116(3), and 2.020(3) Å, respectively, are slightly shorter than the corresponding ones involving palladium, 2.314(1), 2.138(2), and 2.046(2) Å, respectively. This is in keeping with the recent observation that platinum is slightly smaller than palladium.<sup>[7a,14]</sup> On the contrary, the Pt–C(13) bond, 2.040(4) Å, is slightly longer than the Pd–C(13) one, 2.022(3) Å. As pointed out in ref.<sup>[7a]</sup>, this can be due to the different packing forces in the two nonisomorphous crystals. The conformation of the Pd–N(2)–C(10)–C(11)–C(12)–C(13) six-membered ring is irregular, as previously found in **20**, ref.<sup>[7a]</sup>. Atoms Pt, N(2), C(10), and C(13) are approximately planar (maximum distances from their best plane are +0.033(3) Å for N(2) and −0.023(4) Å for C(10)], with atoms C(11) and C(12) lying at −0.336(4) and +0.471(4) Å from this best plane.

Figure 2. ORTEP view of compound **5**. Thermal ellipsoids as in Figure 1.

In the case of compound **3**, the activation of the methyl group directly generates a stereogenic carbon atom  $\beta$  to the metal atom, a result still rare,<sup>[7a]</sup> even if not unprecedented. In agreement, the  $^1\text{H}$  NMR spectrum shows two diastereotopic hydrogens  $\alpha$  to the metal atom ( $\delta_{\text{A}} = 2.66$ , dd;  $\delta_{\text{B}} = 3.07$ , dd).

## Reactivity of the Metallated Species

In contrast with the behaviour of the analogous cyclo-metallated species containing Pt–C( $\text{sp}^2$ ) bonds,<sup>[7d]</sup> displacement of the chloride ligand in complexes **2–5** is easily accomplished in mild conditions by both neutral (e.g. CO,  $\text{PPh}_3$ ) and anionic ligands (e.g.  $\text{CN}^-$ ).

Derivatives **7–12** were obtained in good yields in the presence of  $[\text{BF}_4]^-$  and characterised by analytical and spectroscopic methods. In particular the carbonyl derivatives  $[\text{Pt}(\text{L})\text{CO}][\text{BF}_4]$ , **7** and **8**, show strong IR absorptions in the region around  $2100\text{ cm}^{-1}$  [ $\tilde{\nu}_{\text{max}}(\text{cm}^{-1}) = 2107$ , **7**; 2100, **8**].

In the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **7**, the  $^2J_{\text{Pt-H}}$  and  $^1J_{\text{Pt-C}}$  values relevant to the metallated methylene group are small ( $J_{\text{Pt-H}} = 66$  and  $52$  Hz;  $J_{\text{Pt-C}} = 567$  Hz) in comparison with those of the chloride species **5** ( $J = 89, 79$  and  $736$  Hz, respectively), as previously observed when a strong  $\pi$  acceptor ligand is *cis* to the metal–carbon bond.<sup>[7b]</sup>

Compounds **9–11**,  $[\text{Pt}(\text{L})(\text{PPh}_3)][\text{BF}_4]$ , can be obtained both with a Pt/P 1:1 or 1:2 molar ratio, showing that the terdentate *N,N,C* system is rather robust. The  $^{31}\text{P}$  NMR spectra (see Table 3) are in agreement with a phosphorus *trans* to a nitrogen atom: the  $^1J_{\text{Pt,P}}$  values in the five-membered compounds **9** and **10**, as well as in  $[\text{Pt}(\text{L}^{\text{tb}})(\text{PPh}_3)][\text{BF}_4]$ ,<sup>[7b]</sup> are in the range 4000–4100 Hz, whereas in the six-membered species **11** a greater value, 4453 Hz is found. Similar values (4400–4471 Hz) have been observed in the case of the *N,N,C*( $\text{sp}^2$ ) six-membered compounds derived from substituted benzylbipyridines<sup>[7d]</sup> (see Scheme 1, compounds of type IV,  $\text{M} = \text{Pt}$ ).

The reactivity of compound **5** with the potentially bidentate ligands  $\text{L}'\text{--L}''$  ( $\text{Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2$ , dppm,  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ , dppe, and  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$ , dppae) was studied with the aim of establishing whether square-planar (mono- or dinuclear) or five-coordinated complexes were formed.

The reaction was investigated both with a 1:1 and a 2:1 Pt/ $\text{L}'\text{--L}''$  molar ratio: in the first case mononuclear cationic species of the general formula  $[\text{Pt}(\text{L})(\text{L}'\text{--L}'')]^+$  were formed, whereas dinuclear species containing a not so common unsupported  $\text{L}'\text{--L}''$  bridging unit were isolated in the second case.

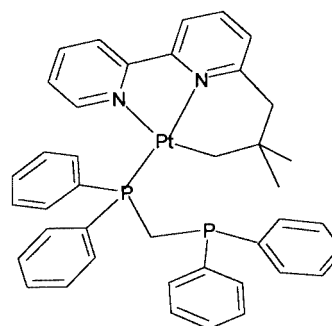
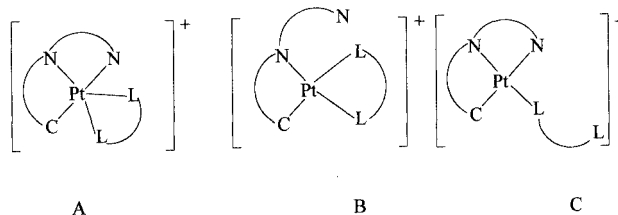
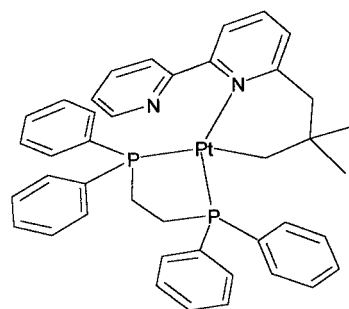
The dinuclear species  $[(\text{L})\text{Pt}(\mu\text{--L}'\text{--L}'')\text{Pt}(\text{L})]^{2+}$ , **12–15**, were characterised mainly on the basis of  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. In particular the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **12–15** deserve comments: the chemical shifts rule out a chelating behaviour of the ligands  $\text{L}'\text{--L}''$  and support a bridging coordination.<sup>[15]</sup> In the analysis of the  $^{31}\text{P}$  NMR spectra, due to the presence of  $^{31}\text{P}$  (100% natural abundance) and  $^{195}\text{Pt}$  (33.8% natural abundance) nuclei, four isotopomers have to be considered.

|     |                                                                                                             |       |
|-----|-------------------------------------------------------------------------------------------------------------|-------|
| I   | $\text{Pt}_\text{A}\text{--P}_\text{A} \text{---} \text{P}_\text{B}\text{--Pt}_\text{B}$                    | 43.8% |
| II  | $^{195}\text{Pt}_\text{A}\text{--P}_\text{A} \text{---} \text{P}_\text{B}\text{--Pt}_\text{B}$              | 22.4% |
| III | $\text{Pt}_\text{A}\text{--P}_\text{A} \text{---} \text{P}_\text{B}\text{--}^{195}\text{Pt}_\text{B}$       | 22.4% |
| IV  | $^{195}\text{Pt}_\text{A}\text{--P}_\text{A} \text{---} \text{P}_\text{B}\text{--}^{195}\text{Pt}_\text{B}$ | 11.4% |

In symmetric species, such as **12** and **14**, the  $^{31}\text{P}$  NMR spectra should consist of a singlet due to isotopomer I located in the centre of a satellite system. If the complex pattern due to IV is ignored owing to its low natural abundance, the satellite system is governed by species II–III, which in symmetric species, are equivalent. Isotopomers II and III give rise to an ABX spin system ( $\text{X} = ^{195}\text{Pt}$ ) and the  $^{31}\text{P}$  spectrum can be described as being formed by two AB subspectra.<sup>[16]</sup> Two different situations are shown by the dppm and dppe bridging systems, respectively: in the for-

mer case no  $^2J_{\text{P,P}}$  has been resolved, but a  $^3J_{\text{Pt,P}}$  (32 Hz) is observed, whereas in the latter case a  $^3J_{\text{P,P}} = 52$  Hz is present but the  $^4J_{\text{Pt,P}}$  is negligible. The reaction with dppe has also been carried out on complex **3**,  $[\text{Pt}(\text{L}^{\text{ip}})\text{Cl}]$ : in this case, due to the presence of a couple of stereogenic centres two diastereomers are expected, and this is reflected by the complex pattern of the  $^1\text{H}$  NMR spectrum. It is also worth noting that in these dinuclear complexes the  $^1J_{\text{Pt,P}}$  is very different in the six- and five-membered species ( $^1J_{\text{Pt,P}} = 4020$  Hz, **13**, and  $^1J_{\text{Pt,P}} = 4412$  Hz, **14**). Compound **15**,  $[(\text{L}^{\text{np}})\text{Pt}(\mu\text{--dppae})\text{Pt}(\text{L}^{\text{np}})][\text{BF}_4]_2$ , at variance with compounds **12–14**, is no longer symmetric so that resonances relevant to two different bipy units are present in the  $^1\text{H}$  NMR spectrum (Table 1).

When the reaction is carried out with a Pt/ $\text{L}'\text{--L}''$  1:1 molar ratio at least three different species should be considered: a pentacoordinated, (A), and two square-planar compounds (B and C).

**16****17**

In the case of dppm a type C species, **16**, is formed as indicated, inter alia, by the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which shows two different signals, corresponding to a coordinated ( $\delta = 7.69$  ppm, doublet,  $^1J_{\text{Pt,P}} = 4421$ ,  $^2J_{\text{P,P}} = 83$  Hz), and to an uncoordinated phosphorus atom ( $\delta = -25.9$  ppm doublet,  $^3J_{\text{Pt,P}} = 94$ ,  $^2J_{\text{P,P}} = 83$  Hz). The  $^1\text{H}$  NMR spectrum, as expected, is almost coincident with that of  $[\text{Pt}(\text{L}^{\text{np}})(\text{PPh}_3)]^+$  (e.g.  $\text{CH}_2\text{-Pt}$ ,  $\delta = 1.60$  ppm, **11**; 1.69, **16**). At variance, with dppe a type-B complex is obtained, **17**: in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum two sets of signals, centred at  $\delta = 44.84$  ppm ( $^1J_{\text{Pt,P}} = 1912$  Hz) and 32.37 ppm, ( $^1J_{\text{Pt,P}} = 4138$  Hz), are consistent with phosphorus atoms *trans* to a carbon and a nitrogen nucleus, respectively. The  $^1\text{H}$  NMR spectrum is complex, which is likely due to the crowded environment, all the protons of the four  $\text{CH}_2$  groups are not equivalent anymore.

The nature of complex **17** has been confirmed by the resolution of the structure.

The crystal consists of the packing of  $[\text{Pt}(\text{L}^{\text{np}})(\text{dppe})]^+$  cations,  $[\text{BF}_4]^-$  anions and  $\text{CH}_2\text{Cl}_2$  molecules in the molar ratio 1:1:1 with no unusual van der Waals contacts. Principal bond parameters are listed in Table 6. An ORTEP view of the cation is shown in Figure 3. The Pt atom displays a square-planar coordination with a slight tetrahedral distortion, with maximum distances from the best plane of  $-0.084(2)$  and  $+0.1035(3)$  Å for atoms C(13) and N(2), respectively. The Pt–P(1) distance, 2.314(1) Å, is markedly longer than the Pt–P(2) one, 2.209(1) Å, because of the strong *trans* influence of the C(13) alkyl atom. Also the Pt–C(13), 2.115(3) Å, and Pt–N(2), 2.127(2) Å, bond lengths are elongated by the *trans* influence of atoms P(1) and P(2), respectively. The Pt–N(2)–C(10)–C(11)–C(12)–C(13) ring is in a boat conformation, with atoms N(2), C(11), C(12), and C(13) approximately planar [maximum distances from their best plane are  $-0.068(2)$  Å for N(2) and  $+0.074(3)$  Å for C(10)] and atoms Pt and C(11) lying at  $-1.289(1)$  and  $-0.615(3)$  Å from the best plane, respectively. The P(1)–Pt–N(2) angle,  $100.9(1)^\circ$ , is larger than the P(2)–Pt–C(13) one,  $92.4(1)^\circ$ , probably as a result of the steric hindrance of the noncoordinated pyridine ring. The two pyridine rings are planar and form a dihedral angle of  $29.2(2)^\circ$ .

Table 6. Selected bond lengths (Å) and angles ( $^\circ$ ) with e.s.d.s in parentheses for cation **17**

|               |          |               |          |
|---------------|----------|---------------|----------|
| Pt–P(1)       | 2.314(1) | Pt–P(2)       | 2.209(1) |
| Pt–N(2)       | 2.127(2) | Pt–C(13)      | 2.115(3) |
| P(1)–Pt–P(2)  | 85.5(1)  | P(1)–Pt–N(2)  | 100.9(1) |
| P(1)–Pt–C(13) | 173.5(1) | P(2)–Pt–N(2)  | 173.0(1) |
| P(2)–Pt–C(13) | 92.4(1)  | N(2)–Pt–C(13) | 81.6(1)  |

The spectroscopic evidences for **18**,  $[\text{Pt}(\text{L}^{\text{np}})(\text{dppae})][\text{BF}_4]$ , indicate a monodentate P coordination of dppae, as for dppm, so that the *N,N,C* coordination environment is retained. The  $^{31}\text{P}\{^1\text{H}\}$  NMR resonance at  $\delta = 15.22$  ppm, is indicative of a nonchelating behaviour of dppae and the  $^1J_{\text{Pt,P}} = 4382$  Hz is typical for a P nucleus *trans* to a pyridinic nitrogen atom. In the  $^1\text{H}$  NMR spectrum the signals of

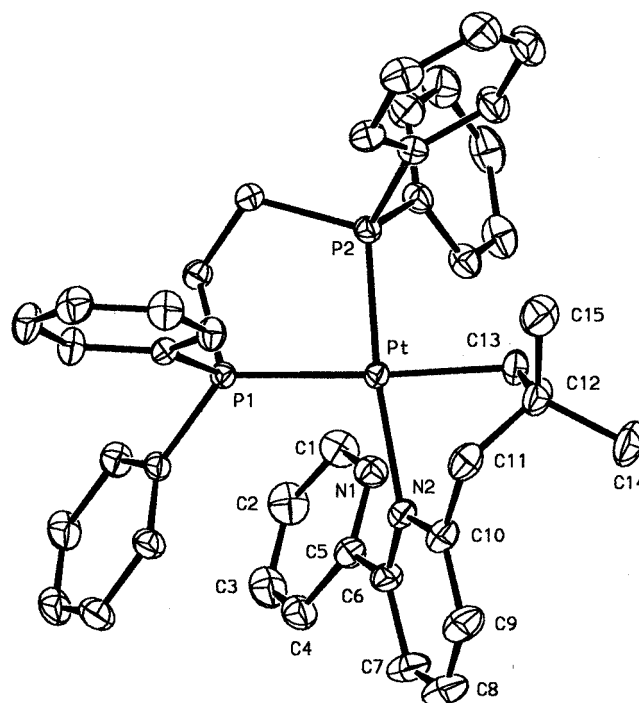


Figure 3. ORTEP view of compound **17**; thermal ellipsoids as in Figure 1

the pyridine rings as well as those of the  $\text{CH}_2\text{-Pt}$  groups are almost superimposable to those of compounds **11** and **16**, providing further evidence for the terdentate behaviour of the *N,N,C* ligand. In crowded species such as **16–18**, it is reasonable to deem that either the different size or the coordinating ability of the As atom with respect to P can direct the reaction towards a different outcome.

## Conclusions

In this paper we have shown that organoplatinum(II) compounds containing an *N,N,C*( $\text{sp}^3$ ) terdentate ligand are readily formed from  $\text{K}_2[\text{PtCl}_4]$  through a direct  $\text{C}(\text{sp}^3)\text{-H}$  bond activation of an unactivated aliphatic chain. Among the species obtained,  $[\text{Pt}(\text{L}^{\text{np}})\text{Cl}]$ , having a rare six-membered cyclometallated *N,C*( $\text{sp}^3$ ) cycle, and  $[\text{Pt}(\text{L}^{\text{ip}})\text{Cl}]$ , where a stereogenic centre has been directly formed through metallation, are of particular interest. The ligands studied have different reactivities: with  $\text{HL}^{\text{et}}$  the metallation can be achieved with difficulty and an adduct species, which can be regarded as an intermediate in the cyclometallation, has been isolated in the solid state and studied by X-ray diffraction. Also the structure of  $[\text{Pt}(\text{L}^{\text{np}})\text{Cl}]$  has been solved, allowing comparisons to be made with the analogous  $\text{Pd}^{\text{II}}$  six-membered *N,C*( $\text{sp}^3$ ) metallacycle. NMR spectroscopic data seem to indicate that in the six-membered  $[\text{Pt}(\text{N,N,C})\text{L}]^{n+}$  species ( $\text{L}$  = neutral,  $n = 1$ ; or anionic ligand,  $n = 0$ ) the Pt–C bond is weaker and the Pt–L ( $\text{L} = \text{PR}_3$ ) bond is stronger than in the five-membered ones, as indicated by  $^1J_{\text{Pt,C}}$  in **2–5** and by  $^1J_{\text{Pt,P}}$  in **9–18**.

In the course of the study on the reactivity of these species the chloride ligand has been shown to be rather labile whereas the *N,N,C* system is rather robust. The chloride ligand can easily be removed by anionic and neutral ligands: in the case of neutral bidentate ligands both mono- and binuclear species can be obtained. Only in one case (with dppe) has the external nitrogen atom of the terdentate *N,N,C* ligand been displaced from the metal to give a crowded  $[\text{Pt}(\text{N,C})(\text{P,P})]^+$  compound whose structure has been resolved in the solid state.

All the new species are remarkably stable towards air and moisture, even in solution, and so all the reactions can be performed in air.

## Experimental Section

The ligands HL were prepared according to literature methods.<sup>[12]</sup>  $\text{K}_2[\text{PtCl}_4]$  (43.035% Pt) was obtained from Engelhard S.r.l. and  $[(\text{DMSO})_2\text{PtCl}_2]$  was synthesised as described in ref<sup>[17]</sup>. All the solvents were purified before use according to standard methods.<sup>[18]</sup> Elemental analyses were performed with a Perkin–Elmer Elemental Analyser 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. Infrared Spectra were recorded with a Perkin–Elmer 983 using Nujol mulls.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9, 75.4 and 121.4 MHz respectively, and are collected in Table 1–3.

Chemical shifts are given in ppm relative to internal TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). The 2D experiments were performed by means of standard pulse sequences.

The mass spectrometric measurements were performed on a VG 7070EQ instrument, equipped with a PDP 11–250 J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix.

### Preparations

**[Pt(HL<sup>et</sup>)Cl<sub>2</sub>] (1):** a) *cis*- $[(\text{DMSO})_2\text{PtCl}_2]$  (215 mg, 0.51 mmol) was added to a solution of HL<sup>et</sup> (92 mg, 0.50 mmol) in  $\text{CHCl}_3$  (50 mL). The yellow solution was stirred for 36 h, then evaporated to dryness. The resulting solid was crystallised from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the analytical sample as a yellow solid. Yield 85% (191 mg). The reaction can also be carried out in other solvents (e.g. EtOH).

b)  $\text{K}_2[\text{PtCl}_4]$  (43.035% Pt, 1.297 g, 2.86 mmol) was dissolved in  $\text{H}_2\text{O}$  (30 mL) and filtered. HL<sup>et</sup> (523.7 mg, 2.85 mmol) and of 2 M HCl (5 mL) were added to the solution. The mixture was stirred at room temperature until the solution became colourless. The precipitate that formed was filtered, washed with  $\text{H}_2\text{O}$ , EtOH and  $\text{Et}_2\text{O}$  and recrystallised from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the analytical sample. Yield 30% (384 mg). M.p. 220 °C.  $\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{N}_2\text{Pt}$  (450.2): calcd. C 32.01; H 2.69; N 6.22; found C 31.97; N 6.25; IR (Nujol):  $\tilde{\nu}$  = 1600 s 1558 s, 1375 s, 335  $\text{cm}^{-1}$ .

**[Pt(L<sup>et</sup>)Cl] (2):** HL<sup>et</sup> (184 mg, 1.00 mmol) and 2 M HCl (3.5 mL) were added to an aqueous solution (30 mL) containing  $\text{K}_2[\text{PtCl}_4]$  (1.00 mmol) in water. The mixture was heated in a water bath for 1 d: the precipitate that formed was filtered, washed with water, EtOH and  $\text{Et}_2\text{O}$  and recrystallised from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . The crude obtained (362 mg) was a mixture ca. 1:1 of compounds **1** and **2** (NMR criterion). The products were separated by column chroma-

tography on silica gel, using a mixture of  $\text{CH}_2\text{Cl}_2/\text{acetone}$  20:1 as eluent. Complex **2** was obtained with a 30% yield. M.p. 258–260 °C (dec).  $\text{C}_{12}\text{H}_{11}\text{ClN}_2\text{Pt}$  (413.8): calcd. C 34.83, H 2.68, N 6.77; found C 35.44, H 2.80, N 6.50%. IR (Nujol):  $\tilde{\nu}$  = 1597 s 1556 w, 328  $\text{cm}^{-1}$ . FAB<sup>+</sup>:  $m/z$  = 413  $[\text{M}^+]$ , 378  $[\text{M} - \text{Cl}]$ , 791  $[\text{M}_2 - \text{Cl}]$ .

**[Pt(L)Cl] (L = L<sup>p</sup>, 3; L = L<sup>np</sup>, 5):** HL (1.00 mmol) and 2 M HCl (3.0 mL) were added to an aqueous solution (30 mL) containing  $\text{K}_2\text{PtCl}_4$  (1.00 mmol). The mixture was heated in a water bath until a colourless solution was obtained and an orange precipitate formed. The suspension was filtered off, washed with water, ethanol and diethyl ether and recrystallised from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ .

**3:** Yield 91% (389 mg), m.p. 245 °C.  $\text{C}_{13}\text{H}_{13}\text{ClN}_2\text{Pt}$  (427.8): calcd. C 36.50, H 3.06, N 6.55; found C 36.50, H 3.05, N 6.25%. IR (Nujol):  $\tilde{\nu}$  = 1596 s, 1552 w, 332  $\text{cm}^{-1}$ . FAB<sup>+</sup>:  $m/z$  = 427  $[\text{M}^+]$ , 392  $[\text{M} - \text{Cl}]$ , 819  $[\text{M}_2 - \text{Cl}]$ .

**5:** Yield 90% (410 mg), m.p.: 233 °C (dec).  $\text{C}_{15}\text{H}_{17}\text{ClN}_2\text{Pt}$  (455.8) calcd. C 39.52, H 3.76, N 6.15; found C 39.27, H 3.84, N 6.04%. IR (Nujol):  $\tilde{\nu}$  = 1600 s, 1564 w, 328  $\text{cm}^{-1}$ . FAB<sup>+</sup>:  $m/z$  = 455  $[\text{M}^+]$ .

**[Pt(L<sup>p</sup>)(CN)] (6):** Complex **3** (175 mg, 0.41 mmol) was added to a methanolic solution (25 mL) of KCN (27 mg, 0.41 mmol) whilst stirring. The mixture was stirred for 1 day, then evaporated to dryness and the solid residue recrystallised from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give the analytical sample as a yellow solid. Yield 56% (96 mg), m.p. 115 °C.  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{Pt}$  (418.3) calcd. C 40.19, H 3.13, N 10.04; found C 39.67, H 3.06, N 9.62%. IR (Nujol):  $\tilde{\nu}$  = 2105 m, 1595 s, 1557  $\text{cm}^{-1}$ .

**[Pt(L)(CO)] [BF<sub>4</sub>] (L = L<sup>p</sup>, 7; L = L<sup>np</sup>, 8):** NaBF<sub>4</sub> (121 mg, 1.00 mmol) was added to a solution of the relevant  $[\text{Pt}(\text{L})\text{Cl}]$  (0.25 mmol) in acetone (20 mL) whilst stirring and carbon monoxide, at atmospheric pressure, was bubbled through the solution. After 6 h the solvent was evaporated to dryness and the solid residue was crystallised from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ .

**7** Yield 70% (89 mg), m.p.: 235 °C.  $\Lambda_{\text{M}}$  ( $5 \cdot 10^{-4}$  M, acetone) = 138  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $\text{C}_{14}\text{H}_{13}\text{BF}_4\text{N}_2\text{OPt}$  (507.2): calcd. C 33.16, H 2.58, N 5.52; found C 33.28, H 2.60, N 5.30%. IR (Nujol):  $\tilde{\nu}$  = 2107 s 1598 s 1563 s 1050 b. FAB<sup>+</sup>:  $m/z$  = 420  $[\text{M}^+]$ , 392  $[\text{M} - \text{CO}]$ .

**8:** Yield: 76% (102 mg), m.p. 182–184 °C.  $\Lambda_{\text{M}}$  ( $5 \cdot 10^{-4}$  M, acetone) = 157  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $\text{C}_{16}\text{H}_{17}\text{BF}_4\text{N}_2\text{OPt}$  (535.2): calcd. C 35.91, H 3.20, N 5.23; found C 35.40, H 3.06, N 5.11%. IR (Nujol):  $\tilde{\nu}$  = 2100 s, 1600 s, 1560 w, 1050  $\text{cm}^{-1}$ .

**[Pt(L)(PPh<sub>3</sub>)] [BF<sub>4</sub>] (L = L<sup>et</sup>, 9; L = L<sup>p</sup>, 10; L = L<sup>np</sup>, 11):** PPh<sub>3</sub> (0.22 mmol) and NaBF<sub>4</sub> (100 mg, 0.900 mmol) were added to a solution of the relevant  $[\text{Pt}(\text{L})\text{Cl}]$  (0.20 mmol) in acetone (30 mL) whilst stirring. The mixture was stirred at room temperature, then evaporated to dryness and crystallised from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ .

**9:** Yield 90% (131 mg), m.p. 253 °C.  $\Lambda_{\text{M}}$  ( $5 \cdot 10^{-4}$  M acetone) = 150  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $\text{C}_{30}\text{H}_{26}\text{BF}_4\text{N}_2\text{PPt}$  (727.4): calcd. C 49.54, H 3.60, N 3.85; found C 48.93, H 3.55, N 3.71%. FAB<sup>+</sup>:  $m/z$  = 640  $[\text{M}^+]$ , 378  $[\text{M} - \text{PPh}_3]$ .

**10:** Yield 76% (113 mg), m.p. 275 °C.  $\Lambda_{\text{M}}$  ( $5 \cdot 10^{-4}$  M, acetone) = 130  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $\text{C}_{31}\text{H}_{28}\text{BF}_4\text{N}_2\text{PPt}$  (741.4): calcd. C 50.22, H 3.81, N 3.78; found C 50.34, H 3.91, N 3.63%. IR (Nujol):  $\tilde{\nu}$  = 1598 s, 1564 w, 1102 s, 1050br. s. FAB<sup>+</sup>:  $m/z$  = 654  $[\text{M}^+]$  392  $[\text{M} - \text{PPh}_3]$ .

**11:** Yield: 77% (118 mg), m.p. 263 °C.  $\Lambda_{\text{M}}$  ( $5 \cdot 10^{-4}$  M, acetone) = 150  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $\text{C}_{33}\text{H}_{32}\text{BF}_4\text{N}_2\text{PPt}$  (769.5): calcd. C 51.51,

H 4.19, N 3.64%; found C 51.26, H 4.09, N 3.65%. IR (Nujol):  $\tilde{\nu}$  = 1602 s, 1568 w, 1050 s, 540 w. FAB<sup>+</sup>:  $m/z$  = 682 [M<sup>+</sup>].

**[Pt<sub>2</sub>(L<sup>np</sup>)<sub>2</sub>(μ-dppm)] [BF<sub>4</sub>]<sub>2</sub> (12):** A mixture containing **5** (42 mg, 0.092 mmol), dppm (17.4 mg, 0.046 mmol) and NaBF<sub>4</sub> (43 mg) in acetone (30 mL) was stirred at room temperature for 4 days, then evaporated to dryness and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, to give the analytical sample as a yellow solid. Yield: 59% (34 mg), m.p. 168 °C (dec.).  $\Lambda_M$  (5 × 10<sup>-4</sup> M, acetone) = 260 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. C<sub>55</sub>H<sub>56</sub>B<sub>2</sub>F<sub>8</sub>N<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub> (1441.2): calcd. C 46.25, H 3.99, N 3.89; found C 46.37, H 4.03, N 3.96%. IR (Nujol):  $\tilde{\nu}$  = 2100 s, 1600 s, 1560 w, 1050 br s cm<sup>-1</sup>. FAB<sup>+</sup>:  $m/z$  = 1224 [M<sup>+</sup>], 1311 [M<sup>+</sup> + BF<sub>4</sub>].

**[Pt<sub>2</sub>(L)<sub>2</sub>(μ-dppe)] [BF<sub>4</sub>]<sub>2</sub> (L = L<sup>ip</sup>, **13**; L = L<sup>np</sup>, **14**):** dppe (0.20 mmol) and NaBF<sub>4</sub> (150 mg) were added to a suspension of the relevant [Pt(L)Cl] (0.40 mmol) in acetone (25 mL) whilst stirring. The mixture was stirred for a few hours, then evaporated to dryness and crystallised by CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample.

**13:** Yield 75% (203 mg); m.p. 280 °C.  $\Lambda_M$  (5.10<sup>-4</sup> M, acetone) = 202 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. C<sub>52</sub>H<sub>50</sub>B<sub>2</sub>F<sub>8</sub>N<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub> (1356.7): calcd. C 46.04, H 3.71, N 4.13; found C 45.74, H 3.74, N 4.01%. IR (Nujol):  $\tilde{\nu}$  = 1598 s 1564 w, 1050 broad cm<sup>-1</sup>.

**14:** (yellow) Yield 93% (279 mg); m.p. 184 °C (dec).  $\Lambda_M$  (5 × 10<sup>-4</sup> M, acetone) = 248 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. C<sub>56</sub>H<sub>58</sub>B<sub>2</sub>F<sub>8</sub>N<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>

(1497.7): calcd. C 45.71, H 4.04, N 3.74; found C 46.26, H 4.18, N 3.71%. IR (Nujol):  $\tilde{\nu}$  = 1602 s, 1569 w, 1050 br s cm<sup>-1</sup>.

**[Pt<sub>2</sub>(L<sup>np</sup>)<sub>2</sub>(μ-dppae)] [BF<sub>4</sub>]<sub>2</sub> (15):** A mixture containing **5** (39 mg, 0.085 mmol), dppae (18.8 mg, 0.0425 mmol) and NaBF<sub>4</sub> (50 mg) in acetone (30 mL) was stirred at room temperature for 1 day, then evaporated to dryness and crystallised from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O, to give the analytical sample as a yellow solid. Yield 80% (51 mg), m.p. 250–255 °C. C<sub>56</sub>H<sub>58</sub>AsB<sub>2</sub>F<sub>8</sub>N<sub>4</sub>P<sub>2</sub>Pt<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub> (1499.2): calcd. C 45.26, H 3.97, N 3.74; found C 45.02, H 3.98, N 3.68%.

**[Pt(L<sup>np</sup>)(L'–L'')][BF<sub>4</sub>] (L'–L'' = dppm, **16**, L'–L'' = dppe, **17**, L'–L'' = dppae, **18**):** NaBF<sub>4</sub> (120 mg) was added to an acetone solution (30 mL) of **5** (103 mg, 0.25 mmol) and L'–L'' (0.25 mmol) whilst stirring. The mixture was stirred for 4 h, then evaporated to dryness. The solid obtained was crystallised from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give the analytical sample as a yellow solid.

L'–L'' = dppm, **16**, pale-yellow. Yield: 90% (201 mg); m.p. 238–240 °C. C<sub>40</sub>H<sub>39</sub>BF<sub>4</sub>N<sub>2</sub>P<sub>2</sub>Pt (891.6): calcd. C 53.88, H 4.41, N 3.14; found C 53.40, H 4.53, N 3.07%.

L'–L'' = dppe, **17**, yellow. Yield: 88% (199 mg). M.p. 182–5 °C (dec).  $\Lambda_M$  (5 × 10<sup>-4</sup> M, acetone) = 133 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. C<sub>41</sub>H<sub>41</sub>BF<sub>4</sub>N<sub>2</sub>P<sub>2</sub>Pt (905.6): calcd. C 54.38, H 4.56, N 3.09; found C 54.42, H 4.56, N 3.11%. IR (Nujol):  $\tilde{\nu}$  = 1600, 1580 w, 1050 s, 540 s cm<sup>-1</sup>.

Table 7. Crystallographic experimental details

| Compound                                                            | <b>1</b>                                                          | <b>5</b> ·CHCl <sub>3</sub>                                       | <b>17</b> [BF <sub>4</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>                                     |
|---------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| Formula                                                             | C <sub>12</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> Pt | C <sub>16</sub> H <sub>18</sub> Cl <sub>4</sub> N <sub>2</sub> Pt | C <sub>42</sub> H <sub>43</sub> BCl <sub>2</sub> F <sub>4</sub> N <sub>2</sub> P <sub>2</sub> Pt |
| <i>M</i>                                                            | 450.24                                                            | 575.24                                                            | 990.57                                                                                           |
| Colour                                                              | yellow                                                            | yellow-orange                                                     | pale yellow                                                                                      |
| Crystal system                                                      | monoclinic                                                        | triclinic                                                         | triclinic                                                                                        |
| Space group                                                         | <i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)                       | <i>P</i> $\bar{1}$ (no. 2)                                        | <i>P</i> $\bar{1}$ (no. 2)                                                                       |
| <i>a</i> /Å                                                         | 14.909(2)                                                         | 9.209(1)                                                          | 11.969(1)                                                                                        |
| <i>b</i> /Å                                                         | 9.503(1)                                                          | 10.813(1)                                                         | 13.307(1)                                                                                        |
| <i>c</i> /Å                                                         | 17.732(2)                                                         | 10.980(1)                                                         | 13.659(1)                                                                                        |
| $\alpha$ /°                                                         | 90                                                                | 78.77(1)                                                          | 75.97(1)                                                                                         |
| $\beta$ /°                                                          | 99.87(2)                                                          | 65.60(1)                                                          | 83.35(1)                                                                                         |
| $\gamma$ /°                                                         | 90                                                                | 82.07(1)                                                          | 89.67(1)                                                                                         |
| <i>V</i> /Å <sup>3</sup>                                            | 2511.2(6)                                                         | 974.6(2)                                                          | 2095.8(3)                                                                                        |
| <i>Z</i>                                                            | 8                                                                 | 2                                                                 | 2                                                                                                |
| <i>F</i> (000)                                                      | 1680                                                              | 548                                                               | 984                                                                                              |
| <i>T</i> /K                                                         | 296                                                               | 296                                                               | 296                                                                                              |
| <i>D<sub>c</sub></i> /g cm <sup>-3</sup>                            | 2.38                                                              | 1.96                                                              | 1.57                                                                                             |
| Crystal dimensions (mm)                                             | 0.33 × 0.45 × 0.50                                                | 0.16 × 0.27 × 0.44                                                | 0.13 × 0.30 × 0.44                                                                               |
| $\mu$ (Mo- <i>K</i> $\alpha$ )/cm <sup>-1</sup>                     | 117.0                                                             | 78.3                                                              | 36.3                                                                                             |
| Min. and max.transmiss. factors                                     | 0.81–1.00                                                         | 0.88–1.00                                                         | 0.59–1.00                                                                                        |
| Scan mode                                                           | $\omega$                                                          | $\omega$                                                          | $\omega$                                                                                         |
| $\omega$ -scan width/°                                              | 1.20 + 0.35 tan $\theta$                                          |                                                                   |                                                                                                  |
| Frame width/°                                                       |                                                                   | 0.30                                                              | 0.30                                                                                             |
| Time per frame/s                                                    |                                                                   | 20                                                                | 20                                                                                               |
| No. of frames                                                       |                                                                   | 2450                                                              | 2450                                                                                             |
| Detector/sample distance/cm                                         |                                                                   | 5.00                                                              | 5.00                                                                                             |
| $\theta$ -range/°                                                   | 3–27                                                              | 3–26                                                              | 3–26                                                                                             |
| Reciprocal space explored                                           | quadrant                                                          | full sphere                                                       | full sphere                                                                                      |
| Measured reflections (total, independent)                           | 5444, 5444                                                        | 12214, 4798                                                       | 32505, 12183                                                                                     |
| <i>R</i> <sub>int</sub>                                             |                                                                   | 0.029                                                             | 0.026                                                                                            |
| Unique observed reflections with <i>I</i> > 3 $\sigma$ ( <i>I</i> ) | 4239                                                              | 3965                                                              | 10764                                                                                            |
| Final <i>R</i> and <i>R'</i> <sup>[a]</sup>                         | 0.030, 0.037                                                      | 0.023, 0.028                                                      | 0.024, 0.033                                                                                     |
| No. of variables                                                    | 308                                                               | 209                                                               | 496                                                                                              |
| Goodness of fit <sup>[b]</sup>                                      | 1.40                                                              | 0.94                                                              | 1.19                                                                                             |

<sup>[a]</sup>  $R = [\Sigma(|F_o| - k|F_c|)]/\Sigma F_o$ ,  $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}$ . <sup>[b]</sup>  $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{1/2}$ , where  $w = 1/[\sigma(F_o)]^2$ ,  $\sigma(F_o) = [\sigma^2(F_o^2) + (0.04F_o^2)^2]^{1/2}/2F_o$ ,  $N_o$  is the number of observations,  $N_v$  the number of variables.

$L'-L'' = \text{dppe}$ , **18**, yellow. Yield: 84% (199 mg), m.p. 205–213 °C (dec).  $\Lambda_M$  ( $5 \times 10^{-4}$  M, acetone) = 147  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ .  $\text{C}_{41}\text{H}_{41}\text{AsBF}_4\text{N}_2\text{PPt}$  (949.6): calcd. C 51.86, H 4.35, N 2.95; found C 51.47, H 4.39, N 2.97%. IR (Nujol):  $\tilde{\nu} = 1600 \text{ s}, 1560 \text{ w}, 1050 \text{ br}, 530 \text{ s cm}^{-1}$ .

**X-ray Data Collection and Structure Determination:** Crystal data and other experimental details are summarised in Table 7. The diffraction experiment concerning **1** was carried out on an Enraf–Nonius CAD-4 diffractometer at room temperature using Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a graphite crystal monochromator in the incident beam. A periodic monitoring of three standard reflections did not reveal any crystal decay. The diffracted intensities were corrected for Lorentz, polarisation, and absorption effects (empirical correction).<sup>[19]</sup>

The diffraction experiments concerning **5**·CHCl<sub>3</sub> and **17** [BF<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub> were carried out on a Bruker SMART CCD area-detector diffractometer at room temperature using Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from the least-squares refinement of 69 reflections (for **5**·CHCl<sub>3</sub>) and of 148 reflections (for **17**[BF<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>) measured in three different sets of 15 frames each, in the range  $3 < \theta < 23^\circ$ . At the end of data collections the first 50 frames, containing 171 and 362 reflections (for **5**·CHCl<sub>3</sub> and **17**[BF<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, respectively) were recollected to have a monitoring of crystal decay, which was not observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,<sup>[20]</sup> and an empirical absorption correction was applied (SADABS<sup>[21]</sup>) to the collected reflections. Scattering factors and anomalous dispersion corrections were taken from ref.<sup>[22]</sup>

The calculations were performed on a Pentium III PC using the Personal Structure Determination Package<sup>[23]</sup> and the physical constants tabulated therein.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimising the function  $\Sigma w(F_o - k|F_c|)$  (refinement on  $F$ ). In compound **17**[BF<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub> three fluorine atoms of the BF<sub>4</sub><sup>−</sup> anion are disordered. Anisotropic thermal factors were refined for all the non-hydrogen atoms. Hydrogen atoms were placed in their ideal positions (C–H: 0.97 Å, B: 1.10 times that of the carbon atom to which they are attached) and not refined. The final Fourier maps showed maximum residuals of 1.34(19) e/Å<sup>3</sup> at 0.87 Å from Pt<sub>A</sub> (in compound **1**), 1.22(11) e/Å<sup>3</sup> at 0.96 Å from Pt (in compound **5**·CHCl<sub>3</sub>), and of 1.18(9) e/Å<sup>3</sup> at 0.83 Å from Pt (in compound **17**[BF<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>). The atomic coordinates of the structure models have been deposited with the Cambridge Data File.

CCDC-181834 (**1**), -181835 (**5**·CHCl<sub>3</sub>) and -181836 (**17**[BF<sub>4</sub>]·CH<sub>2</sub>Cl<sub>2</sub>) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## Acknowledgments

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