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Polynuclear homo- or heterometallic palladium(II)–platinum(II) pentafluorophenyl complexes containing bridging diphenylphosphido ligands. Synthesis and crystal structure of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$ *

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Abstract

The binuclear anionic derivatives $(NBu_4)_2[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)_2]$ ($M = M' = Pd$, **1**; $M = M' = Pt$, **2**; $M = Pd$, $M' = Pt$, **3**) have been obtained by treating either $(NBu_4)_2[(C_6F_5)_2M(\mu\text{-}X)_2M'(C_6F_5)_2]$ ($X = Cl$, Br) with $LiPPh_2$ (**1**,**2**) or $[cis\text{-}M(C_6F_5)_2(PPh_2)_2]^{2-}$ with $M'(C_6F_5)_2(THF)_2$ (**1**,**2**,**3**). These binuclear derivatives react with HCl yielding the tetranuclear complexes $(NBu_4)_2[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(\mu\text{-}Cl)_2M'(\mu\text{-}PPh_2)_2M(C_6F_5)_2]$ (**7**: $M = M' = Pt$; **8**: $M = M' = Pd$; **9**: $M = Pt$, $M' = Pd$). However, **2** and **3** react with HCl in the presence of PPh_3 to yield the binuclear asymmetric complexes $(NBu_4)[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)(PPh_3)]$ (**10**: $M = M' = Pt$; **11**: $M = Pt$, $M' = Pd$). The tetranuclear complexes **7**, **8**, and **9** react with bidentate ligands yielding the neutral asymmetric binuclear complexes $[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(L\text{–}L)]$ (**5**: $M = M' = Pt$; L–L = dppm; **12**: L–L = phen; **13**: $M = M' = Pd$, L–L = bipy). The salts $Li_2[M(C_6F_5)_2(PPh_2)_2]$ ($M = Pd$, Pt) react with $PtCl_2(dppm)$, $[Pt(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ or $PtCl_2$ to yield $[(C_6F_5)_2M(\mu\text{-}PPh_2)_2Pt(dppm)]$ (**4**: $M = Pd$; **5**: $M = Pt$), $(NBu_4)[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)(tht)]$ (**6**) or $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (**7**), respectively. These complexes have been characterized by IR and ^{19}F and ^{31}P NMR spectroscopy, the latter indicating that in all cases no metal–metal bonds are present. The molecular structure of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$ has been established by an X-ray diffraction study. The Pt...Pt distance (3.5711(9) Å) confirms that there is no Pt–Pt bond.

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* Dedicated to Prof. F.G.A. Stone on the occasion of his 65th birthday.

Introduction

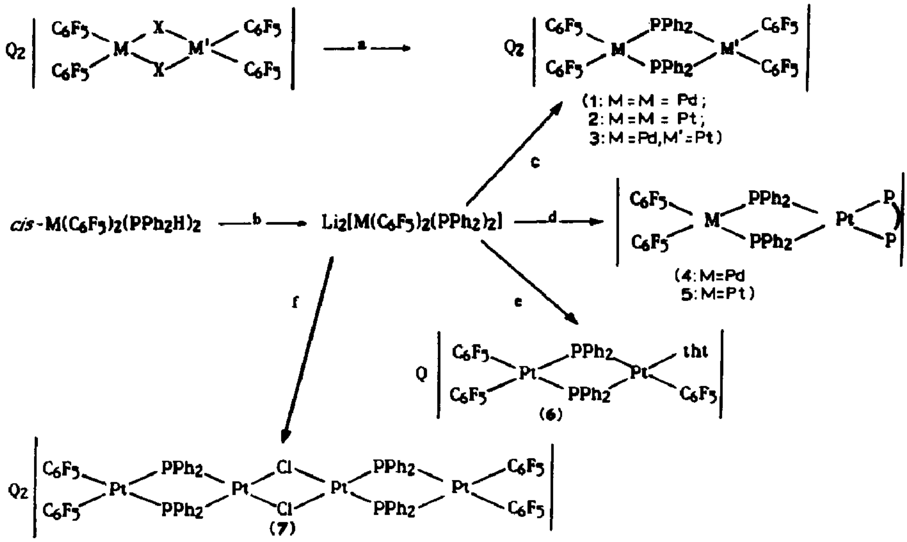
Polynuclear transition metal complexes containing bridging phosphide (PR_2^-) groups have recently attracted considerable attention, not only from a synthetic and structural viewpoint but also because in most cases the versatility of the PR_2 groups as supporting ligands allows the retention of the polynuclear framework during chemical reactions [1–8]. In the course of our researches on pentafluorophenyl-palladium or -platinum complexes we have synthesized homo- and hetero-metallic, bi- or tetra-nuclear, neutral or anionic Pd^{II} or Pt^{II} complexes containing diphenylphospido bridging groups.

The structures of the complexes reported have been established by IR and ^{19}F and ^{31}P NMR spectroscopy, and the molecular structure of the asymmetric compound $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$ has been determined by a single-crystal X-ray diffraction study. There are no metal–metal bonds in these polynuclear complexes.

Results and discussion

(a) Preparation of complexes

The binuclear anionic complexes $(NBu_4)_2[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)_2]$ (**1**: M = M' = Pd; **2**: M = M' = Pt) can be obtained by reaction of the corresponding halo complexes $(NBu_4)_2[M_2(\mu\text{-}X)_2(C_6F_5)_4]$ (M = Pd, X = Br; M = Pt, X = Cl) with an excess of $LiPPh_2$ (molar ratio ~ 1/4) (Scheme 1a). If the reaction is carried out in a 1/1 molar ratio with the intention of preparing binuclear complexes containing both (μ-X) and (μ-PR_2) bridging ligands, a mixture of the corresponding starting material and complex **1** or **2**, respectively, is obtained. Different behaviour has been observed for binuclear rhodium(I) halide-bridged complexes, which react with $LiPPh_2$ (molar ratio 1/1) to give binuclear $>Rh(\mu\text{-}Cl)(\mu\text{-}PR_2)Rh<$ complexes [9].



Scheme 1. Q = NBu_4; (a) $LiPPh_2$, THF; (b) Li^nBu, THF; (c) $M'(C_6F_5)_2(THF)_2$, M = Pd, Pt; (d) $PtCl_2(dppm)$; (e) $[Pt(\mu\text{-}Cl)(C_6F_5)(tht)]_2$, $QClO_4$ (tht = tetrahydrothiophene); (f) $PtCl_2$, $QClO_4$.

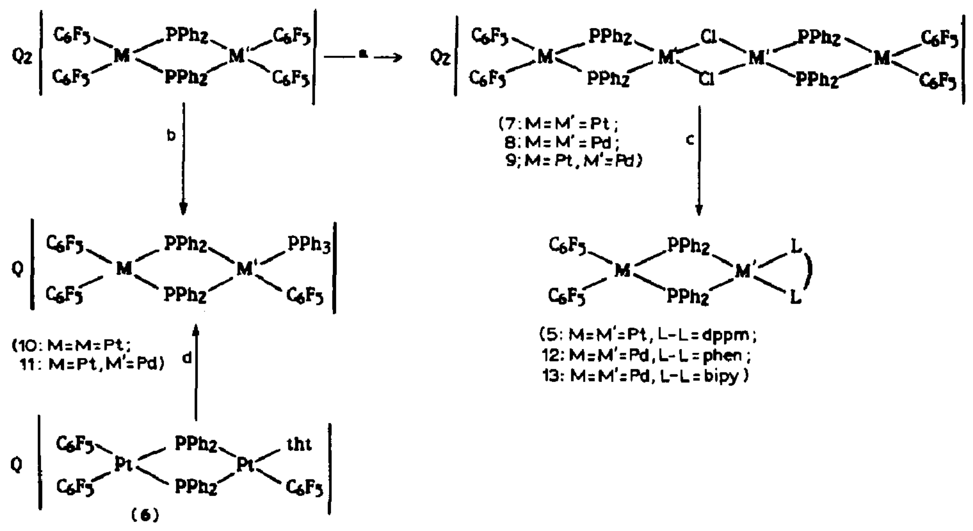
On the other hand, the reaction between *cis*-$M(C_6F_5)_2(THF)_2$ (THF = tetrahydrofuran) and $Li_2[M(C_6F_5)_2(PPh_2)_2]$ (1/1) (prepared "in situ" by treating *cis*-$M(C_6F_5)_2(PPh_2H)_2$ with Li^nBu in a 1/2 molar ratio in THF) yields, after addition of NBu_4ClO_4, complexes **1** and **2** in similar yields. The heterobimetallic complex $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(C_6F_5)_2]$ (**3**) can be obtained from the reaction between $Li_2[Pt(C_6F_5)_2(PPh_2)_2]$ and *cis*-$Pd(C_6F_5)_2(THF)_2$ (1/1) in THF (Scheme 1c).

The terminal phosphido ligands in $Li_2[cis\text{-}M(C_6F_5)_2(PPh_2)_2]$ are sufficiently nucleophilic to displace halide ligands from other mononuclear or binuclear platinum(II) complexes; for example, $Li_2[M(C_6F_5)_2(PPh_2)_2]$ (M = Pd, Pt) reacts with $PtCl_2(dppm)$ (dppm = bis(diphenylphosphinomethane)) in THF (molar ratio 1/1) to yield the binuclear asymmetric neutral complexes $[(C_6F_5)_2M(\mu\text{-}PPh_2)_2Pt(dppm)]$ (**4**: M = Pd; **5**: M = Pt) (Scheme 1d). Similarly the reaction between $Li_2[cis\text{-}Pt(C_6F_5)_2(PPh_2)_2]$ and $[Pt(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (tht = tetrahydrothiophene) in THF (molar ratio 2/1) yields, after addition of NBu_4ClO_4, $(NBu_4)[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)(tht)]$ (**6**) (Scheme 1e). However, no reaction takes place when a THF solution of $Li_2[cis\text{-}Pt(C_6F_5)_2(PPh_2)_2]$ and $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$ (molar ratio 2/1) is stirred at room temperature for 1.5 h.

In an attempt to prepare the binuclear asymmetric compound $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2PtCl_2]$ we carried out the reaction between $Li_2[cis\text{-}Pt(C_6F_5)_2(PPh_2)_2]$ and $PtCl_2$ in THF at 0 °C (molar ratio 1/1), but after addition of NBu_4ClO_4 to the resulting solution, the tetranuclear compound $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (**7**) was obtained (Scheme 1f). The isolation of this tetranuclear complex does not rule out the presence of the binuclear one in solution, since **7** could be formed from the binuclear derivative, as in eq. 1, and its lower solubility could be responsible for the separation of **7**.

$$2\left[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2PtCl_2\right]^{2-} \rightleftharpoons \left[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2\right]^{2-} + 2Cl^- \quad (1)$$

Complex **7** or other similar tetranuclear derivatives can be prepared by an alternative route. Acetone solutions of $(NBu_4)_2[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)_2]$ (**1**: M = M' = Pd; **2**: M = M' = Pt; **3**: M = Pd, M' = Pt) react with an aqueous solution of HCl, molar ratio 1/2) to yield the tetranuclear derivatives $(NBu_4)_2[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(\mu\text{-}Cl)_2M'(\mu\text{-}PPh_2)_2M(C_6F_5)_2]$ (**7**: M = M' = Pt; **8**: M = M' = Pd; **9**: M = Pt, M' = Pd) (Scheme 2a). As can be seen, HCl cleaves two M–C bonds on the same metal atom, and although the intermediate $(NBu_4)_2[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'Cl_2]$ cannot be isolated, the tetranuclear species are obtained (eq. 1). In the case of the heterobinuclear complex **3**, HCl selectively cleaves the Pd–C bonds to give **9**, and there is no evidence for the formation of the isomer $(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}PPh_2)_2Pd(C_6F_5)_2]$. When the reaction between the binuclear complexes **1** or **2** and HCl is carried out in a 1/1 molar ratio, a mixture of the tetranuclear complex **7** or **8** and the corresponding starting material (identified by its IR spectrum) is obtained. These results indicate that once $[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)Cl]^{2-}$ is formed, the HCl acts selectively on the $M'\text{–}C_6F_5$ bond of this anion and not on the residual starting material $[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)_2]^{2-}$. Similar behaviour has been observed for $(NBu_4)_2[M(C_6X_5)_4]$



Scheme 2. (a) HCl; (b) HCl, PPh_3; (c) L–L = dppm, bipy, or phen, respectively; (d) PPh_3.

(M = Pd, X = F, Cl; M = Pt, X = Cl), which react with HCl (molar ratio 1/1) to yield the corresponding binuclear complexes $(NBu_4)_2[(C_6X_5)_2M(\mu\text{-}Cl)_2M(C_6X_5)_2]$, along with unchanged starting material, although $(NBu_4)_2[Pt(C_6F_5)_4]$ under similar conditions gives the mononuclear compound $(NBu_4)_2[Pt(C_6F_5)_3Cl]$ [10,11]. However, the binuclear complexes $(NBu_4)[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)(PPh_3)]$ (**10**: M = M' = Pt; **11**: M = Pt, M' = Pd) are obtained when acetone solutions of **2** or **3** are treated with aqueous HCl in the presence of PPh_3 (molar ratio 1/1/1) (Scheme 2b), so that only one $M\text{–}C_6F_5$ bond per binuclear anion is cleaved. This different behaviour of HCl towards the binuclear derivatives **2** or **3** in the presence of PPh_3 may indicate that the reaction takes place stepwise, and that in the presence of PPh_3 the formation of the complexes $[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)(PPh_3)]^-$, which have smaller charges, is prefered, and furthermore that these must be less reactive towards the H^+ than are $[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)]^{2-}$. Similar behaviour of $M\text{–}C_6X_5$ bonds towards HCl and L has been observed in other cases; e.g. $(NBu_4)_2[Pt(C_6Cl_5)_4]$ reacts with HCl in the presence of L (L = phosphines, stibines) (molar ratio 1/1/1) to yield $(NBu_4)_2[Pt(C_6Cl_5)_3L]$ rather than the binuclear derivative obtained in the absence of L [11,12]. Furthermore the action of an excess of HCl and PPh_3 on $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (molar ratio 2/2/1) leads to formation only of **10**, no further $M\text{–}C_6F_5$ bonds being cleaved.

All the above results are summarized in Scheme 2. In no case is the HCl able to protonate a phosphido bridging ligand to give a terminal PPh_2H group, although it has recently been reported that some phosphido complexes can be protonated by acids with fragmentation of the binuclear framework $M(\mu\text{-}PPh_2)_2M$ and formation of mononuclear species containing terminal PPh_2H ligands [13,14].

The tetranuclear derivatives **7**, **8** and **9** are useful intermediates for the synthesis of neutral asymmetric complexes since their reactions with bidentate ligands (L–L) such as dppm, bipy, or phen, in acetone (molar ratio 1/2) yield the corresponding $[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(L\text{–}L)]$ (**5**: M = M' = Pt, L–L = dppm; **12**: L–L = phen; **13**: M = M' = Pd, L–L = bipy) complexes (Scheme 2c). When the reaction is carried out in a 1/1 molar ratio the binuclear complexes **5**, **12**, **13** are obtained

Table 1

Analyses, conductivities [a], and relevant IR data (cm^{-1}) for the complexes

Complex	Analysis (Found (calcd.)(%))			ΛM (ohm^{-1} cm^2 mol^{-1})	X-sensitive	Other bands
	C	H	N			
$Q_2[(C_6F_5)_2Pd(\mu\text{-}PPh_2)_2Pd(C_6F_5)_2]$	55.43	5.56	1.63	176	762, 752	
(1)	(55.34)	(5.34)	(1.61)			
$Q_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$	49.95	4.72	1.39	172	774, 762	
(2)	(50.21)	(4.84)	(1.46)			
$Q_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(C_6F_5)_2]$	52.89	5.39	1.47	166	774, 762, 750	
(3)	(52.65)	(5.00)	(1.53)			
$(C_6F_5)_2Pd(\mu\text{-}PPh_2)_2Pt(dppm)$	52.83	3.21	-	n.c.	778, 770	
(4)	(52.71)	(3.04)				
$(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(dppm)$	49.42	2.92	-	n.c.	768. 761	
(5)	(49.54)	(2.86)				
$Q[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)(tht)]$	46.81	4.50	0.99	81	779, 762	
(6)	(46.76)	(4.05)	(0.88)			
$Q_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)]_2$	45.41	4.30	0.94	168	779, 770	250 [b]
(7)	(45.50)	(4.11)	(1.02)			
$Q_2[(C_6F_5)_2Pd(\mu\text{-}PPh_2)_2Pd(\mu\text{-}Cl)]_2$	52.37	4.67	1.03	192	767, 760	248 [b]
(8)	(52.25)	(4.72)	(1.17)			
$Q_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}Cl)]_2$	48.40	4.38	0.92	168	781, 771	248 [b]
(9)	(48.65)	(4.40)	(1.09)			
$Q[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)\text{-}(PPh_3)]$	51.58	4.26	0.61	81	783, 775, 767	
(10)	(51.68)	(4.05)	(0.79)			
$Q[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(C_6F_5)\text{-}(PPh_3)]$	53.95	4.35	0.91	92	773, 765	
(11)	(54.41)	(4.26)	(0.83)			
$[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$	45.00	2.30	2.31	n.c.	778, 770	
(12)	(45.22)	(2.21)	(2.20)			
$[(C_6F_5)_2Pd(\mu\text{-}PPh_2)_2Pd(bipy)]$	51.47	2.63	2.61	n.c.	[c]	
(13)	(51.09)	(2.60)	(2.44)			
cis-$Pd(C_6F_5)_2(PPh_2H)_2$	53.25	2.73	-	n.c.	782, 774	2324 [d]
(14)	(53.21)	(2.73)				
cis-$Pt(C_6F_5)_2(PPh_2H)_2$	48.56	2.64	-	n.c.	794, 783	2329 [d]
(15)	(47.96)	(2.46)				

[a] In $\sim 5\times10^{-4}$mol dm^{-3}; n.c. = non-conducting. [b] ν(M–Cl). [c] Absorptions due to bipy in this region precludes unambiguous assignment. [d] ν(P–H).

along with unchanged starting material. On the other hand, complex **12** reacts with dppm in CH_2Cl_2 (molar ratio 1/1) to yield **5**.

Finally, complex **6** reacts with PPh_3 in CH_2Cl_2 (molar ratio 1/1) by displacement of the tetrahydrothiophene (tht) to yield **10** (Scheme 2d). In no case does the action of neutral monodentate or bidentate ligand, even in an excess, on these polynuclear complexes lead to cleavage of the $M(\mu\text{-}PPh_2)_2M'$ system.

Analytical and conductivity data along with relevant infrared absorptions related to the C_6F_5 group are listed in Table 1.

(b) Spectroscopic characterization of the complexes

The IR spectra of all the complexes show bands characteristic of the C_6F_5 group near 1500, 1050, 950 and 800 cm^{-1} [15]. Table 1 lists the absorptions assigned to the

Table 2

^{19}F NMR spectroscopic data [a]

Complex	$\delta(F_o)$	$\delta(F_m)$		$\delta(F_p)$		$J(Pt-F_o)$
1	−108.3	−165.3		−167.0		–
2	−111.9	−166.3		−168.2		316.0
3	−108.5	−165.3		−167.0		–
	−111.7	−166.6		−168.0		325.9
4	−110.2		−164.5		–	
5	−113.3		−165.6			309.6
6	−112.6	[b]		[b]		326.2
	−113.0					322.6
	−114.6					260.2
7	−113.8	−165.7		−166.5		329.8
8	−110.5	−164.9		−165.5		–
9	−113.7	−165.8		−166.5		316.9
10	−112.4 [c]	[b]		[b]		323.4
	−113.1					222.8
11	−110.6	−167.1		−164.7		–
	−112.2 [c]	−166.0		−163.5		329.8
12	−113.7	−165.5		−165.8		315.6
13	−110.3	−164.5		−164.3		–
14 [d]	−116.3	−164.1		−162.0		–
15 [d]	−118.9	−164.8		−162.7		335.4

[a] δ relative to $CFCl_3$, J in Hz; solvent acetone-d_6. [b] Complex multiplets which could not be unabiguously assigned. [c] This signal is due to the C_6F_5 groups bonded to the same platinum centre. Although the two groups are inequivalent, only one signal, with double intensity is observed. [d] in $CDCl_3$.

X-sensitive mode of this group that are of structural interest. Two bands with the same intensity are observed for complexes containing two C_6F_5 groups per metal centre, which indicates [16] that the C_6F_5 groups are mutually *cis*. Complex **3** shows three bands, indicating that the C_6F_5 groups are bonded to different metal centres Complexes **6** and **11** were expected to show three bands in view of their stoichiometry but only two of them were observed.

Bands in the 500 cm^{-1} region due to the PPh_2 group are observed in the phosphido complexes. Complexes **14** and **15** show absorptions in the ~ 850 and 2300 cm^{-1} regions, assigned respectively to a P–H deformation mode and ν(P–H) of the PPh_2H ligand [17].

^{19}F and ^{31}P NMR specta. The ^{19}F NMR spectral data for solutions in acetone-d_6 are listed in Table 2, and are consistent with the proposed structures. As usual, in all cases the *o*-F and *m*-F of each C_6F_5 group are isochronous. The ^{31}P NMR spectra provide valuable information on the structure of the complexes (Table 3). The corresponding δ ^{31}P (PPh_2) signals appear in all cases at very high field (in the range −95 to −150 ppm (relative to H_3PO_4)), indicating the absence of metal–metal bonds in the complexes.

Published data show that upfield (δ +50 to −200) resonance are usually found for μ-PPh_2 ligands bridging two metals not joined by a metal–metal bond [18–20]. Complexes **1, 2, 3, 7, 8, 9, 12, 13**, containing two equivalents (μ-PPh_2) ligands, show one signal assignable to the phosphido groups; for complexes containing platinum atoms, platinum satellites due to the ^{195}Pt (33.7% I $\frac{1}{2}$) are observed with ^{1}J(Pt–P) values ranging from 2615 to 1668 Hz. No ^{3}J(Pt–P) coupling was observed for complex **7**. The spectrum of **6** shows a characteristic first order AB system, indicating the presence of two inequivalent (μ-PPh_2) ligands. Since both platinum atoms are inequivalent four ^1J(Pt–P) coupling constants can be observed. The coupling constants (^1J(Pt–P)) corresponding to the signal at δ −148.3 ppm are 1623 and 1776 Hz, and the signal at δ −130.7 shows platinum satellites with ^1J(Pt–P) 1911 and 2134 Hz. In the light of these observations it seems reasonable to assume that the signal at δ −148.3 ppm is due to the phosphido ligand *cis* to the tht group, since the coupling constants for this signal are more similar than are those ones for the other signal. The spectrum of **11** is consistent with the presence of three inequivalent P atoms. The signal at lowest field can be assigned to the PPh_3 ligand. It should be noticed that $^2J(PR_3–PR_2{}^-{}_{trans})$ is larger than $^2J(PR_2{}^-–PR_2{}^-)$, and that no $^2J(PR_3–PR_2{}^-{}_{cis})$ coupling is observed. For **10** the complexity of the signals in the region corresponding to PPh_2 precludes and unequivocal assignment of the various parameters, but the parameters for the PPh_3 signal can be assigned.

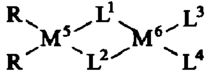
The spectra of **4** and **5** can be analyzed in terms of an AA′XX′ spin system with platinum satellites. The various parameters related to these spectra have been computed by standard methods [21,22] and are listed in Table 3. Figure 1 shows the half spectrum in the dppm region for complex **4**.

(c) Structure of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$ (12)

The structure of **12** was determined by a single-crystal X-ray diffraction study. General crystallographic information is presented in Table 4. Fractional coordinates of non-hydrogen atoms are given in Table 5. Bond distances and bond angles are listed in Table 6. The structure of **12** (Fig. 2) consists of a binuclear complex formed

Table 3

$^{31}P\{^1H\}$ NMR data (δ in ppm, J in Hz) (relative to H_3PO_4, solvent acetone-d_6)



	$\delta_{1.2}$	$\delta_{3.4}$	$^1J_{1.5}$	$^1J_{1.6}$	$^1J_{2.5}$	$^1J_{2.6}$	$^1J_{3.6}$	$^2J_{1.2}$	$^2J_{1.3}$	$^2J_{2.3}$	$^2J_{3.4}$
1	−105.6										
2	−146.9		1787								
3	−128.2		1668								
4	−105.6	−28.9		1603			1694	158 [a]	18	270	30 [a]
5	−105.6	−29.0	{1609 [b] 1589				1697	159 [a]	17	272	30 [a]
6	−148.3		{1623 [b] 1777					142			
	−130.7				1911 [c]	2134 [c]					
7	−139.4		1941 [c]	2616 [c]							
8	−113.1										
9	−133.2		1761								
10	[d]	19.9					2129			316	
11	−132.2	21.4	1602					163		326	
	−109.4				1737						
12	−132.0		1849 [c]	2163 [c]							
13	−96.0										

[a] $|J_{AA'}|$ and $|J_{XX'}|$. [b] The two coupling constants could not be assigned unequivocally. [c] These values were assigned by taking into account the high *trans*-influence of the C_6F_5 group. [d] See text.

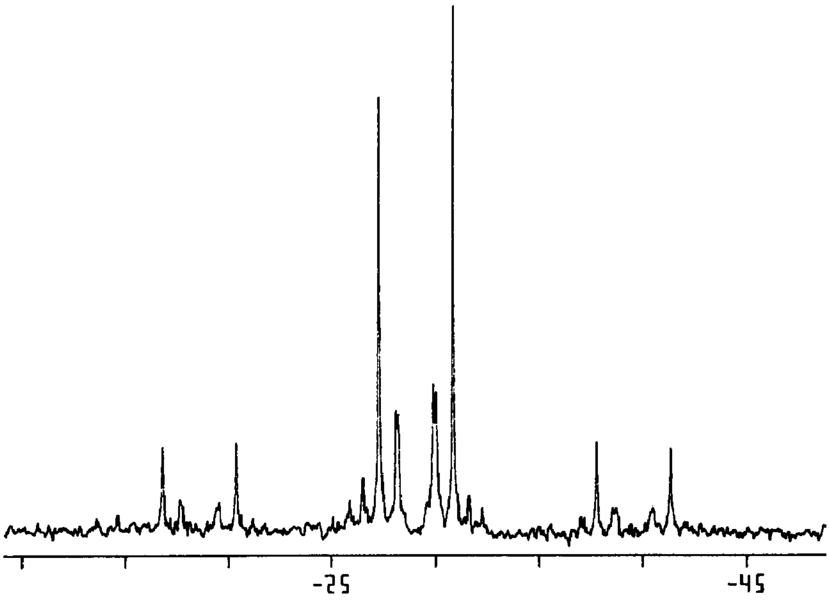


Fig. 1. The half spectrum (^{31}P NMR) of the dppm area for $[(C_6F_5)_2Pd(\mu\text{-}PPh_2)_2Pt(dppm)]$ (4). The horizontal axis is labeled in ppm.

by two different and distorted square planar platinum environments which share an edge containing the P atoms of both PPh_2 bridging ligands. Within the Pt_2P_2 ring, the Pt–Pt distance (3.5711(9) Å) [29] indicates that no metal–metal bond is present (in agreement with the ^{31}P NMR data). Because of the long Pt–Pt distance, the

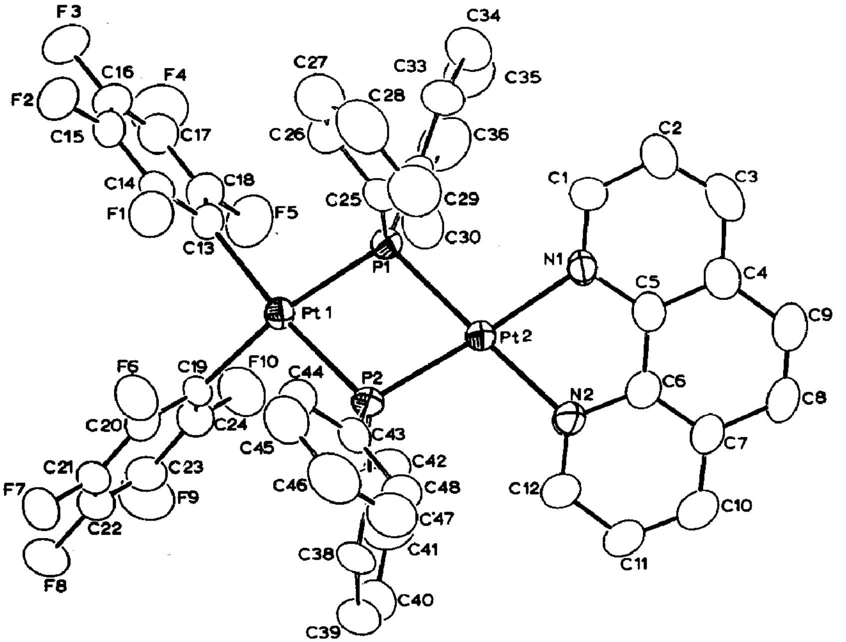


Fig. 2. Molecular structure of $[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)]$ (12) showing the atom labelling scheme.

Table 4

Crystal data and details of the crystallographic study of $(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)$ [a]

Formula	$C_{48}H_{28}N_2F_{10}P_2Pt_2$
M	1274.9
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
a (Å)	11.155(2)
b (Å)	11.935(3)
c (Å)	17.575(4)
α (°)	72.301(21)
β (°)	72.142(17)
γ (°)	78.211(18)
V (Å^3)	2077.4
Diffractometer	Enraf-Nonius CAD 4
T (K)	293 ± 1
Radiation	Mo-K_α
λ (Å)	0.71069
μ (Mo-K_α) (cm^{-1})	70.9, empirical absorption correction was applied [35].
θ-range (°)	1–25°
Mode	θ–2θ scans
Data measured	7815
Data used	6279 ($F > 4\sigma(F)$)
Solution	Direct methods, ΔF syntheses
Refinement	Full-matrix least squares
Model	All atoms anisotropic. H atoms non resolved. Rigid planar hexagons for C_6H_5 groups.
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.002009(F^2)$
R_w	0.0382
R	0.0323
Variables	529

[a] Suitable crystals were obtained by slow diffusion (ca. 2 weeks at −30 °C) of n-hexane into a solution of the complex in acetone.

Pt–P–Pt angles are 102.7(1) and 103.2(1)°. Similar Pt...Pt distances (3.585(1) or 3.699(1) Å) and Pt–P–Pt angles (102.8(1), 103.9(1)°) have been observed for other neutral $[PtCl(PPh_2)(PPh_2H)]_2$ or cationic $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$ platinum(II) phosphido complexes [18] without Pt–Pt bonds. The small P–Pt–P angles (74.7(1) and 75.4(1)°) are the result of the long Pt(1)...Pt(2) distance and the large Pt(1)–P–Pt(2) angles. The Pt_2P_2 ring is not planar, the dihedral angles formed by the planes Pt(1)–P(1)–P(2) and Pt(2)–P(1)–P(2) or Pt(1)–P(1)–Pt(2) and Pt(1)–P(2)–Pt(2) being 160.93(7) and 155.64(8)°, respectively. The four Pt–P distances are slightly different, and fall in the range 2.269(1)–2.294(1) Å.

The square planar environments of both platinum atoms are different. Pt(1) is bonded to two phosphido and two pentafluorophenyl groups, and the corresponding Pt–C distances (2.099(6) and 2.069(5) Å) lie close to the top of the range found for Pt–C distances in other pentafluorophenylplatinum(II) complexes [23–27]; shorter Pt–C distances have been found in complexes such as $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}Cl)_2Pt(C_6F_5)_2]$ (1.977(10) and 1.991(10) Å) [26] or $[Pt(C_6F_5)_2(\mu\text{-}Br)Pd(\eta^4\text{-}1,5\text{-}$

Table 5

Fractional atomic coordinates (×10^4) and their estimated standard deviations for $(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)$

	x	y	z	B (Å^2) ^{a}
Pt1	2099(1)	7006(1)	2162(1)	2.36(2)
Pt2	65(1)	9669(1)	2413(1)	2.51(2)
P1	391(1)	7718(1)	3084(1)	2.46(10)
P2	2037(1)	9024(1)	1722(1)	2.58(10)
N1	−1661(5)	10244(4)	3206(3)	2.99(37)
N2	−345(5)	11438(4)	1712(3)	3.13(37)
C1	−2245(6)	9696(6)	3956(4)	3.45(46)
C2	−3298(7)	10211(7)	4462(5)	4.26(56)
C3	−3785(7)	11321(7)	4148(5)	4.47(59)
C4	−3191(6)	11983(6)	3339(5)	3.80(51)
C5	−2113(6)	11408(5)	2887(4)	3.08(45)
C6	−1458(6)	12039(5)	2103(4)	3.04(44)
C7	−1872(6)	13185(6)	1757(5)	3.89(52)
C8	−3013(7)	13761(6)	2217(6)	4.62(60)
C9	−3626(7)	13193(7)	2965(6)	4.89(64)
C10	−1202(8)	13751(7)	958(6)	5.29(66)
C11	−107(7)	13149(6)	565(5)	4.64(58)
C12	305(7)	11993(6)	971(5)	4.12(53)
C13	2003(6)	5182(5)	2675(4)	2.84(42)
C14	2648(6)	4519(6)	3243(4)	3.39(46)
C15	2608(7)	3326(6)	3588(4)	4.15(51)
C16	1881(7)	2752(6)	3377(5)	4.27(55)
C17	1268(7)	3337(6)	2792(5)	4.31(57)
C18	1334(7)	4550(6)	2454(4)	3.73(51)
C19	3630(6)	6688(5)	1200(4)	2.59(39)
C20	4874(6)	6584(5)	1211(4)	3.35(47)
C21	5881(6)	6490(6)	555(4)	3.79(49)
C22	5669(8)	6450(6)	−173(5)	5.06(61)
C23	4476(8)	6520(6)	−232(4)	3.93(52)
C24	3474(7)	6624(6)	462(5)	3.81(51)
C25	651(4)	7574(3)	4084(2)	2.67(39)
C26	792(4)	6460(3)	4630(2)	4.12(52)
C27	1075(4)	6353(3)	5371(2)	5.26(67)
C28	1219(4)	7360(3)	5565(2)	5.55(73)
C29	1078(4)	8474(3)	5018(2)	5.32(71)
C30	794(4)	8581(3)	4277(2)	4.10(54)
C31	−1080(3)	7090(4)	3299(3)	2.93(40)
C32	−1903(3)	6765(4)	4086(3)	4.49(55)
C33	−3041(3)	6355(4)	4185(3)	5.44(68)
C34	−3356(3)	6271(4)	3496(3)	6.44(83)
C35	−2533(3)	6596(4)	2709(3)	6.52(87)
C36	−1395(3)	7005(4)	2611(3)	4.27(56)
C37	2388(4)	9621(4)	610(2)	2.94(40)
C38	3386(4)	10283(4)	139(2)	3.80(47)
C39	3579(4)	10703(4)	−717(2)	4.73(56)
C40	2773(4)	10460(4)	−1101(2)	4.71(57)
C41	1775(4)	9797(4)	−630(2)	6.00(74)
C42	1582(4)	9377(4)	226(2)	4.55(58)
C43	3107(4)	9580(3)	2092(3)	3.01(42)
C44	3739(4)	8769(3)	2643(3)	3.78(49)
C45	4515(4)	9157(3)	2976(3)	4.69(61)
C46	4658(4)	10358(3)	2758(3)	5.01(66)
C47	4026(4)	11169(3)	2207(3)	4.75(62)

Table 5 (continued)

	x	y	z	B (Å^2) ^{a}
C48	3250(4)	10781(3)	1874(3)	3.66(48)
F1	3392(4)	5044(4)	3496(3)	4.52(32)
F2	3288(5)	2726(4)	4148(3)	6.12(38)
F3	1845(5)	1583(3)	3731(3)	6.91(43)
F4	599(6)	2775(4)	2549(3)	7.03(50)
F5	678(5)	5091(4)	1882(3)	5.27(38)
F6	5154(4)	6590(4)	1909(3)	4.81(34)
F7	7092(4)	6416(4)	590(3)	5.56(36)
F8	6680(5)	6331(4)	−838(3)	6.88(41)
F9	4290(5)	6451(5)	−916(3)	6.43(44)
F10	2317(4)	6669(4)	367(3)	5.25(39)

^{a} B_{eq} anisotropic atoms.

$C_8H_{12})(\mu$-Br)Pt$(C_6F_5)_2(\mu$-Br)Pd$(\eta^4$-1,5-$C_8H_{12})(\mu$-Br)] (1.974(9), 1.967(9) Å) [28] probably as a consequence of the high *trans*-influence of the bridging phosphido group. On the other hand, P(1) and P(2) are both closer to Pt(2) (2.279(1), 2.269(1) Å) than they are to Pt(1) (2.294(1), 2.288(1) Å), in accordance with the higher *trans*-influence of C_6F_5 than of the N donor ligand. As a consequence of the small P(1)–Pt(1)–P(2) angle (74.7°), the remaining angles at the Pt(1) atom are all greater than 90°, the P–Pt(1)–C angles being larger (94.9(2) and 99.3(2)°) than the corresponding C(13)–Pt(1)–C(19) (91.1(2)°) angle. The Pt(1) environment is very close to planar; the dihedral angles formed by the planes C(13)–Pt(1)–C(19) and P(1)–Pt(1)–P(2) or P(1)–Pt(1)–C(13) and P(2)–Pt(1)–C(19) are 177.58(16) and 177.74(18)°, respectively [29]. Pt(2) is bonded to two phosphido groups and to the phen ligand, and because of the small values of the P(1)–Pt(2)–P(2) (75.4(0)°) and N(1)–Pt(2)–N(2) (78.7(2)°) [30], the corresponding P(1)–Pt(2)–N(1) and P(2)–Pt(2)–N(2) are larger than 90° (101.6(1) and 105.2(1)°, respectively). The Pt(2) environment deviates more from planarity than does that of Pt(1). The corresponding dihedral angles formed by the planes N(1)–Pt(2)–N(2) and P(1)–Pt(2)–P(2) or P(1)–Pt(2)–N(1) and P(2)–Pt(2)–N(2) are 168.78(14) and 171.05(12)°, respectively [29].

Experimental

C, H and N analyses were carried out with a Perkin Elmer 240B microanalyzer. IR spectra were recorded on a Perkin Elmer 599 spectrophotometer (range 4000–200 cm^{-1}) with Nujol mulls between polyethylene plates. ^{19}F and ^{31}P NMR spectra were recorded on a Varian XL200 instrument (200 Mz for ^1H). Conductivities were measured with a Philips PW 9501/01 conductimeter (acetone solutions, c ~ 5×10^{-4} *M*).

Published methods were used to prepare the following starting materials: *cis*-Pt$(C_6F_5)_2(THF)_2$ [28], *cis*-Pd$(C_6F_5)_2(THF)_2$ [28], LiPPh$_2$ [31], $(NBu_4)_2[Pt_2(\mu$-$Cl)_2(C_6F_5)_4]$, [32], $(NBu_4)_2[Pd_2(\mu$-$Br)_2(C_6F_5)_4$ [33], [Pt$(\mu$-Cl$)(C_6F_5)$(tht)]$_2$ [34].

cis-$M(C_6F_5)_2(PPh_2H)_2$ (14: $M = Pd$; 15: $M = Pt$)

M = Pt: To a CH_2Cl_2 (20 ml) solution of *cis*-Pt$(C_6F_5)_2(THF)_2$ (0.700 g, 1.039 mmol) was added PPh$_2$H (0.362 ml, 2.078 mmol), and the mixture was stirred at

Table 6

Bond distances (Å) and bond angles (°) and their estimated standard deviations for $(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(phen)$

(a) Bond distances (Å)							
P1–Pt1	2.294 (1)	C11–C10	1.383 (11)	P2–Pt1	2.288 (1)	C12–C11	1.403 (9)
C13–Pt1	2.099 (6)	C14–C13	1.367 (9)	C19–Pt1	2.069 (5)	C18–C13	1.364 (12)
P1–Pt2	2.279 (1)	C15–C14	1.371 (9)	P2–Pt2	2.269 (1)	F1–C14	1.373 (10)
N1–Pt2	2.127 (5)	C16–C15	1.352 (13)	N2–Pt2	2.135 (5)	F2–C15	1.366 (9)
C25–P1	1.818 (5)	C17–C16	1.347 (12)	C31–P1	1.829 (4)	F3–C16	1.347 (7)
C37–P2	1.810 (3)	C18–C17	1.396 (9)	C43–P2	1.830 (5)	F4–C17	1.328 (12)
C1–N1	1.308 (8)	F5–C18	1.352 (9)	C5–N1	1.383 (7)	C20–C19	1.374 (10)
C6–N2	1.394 (8)	C24–C19	1.386 (11)	C12–N2	1.323 (8)	C21–C20	1.354 (9)
C2–C1	1.395 (9)	F6–C20	1.358 (10)	C3–C2	1.342 (10)	C22–C21	1.388 (13)
C4–C3	1.426 (9)	F7–C21	1.355 (9)	C5–C4	1.400 (9)	C23–C22	1.350 (13)
C9–C4	1.445 (9)	F8–C22	1.373 (9)	C6–C5	1.405 (8)	C24–C23	1.396 (9)
C7–C6	1.365 (8)	F9–C23	1.309 (11)	C8–C7	1.448 (10)	F10–C24	1.339 (10)
C10–C7	1.405 (1)			C9–C8	1.322 (11)		
(b) Bond angles (°)							
P2–Pt1–P1	74.7 (1)	C12–C11–C10	119.4 (7)	C13–Pt1–P1	99.3 (2)	C11–C12–N2	122.1 (6)
C13–Pt1–P2	174.0 (2)	C14–C13–Pt1	122.3 (6)	C19–Pt1–P1	169.3 (2)	C18–C13–Pt1	123.3 (5)
C19–Pt1–P2	94.9 (2)	C18–C13–C14	114.3 (6)	C19–Pt1–C13	91.1 (2)	C15–C14–C13	123.7 (8)

P2–Pt2–P1	75.4 (1)	F1–C14–C13	120.0 (6)	N1–Pt2–P1	101.6 (1)	F1–C14–C15	116.3 (6)
N1–Pt2–P2	171.5 (2)	C16–C15–C14	119.6 (7)	N2–Pt2–P1	173.8 (2)	F2–C15–C14	120.1 (8)
N2–Pt2–P2	105.2 (1)	F2–C15–C16	120.3 (6)	N2–Pt2–N1	78.7 (2)	C17–C16–C15	119.8 (6)
Pt2–P1–Pt1	102.7 (1)	F3–C16–C15	118.7 (7)	C25–P1–Pt1	114.8 (1)	F3–C16–C17	121.4 (8)
C25–P1–Pt2	110.1 (1)	C18–C17–C16	118.7 (9)	C31–P1–Pt1	115.4 (2)	F4–C17–C16	120.7 (6)
C31–P1–Pt2	107.1 (1)	F4–C17–C18	120.6 (7)	C31–P1–C25	106.4 (2)	C17–C18–C13	123.6 (7)
Pt2–P2–Pt1	103.2 (1)	F5–C18–C13	120.5 (6)	C37–P2–Pt1	114.7 (2)	F5–C18–C17	115.9 (8)
C37–P2–Pt2	114.0 (1)	C20–C19–Pt1	123.9 (5)	C43–P2–Pt1	112.6 (1)	C24–C19–Pt1	121.8 (5)
C43–P2–Pt2	104.4 (1)	C24–C19–C20	114.2 (6)	C43–P2–C37	107.5 (2)	C21–C20–C19	124.3 (7)
C1–N1–Pt2	128.9 (4)	F6–C20–C19	119.9 (5)	C5–N1–Pt2	112.3 (4)	F6–C20–C21	115.8 (7)
C5–N1–C1	118.4 (5)	C22–C21–C20	119.0 (7)	C6–N2–Pt2	113.3 (3)	F7–C21–C20	122.2 (8)
C12–N2–Pt2	128.2 (4)	F7–C21–C22	118.7 (6)	C12–N2–C6	118.5 (5)	C23–C22–C21	120.5 (7)
C2–C1–N1	124.2 (6)	F8–C22–C21	119.7 (8)	C3–C2–C1	118.1 (6)	F8–C22–C23	119.8 (9)
C4–C3–C2	120.9 (6)	C24–C23–C22	118.0 (8)	C5–C4–C3	116.9 (6)	F9–C23–C22	119.8 (7)
C9–C4–C3	124.5 (6)	F9–C23–C24	122.1 (8)	C9–C4–C5	118.6 (6)	C23–C24–C19	123.9 (7)
C4–C5–N1	121.3 (5)	F10–C24–C19	121.1 (6)	C6–C5–N1	119.5 (5)	F10–C24–C23	115.0 (8)
C6–C5–C4	119.2 (5)	C26–C25–P1	120.5 (4)	C5–C6–N2	116.2 (5)	C30–C25–P1	119.3 (3)
C7–C6–N2	122.1 (5)	C32–C31–P1	124.0 (4)	C7–C6–C5	121.7 (5)	C36–C31–P1	115.9 (3)
C8–C7–C6	118.7 (6)	C38–C37–P2	124.4 (3)	C10–C7–C6	118.9 (6)	C42–C37–P2	115.6 (3)
C10–C7–C8	122.3 (6)	C44–C43–P2	117.7 (3)	C9–C8–C7	120.5 (6)	C48–C43–P2	122.2 (3)
C8–C9–C4	121.3 (7)			C11–C10–C7	118.8 (6)		

room temperature for 1 h. The solution was concentrated to ca. ~ 2 ml and n-hexane (20 ml) was added. The white precipitate was washed with n-hexane **15**, 90% yield. **14** was prepared similarly in 85% yield.

$(NBu_4)_2[MM'(\mu\text{-}PPh_2)_2(C_6F_5)_4]$ (*1: M = M' = Pd; 2: M = M' = Pt; 3: M = Pt, M' = Pd*)

Preparation of 2

(a) From $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$. To a solution of $LiPPh_2$ (2.027 mmol) in THF (10 ml) at 0 °C, was added $(NBu_4)_2[Pt_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ (0.800 g, 0.496 mmol) and the mixture stirred at room temperature for 7 h. The solution was evaporated to dryness and the oily residue was extracted with Et_2O (10 ml) and the extract was evaporated to dryness. The resulting white solid was washed with ^iPrOH and recrystallized from $CH_2Cl_2/^iPrOH$, 67% yield.

(b) From cis-$Pt(C_6F_5)_2(PPh_2H)_2$. A THF (10 ml) solution of *cis*-$Pt(C_6F_5)_2(PPh_2H)_2$ (0.527 g, 0.584 mmol) was treated with Li^nBu (1.703 mmol) in hexane and *cis*-$Pt(C_6F_5)_2(THF)_2$ (0.394 g, 0.585 mmol) was subsequently added. The mixture was stirred at room temperature for 20 min, then evaporated to dryness. The residue was extracted with Et_2O (20 ml) and the extract evaporated to dryness. The residue was treated with ^iPrOH (30 ml) and NBu_4ClO_4 (0.400 g, 1.169 mmol) was added to the filtered solution to produce white crystals of **2**, which was washed with ^iPrOH. Yield 62%.

Complex **1** was prepared by treating $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (0.836 g, 0.548 mmol) with $LiPPh_2$ (1.953 mmol). The work up was similar to that for **2** (method a). Yield 46%.

Complex 3 was obtained in the same way as **2** (method b), *cis*-$Pt(C_6F_5)_2(PPh_2H)_2$ (0.400 g, 0.444 mmol); 0.945 mmol of Li^nBu; *cis*-$Pd(C_6F_5)_2(THF)_2$ (0.260 g, 0.444 mmol). After the extraction with Et_2O and removal of the ether, the residue was extracted with 20 ml of CH_2Cl_2 and the extract evaporated to dryness. The residue was taken up in MeOH (20 ml) and NBu_4ClO_4 (0.304 g, 0.888 mmol) was added, to produce a yellow solid (**3**), which was washed with MeOH. Yield 45%.

$(NBu_4)[(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(C_6F_5)L]$ (*6: M = M' = Pt, L = tht; 10: M = M' = Pt, L = PPh₃; 11: M = Pt, M' = Pd, L = PPh₃*)

Complex 6. To a THF solution (15 ml) of *cis*-$Pt(C_6F_5)_2(PPh_2H)_2$ (0.400 g, 0.444 mmol) and 0.945 mmol of Li^nBu was added $[Pt(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ (0.215 g, 0.221 mmol). The mixture was stirred at room temperature for 3 h. The solution was evaporated to dryness, the residue extracted with 30 ml of CH_2Cl_2 and the extract was filtered and evaporated to dryness. The residue was taken up in ^iPrOH (30 ml), the colourless mixture was filtered, and NBu_4ClO_4 (0.152 g, 0.444 mmol) added, to give crystalline **6**, which was washed with ^iPrOH. Yield 67%.

Complex 10

(a) From 6. To a colourless dichloromethane solution of **6** (0.100 g, 0.063 mmol) was added PPh_3 (0.0165 g, 0.063 mmol). The mixture was stirred at room temperature for 24 h, then evaporated almost to dryness. Addition of ^iPrOH (20 ml) produced a precipitate of **10**, which was washed with ^iPrOH. Yield 45%.

(b) From 2. A solution of 0.150 g (0.078 mmol) of **2** in acetone (15 ml), was treated at room temperature with 0.078 mmol of HCl in water and PPh_3 (0.020 g,

0.078 mmol). The mixture was kept for 5 h then evaporated almost to dryness and ^{i}PrOH (15 ml) was added. The white precipitate (**10**) was washed with ^{i}PrOH. Yield 76%.

Complex **11** was obtained similarly from **3** (0.150 g, 0.082 mmol), HCl (0.082 mmol) and PPh_3 (0.0215 g, 0.082 mmol). Recrystallization was from acetone/isopropanol. Yield 71%.

$(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pt(\mu\text{-}Cl)_2Pt(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (7)

(a) From 2. To an acetone (20 ml) solution of **2** (0.150 g, 0.078 mmol) was added 0.156 mmol HCl in water and the mixture was stirred at room temperature for 5 h. The solution was evaporated almost to dryness and addition of ^{i}PrOH (15 ml) with vigorous stirring gave a precipitate of **7**, which was washed with ^{i}PrOH. Yield 80%.

(b) From cis-$Pt(C_6F_5)_2(PPh_2H)_2$. $PtCl_2$ (0.050 g, 0.188 mmol) was added to a THF (10 ml) solution of Li^{n}Bu (0.399 mmol) and *cis*-$Pt(C_6F_5)_2(THF)_2$ (0.168 g, 0.186 mmol) at −10 °C, and the mixture was stirred for 90 min then evaporated to dryness. The residue was extracted with CH_2Cl_2 (20 ml) and the extract evaporated to dryness. Addition of ^{i}PrOH produced a dark solution, the addition of NBu_4ClO_4 (0.063 g, 0.186 mmol) resulted in crystallization of **7**. Yield 43%.

$(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}PPh_2)_2Pd(\mu\text{-}Cl)_2Pd(\mu\text{-}PPh_2)_2Pd(C_6F_5)_2]$ (8)

This compound was synthesized in the same way as **7** (method a) from **1** (0.083 g, 0.047 mmol) and aqueous HCl (0.094 mmol). The oily residue obtained after evaporation to dryness was disolved in a mixture of acetone (10 ml) and ^{i}PrOH (15 ml), and concentration of the solution to ~ 10 ml yielded **8**, which was washed with ^{i}PrOH. Yield 70%.

$(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}PPh_2)_2Pd(\mu\text{-}Cl)_2Pd(\mu\text{-}PPh_2)_2Pt(C_6F_5)_2]$ (9)

Complex **9** was obtained similarly from **3** (0.150 g, 0.082 mmol) and aqueous HCl (0.164 mmol). Yield 94%.

$(C_6F_5)_2M(\mu\text{-}PPh_2)_2M'(L\text{–}L)$ (5: $M = M' = Pt$, $L\text{–}L$ = dppm; 4: $M = Pd$, $M' = Pt$, L = dppm; 12: $M = M' = Pt$, $L\text{–}L$ = phen; 13: $M = M' = Pd$, $L\text{–}L$ = bipy)

Complex 5. To a THF (10 ml) solution of *cis*-$Pt(C_6F_5)_2(PPh_2H)_2$ (0.150 g, 0.166 mmol) and Li^{n}Bu (0.424 mmol), at 0 °C, was added $PtCl_2$(dppm) (0.108 g, 0.166 mmol). The mixture was stirred for 2 h at 0 °C and overnight at room temperature, and then evaporated to dryness. The residue was extracted at room temperature with Et_2O (5 ml) and the extract evaporated to dryness. The residue was extracted with CH_2Cl_2 (20 ml) and the extract evaporated to ca. 5 ml. Addition of $CHCl_3$ (15 ml) and concentration to ca. 2 ml produced a yellow precipitate of **5** which was washed with 1 ml of $CHCl_3$ and 2 × 2 ml of Et_2O. Yield 43%.

Complex **4** was obtained similarly. Yield 23%.

Complex 12. To an acetone (15 ml) solution of **7** (0.100 g, 0.036 mmol) was added 1,10-phen · H_2O (0.015 g, 0.076 mmol), and the mixture stirred at room temperature for 7 h. The solution was evaporated to ca. 3 ml, and addition of MeOH (~ 5 ml) then gave **12**, which was washed with MeOH. Yield 77%.

Complex 13. To an acetone (~ 15 ml) solution of **8** (0.066 g, 0.027 mmol) was added 2,2′-bipy (0.0094 g, 0.060 mmol). The mixture was stirred at room temperature for 5 h, then evaporated almost to dryness. Addition of ^{i}PrOH (~ 20 ml) gave solid **13** (93% yield), which was washed with ^{i}PrOH.

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