

# Some platinum(II) complexes containing bis(diphenylphosphino)-acetylene $\text{PPh}_2\text{C}\equiv\text{CPh}_2$ : synthesis, characterisation and crystal structures †

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The reactivity of *cis*-[Pt(C≡CR)<sub>2</sub>(COD)] (R = Bu<sup>t</sup>, Ph) and *cis/trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tht)<sub>2</sub>] towards PPh<sub>2</sub>C≡CPh<sub>2</sub> (dppa) in several molar ratios has been explored. Treatment of *cis*-[Pt(C≡CR)<sub>2</sub>(COD)] with 1 equiv. of dppa leads to novel alkynyl Pt(II) dimers [Pt<sub>2</sub>(C≡CR)<sub>4</sub>(μ-dppa)<sub>2</sub>] (R = Bu<sup>t</sup> **1**, Ph **2**) with a double dppa-bridged system. However, the reactions with 2 equiv. of dppa only give mixtures of **1** or **2** and the expected *cis*-[Pt(C≡CR)<sub>2</sub>(dppa-κP)] (R = Bu<sup>t</sup> **3**, Ph **4**). The analogous reactions using *cis*- or *trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tht)<sub>2</sub>] (tht = tetrahydrothiophene) as precursors afford, in 1 : 1 molar ratio, the homologous pentafluorophenyl-bis(μ-dppa) diplatinum species [Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>(μ-dppa)<sub>2</sub>] **5** or the polymer *trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(μ-dppa)]<sub>n</sub> **7** and, in 1 : 2 molar ratio, the mononuclear *cis*- or *trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(dppa-κP)]<sub>2</sub> (**6**, **8**) derivatives. The molecular structure of **5** has been confirmed by X-ray diffraction. Furthermore, [Pt<sub>2</sub>(C≡CR)<sub>4</sub>(μ-dppa)<sub>2</sub>] **1** and **2** react with 2 equiv. of *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] to afford the tetranuclear bis(μ-alkynyl)bis(μ-dppa) platinum complexes [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-C≡CR)<sub>2</sub>Pt(μ-dppa)]<sub>2</sub> (R = Bu<sup>t</sup> **9**, Ph **10**). However, a mixture of **9/10** and [(RC≡C)<sub>2</sub>Pt(μ-dppa)<sub>2</sub>Pt(μ-C≡CR)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (R = Bu<sup>t</sup> **11**, Ph **12**) is observed if the reactions are carried out in 1 : 1 molar ratios. Finally, dinuclear P-bonded mono μ-dppa complexes of type Q<sub>2</sub>[*cis*-{Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>X}<sub>2</sub>(μ-dppa)] [Q = NBu<sub>4</sub>, X = C<sub>6</sub>F<sub>5</sub> **13**, X = Cl **14**; Q = PMePh<sub>3</sub>, X = C≡CPh **15** (X-ray)] have also been prepared starting from the appropriate precursors and dppa.

The acetylenic ditertiary phosphine bis(diphenylphosphino)-acetylene PPh<sub>2</sub>C≡CPh<sub>2</sub> (dppa), a potential trifunctional ligand, has been used extensively in transition metal chemistry,<sup>1-7</sup> forming binuclear,<sup>2</sup> polynuclear<sup>2f,k,3,4a</sup> or even polymeric<sup>5</sup> complexes. The dominant coordination modes, which leave the ligand intact, are end-on terminal<sup>4</sup> and end-on bridging<sup>2</sup> coordination through the phosphorus functions. In the latter case, the diphosphine can connect separated metal-ligand fragments<sup>2a-m</sup> or homo and hetero cluster moieties.<sup>2f,3a-g</sup> This ligand is also capable of bridging one metal-metal cluster edge,<sup>3h-k</sup> as observed in Re<sub>3</sub><sup>3h</sup> and Ir<sub>3</sub>W<sup>3i</sup> clusters, but obviously due to its rigidity it is not capable of acting as a κ<sup>2</sup>PP' chelating ligand.

Coordination to a metal site through the alkyne functionality (η<sup>2</sup>-fashion) is observed on rare occasions.<sup>4b,6</sup> Ward and Templeton<sup>4b</sup> have reported the complex [W(CO)(Ph<sub>2</sub>PC≡CPh<sub>2</sub>)(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>], in which the dppa ligand is coordinated through the C≡C linkage as a four-electron donor; this coordination results in a distortion of the skeleton of the alkyne function, which enables the W-coordinated η<sup>2</sup>-dppa to bridge a Co-Co bond (μ<sub>3</sub>-dppa-η<sup>2</sup> : κP : κP') or even to chelate (μ<sub>3</sub>-dppa-η<sup>2</sup> : κ<sup>2</sup>PP') a tetracarbonyl metal fragment using the lone pairs of the P atoms.<sup>7</sup>

In addition, in some ruthenium, osmium and rhenium carbonyl cluster compounds with P-coordinated dppa ligands, one or two of the PPh<sub>2</sub> groups may be cleaved thermally or under photoinduced conditions to yield ligand fragments such

as Ph<sub>2</sub>P along with C<sub>2</sub>PPh<sub>2</sub>,<sup>3g,8</sup> PhC<sub>2</sub>PPh<sub>2</sub><sup>8b</sup> or C<sub>2</sub>.<sup>3h,9</sup> These fragments, coordinated in the clusters as ligands, may also take part in C-C coupling reactions in the presence of unsaturated molecules.<sup>10</sup>

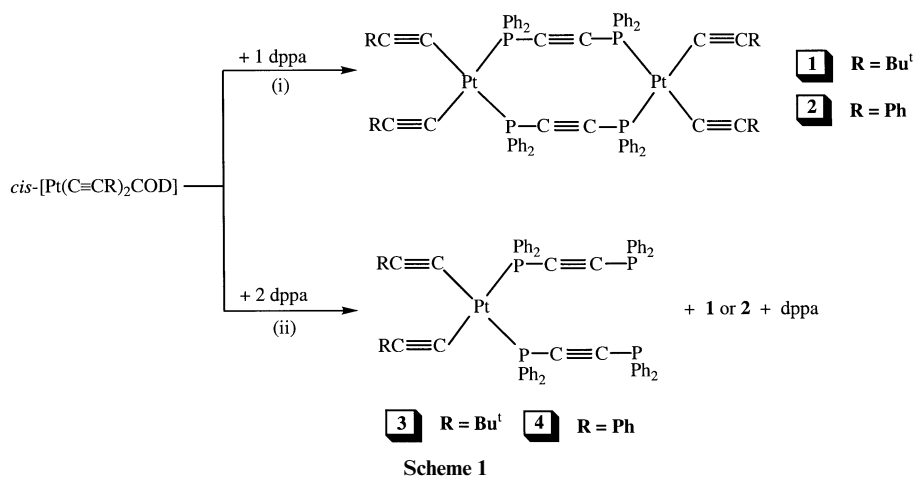
In connection with our work on polymetallic alkynyl platinum complexes, we recently explored the synthesis of the phosphinoalkyne (PPh<sub>2</sub>C≡CR') derivatives *cis*-[PtX<sub>2</sub>(PPh<sub>2</sub>C≡CR')<sub>2</sub>] (X = Cl,<sup>11a</sup> C≡CR,<sup>11b</sup> C<sub>6</sub>F<sub>5</sub>,<sup>11c</sup> R, R' = Ph, Bu<sup>t</sup>) and their reactivity towards the labile neutral species *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] (thf = tetrahydrofuran) as an accessible route for obtaining homobridged (μ-X)<sub>2</sub> (X = Cl, C≡CR), heterobridged (μ-PPh<sub>2</sub>C≡CPh)(μ-X) or unusual C-C coupled homo- or hetero-dinuclear complexes. These results prompted us to study the reactivity of alkynyl and pentafluorophenyl platinum complexes towards dppa in several molar ratios. We describe here the synthesis of novel Pt(II) monomers containing P-bonded dppa [PtX<sub>2</sub>(dppa-κP)]<sub>2</sub>, dimers with double dppa-bridged systems [Pt<sub>2</sub>X<sub>4</sub>(μ-dppa)<sub>2</sub>] and the polynuclear complex *trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(μ-dppa)]<sub>n</sub>. We also describe the reactivity of [Pt<sub>2</sub>(C≡CR)<sub>4</sub>(μ-dppa)<sub>2</sub>] towards *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] in either a 1 : 1 or 1 : 2 molar ratio and finally, the synthesis and characterisation of new binuclear mono(dppa) bridged platinum complexes.

## Results and discussion

### [Pt<sub>2</sub>X<sub>4</sub>(μ-dppa)<sub>2</sub>] and [PtX<sub>2</sub>(dppa-κP)]<sub>2</sub> (X = C≡CR, C<sub>6</sub>F<sub>5</sub>)

A general synthetic route for preparing *cis*-bis(alkynyl)bis(phosphine) derivatives is based in the easy displacement of

† Dedicated to Professor Rafael Usón on the occasion of his 75<sup>th</sup> birthday.



labile COD from the precursor complexes  $cis\text{-[Pt(C}\equiv\text{CR)}_2(\text{COD})]$  (COD) by the incoming phosphine ligand.<sup>11b,12a,b</sup> Thus, we assume that these complexes (R = Bu<sup>t</sup>,<sup>12b</sup> Ph<sup>12c</sup>) are suitable starting materials for the preparation of the corresponding derivatives with the stoichiometry  $cis\text{-[Pt(C}\equiv\text{CR)}_2(\text{dppa-}\kappa\text{P})_2]$  and  $cis\text{-[Pt(C}\equiv\text{CR)}_2(\text{dppa})]$ . In the latter, the ligand is not capable of chelating ( $\kappa^2\text{PP}'$ ) a single metal centre and the formulation may correspond to a dimer stabilised by two bridging  $\mu\text{-}\kappa\text{P} : \kappa\text{P}'$  dppa ligands.

As is shown in Scheme 1 (path i), treatment of the complexes  $cis\text{-[Pt(C}\equiv\text{CR)}_2(\text{COD})]$  (R = Bu<sup>t</sup>, Ph) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature with dppa (1 : 1 molar ratio) leads to the formation of the novel alkyne Pt(II) dimers  $[\text{Pt}_2(\text{C}\equiv\text{CR})_4(\mu\text{-dppa})_2]$  (R = Bu<sup>t</sup> **1**, Ph **2**) in moderate yields (61% **1**, 66% **2**). Complexes **1** (white) and **2** (pale yellow) are air stable solids, soluble in the usual organic solvents, and display spectral properties (see Experimental section and Table 1) consistent with their formulation. Thus, although only **2** shows one medium absorption at 2124 cm<sup>-1</sup> in its IR spectrum attributed to the  $\nu(\text{C}\equiv\text{C})$  of the terminal alkyne ligands (the  $\nu(\text{C}\equiv\text{C})$  mode of the symmetric dppa is not observed),<sup>2a</sup> the <sup>1</sup>H NMR spectrum of **1** exhibits the expected singlet due to the equivalent C≡CBu<sup>t</sup> at  $\delta$  0.86 with the correct integration ratio. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra show only a signal at  $\delta$  -7.84 (**1**) and -7.52 (**2**) with <sup>1</sup>J(<sup>195</sup>Pt<sup>31</sup>P) [2269 (**1**) and 2290 Hz (**2**)] clearly lower than those observed for other Pt(II) dimers containing two bridging dppa ligands  $\{[\text{Pt}_2\text{X}_4(\mu\text{-dppa})_2]$  (X = halide,<sup>2i</sup> SR<sup>2m</sup>) in agreement with the strong *trans* influence of the alkyne ligands. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectra, the alkyne carbons (second order AXX' spin systems, see Experimental section for details) are found in typical chemical shift ranges [ $C_\alpha/C_\beta$ ,  $\delta$  82.7/118.1 **1**; 98.7/110.4 ppm **2**;  ${}^2J(C_\alpha P_{trans}) + {}^2J(C_\alpha P_{cis})/{}^3J(C_\beta P_{trans}) + {}^3J(C_\beta P_{cis})$ ] 179.5/35.7 Hz **1**; 178.0/36.3 Hz **2**], the magnitude of the <sup>13</sup>C-<sup>195</sup>Pt coupling constants [<sup>1</sup>J(CPt) 1156 Hz **1**, 1165 Hz **2**; <sup>2</sup>J(CPt) 312 Hz **1**, 317 Hz **2**] being comparable to those observed in neutral bis(alkynyl) complexes of the type  $[\text{Pt}(\text{C}\equiv\text{CR})_2\text{L}_2]$  (L = phosphine).<sup>11b,12a,13</sup> The signals due to the equivalent acetylenic carbons of the bridging dppa occur at a chemical shift intermediate between the C<sub>α</sub> and C<sub>β</sub> resonances of the alkyne ligands, with the appearance of a doublet of pseudotriplets (dpst) ( $\delta$  100.7 **1**, 100.8 **2**) due to a more complex A[X]<sub>3</sub> or A[X]<sub>4</sub> (A = <sup>13</sup>C; X = <sup>31</sup>P) spin system. The phenyl rings of the dppa ligands appear as magnetically equivalent.

In order to force the formation of the mononuclear derivatives containing two *cis* dppa ligands, the reactions of  $cis\text{-[Pt(C}\equiv\text{CR)}_2(\text{COD})]$  with 2 equiv. of dppa were also explored (Scheme 1, path ii). <sup>31</sup>P{<sup>1</sup>H} NMR monitoring of these reactions indicates the presence of mixtures of dimers  $[\text{Pt}_2(\text{C}\equiv\text{CR})_4(\mu\text{-dppa})_2]$  (**1** or **2**) and the expected monomers  $cis\text{-[Pt(C}\equiv\text{CR)}_2(\text{dppa-}\kappa\text{P})_2]$  (R = Bu<sup>t</sup> **3**, Ph **4**), together with free dppa in ratios of 1 : 2 (**1** : **3**, 30 min of reaction) or 2.2 : 1 (**2** : **4**, 10 min), respectively. A gradual increase in the dimer species

(**1** or **2**) is observed after 2 hours of reaction, precluding the isolation of the mononuclear complexes **3** or **4** as pure solids. However, **3** and **4** could be characterised from the reaction mixtures by spectroscopic methods. Thus, in the <sup>31</sup>P{<sup>1</sup>H} spectra, besides the signals attributed to the dimers **1** or **2** and the signal of free dppa ( $\delta$  -32.1), two singlets are observed. The low-field resonance ( $\delta$  -5.54 **3**, -5.61 **4**) is assigned to the phosphorus atom bonded to the Pt centre with <sup>1</sup>J(PtP) slightly higher (see Table 1) than those observed in the dimers **1** or **2**; and the high-field resonance, with chemical shifts similar to that of free dppa ( $\delta$  -31.64 **3**, -31.62 **4**) can be assigned to the free end of the dppa. As is expected, in the <sup>1</sup>H NMR of the mixture **1/3** (molar ratio 1 : 2) two singlets, due to the Bu<sup>t</sup> groups, with the appropriate integration ratio, are observed ( $\delta$  0.86 **1**, 0.85 **3**).

The reactivity of *cis*- and *trans*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{tht})_2]$  (tht = tetrahydrothiophene) towards dppa in 1 : 1 and 1 : 2 molar ratios, has also been studied (see Scheme 2, paths a, b). Thus, the double-bridging dppa dimer  $[\text{Pt}_2(\text{C}_6\text{F}_5)_4(\mu\text{-dppa})_2]$  **5** is easily obtained by treatment of the mononuclear complex *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{tht})_2]$  with 1 equiv. of dppa in CH<sub>2</sub>Cl<sub>2</sub> (path a, i). The synthesis of the mononuclear derivative *cis*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{dppa-}\kappa\text{P})_2]$  **6** is optimal with the use of an excess of dppa (1 : 2.35) in CH<sub>2</sub>Cl<sub>2</sub> for 1 hour (path a, ii). The use of a lesser amount of dppa (1 : 2 or 1 : 2.25 molar ratios) yields a mixture of **5** and **6**, while larger excesses (1 : 2.5 or 1 : 3 molar ratios) afford a solid which is a mixture of **6** and dppa.

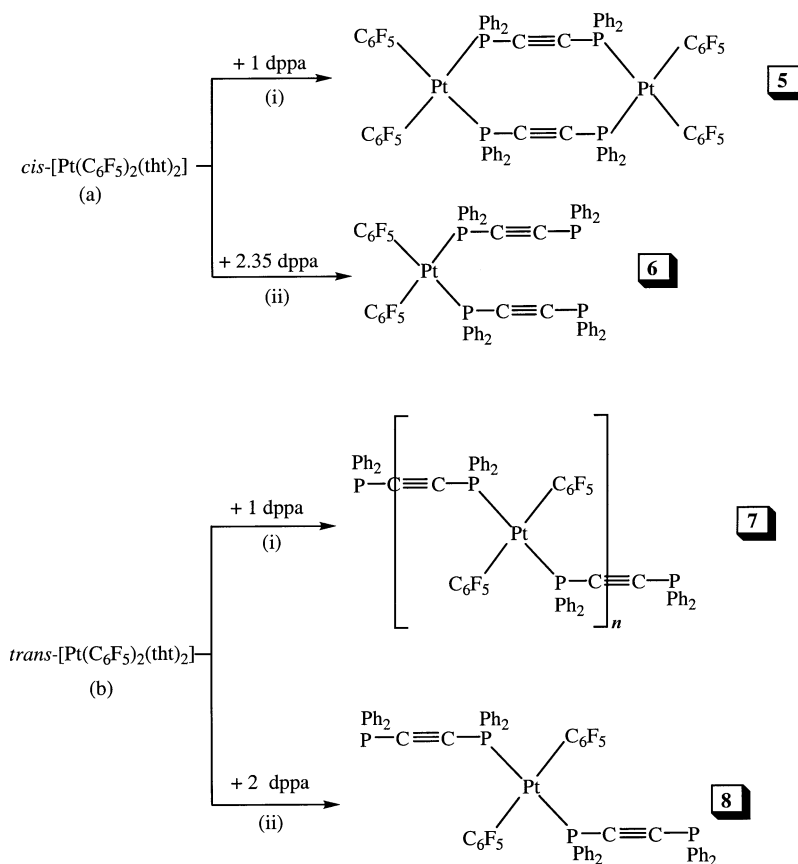
When *trans*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{tht})_2]$  is reacted with 1 equiv. of dppa in CH<sub>2</sub>Cl<sub>2</sub>, a very insoluble white solid is formed (path b, i), which is formulated as *trans*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-dppa})_n]$  **7** on the basis of analytical data and its IR spectrum, which confirms a *trans* arrangement of the C<sub>6</sub>F<sub>5</sub> groups. However, when 2 equiv. of dppa are used, the mononuclear compound *trans*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{dppa-}\kappa\text{P})_2]$  **8** is isolated (path b, ii) as a white, air stable solid (see Experimental section).

As is expected, only the derivatives **6** and **8**, which contain the monodentate dppa ligand, show a weak absorption assignable to  $\nu(\text{C}\equiv\text{C})$  (2104 cm<sup>-1</sup> **6**, 2119 cm<sup>-1</sup> **8**) in their IR spectra. As expected, the IR spectra of the *cis* derivatives (**5** and **6**) exhibit two X-sensitive C<sub>6</sub>F<sub>5</sub> absorptions in the 782–794 cm<sup>-1</sup> range and the *trans* complexes (**7** and **8**) only one, confirming the retention of the configurations during the reactions. The <sup>19</sup>F NMR spectra display three signals of relative intensity 2 : 1 : 2, confirming that not only the C<sub>6</sub>F<sub>5</sub> groups but also the two halves of each ring are equivalent at least on the NMR time-scale. The most noticeable difference is the lower coupling constant <sup>3</sup>J(PtF<sub>5</sub>) in the *trans* derivative **8** (236 Hz) in relation to those observed in the *cis* species (336 Hz **5**, ~308 Hz **6**), in accord with the greater *trans* influence of the C<sub>6</sub>F<sub>5</sub> group compared to the phosphorus donor atom. The signal due to the equivalent phosphorus atoms in complex **5** appears in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum as a singlet ( $\delta$  -4.82) with a coupling constant [<sup>1</sup>J(PtP) = 2263 Hz] comparable to those observed in

Table 1  $^1\text{H}$ ,  $^3\text{P}\{^1\text{H}\}$  and  $^{19}\text{F}$  NMR data in  $\text{CDCl}_3$  for the complexes **1–15** ( $\delta$  in ppm and  $J$  in Hz)<sup>a</sup>

Compound	$^1\text{H}$		$^3\text{P}$		$^{19}\text{F}$		
	$\delta(\text{Bu}^t)$	$\delta(\text{Ph})$	$\delta(\text{P}_1)$ [ $J(\text{PtP}_1)$ ]	$\delta(\text{P}_2)$ [ $J(\text{PtP}_2)$ ]	$\delta(\text{F}_o)^b$	$\delta(\text{F}_p)$	$\delta(\text{F}_m)$
<b>1</b>	0.86 (s, 36H)	7.51 (m, 16H), 7.30 (m, 8H) 7.14 (m, 16H)	-7.84 (s) [2269]	—	—	—	—
<b>2</b>	—	7.58 (m, 16H), 7.35 (m, 8H) 7.18 (m, 16H), 7.02 (m, 12H)	-7.52 (s) [2290]	—	—	—	—
<b>3<sup>c</sup></b>	0.85 (s)	6.85 (m, 8H) <sup>d</sup>	-5.54 (s) [2302]	-31.64 (s)	—	—	—
<b>4<sup>c</sup></b>	—	<sup>d</sup>	-5.61 (s) [2324]	-31.62 (s)	—	—	—
<b>5</b>	—	7.40 (m, 24H), 7.17 (m, 16H)	-4.82 (s) [2263]	—	-117.6 (m)	-161.4 (t)	-163.3 (m)
<b>6</b>	—	7.49 (m, 8H), 7.38–7.20 (m, 24H), 7.10 (t, 8H)	-5.41 (s) [2366]	-31.84 (s)	[336]	-162.4 (t)	-163.8 (t)
<b>8</b>	—	7.52 (m), 7.41 (m), 7.31 (m), 7.24 (m) (40H)	-5.08 (s) [2879]	-31.72 (s)	[ $\approx$ 308]	-161.7 (t)	-163.7 (m)
<b>9</b>	0.80 (s, 18H) 0.79 (s, 18H) 0.76 (sh)	7.56 (m), 7.42 (m) 7.23 (m) (40H)	-10.88 (s) [2606]	—	[236]	-163.8 (t, 3F <sub>p</sub> + t, 1F <sub>p</sub> )	-165.1 (m, 4F <sub>m</sub> ) -166.0 (m, 1F <sub>m</sub> ) -166.4 (m, 3F <sub>m</sub> )
<b>10</b>	—	7.62 (m, 12H), 7.45 (t, 8H) 7.27 (m, 24H), 7.07 (t, 8H) 6.84 (d, 8H)	-10.71 (s) [2604]	—	[ $\approx$ 468]	-163.3 (t)	-165.9 (s, br)
<b>11<sup>c</sup></b>	<sup>e</sup>	<sup>d</sup>	-11.44 (s) [2614]	-7.22 (s) [2260]	—	<sup>d</sup>	—
<b>12<sup>c</sup></b>	—	<sup>f</sup>	-11.07 (s) [2612]	-7.06 (s) [2281]	—	<sup>g</sup>	—
<b>13<sup>h,i</sup></b>	—	7.59 (m), 7.35 (m) 7.26 (m) (20H)	-4.81 (s) [2659]	—	-114.5 (dm, 8F <sub>o</sub> ) [315]	-166.2 (m, 6F <sub>p</sub> + 8F <sub>m</sub> )	—
<b>14<sup>h</sup></b>	—	7.78 (m, 8H) 7.21 (m, 12H)	-1.94 (s) [2564]	—	-115.1 (m, 4F <sub>o</sub> ) [410]	-166.8 (4F <sub>m</sub> ) -165.5 (m, 4F <sub>m</sub> )	—
<b>15<sup>i,j</sup></b>	—	8.03–7.78 (m, 36H) 7.26–7.15 (m, 14H) 6.91–6.74 (m, 10H)	-5.67 (s, br) [2550]	—	[440]	-164.8 (t, 2F <sub>p</sub> ) -165.7 (t, 2F <sub>p</sub> ) -166.2 (m, 4F <sub>p</sub> + 2F <sub>m</sub> )	—

<sup>a</sup> Compound **7** is extremely insoluble. <sup>b</sup>  $J(\text{PtF}_o)$  in square brackets. <sup>c</sup> Identified spectroscopically in a mixture containing the 1 : 1 and 1 : 2 products. <sup>d</sup> It cannot be determined: in this region the signals of the 1 : 1 and 1 : 2 products overlap. <sup>e</sup>  $\delta$  0.80, 0.79, 0.77 (9 + 11) bridging; 0.87 (1), 0.88 (11) terminal. <sup>f</sup> Signals in identical positions as in the product **10**. <sup>g</sup>  $\delta$  -117.1 [380] (s, br; F<sub>o</sub> **10** + **12**), -163.34 (t, F<sub>m</sub> **10**), -163.42 (t, F<sub>m</sub> **12**), -165.9 (s, br; F<sub>m</sub> **10** + **12**). <sup>h</sup> The complexes **13** and **14** show signals due to the NBu<sub>4</sub><sup>+</sup> cation at  $\delta$  0.99/0.88 (CH<sub>3</sub>), 1.42/1.31 ( $\alpha$ -CH<sub>2</sub>), 1.83/1.46 ( $\beta$ -CH<sub>2</sub>), 3.45/3.00 ( $\gamma$ -CH<sub>2</sub>). <sup>i</sup> In CD<sub>3</sub>COCD<sub>3</sub>. <sup>j</sup> Additionally it shows a singlet at  $\delta$  22.4 in its  $^3\text{P}$  spectrum due to the PMePh<sub>3</sub><sup>+</sup> cation.



**1** and **2**, which contain a similar double bridge system. Complexes **6** and **8** show the expected coordinated and free phosphorus resonances of the dppa as singlets ( $\delta -5.41$  Pt–P,  $-31.84$  PtPC $\equiv$ CP **6**;  $\delta -5.08$ ,  $-31.72$  **8**) and again, in agreement with the larger *trans* influence of the C<sub>6</sub>F<sub>5</sub> groups, the magnitude of  $^1J(\text{PtP})$  (2879 Hz) in **8** is clearly greater than that in the corresponding *cis* derivatives (2263 Hz **5**, 2366 Hz **6**).

The dimeric nature of the complexes [Pt<sub>2</sub>L<sub>4</sub>(dppa)<sub>2</sub>] (L = C<sub>6</sub>F<sub>5</sub> **5**, C $\equiv$ CR **1**, **2**) has been unambiguously confirmed by an X-ray diffraction study carried out on crystals of [Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>( $\mu$ -dppa)<sub>2</sub>] **5** (Fig. 1a). Relevant bond lengths and angles are listed in Table 2. As can be seen, the double dppa bridges connect the two platinum centres in a *cis* disposition. The square-planar coordination of the platinum atoms is slightly distorted, the P–Pt–P angles being larger than ideal [94.57(11) $^\circ$  and 95.48(10) $^\circ$ ] and with smaller C(C<sub>6</sub>F<sub>5</sub>)–Pt–C(C<sub>6</sub>F<sub>5</sub>) angles of 85.6(4) $^\circ$  and 84.2(4) $^\circ$ , and *trans* angles in the range 171.3(4)–174.2(3) $^\circ$ .

The two dppa bridges have different orientations (see Fig. 1b), the dihedral angle between the two coordination planes being 31.27(1) $^\circ$ ; the torsion angles Pt(1)–P(1)–P(4)–Pt(2) and Pt(1)–P(2)–P(3)–Pt(2) are 11.72(6) $^\circ$  and 121.34(5) $^\circ$ , respectively. A similar disposition has been found previously in related [Pt<sub>2</sub>X<sub>4</sub>( $\mu$ -dppa)<sub>2</sub>] (X = Cl, I) complexes.<sup>2f</sup> The formation of the strained 10-membered Pt<sub>2</sub>P<sub>4</sub>C<sub>4</sub> ring causes a considerable bowing of both PC $\equiv$ CP backbones with the C $\equiv$ CP angles lying in the range 176.2(10)–170.3(11) $^\circ$  and, correspondingly, with the M–P–C angles in the range 104.6(4)–115.6(4) $^\circ$ .

#### Reactivity of [Pt<sub>2</sub>(C $\equiv$ CR)<sub>4</sub>( $\mu$ -dppa)<sub>2</sub>] towards *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>]

With the purpose of synthesising complexes containing Ph<sub>2</sub>PC $\equiv$ CPh<sub>2</sub> acting as a tridentate ligand we tried to force the coordination of the alkyne functions by exploring the reactivity of the pentafluorophenyl derivative **5** towards *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] or [Pt( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>]. Unfortunately, neither at room

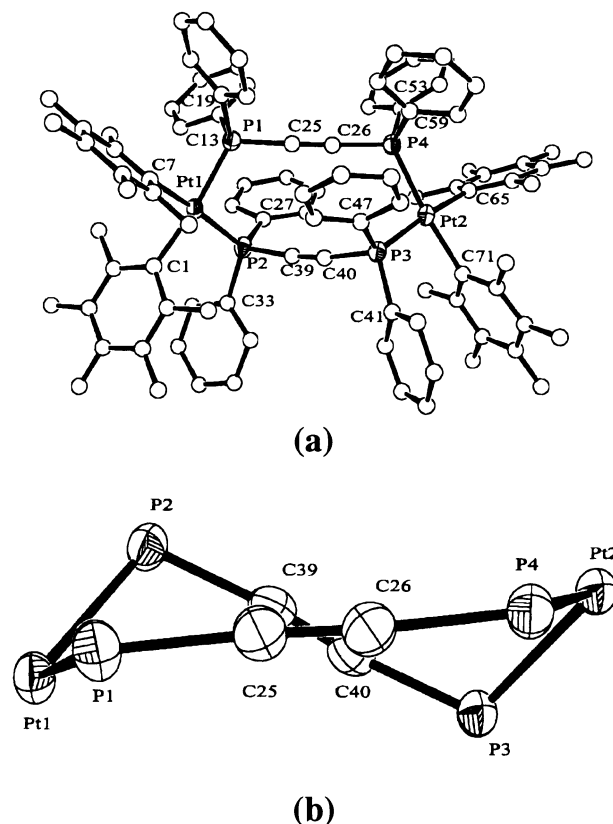
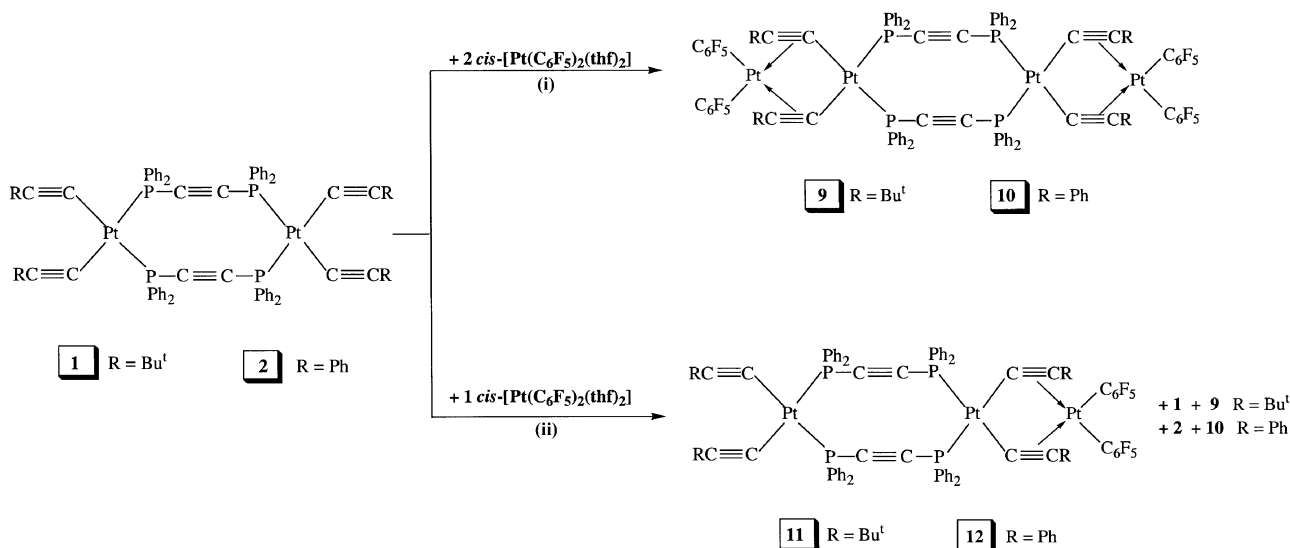


Fig. 1 (a) Molecular structure of [Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>( $\mu$ -dppa)<sub>2</sub>] **5**; (b) central core of [Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>( $\mu$ -dppa)<sub>2</sub>] **5**.

temperature nor at reflux did these reactions give the expected results, and only the starting materials were recovered in all cases. However, higher nuclearity species have been obtained by reacting **1** and **2** with *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>]. As shown in



Scheme 3

**Table 2** Selected bond lengths (Å) and angles (deg) for  $[\text{Pt}_2(\text{C}_6\text{F}_5)_4(\mu\text{-dppa})_2]$  **5**

Pt(1)–P(1)	2.290(3)	Pt(1)–P(2)	2.307(3)
Pt(2)–P(3)	2.285(3)	Pt(2)–P(4)	2.304(3)
Pt(1)–C(1)	2.057(11)	Pt(1)–C(7)	2.097(10)
Pt(2)–C(65)	2.057(11)	Pt(2)–C(71)	2.066(11)
P(1)–C(25)	1.787(12)	P(2)–C(39)	1.835(12)
P(3)–C(40)	1.772(12)	P(4)–C(26)	1.768(12)
C(25)–C(26)	1.20(2)	C(39)–C(40)	1.17(2)
C(1)–Pt(1)–C(7)	85.6(4)	P(1)–Pt(1)–P(2)	94.57(11)
C(7)–Pt(1)–P(1)	90.5(3)	C(1)–Pt(1)–P(2)	90.0(3)
C(65)–Pt(2)–C(71)	84.2(4)	P(3)–Pt(2)–P(4)	95.48(10)
C(71)–Pt(2)–P(3)	90.5(3)	C(65)–Pt(2)–P(4)	89.9(3)
C(7)–Pt(1)–P(2)	171.3(4)	C(1)–Pt(1)–P(1)	173.1(3)
C(65)–Pt(2)–P(3)	174.2(3)	C(71)–Pt(2)–P(4)	173.5(3)
C(26)–C(25)–P(1)	176.2(10)	C(25)–C(26)–P(4)	175.4(11)
C(40)–C(39)–P(2)	172.7(11)	C(39)–C(40)–P(3)	170.3(11)
C(25)–P(1)–Pt(1)	115.1(4)	C(13)–P(1)–Pt(1)	113.7(4)
C(19)–P(1)–Pt(1)	116.8(4)	C(39)–P(2)–Pt(1)	104.6(4)
C(33)–P(2)–Pt(1)	117.9(4)	C(27)–P(2)–Pt(1)	118.6(4)
C(40)–P(3)–Pt(2)	107.8(4)	C(41)–P(3)–Pt(2)	116.6(4)
C(47)–P(3)–Pt(2)	118.4(4)	C(26)–P(4)–Pt(2)	115.6(4)
C(59)–P(4)–Pt(2)	112.3(4)	C(53)–P(4)–Pt(2)	116.6(4)

Scheme 3i, treatment of  $[\text{Pt}_2(\text{C}\equiv\text{CR})_4(\mu\text{-dppa})_2]$  ( $\text{R} = \text{Bu}^t$  **1**, **Ph** **2**) with 2 equiv. of  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$  at room temperature affords the homotetranuclear derivatives  $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-C}\equiv\text{CR})_2\text{-Pt}(\mu\text{-dppa})_2]$  ( $\text{R} = \text{Bu}^t$  **9**, **Ph** **10**) as white microcrystalline solids in moderate (46%, **9**) or high yield (80%, **10**). For complex **9** an X-ray crystallographic study was carried out, but unfortunately the poor quality of the data obtained prevented a satisfactory refinement. Notwithstanding, this study indicates that in the tetranuclear species, the two central platinum atoms are connected through a double dppa bridge system, while the two platinum atoms at each end are bridged through a double alkynyl ( $\text{C}\equiv\text{CBu}^t$ ) system, as represented in Scheme 3. The equivalent phosphorus atoms of the dppa ligands appear in their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra at lower frequencies ( $\delta -10.88$  **9**,  $-10.71$  **10**) than the values observed in the precursors **1** and **2**. The magnitude of  $^1J(\text{PtP})$  (2606 **9**, 2604 Hz **10**) is slightly larger than that in the corresponding dinuclear starting material with terminal alkynyl ligands **1** and **2**, confirming the lesser *trans* influence of a bridging alkynyl ligand, as has been observed in similar systems.<sup>11b</sup> The  $^1\text{H}$  NMR spectrum of the *tert*-butyl derivative (**9**) shows two singlets at  $\delta$  0.80 and 0.79 with a shoulder at  $\delta$  0.76, indicating that the  $\text{Bu}^t$  groups of the alkynyl ligands are inequivalent, probably as a consequence of the rigid behaviour of the molecule on the NMR time-scale. In the same

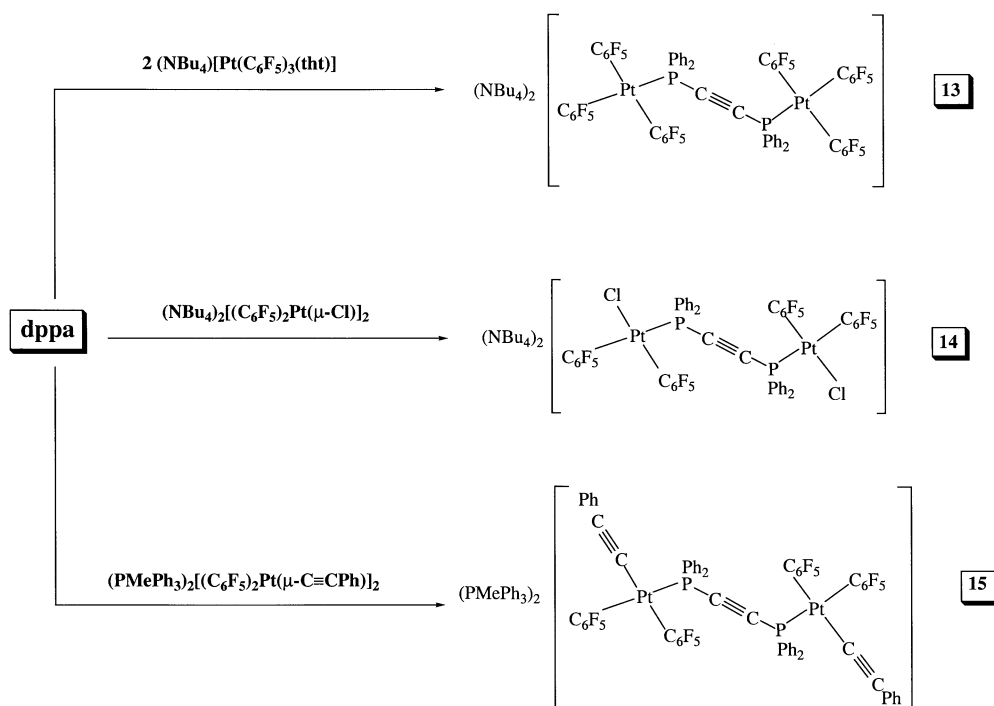
vein, its  $^{19}\text{F}$  NMR spectrum at room temperature confirms the presence of three types of  $\text{C}_6\text{F}_5$  groups: two  $\text{C}_6\text{F}_5$  rings are chemically inequivalent while the other two are equivalent (**2A**, **B**, **C**) and in one of the rings (**B** or **C**), the *endo* and *exo o*-F and *m*-F are inequivalent (see Table 1 for details). In contrast, the room temperature  $^{19}\text{F}$  NMR spectrum of the phenyl derivative **10**, shows only one type of  $\text{C}_6\text{F}_5$  (three signals of relative intensity 2 : 1 : 2), indicating that this complex is not rigid in solution.

NMR monitoring of the reactions between  $[\text{Pt}_2(\text{C}\equiv\text{CR})_4(\mu\text{-dppa})_2]$  ( $\text{R} = \text{Bu}^t$  **1**, **Ph** **2**) with 1 equiv. of  $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$  (Scheme 3ii) clearly indicates the formation of mixtures of compounds in which the precursors  $[\text{Pt}_2(\text{C}\equiv\text{CR})_4(\mu\text{-dppa})_2]$  ( $\text{R} = \text{Bu}^t$  **1**, **Ph** **2**) and the tetranuclear derivatives  $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-C}\equiv\text{CR})_2\text{-Pt}(\mu\text{-dppa})_2]$  ( $\text{R} = \text{Bu}^t$  **9**, **Ph** **10**) coexist with the expected trinuclear species  $[(\text{RC}\equiv\text{C})_2\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\mu\text{-C}\equiv\text{CR})_2\text{-Pt}(\text{C}_6\text{F}_5)_2]$  ( $\text{R} = \text{Bu}^t$  **11**, **Ph** **12**), initially in relative proportions of  $\approx 1 : 0.9$  (**9** : **11**) or  $\approx 1 : 1$  (**10** : **12**), respectively. Although all attempts to isolate the pure complexes **11** and **12** have failed, these products have been identified spectroscopically in the reaction mixture. Thus, the  $^{31}\text{P}\{^1\text{H}\}$  spectra of these mixtures show, in addition to the signals corresponding to the complexes **1/9** or **2/10**, two singlets at  $\delta -11.44$ ,  $-7.22$  (**11**) or  $-11.07$ ,  $-7.06$  (**12**). The high-field resonances are assigned to the phosphorus atoms closest to the  $(\mu\text{-C}\equiv\text{CR})_2$  system by comparison to those observed in the tetranuclear derivatives **9** or **10**; and, as expected, the coupling constants of these signals are larger than those seen in the signal corresponding to the phosphorus atoms nearest to the terminal  $\text{C}\equiv\text{CR}$  ligand (2614 vs. 2260 **11**, 2612 vs. 2281 **12**) in keeping with the lower *trans* influence of the bridging alkynyl ligand. The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra are less informative since the signals observed overlap with those seen for **9** and **10**, respectively (see Table 1 for details).

#### Mono $\mu\text{-dppa}$ complexes

The synthesis of dinuclear P-bonded mono( $\mu\text{-dppa}$ ) complexes was also explored. As can be seen in Scheme 4, when the platinum-containing substrate  $(\text{NBu}_4)[\text{Pt}(\text{C}_6\text{F}_5)_3(\text{tht})]$  ( $\text{tht}$  = tetrahydrothiophene) reacts with 0.5 equiv. of dppa in  $\text{CH}_2\text{Cl}_2$ , the dinuclear  $\mu\text{-}\kappa\text{P} : \kappa\text{P}'$  dppa complex  $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}_6\text{F}_5)_3\}_2(\mu\text{-dppa})]$  **13**, is isolated in high yield (67%), and similar mono  $\mu\text{-dppa}$  binuclear complexes can also be obtained by reaction of the dimers  $\text{Q}_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-X})_2]$  ( $\text{Q} = \text{NBu}_4$ ,  $\text{X} = \text{Cl}$ ;  $\text{Q} = \text{PMePh}_3$ ,  $\text{X} = \text{C}\equiv\text{CPh}$ ) with dppa. Thus, the reaction between  $(\text{NBu}_4)_2[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-Cl})_2]$  and 1 equiv. of dppa in  $\text{CH}_2\text{Cl}_2$  (Scheme 4) gives the anionic compound  $(\text{NBu}_4)_2[\text{cis-}\{\text{Pt}(\text{C}_6\text{F}_5)_2\text{Cl}\}_2(\mu\text{-dppa})]$  **14**. Analogously, treatment of





Scheme 4

$\text{(PMePh}_3\text{)}_2\text{[(C}_6\text{F}_5\text{)}_2\text{Pt}(\mu\text{-C}\equiv\text{CPh)}\text{]}_2$  with 1 equiv. of dppa in  $\text{CH}_2\text{Cl}_2$  allows the isolation, in low yield (17%), of the homologous  $\text{(PMePh}_3\text{)}_2\text{[cis-}\{\text{Pt(C}_6\text{F}_5\text{)}_2\text{(C}\equiv\text{CPh)}\}_2\text{(}\mu\text{-dppa)}\text{]}^-$  **15**. However, under similar reaction conditions (27 hours, room temperature) the dinuclear *tert*-butyl derivative  $\text{(NBu}_4\text{)}_2\text{[(C}_6\text{F}_5\text{)}_2\text{Pt}(\mu\text{-C}\equiv\text{CBu}^t)\text{]}_2$  does not react with the dppa ligand. For complexes **14** and **15**, their mass spectra (es – **14**, FAB – **15**) confirm the binuclear nature, through the observation of peaks whose isotopic distribution correspond to those expected for the binuclear anion with Q [Q =  $\text{NBu}_4$  **14**, (base peak),  $\text{PMePh}_3$  **15**]. The IR spectra show two bands in the  $806\text{--}774 \text{ cm}^{-1}$  region (for **13** one of them broad), due to the expected two (**14**, **15**) or three (**13**) IR-active  $\nu(\text{X-sensitive C}_6\text{F}_5)$  modes; and **15** also shows a strong  $\nu(\text{C}\equiv\text{C})$  band at  $2094 \text{ cm}^{-1}$ , confirming the presence of terminal alkynyl groups. In agreement with the formulation given, their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra exhibit one singlet signal, showing platinum–phosphorus constants [ $^1J(\text{PtP})/\text{Hz}$  2659 **13**, 2564 **14**, 2550 **15**] larger than those observed in the double ( $\mu\text{-dppa}$ ) derivatives **1**, **2** and **5**, probably due to a better bonding interaction between platinum and phosphorus as the result of less steric constraint. The presence of two types of  $\text{C}_6\text{F}_5$  groups in the expected 2 : 1 ratio for **13** or 1 : 1 for **14** and **15** is confirmed by  $^{19}\text{F}$  NMR spectroscopy (see Table 1 for details). Complex **15** was also characterised by single-crystal X-ray diffraction analysis, which provided an unambiguous structural assignment of the anion as illustrated in Fig. 2. Selected interatomic distances and angles are collected in Table 3. The anion is formed by two identical moieties “*cis*- $\text{Pt(C}_6\text{F}_5\text{)}_2\text{(C}\equiv\text{CPh)}$ ” connected by a P-bonded  $\mu\text{-}\kappa\text{P} : 2\kappa\text{P}'\text{-PPH}_2\text{C}\equiv\text{CPh}$  ligand. The presence of a dppa molecule as the unique bridging ligand between two metal fragments is not very usual.<sup>2d,f,3e,f</sup>

The fragment P–C–P is almost linear [P(1)–C(21)–C(21')]  $176.5(17)^\circ$  and the Pt–P(1)  $2.262(3) \text{ \AA}$ , P(1)–C(21)  $1.772(12) \text{ \AA}$  and C(21)–C(21')  $1.20(2) \text{ \AA}$  distances are in agreement with those expected. The P–P vector forms an angle of  $31.2^\circ$  with an imaginary line joining the platinum centres, and the angle Pt–P(1)–C(21) has a value of  $116.7(4)^\circ$ . The molecule is centrosymmetric and thus the platinum fragments are in identical environments adopting an *anti* disposition. This arrangement leaves the terminal alkynyl ligands in a *transoidal* disposition; the unique C=C distance is  $1.23(2) \text{ \AA}$  and the angles at  $\text{C}_\alpha$  and

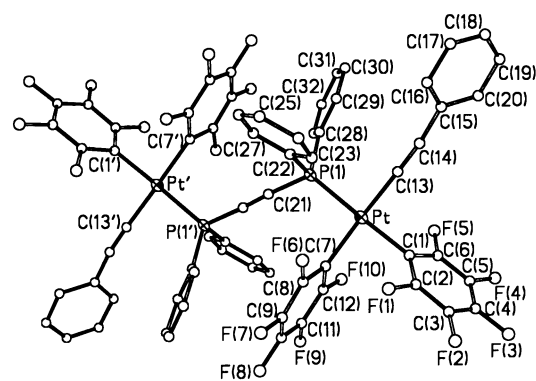


Fig. 2 Molecular structure of the anion of **15**,  $[\text{cis-}\{\text{Pt(C}_6\text{F}_5\text{)}_2\text{(C}\equiv\text{CPh)}\}_2\text{(}\mu\text{-dppa)}\text{]}^{2-}$ .

Table 3 Selected bond lengths ( $\text{\AA}$ ) and angles (deg) for  $\text{(PMePh}_3\text{)}_2\text{[cis-}\{\text{Pt(C}_6\text{F}_5\text{)}_2\text{(C}\equiv\text{CPh)}\}_2\text{(}\mu\text{-dppa)}\text{]}^-$  **15**

Pt–P(1)	2.262(3)	Pt–C(1)	2.055(10)
Pt–C(7)	2.050(12)	Pt–C(13)	1.987(12)
C(13)–C(14)	1.23(2)	C(21)–C(21')	1.20(2)
P(1)–C(21)	1.772(12)	P(1)–C(22)	1.827(14)
P(1)–C(28)	1.829(12)		
C(7)–Pt–P(1)	93.3(3)	C(13)–Pt–P(1)	89.8(3)
C(7)–Pt–C(1)	88.0(4)	C(13)–Pt–C(1)	88.9(4)
C(14)–C(13)–Pt	172.8(13)	C(13)–C(14)–C(15)	173.1(15)
C(21')–C(21)–P(1)	176.5(17)	C(21)–P(1)–Pt	116.7(4)
C(22)–P(1)–Pt	113.4(5)	C(28)–P(1)–Pt	117.1(4)

The symmetry transformation used to generate the equivalent C(21') atom is  $x, -y, -z$ .

$\text{C}_\beta$  are  $172.8(13)^\circ$  and  $173.1(15)^\circ$ . The square-planar environment for both platinum centres is completed by two mutually *cis*  $\text{C}_6\text{F}_5$  groups. The Pt $\cdots$ Pt distance is  $7.850(1) \text{ \AA}$ .

In summary, mono- (**3**, **4**, **6**, **8**), bi- (**1**, **2**, **5**, **13–15**), tri- (**11**, **12**) and tetra-nuclear (**9**, **10**) alkynyl or pentafluorophenyl platinum complexes stabilised by terminal or bridging dppa have been isolated starting from suitable precursors. X-Ray structures of **5** and **15** confirm the expected formulations with double (**5**) or single (**15**) dppa bridging systems.

## Experimental

Reactions were carried out under an atmosphere of argon by using conventional Schlenk techniques. Solvents were purified according to standard procedures. Microanalyses were determined with a Perkin-Elmer 2400 CHNS/O microanalyser. Infrared spectra (KBr) were recorded on a Perkin-Elmer FT-IR 1000 spectrophotometer. NMR spectra were obtained on a Bruker ARX-300 with chemical shifts reported in ppm relative to external standards (SiMe<sub>4</sub> for <sup>1</sup>H and <sup>13</sup>C, CFCl<sub>3</sub> for <sup>19</sup>F and 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P). The mass spectra (FAB+ or -) were carried out on a VG Autospec spectrometer and the electrospray mass (em) spectra on an HP5989B with interphase API-ES HP59987A (in the negative ion mode with methanol as mobile phase). The starting materials *cis*-[Pt(C≡CR)<sub>2</sub>(COD)] (R = Bu<sup>t</sup>, <sup>12b</sup>, Ph <sup>12c</sup>), *cis/trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tht)<sub>2</sub>]<sup>14</sup>, *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>]<sup>15</sup>, (NBu<sub>4</sub>)[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(tht)]<sup>14</sup>, (NBu<sub>4</sub>)<sub>2</sub>[(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-Cl)]<sub>2</sub><sup>16</sup>, (PMePh<sub>3</sub>)<sub>2</sub>[(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-C≡CPh)]<sub>2</sub><sup>12b</sup> were prepared by published methods. Dppa was purchased from commercial suppliers.

### Reaction of *cis*-[Pt(C≡CR)<sub>2</sub>(COD)] with dppa: synthesis of [Pt<sub>2</sub>(C≡CR)<sub>4</sub>(μ-dppa)<sub>2</sub>] (R = Bu<sup>t</sup> **1**, R = Ph **2**). Identification of *cis*-[Pt(C≡CR)<sub>2</sub>(dppa-κP)]<sub>2</sub> (R = Bu<sup>t</sup> **3**, Ph **4**)

**1 : 1 molar ratio.** A suspension of *cis*-[Pt(C≡CBu<sup>t</sup>)<sub>2</sub>(COD)] (0.100 g, 0.215 mmol) in 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was treated with dppa (97%, 0.087 g, 0.215 mmol). After 5 min of stirring the resulting colourless solution was evaporated to dryness and the residue was treated with EtOH (10 cm<sup>3</sup>) to give **1** as a white solid (0.098 g, 61%).

Complex **2** was obtained similarly as a pale-yellow solid, starting from *cis*-[Pt(C≡CPh)<sub>2</sub>(COD)] (0.200 g, 0.396 mmol) and dppa (0.161 g, 0.396 mmol) (0.207 g, 66%).

Data for **1**: (Found: C, 60.29; H, 4.93%; *M* 1504. C<sub>76</sub>H<sub>76</sub>P<sub>4</sub>Pt<sub>2</sub> requires C, 60.71; H, 5.09%); *v*<sub>max</sub>/cm<sup>-1</sup>: (C≡CR) is not observed (Nujol); δ<sub>C</sub> (CDCl<sub>3</sub>, 16 °C) 133.6 [AXX', t, <sup>2</sup>J(CP) + <sup>4</sup>J(CP)] 12.4 Hz, C<sub>o</sub>, PPh<sub>2</sub>, 130.4 (s, C<sub>p</sub>, PPh<sub>2</sub>), 129.6 [AXX' five line pattern, <sup>1</sup>J(CP) + <sup>3</sup>J(CP)] 66.1 Hz, C<sub>i</sub>, PPh<sub>2</sub>, 127.9 [AXX', t, <sup>3</sup>J(CP) + <sup>5</sup>J(CP)] 11.6 Hz, C<sub>m</sub>, PPh<sub>2</sub>, 118.1 [AXX' five line pattern, <sup>3</sup>J(C<sub>β</sub>P<sub>trans</sub>) + <sup>3</sup>J(C<sub>β</sub>P<sub>cis</sub>)] 35.7 Hz, <sup>2</sup>J(C<sub>β</sub>Pt) ≈ 312 Hz, C<sub>β</sub>, C<sub>α</sub>≡C<sub>β</sub>R], 100.7 [A[X]<sub>3</sub> or A[X]<sub>4</sub>, dpst, PC≡CP), 82.7 [AXX', <sup>2</sup>J(C<sub>α</sub>P<sub>trans</sub>) + <sup>2</sup>J(C<sub>α</sub>P<sub>cis</sub>)] 179.5 Hz, <sup>1</sup>J(C<sub>α</sub>Pt) 1156 Hz, C<sub>α</sub>, C<sub>α</sub>≡C<sub>β</sub>R], 31.4 [s, <sup>4</sup>J(CPt) ≈ 8 Hz, C(CH<sub>3</sub>)<sub>3</sub>], 28.8 [s, <sup>3</sup>J(CPt) 20.8 Hz, CMe<sub>3</sub>]. Iteration of the AXX' spin system of C<sub>α</sub> and C<sub>β</sub> nuclei gives the following data: C<sub>α</sub> <sup>2</sup>J(PP') 16.54 Hz, <sup>2</sup>J(C<sub>α</sub>P) 155.37, <sup>2</sup>J(C<sub>α</sub>P') 24.12 Hz; C<sub>β</sub> <sup>2</sup>J(PP') 16.54, <sup>3</sup>J(C<sub>β</sub>P) 36.01, <sup>3</sup>J(C<sub>β</sub>P') -0.31 Hz (P = P<sub>trans</sub>, P' = P<sub>cis</sub>); *m/z* (%) 1504 (M<sup>+</sup> 15), 1422 ([M - C≡CBu<sup>t</sup> + 1]<sup>+</sup> 33), 1342 ([M - 2C≡CBu<sup>t</sup> + 2]<sup>+</sup> 33), 1260 ([M - 3C≡CBu<sup>t</sup> + 3]<sup>+</sup> 38), 1178 ([Pt<sub>2</sub>(dppa)<sub>2</sub>]<sup>+</sup> 100), 1101 ([Pt<sub>2</sub>(dppa)<sub>2</sub> - Ph]<sup>+</sup> 52).

Data for **2**: (Found: C, 64.03; H, 3.54%; *M* 1584. C<sub>84</sub>H<sub>60</sub>P<sub>4</sub>Pt<sub>2</sub> requires C, 63.72; H, 3.82%); *v*<sub>max</sub>/cm<sup>-1</sup>: (C≡CR) 2124m (Nujol); δ<sub>C</sub> (CDCl<sub>3</sub>, 16 °C) 133.4 [AXX', t, <sup>2</sup>J(CP) + <sup>4</sup>J(CP)] 12.6, C<sub>o</sub>, PPh<sub>2</sub>, 131.4 [s, <sup>4</sup>J(PtC) 4.1 Hz, C<sub>o</sub>, C≡CPh], 130.9 (s, C<sub>p</sub>, PPh<sub>2</sub>), 128.7 [AXX' five line pattern, <sup>1</sup>J(CP) + <sup>3</sup>J(CP)] 67.2 Hz, <sup>2</sup>J(CPt) ≈ 19, C<sub>i</sub>, PPh<sub>2</sub>, 128.3 [AXX', t, <sup>3</sup>J(CP) + <sup>5</sup>J(CP)] 11.8 Hz, C<sub>m</sub>, PPh<sub>2</sub>, 127.2 (s, C<sub>m</sub>, C≡CPh), 127.1 (s, C<sub>i</sub>, C≡CPh), 125.6 (s, C<sub>p</sub>, C≡CPh), 110.4 [AXX' five line pattern, <sup>3</sup>J(C<sub>β</sub>P<sub>trans</sub>) + <sup>3</sup>J(C<sub>β</sub>P<sub>cis</sub>)] 36.3 Hz, <sup>2</sup>J(C<sub>β</sub>Pt) 317 Hz, C<sub>β</sub>, C<sub>α</sub>≡C<sub>β</sub>R], 100.8 [A[X]<sub>3</sub> or A[X]<sub>4</sub>, dpst, PC≡CP), 98.7 [AXX', <sup>2</sup>J(C<sub>α</sub>P<sub>trans</sub>) + <sup>2</sup>J(C<sub>α</sub>P<sub>cis</sub>)] 178.0 Hz, <sup>1</sup>J(C<sub>α</sub>Pt) 1165 Hz, C<sub>α</sub>, C<sub>α</sub>≡C<sub>β</sub>R]. Iteration of the AXX' spin system of C<sub>α</sub> and C<sub>β</sub> nuclei gives the following data: C<sub>α</sub> <sup>2</sup>J(PP') 16.00 Hz, <sup>2</sup>J(C<sub>α</sub>P) 155.30, <sup>2</sup>J(C<sub>α</sub>P') 22.70 Hz; C<sub>β</sub> <sup>2</sup>J(PP') 16.00 Hz, <sup>3</sup>J(C<sub>β</sub>P) 37.33, <sup>3</sup>J(C<sub>β</sub>P') -1.03 Hz (P = P<sub>trans</sub>, P' = P<sub>cis</sub>); *m/z* (%) 1584 (M<sup>+</sup> 21), 1483 ([M - C≡CPh + 1]<sup>+</sup> 16), 1381 ([M - 2C≡CPh + 2]<sup>+</sup> 35), 1279 ([M - 3C≡CPh + 3]<sup>+</sup> 21), 1178 ([Pt<sub>2</sub>(dppa)<sub>2</sub>]<sup>+</sup> 100), 1101 ([Pt<sub>2</sub>(dppa)<sub>2</sub> - Ph]<sup>+</sup> 52).

**1 : 2 molar ratio.** Dppa (97%, 0.175 g, 0.430 mmol) was added to a stirred suspension of *cis*-[Pt(C≡CBu<sup>t</sup>)<sub>2</sub>(COD)] (0.100 g, 0.215 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and the mixture was stirred

for 30 min. Monitoring by NMR spectroscopy indicates the mixture to be composed of dppa, [Pt<sub>2</sub>(C≡CBu<sup>t</sup>)<sub>4</sub>(μ-dppa)<sub>2</sub>] **1** and a new compound identified as *cis*-[Pt(C≡CBu<sup>t</sup>)<sub>2</sub>(dppa-κP)]<sub>2</sub> **3** (molar ratios **1** : **3**, ≈ 1 : 2, based on <sup>31</sup>P NMR). After 2 hours, the intensity of the signal due to the dinuclear complex **1** increases (≈ 1 : 1.6, **1** : **3**), and all attempts to obtain pure **3** from the mixture were unsuccessful.

Under similar reaction conditions, the reaction of *cis*-[Pt(C≡CPh)<sub>2</sub>(COD)] (0.1 g, 0.198 mmol) and dppa (0.161 g, 0.396 mmol) shows an initial proportion of **2** and **4** of ca. 1 : 1 (based on <sup>31</sup>P NMR), but in a few minutes the signal due to **2** increases [10 min, 2.2 : 1; 3 h, 3 : 1 proportion (**2** : **4**)]. Complex **2** can be obtained as a yellow solid if the resulting solution is evaporated to dryness, after 3 hours of stirring, and treated with EtOH (10 cm<sup>3</sup>) (0.110 g, 70%). However, all attempts to obtain **4** were unsuccessful. Compounds **3** and **4** were only characterised in solution by NMR spectroscopy (see Table 1).

### Synthesis of [Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>(μ-dppa)<sub>2</sub>] **5**

A suspension of *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tht)<sub>2</sub>] (0.150 g, 0.213 mmol) in 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was treated with dppa (97%, 0.087 g, 0.213 mmol). After 2 hours of stirring, the resulting solution was concentrated to ca. 2 cm<sup>3</sup>. Addition of 10 cm<sup>3</sup> of EtOH rendered **5** as a white solid (0.081 g, 41%) (Found: C, 49.06; H, 2.33%; *M* 1848. C<sub>76</sub>F<sub>20</sub>H<sub>40</sub>P<sub>4</sub>Pt<sub>2</sub> requires C, 49.44; H, 2.18%). *v*<sub>max</sub>/cm<sup>-1</sup>: (X-sens C<sub>6</sub>F<sub>5</sub>) 798vs, 788sh (Nujol); *m/z* (%) no peaks are observed in FAB(+).

### Synthesis of *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(dppa-κP)]<sub>2</sub> **6**

Dppa (97%, 0.270 g, 0.665 mmol) was added to a suspension of *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tht)<sub>2</sub>] (0.200 g, 0.283 mmol) in 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred at room temperature for 1 hour. The resulting solution was evaporated to dryness and the residue treated with 1 cm<sup>3</sup> of acetone and 10 cm<sup>3</sup> of EtOH, affording a white solid, which was filtered off, washed with EtOH (2 × 2 cm<sup>3</sup>) and identified as **6** (0.276 g, 74%). If 1 : 2, 1 : 2.25 or 1 : 3 molar ratios are used, mixtures of **5** and **6**, or **6** and dppa are obtained using a similar work-up (Found: C, 58.32; H, 3.03%; *M* 1318. C<sub>64</sub>F<sub>10</sub>H<sub>40</sub>P<sub>4</sub>Pt requires C, 58.32; H, 3.06%). *v*<sub>max</sub>/cm<sup>-1</sup>: (C≡CR) 2104m; (X-sens C<sub>6</sub>F<sub>5</sub>) 794m, 782m (KBr); *m/z* (%) 1318 (M<sup>+</sup> 100), 1241 ([M - Ph]<sup>+</sup> 40), 1200 ([M - 2Ph]<sup>+</sup> 5), 1150 ([M - C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> 55), 1073 ([M - C<sub>6</sub>F<sub>5</sub> - Ph]<sup>+</sup> 30), 923 ([M - dppa]<sup>+</sup> 30).

### Synthesis of *trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(μ-dppa)]<sub>2</sub> **7**

A suspension of *trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tht)<sub>2</sub>] (0.15 g, 0.213 mmol) in 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was treated with dppa (97%, 0.087 g, 0.213 mmol) and the resulting solution was stirred at room temperature. After 15 min a white solid began to precipitate. The mixture was stirred for 2 hours and then the resulting solid **7** was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 2 cm<sup>3</sup>) (0.132 g, 67%) (Found: C, 49.80; H, 2.29%; *M* 924. C<sub>38</sub>F<sub>10</sub>H<sub>20</sub>P<sub>2</sub>Pt requires C, 49.42; H, 2.18%). *v*<sub>max</sub>/cm<sup>-1</sup>: (C≡CR) is not observed; (X-sens C<sub>6</sub>F<sub>5</sub>) 780s (br) (Nujol); NMR data cannot be obtained due to the insolubility of **7** in common solvents.

### Synthesis of *trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(dppa-κP)]<sub>2</sub> **8**

Dppa (97%, 0.115 g, 0.284 mmol) was added to a suspension of *trans*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tht)<sub>2</sub>] (0.100 g, 0.142 mmol) in 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was stirred for 2 hours and filtered through Celite. The solvent was removed, and the addition of EtOH (10 cm<sup>3</sup>) to the residue yielded **8** as a white solid (0.127 g, 68%) (Found: C, 58.04; H, 3.15%; *M* 1318. C<sub>64</sub>F<sub>10</sub>H<sub>40</sub>P<sub>4</sub>Pt requires C, 58.32; H, 3.06%); *v*<sub>max</sub>/cm<sup>-1</sup>: (C≡CR) 2119w; (X-sens C<sub>6</sub>F<sub>5</sub>) 781s (Nujol); *m/z* (%) 2241 ([2M + 4]<sup>+</sup> 20), 1318 ([M]<sup>+</sup> 88), 1241 ([M - Ph]<sup>+</sup> 22), 1182 ([M - 2Ph]<sup>+</sup> 18), 1150 ([M - C<sub>6</sub>F<sub>5</sub>]<sup>+</sup> 35).

**Reactions of [Pt<sub>2</sub>(C≡CR)<sub>4</sub>(μ-dppa)<sub>2</sub>] (R = Bu<sup>1</sup> **1**, Ph **2**) with *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>]: synthesis of [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-C≡CR)<sub>2</sub>Pt(μ-dppa)]<sub>2</sub> (R = Bu<sup>1</sup> **9**, Ph **10**). Identification of [(RC≡C)<sub>2</sub>Pt(μ-dppa)<sub>2</sub>Pt(μ-C≡CR)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (R = Bu<sup>1</sup> **11**, Ph **12**)**

**1 : 2 molar ratio.** *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] (0.112 g, 0.166 mmol) was added to a solution of [Pt<sub>2</sub>(C≡CBu<sup>1</sup>)<sub>4</sub>(μ-dppa)<sub>2</sub>] **1** (0.125 g, 0.083 mmol) in 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>. The resulting brown solution was stirred for 30 min, filtered through Celite and the filtrate evaporated to small volume (*ca.* 2 cm<sup>3</sup>). Addition of Et<sub>2</sub>O (10 cm<sup>3</sup>) gave [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-C≡CBu<sup>1</sup>)<sub>2</sub>Pt(μ-dppa)]<sub>2</sub> **9** as a white solid (0.098 g, 46%).

The complex [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-C≡CPh)<sub>2</sub>Pt(μ-dppa)]<sub>2</sub> **10** was prepared by following a procedure similar to that described for complex **9**, but starting from [Pt<sub>2</sub>(C≡CPh)<sub>4</sub>(μ-dppa)<sub>2</sub>] **2** (0.150 g, 0.095 mmol) and *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] (0.127 g, 0.189 mmol). The mixture was stirred for 15 min and the complex precipitated with *n*-hexane (10 cm<sup>3</sup>) (0.199 g, 80%).

Data for **9**: (Found: C, 46.86; H, 2.88%; *M* 2562. C<sub>100</sub>F<sub>20</sub>H<sub>76</sub>P<sub>4</sub>Pt<sub>4</sub> requires C, 46.89; H, 2.99%);  $\nu_{\max}/\text{cm}^{-1}$ : (C≡CR) is not observed; (X-sens C<sub>6</sub>F<sub>5</sub>) 802m, 791w (Nujol); *m/z* (%) 1208 ([Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(dppa) – Ph]<sup>+</sup> 40), 1131 ([Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(dppa) – 2Ph]<sup>+</sup> 60), 1055 ([Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(dppa) – 3Ph]<sup>+</sup> 65), 754 ([Pt(C≡CBu<sup>1</sup>)<sub>2</sub>(dppa) + 2]<sup>+</sup> 50), 528 ([Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> – 1]<sup>+</sup> 72), 363 ([Pt(C<sub>6</sub>F<sub>5</sub>) + 1]<sup>+</sup> 100).

Data for **10**: (Found: C, 48.82; H, 1.98%; *M* 2642. C<sub>108</sub>F<sub>20</sub>H<sub>60</sub>P<sub>4</sub>Pt<sub>4</sub> requires C, 49.10; H, 2.29%);  $\nu_{\max}/\text{cm}^{-1}$ : (C≡CR) is not observed; (X-sens C<sub>6</sub>F<sub>5</sub>) 806s, 796m (Nujol); *m/z* (%) 1322 ([Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C≡CPh)<sub>2</sub>(dppa)]<sup>+</sup> 12), 1155 ([Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)(C≡CPh)<sub>2</sub>(dppa)]<sup>+</sup> 20).

**1 : 1 molar ratio.** A solution of [Pt<sub>2</sub>(C≡CBu<sup>1</sup>)<sub>4</sub>(μ-dppa)<sub>2</sub>] **1** (0.125 g, 0.083 mmol) in 15 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was treated with *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] (0.056 g, 0.083 mmol). The resulting brown solution was immediately evaporated to dryness, and the residue treated with 10 cm<sup>3</sup> of *n*-hexane to give a pale-brown solid (0.147 g) identified by NMR spectroscopy as a mixture of **9** and [(Bu<sup>1</sup>C≡C)<sub>2</sub>Pt(μ-dppa)<sub>2</sub>Pt(μ-C≡CBu<sup>1</sup>)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] **11**. Monitoring of this reaction by <sup>31</sup>P{<sup>1</sup>H} NMR at 20 °C showed the presence of a mixture of **1**, **9** and **11** in an ≈0.43 : 1 : 0.9 proportion.

Similarly, when the reaction between [Pt<sub>2</sub>(C≡CPh)<sub>4</sub>(μ-dppa)<sub>2</sub>] **2** (0.030 g, 0.019 mmol) and *cis*-[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(thf)<sub>2</sub>] (0.013 g, 0.019 mmol) in 0.5 cm<sup>3</sup> of CDCl<sub>3</sub> was examined by NMR spectroscopy, an initial mixture of **2**, **10** and [(PhC≡C)<sub>2</sub>Pt(μ-dppa)<sub>2</sub>Pt(μ-C≡CPh)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] **12** (0.2 : 1 : 1 approximate proportions) was observed. After 12 hours, complex **10** was the main component of the reaction mixture (0.05 : 1 : 0.38, **2** : **10** : **12**).

All attempts to obtain pure **11** or **12** from these mixtures were unsuccessful; therefore, complexes **11** or **12** were only characterised spectroscopically.

**Synthesis of (NBu<sub>4</sub>)<sub>2</sub>[(Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(μ-dppa)] **13****

Dppa (0.059 g, 0.146 mmol) was added to a solution of (NBu<sub>4</sub>)<sub>2</sub>[Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(tht)] (0.300 g, 0.292 mmol) in 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> and the mixture was stirred for 18 hours. The solution was evaporated to small volume (2 cm<sup>3</sup>) and the residue treated with Et<sub>2</sub>O (10 cm<sup>3</sup>) to give **13** as a white solid (0.222 g, 67%) (Found: C, 49.87; H, 3.82; N, 1.15%; *M* 2272. C<sub>94</sub>F<sub>30</sub>H<sub>92</sub>N<sub>2</sub>P<sub>2</sub>Pt<sub>2</sub> requires C, 49.70; H, 4.08; N, 1.23%);  $\nu_{\max}/\text{cm}^{-1}$ : (C≡CR) is not observed; (X-sens C<sub>6</sub>F<sub>5</sub>) 794m (br), 774m (Nujol); *m/z* (%) es(–): 1090 ([Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(dppa)]<sup>–</sup> 1), 696 ([Pt(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup> 100).

**Synthesis of (NBu<sub>4</sub>)<sub>2</sub>[*cis*-{Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Cl}<sub>2</sub>(μ-dppa)] **14****

A solution of (NBu<sub>4</sub>)<sub>2</sub>[(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-Cl)]<sub>2</sub> (0.500 g, 0.310 mmol) in 15 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was treated with dppa (0.126 g, 0.310 mmol) and the mixture stirred for 7 hours. The resulting solution was evaporated to a small volume (*ca.* 2 cm<sup>3</sup>) and the addition of isopropanol (10 cm<sup>3</sup>) caused the precipitation of **14**

**Table 4** Crystal data and structure refinement for **5** and 15·C<sub>6</sub>H<sub>14</sub>

Complex	<b>5</b>	15·C <sub>6</sub> H <sub>14</sub>
Empirical formula	C <sub>76</sub> H <sub>40</sub> F <sub>20</sub> P <sub>4</sub> Pt <sub>2</sub>	C <sub>104</sub> H <sub>66</sub> F <sub>20</sub> P <sub>4</sub> Pt <sub>2</sub> ·C <sub>6</sub> H <sub>14</sub>
Formula weight	1847.14	2295.80
<i>T</i> /K	200(2)	150(2)
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	17.323(3)	14.7657(11)
<i>b</i> /Å	20.918(4)	20.3282(15)
<i>c</i> /Å	19.549(4)	15.9687(14)
$\beta$ /°	101.74(3)	104.139(10)
<i>V</i> /Å <sup>3</sup>	6936(2)	4648.0(6)
<i>Z</i>	4	2
Absorption coefficient/mm <sup>–1</sup>	4.220	3.166
Reflections collected	12822	7807
Unique reflections	10871 [ <i>R</i> (int) = 0.0691]	7471 [ <i>R</i> (int) = 0.0586]
Final <i>R</i> indices	<i>R</i> 1 = 0.0537, [ <i>I</i> > 2σ( <i>I</i> )] <i>wR</i> <sub>2</sub> = 0.1175	<i>R</i> 1 = 0.0614, <i>wR</i> <sub>2</sub> = 0.1239
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1059, <i>wR</i> <sub>2</sub> = 0.1629	<i>R</i> 1 = 0.1478, <i>wR</i> <sub>2</sub> = 0.1587

as a white solid (0.510 g, 82%) (Found: C, 49.23; H, 4.09; N, 1.21%; *M* 2009. C<sub>82</sub>Cl<sub>2</sub>F<sub>20</sub>H<sub>92</sub>N<sub>2</sub>P<sub>2</sub>Pt<sub>2</sub> requires C, 49.03; H, 4.62; N, 1.39%).  $\nu_{\max}/\text{cm}^{-1}$ : (C≡CR) is not observed; (X-sens C<sub>6</sub>F<sub>5</sub>) 800s, 782s (Nujol); *m/z* (%) es(–): 1766 ([M<sup>2–</sup> + NBu<sub>4</sub>]<sup>–</sup> 100), 1488 ([M<sup>2–</sup> – Cl]<sup>–</sup> 12).

**Synthesis of (PMePh<sub>3</sub>)<sub>2</sub>[*cis*-{Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C≡CPh)<sub>2</sub>(μ-dppa)] **15****

A solution of (PMePh<sub>3</sub>)<sub>2</sub>[(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt(μ-C≡CPh)]<sub>2</sub> (0.125 g, 0.069 mmol) in 15 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was treated with dppa (0.028 g, 0.069 mmol). Prolonged stirring for 15 hours produced a white precipitate (**15**) which was filtered off and washed with cold CH<sub>2</sub>Cl<sub>2</sub> (2 × 2 cm<sup>3</sup>) (0.026 g, 17%). The <sup>19</sup>F NMR of the filtrate only shows signals assigned to the starting material and the <sup>31</sup>P{<sup>1</sup>H} NMR shows the signal of the dppa and of other unidentified products (Found: C, 56.06; H, 3.15%; *M* 2210. C<sub>104</sub>F<sub>20</sub>H<sub>66</sub>P<sub>4</sub>Pt<sub>2</sub> requires C, 56.53; H, 3.01%).  $\nu_{\max}/\text{cm}^{-1}$ : (C≡CR) 2094s; (X-sens C<sub>6</sub>F<sub>5</sub>) 806m, 801m (Nujol); *m/z* (%) FAB(–): 1931 ([M<sup>2–</sup> + PMePh<sub>3</sub>]<sup>–</sup> 5), 1788 ([Pt<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>6</sub>(dppa) + 2]<sup>–</sup> 100), 1024 ([Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C≡CPh)(dppa)]<sup>–</sup> 5), 630 ([Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(C≡CPh)]<sup>–</sup> 35).

**X-Ray crystallography**

Crystal data and other details of the structure analyses are presented in Table 4. For **5**, a crystal was mounted at the end of a glass fibre and held in place with an epoxy resin adhesive. For 15·C<sub>6</sub>H<sub>14</sub>, a crystal was mounted at the end of a quartz fibre and held in place with a fluorinated oil. All diffraction measurements were made on a Siemens P4 diffractometer for **5**, and on an Enraf-Nonius CAD4 diffractometer, for 15·C<sub>6</sub>H<sub>14</sub>, using graphite monochromated Mo-Kα X-radiation. Empirical absorption corrections based on  $\psi$  scans were applied. The structures were solved by Patterson and Fourier methods. All non-hydrogen atoms were assigned anisotropic displacement parameters. For 15·C<sub>6</sub>H<sub>14</sub>, a common set of anisotropic thermal parameters was used for all the carbon atoms of the half *n*-hexane molecule, and the interatomic distances in this moiety were restrained to sensible geometries. Least square calculations were carried out using the program SHELXL-93.<sup>17</sup> CCDC reference numbers 164450 and 164451.

See <http://www.rsc.org/suppdata/dt/b1/b101558n/> for crystallographic data in CIF or other electronic format.

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