

**SYNTHESIS AND REACTIVITY OF MIXED  
 PENTAFLUOROPHENYLPALLADIUM(I)-PLATINUM(I) DERIVATIVES.  
 MOLECULAR STRUCTURE OF  $\text{ClPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)$  \***

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**Summary**

$\text{XPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)$  ( $\text{X} = \text{Cl}$  (I),  $\text{Br}$  (II),  $\text{C}_6\text{F}_5$  (III)) have been prepared by treating  $\text{PdX}(\text{C}_6\text{F}_5)(\eta^1\text{-dppm})_2$  with  $\text{Pt}(\text{COD})_2$  or  $\text{Pt}(\text{PPh}_3)_4$ . Substitution reactions of I yield neutral ( $\text{SCN}$ ) or cationic ( $\text{PPh}_3$ ,  $\text{py}$ ) derivatives. The species  $\text{R}_2\text{N}^+$ ,  $\text{SO}_2$  or  $\text{RC}\equiv\text{CR}$  ( $\text{R} = \text{COOMe}$ ) insert into the  $\text{Pd-Pt}$  bond of I to give A-frame  $\text{Pd}^{\text{II}}\text{-Pt}^{\text{II}}$  complexes, but reaction with  $\text{SnCl}_2$  gives the  $\text{SnCl}_3^-$  derivative. The reactions of  $\text{X-Pt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)$  ( $\text{X} = \text{Cl}$  (I),  $\text{C}_6\text{F}_5$  (III)) with isonitriles  $\text{RNC}$  ( $\text{R} = p\text{-Tol}$ ,  $\text{Cy}$ ,  $t\text{-Bu}$ ) has been studied; the nature of the products obtained depends on the starting material, the isonitrile, and the reaction conditions.

The molecular structure of  $\text{ClPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)$  has been established by a single crystal X-ray study.

**Introduction**

The ability of  $\text{dppm}$  (= 1,2-bis(diphenylphosphino)methane) to form bridged binuclear complexes has prompted interest in this and related ligands [1]. Homo-binuclear palladium(I) or platinum(I) complexes containing a  $\text{Pd-Pd}$  or  $\text{Pt-Pt}$  bond and two bridging  $\text{dppm}$  ligands have been much studied recently [2], but hetero-binuclear  $\text{Pd}^{\text{I}}\text{-Pt}^{\text{I}}$  complexes of this type have received little attention [3].

We previously described the synthesis and reactions of some homo-binuclear perhalophenyl palladium(I) [4] or platinum(I) [5] derivatives containing  $\text{dppm}$  as

\* Dedicated to Prof. R. Usón on the occasion of his 60th birthday.

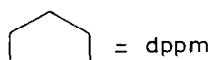
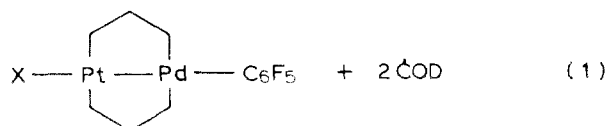
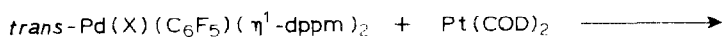
bridging ligand. In this paper we report the synthesis of the related hetero-binuclear pentafluorophenyl palladium(I)-platinum(I) derivatives  $[XPt(\mu\text{-dppm})_2Pd(C_6F_5)]$  ( $X = Cl, Br, C_6F_5, SCN, SnCl_3$ ) and their reactivity in the formation of the cationic complexes  $[L^+Pt(\mu\text{-dppm})_2Pd(C_6F_5)]^+$  ( $L^+ = RNC, PPh_3, py$ ); insertions of groups such as  $RNC, SO_2, N_2R^+$ , and  $RC\equiv CR$  into the Pd-Pt bond have also been studied.

The molecular structure of  $[ClPt(\mu\text{-dppm})_2Pd(C_6F_5)]$  has been established by an X-ray diffraction study.

## Results and discussion

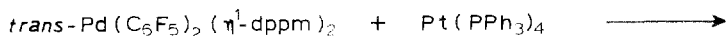
*Synthesis of hetero-binuclear palladium(I)-platinum(I) complexes  $[XPt(\mu\text{-dppm})_2Pd(C_6F_5)]$  ( $X = Cl, Br, SnCl_3, C_6F_5$ )*

Reactions of complexes  $trans\text{-Pd}(X)(C_6F_5)(\eta^1\text{-dppm})_2$  ( $X = Cl, Br, C_6F_5$ ) with  $Pt(COD)_2$  in oxygen-free benzene give the corresponding deep-yellow or orange hetero-binuclear metal-metal bonded  $Pd^I\text{-Pt}^I$  complexes  $[XPt(\mu\text{-dppm})_2Pd(C_6F_5)]$  ( $X = Cl, Br, C_6F_5$ ), according to eqn. 1:

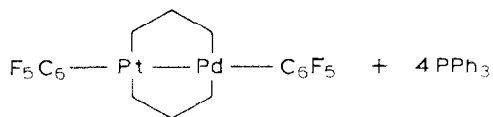


(  $X = Cl$  (I) ,  $Br$  (II) ,  $C_6F_5$  (III) )

Complex III can also be obtained by using  $Pt(PPh_3)_4$  as the  $Pt^0$  starting material, according to eq. 2:



( 2 )



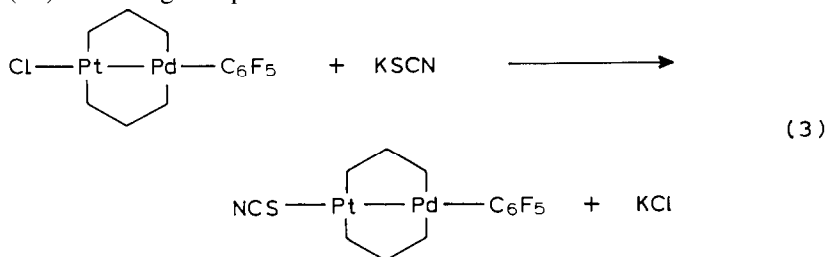
The X-ray structure and  $^{19}F$  NMR spectrum of complex I (see below) show that the redox condensation process (eq. 1) takes place through the migration of the X group from the  $Pd^{II}$  to  $Pt^0$  center.

In the  $^{19}F$  NMR spectrum of complex I, the signal,  $F_o$ , from the *ortho*-fluorines at  $\delta -117.9$  ppm, is basically a doublet (owing to coupling with the neighbouring *meta*-fluorines), with platinum satellites, the  $^4J(Pt-F_o)$ , 104 Hz having a value similar to that value in similar systems [5], in keeping with the presence of a  $C_6F_5$  group attached to the  $Pd^I$  center. As expected, the  $F_o$  resonance in complex III appears as two signals: one corresponding to the two *ortho*-fluorines of the  $C_6F_5$

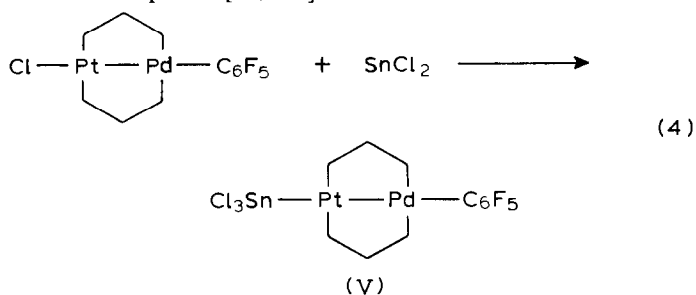
group bonded to Pt ( $\delta -116.4$  ppm), and the other to the two *ortho*-fluorines of the  $C_6F_5$  group bonded to Pd ( $\delta -109.7$  ppm); both signals are basically doublets, owing to coupling to the neighbouring *meta*-fluorines; the first signal shows platinum satellites with  $^3J(\text{Pt}-F_o)$  229 Hz and the other shows platinum satellites with  $^4J(\text{Pt}-F_o)$  56 Hz.

Reaction 2 gives a better yield (77%) of complex III than does reaction 1 (40%); on the other hand, samples of complex III made by reaction 1 contain small amounts of an impurity, which was identified by  $^{19}\text{F}$  NMR spectroscopy as the homo-binuclear complex of  $\text{Pd}^{\text{I}}$ :  $[(C_6F_5)_2Pd(\mu\text{-dppm})_2Pd(C_6F_5)]$  ( $\delta(F_o) -111.8$  ppm).

Complex I reacts with KSCN in methanol to give  $[(\text{NCS})Pt(\mu\text{-dppm})_2Pd(C_6F_5)]$  (IV) according to eq. 3:



Treatment of complex I with an equimolar amount of  $\text{SnCl}_2$  leads to insertion of  $\text{SnCl}_2$  into the Pt-Cl bond according to eq. 4, as previously observed for other  $\text{Pd}^{\text{I}}$  and  $\text{Pt}^{\text{I}}$  complexes [4c,5-7]:



Analytical, conductivity and melting point data are listed in Table 1. Complexes I-V are non-conducting in  $\sim 5 \times 10^{-4}$  M acetone solution (see Table 1).

The IR spectra of complexes I-V show the characteristic absorptions of the dppm ligand ( $600-400$   $\text{cm}^{-1}$  region) along with those of the  $C_6F_5$  group at  $\sim 1500$ ,  $\sim 950$   $\text{cm}^{-1}$  [8]. It is noteworthy that the band at ca.  $950$   $\text{cm}^{-1}$  is shifted to lower wavenumbers relative to its position in the palladium(II) precursors, as expected for a decrease in the formal oxidation state of the metal [4a,5]. Complex III shows two close bands ( $945$ ,  $940$   $\text{cm}^{-1}$ ) in this IR region owing to the presence of two different  $C_6F_5$  groups, one attached to  $\text{Pd}^{\text{I}}$  and the other to  $\text{Pt}^{\text{I}}$ . Complex I shows  $\nu(\text{Pt}-\text{Cl})$  at  $247\text{m,w}$   $\text{cm}^{-1}$ , (compare  $249$   $\text{cm}^{-1}$  for  $[\text{ClPt}(\mu\text{-dppm})\text{PdCl}]$  [3]). Complex IV exhibits an absorption at  $2085$   $\text{cm}^{-1}$  assignable to  $\nu(\text{C}\equiv\text{N})$  of the SCN group [9]. Complex V shows IR bands in the  $320-260$  region due to  $\nu(\text{Sn}-\text{Cl})$  [10]. (see Table 2).

#### Insertion reactions

Insertions of a variety of small molecules into the Pd-Pt bond in the complexes  $[\text{XPt}(\mu\text{-dppm})_2\text{Pd}(C_6F_5)]$  ( $\text{X} = \text{Cl}$  (I),  $C_6F_5$  (III)) give new asymmetric "A-frame"

TABLE 1  
 ANALYTICAL DATA, CONDUCTIVITIES AND MELTING POINTS

Complex	Analysis (Found (calcd.) (%))			$\Lambda_M^a$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	M.p. (°C)
	C	H	N		
ClPt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> ) (I)	52.85 (52.85)	3.46 (3.48)	—	0.80	190d
BrPt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> ) (II)	50.67 (51.06)	3.35 (3.37)	—	0.67	180d
(C <sub>6</sub> F <sub>5</sub> )Pt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> ) (III)	53.03 (53.05)	3.30 (3.16)	—	0.08	198d
(SCN)Pt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> ) (IV)	52.09 (52.84)	3.04 (3.42)	1.19 (1.08)	nc	212d
(Cl <sub>3</sub> Sn)Pt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> ) (V)	45.70 (45.99)	3.35 (3.03)	—	nc	225d
[ClPt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -N <sub>2</sub> - <i>p</i> -Tol)Pd(C <sub>6</sub> F <sub>5</sub> )]BF <sub>4</sub> (VI)	50.55 (51.17)	3.55 (3.47)	1.96 (1.89)	114	230d
[(C <sub>6</sub> F <sub>5</sub> )Pt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -N <sub>2</sub> - <i>p</i> -Tol)Pd(C <sub>6</sub> F <sub>5</sub> )]BF <sub>4</sub> (VII)	51.58 (51.46)	3.28 (3.00)	1.74 (2.02)	124	267d
[ClPt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -N <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>o</i> -NO <sub>2</sub> )Pd(C <sub>6</sub> F <sub>5</sub> )]BF <sub>4</sub> (VIII)	49.17 (49.23)	3.03 (3.20)	3.20 (2.78)	117	230d
[(C <sub>6</sub> F <sub>5</sub> )Pt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -N <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>o</i> -NO <sub>2</sub> )Pd(C <sub>6</sub> F <sub>5</sub> )]BF <sub>4</sub> (IX)	49.27 (49.76)	2.82 (2.94)	2.56 (2.56)	110	248d
[ClPt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -C <sub>2</sub> (CO <sub>2</sub> Me) <sub>2</sub> )Pd(C <sub>6</sub> F <sub>5</sub> )] (X)	51.71 (52.63)	3.56 (3.56)	—	nc	245d
[(C <sub>6</sub> F <sub>5</sub> )Pt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -C <sub>2</sub> (CO) <sub>2</sub> Me) <sub>2</sub> )Pd(C <sub>6</sub> F <sub>5</sub> )] (XI)	52.49 (52.81)	3.67 (3.25)	—	nc	270d
[ClPt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -SO <sub>2</sub> )Pd(C <sub>6</sub> F <sub>5</sub> )]·CH <sub>2</sub> Cl <sub>2</sub> (XII)	48.19 (48.15)	3.28 (3.26)	—	nc	182d
[(C <sub>6</sub> F <sub>5</sub> )Pt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -SO <sub>2</sub> )Pd(C <sub>6</sub> F <sub>5</sub> )] (XIII)	50.21 (50.71)	3.35 (3.02)	—	nc	170d
[ClPt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ - <i>p</i> -TolNC)Pd(C <sub>6</sub> F <sub>5</sub> )] (XIV)	54.78 (55.30)	3.76 (3.69)	1.01 (1.00)	9.5	160d
[(C <sub>6</sub> F <sub>5</sub> )Pt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ - <i>p</i> -TolNC)Pd(C <sub>6</sub> F <sub>5</sub> )] (XV)	55.71 (55.26)	3.50 (3.79)	0.81 (0.92)	nc	156d
[( <i>p</i> -TolNC)Pt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )]BPh <sub>4</sub> (XVI)	63.26 (63.15)	4.27 (4.27)	0.84 (0.83)	72.9	132d
[( <i>p</i> -TolNC)Pt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ - <i>p</i> -TolNC)Pd(C <sub>6</sub> F <sub>5</sub> )]BPh <sub>4</sub> (XVII)	64.01 (64.38)	4.57 (4.38)	1.33 (1.56)	72.5	140d
[(CyNC)Pt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )]BPh <sub>4</sub> (XVIII)	62.14 (62.73)	4.62 (4.53)	0.91 (0.84)	86.7	132d
[(CyNC)Pt( $\mu$ -dppm) <sub>2</sub> ( $\mu$ -CyNC)Pd(C <sub>6</sub> F <sub>5</sub> )]BPh <sub>4</sub> (XIX)	63.50 (63.61)	4.91 (4.88)	1.48 (1.57)	94.4	126d
[( <i>t</i> -BuNC)Pt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )]BPh <sub>4</sub> (XX)	62.61 (62.26)	4.85 (4.48)	0.81 (0.85)	87.0	136d
[(Ph <sub>3</sub> P)Pt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )]BPh <sub>4</sub> (XXI)	64.83 (64.71)	4.68 (4.37)	—	64.0	152d
[(py)Pt( $\mu$ -dppm) <sub>2</sub> Pd(C <sub>6</sub> F <sub>5</sub> )]BPh <sub>4</sub> (XXII)	62.92 (62.41)	4.30 (4.25)	1.00 (0.85)	82.3	134d

<sup>a</sup> nc = non-conducting.

hetero-bimetallic Pd-Pt compounds. Thus, treatment of I and III with the diazonium salts (N<sub>2</sub>R)BF<sub>4</sub> (R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, or *o*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) gives complexes VI–IX. MeOCC≡CCOOMe reacts slowly with complexes I and III to give complexes X

TABLE 2  
SOME RELEVANT IR ABSORPTIONS

Complex	$\nu(\text{cm}^{-1})$			
	$\text{C}_6\text{F}_5$	$\nu(\text{C}\equiv\text{N})$ or $\nu(\text{C}=\text{N})$	600–400 region	Others
I	1493s,945s		512s,498m,478s,450m,425m	247m <sup>a</sup>
II	1490s,945s		515s,503m,482s,425m	
III	1490s,945s,940s		518s,508m,489s,440m,425m	
IV	1493s,946s		517s,503m,482s,435m,425sh	2085s <sup>b</sup>
V	1495s,946s		520s,505m,483s,445m,425w	318s,298m,292m <sup>c</sup>
VI	1502s,951s		513s,479s	1060s,br <sup>d</sup>
VII	1500s,954s		515s,483s	1060s,br <sup>d</sup>
VIII	1500s,958s		514s,482s	1060s,br <sup>d</sup> ,1525m <sup>e</sup>
IX	1500s,955s		515s,485s	1060s,br <sup>d</sup> ,1525m <sup>e</sup>
X	1500s,950s		516s,490s	1702s <sup>f</sup>
XI	1498s,948s		510s,493m,478m	1720s <sup>f</sup>
XII	1498s,951s		512s,496s,470m,423m	1140s,1025m <sup>g</sup>
XIII	1498s,951s		511s,497s,476m,428m	1145s,1025s <sup>g</sup>
XIV	1492s,947s	1620(s,br)	512s,507s,480m,472m	
XV	1490s,946s	1620s,br	510s,500s,485m,475m	1580m,610m <sup>h</sup>
XVI	1495s,948s	2160s	515s,502m,482s	1580m,610m <sup>h</sup>
XVII	1497s,948s	2170s,1620s,br	518s,509s,485s	1580m,610m <sup>h</sup>
XVIII	1490s,947s	2165s	513s,498m,480s	1580m,610m <sup>h</sup>
XIX	1490s,945s	2167s,1620s,br	505s,475m	1580m,610m <sup>h</sup>
XX	1490s,947s	2150s	517s,500m,482s	1580m,610m <sup>h</sup>
XXI	1490s,943s		515s,505m,487s	1580m,610m <sup>h</sup>
XXII	1487s,942s		512s,503m,485s	1595m <sup>i</sup> ,1580m,610m <sup>h</sup>

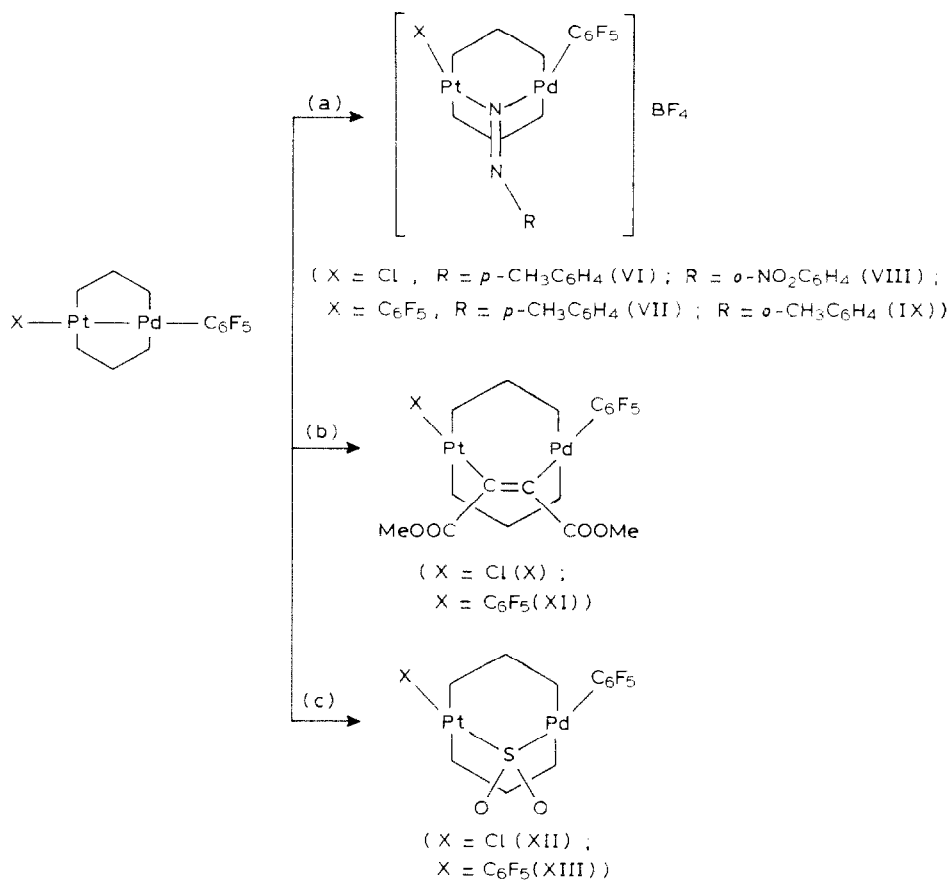
<sup>a</sup>  $\nu(\text{Pt-Cl})$ . <sup>b</sup>  $\nu(\text{C}\equiv\text{N})$ , SCN group. <sup>c</sup>  $\nu(\text{Sn-Cl})$ . <sup>d</sup>  $\text{BF}_4^-$ . <sup>e</sup>  $\nu_{as}(\text{NO}_2)$ . <sup>f</sup>  $\nu_s(\text{C=O})$ . <sup>g</sup>  $\nu(\text{SO}_2)$ . <sup>h</sup>  $\text{BPh}_4^-$ . <sup>i</sup> py.

and XI, respectively. Bubbling of  $\text{SO}_2$  through a  $\text{CH}_2\text{Cl}_2$  solution of complexes I and III gives complexes XII and XIII, respectively (Scheme 1).

Complexes XII and XIII are stable, and no loss of  $\text{SO}_2$  was observed under the conditions employed.

Analytical data are listed in Table 1. In acetone solution ( $c \sim 5 \times 10^{-4} M$ ) [11] complexes X–XIII are non conducting whereas complexes VI–IX behave as 1:1 electrolytes.

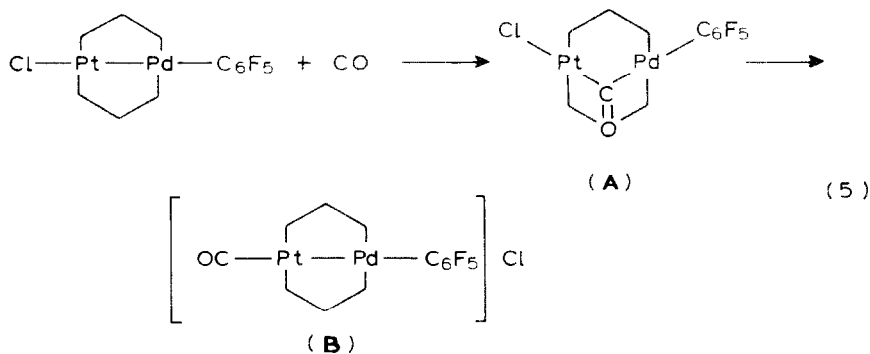
The IR spectra of the complexes show the characteristic absorptions of the dpmm ligand (600–400  $\text{cm}^{-1}$  region) along with those of  $\text{C}_6\text{F}_5$  group (see above). The change in the formal oxidation state of the metal (Pd, Pt) was expected to increase the frequencies of the  $\text{C}_6\text{F}_5$  absorption near 950  $\text{cm}^{-1}$  relative to those in the starting complexes I and III, and this was found to be the case for complexes VI–XIII, the increase being larger for the cationic than for the neutral complexes, as expected. Complexes VI–IX show a strong and broad absorption at  $\sim 1060 \text{ cm}^{-1}$  due to the counterion  $\text{BF}_4^-$  [12]. Complexes VIII–IX exhibit a band at 1525  $\text{cm}^{-1}$  due to  $\nu_{as}(\text{NO}_2)$  of the  $\text{N}_2\text{R}^+$  group [13]. Complexes X and XI show a strong absorption at  $\sim 1700 \text{ cm}^{-1}$  due to  $\nu_s(\text{C=O})$  of the inserted group, shifted to lower energies compared with that for free acetylene ligand (1740  $\text{cm}^{-1}$ ). Complexes XII and XIII show absorptions at  $\sim 1145$  and  $\sim 1125 \text{ cm}^{-1}$  due to the symmetric and asymmetric  $\nu(\text{S-O})$  stretching frequencies, respectively [14].



SCHEME 1. (a) [N<sub>2</sub>R]BF<sub>4</sub>; (b) MeOOC≡CCOOMe; (c) SO<sub>2</sub>.

#### Reaction with CO

As observed for [(C<sub>6</sub>F<sub>5</sub>)Pd(μ-dppm)<sub>2</sub>Pd(C<sub>6</sub>F<sub>5</sub>)] and [(C<sub>6</sub>F<sub>5</sub>)Pt(μ-dppm)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)] [15], complex III does not react with CO in benzene or dichloromethane. In contrast, although complex I also does not react with CO in benzene, when CO was bubbled for 15 min through a dichloromethane solution of complex I the appearance of absorptions at 1710s and 2055w cm<sup>-1</sup> indicated the presence of a mixture of complexes, one of which contains inserted CO (**A**) and the other coordinated CO (**B**) (eq. 5).

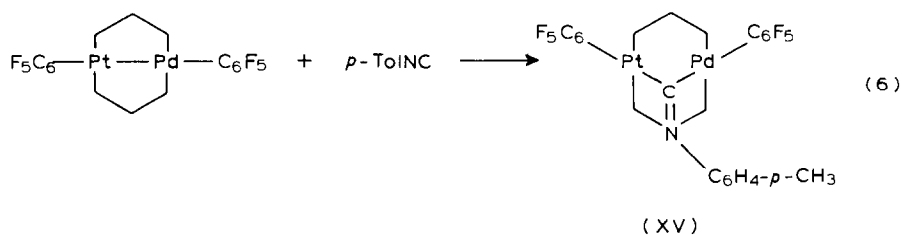


After the CO has been passed for 1 h, the IR spectrum of the dichloromethane solution shows only the absorption at  $2055\text{ cm}^{-1}$  indicating the exclusive presence of the coordinated species **B**, suggesting that the reaction initially gives the insertion product **A** (eq. 5). All attempts to isolate compound **B** gave only the starting complex **I**. The addition of  $\text{NaBPh}_4$  to the dichloromethane solution and partial evaporation yielded a solid which showed absorptions assignable to  $\nu(\text{C}=\text{O})$  ( $2045\text{ cm}^{-1}$ ) and to the  $\text{BPh}_4^-$  ( $610\text{ cm}^{-1}$ ), but the analytical results indicate that this solid is not a single species and may be a mixture of the carbonyl derivative  $[(\text{OC})\text{Pt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]\text{BPh}_4$  and the starting material  $[\text{ClPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]$ . This behaviour contrasts with that of similar pentafluorophenyl derivatives of palladium(I) or platinum(I). Bubbling of CO for 30 min through a dichloromethane solution of  $[\text{ClPt}(\mu\text{-dppm})_2\text{Pt}(\text{C}_6\text{F}_5)]$  gives rise to an IR spectrum with a strong absorption at 2052 but none near  $1700\text{ cm}^{-1}$ , indicating the presence of  $[\text{COPt}(\mu\text{-dppm})_2\text{Pt}(\text{C}_6\text{F}_5)]\text{Cl}$ , but attempts to isolate this compound gave only starting material; however when the reaction was carried out in the presence of  $\text{NaBPh}_4$ ,  $[(\text{CO})\text{Pt}(\mu\text{-dppm})_2\text{Pt}(\text{C}_6\text{F}_5)]\text{BPh}_4$  was obtained [5]. Bubbling of CO for 30 min through a dichloromethane solution of  $[\text{ClPd}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]$  gives rise to absorption at 1715 but none at  $\sim 2100\text{ cm}^{-1}$ , indicating the exclusive presence of  $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-CO})\text{Pd}(\text{C}_6\text{F}_5)]$  however, only the starting material  $[\text{ClPd}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]$  was isolated from the solution.

In view of the reactions of  $[\text{XM}(\mu\text{-dppm})_2\text{M}'\text{-X}']$  ( $\text{X}' = \text{X} = \text{Cl}$ ,  $\text{M} = \text{M}' = \text{Pd}$  [16],  $\text{Pt}$  [17];  $\text{X} = \text{Cl}$ ,  $\text{X}' = \text{C}_6\text{F}_5$ ,  $\text{M} = \text{M}' = \text{Pd}$  [15],  $\text{Pt}$  [5];  $\text{X} = \text{X}' = \text{C}_6\text{F}_5$ ,  $\text{M} = \text{M}' = \text{Pd}$  [15],  $\text{Pt}$  [15];  $\text{X}' = \text{X} = \text{Cl}$ ,  $\text{M} = \text{Pd}$ ,  $\text{M}' = \text{Pt}$  [3];  $\text{X} = \text{Cl}$ ,  $\text{X}' = \text{C}_6\text{F}_5$ ,  $\text{M} = \text{Pt}$ ,  $\text{M}' = \text{Pd}$  and  $\text{X} = \text{X}' = \text{C}_6\text{F}_5$ ,  $\text{M} = \text{Pt}$ ,  $\text{M}' = \text{Pd}$  (this work)) with CO, it can be concluded that the insertion of CO into the M–M' bond is hindered by the presence of  $\text{C}_6\text{F}_5$  groups, and that  $[(\text{OC})\text{M}(\mu\text{-dppm})\text{M}'\text{X}]\text{X}'$  formation is only possible if the CO group can be coordinated to a platinum center.

#### Reaction with isonitriles RNC

The complex  $[(\text{C}_6\text{F}_5)\text{Pt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]$  (III) reacts with *p*-TolNC in benzene to give the insertion products XV (eq. 6), but III does not react with CyNC or *t*-BuNC under the same conditions.



The reaction of  $[\text{ClPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]$  (I) with RNC is more complicated, because the isonitrile (RNC) can insert into the M–M bond and/or can cause displacement of the terminal halide. The nature of the products obtained depends on the isonitrile and on the solvent used.

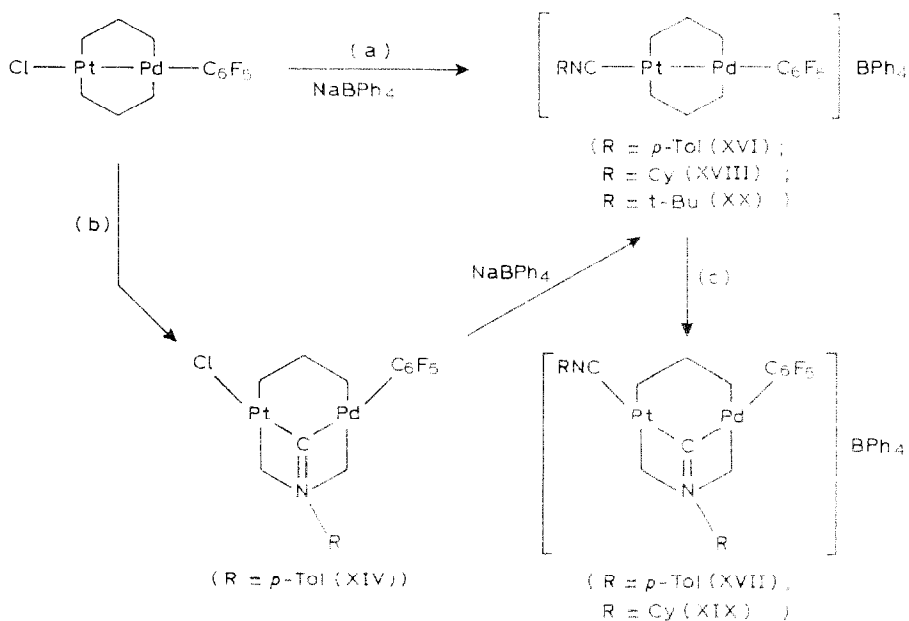
Complex **I** reacts in benzene with a stoichiometric amount of *p*-TolNC to give the insertion product **XIV**. On the other hand, when CyNC is added to a solution of complex **I** in benzene (1/1 molar ratio) the IR spectrum of the solution shows an

absorption due to  $\nu(\text{C}=\text{N})$ , indicating that the inserted isonitrile compound is present. However, the solid obtained by partial evaporation and addition of *n*-hexane shows bands due to  $\nu(\text{C}\equiv\text{N})$  and  $\nu(\text{C}=\text{N})$  that reveal that this solid is a mixture of two isomers  $[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-CNCy})\text{Pd}(\text{C}_6\text{F}_5)]$  and  $[\text{CyNCPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]\text{Cl}$ . Treatment of a solution of complex I with *t*-BuNC (molar ratio 1/1) gives a mixture of both coordinated and inserted derivatives, and the solid isolated from the solution is a mixture of  $[\text{t-BuNCPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]\text{Cl}$  and starting material.

In order to obtain unitary cationic derivatives the reaction of complex I with RNC (molar ratio 1/1) was carried out in acetonitrile and in the presence of  $\text{NaBPh}_4$  (See Scheme 2). When an excess of RNC ( $\text{R} = p\text{-TolNC}$ ,  $\text{CyNC}$ ) is used, the corresponding cationic complexes  $[\text{RNCPt}(\mu\text{-dppm})_2(\mu\text{-RNC})\text{Pd}(\text{C}_6\text{F}_5)]\text{BPh}_4$  ( $\text{R} = p\text{-Tol}$  (XVII),  $\text{Cy}$  (XIX)) containing both inserted and coordinated isonitriles are obtained. Reaction of I with an excess of *t*-BuNC under the same conditions gives the cationic derivative containing only coordinated isonitrile,  $[\text{t-BuNCPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]\text{BPh}_4$  (XX).

Addition of  $\text{NaBPh}_4$  to an acetonitrile solution of  $[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-}p\text{-TolNC})\text{Pd}(\text{C}_6\text{F}_5)]$  (XIV) results, as expected, in bridging-to-terminal migration of the isonitrile and formation of the cationic derivative  $[(p\text{-TolNC})\text{Pt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)]\text{BPh}_4$  (XVI). The reactions of RNC with I are summarized in Scheme 2.

The tendency of RNC to give insertion products decreases in the sequence  $p\text{-TolNC} > \text{CyNC} > \text{t-BuNC}$ , in agreement with our previous observations on palladium(I) or platinum(I) derivatives [4a,4c,5], and in keeping with the insertion of isocyanides into M-C bonds [18,19].

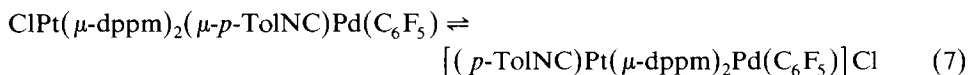


SCHEME 2. (a) RNC in acetonitrile; (b) RNC in benzene; (c) RNC in an excess.



The IR spectra of the isocyanide complexes were very valuable for showing the presence of coordinated  $C\equiv N$ , with  $\nu$  2100–2200  $\text{cm}^{-1}$ , and/or inserted  $C=N$ , with  $\nu$  1500–1650  $\text{cm}^{-1}$  (see Table 2). It is noteworthy that complexes XIV, XV, XVII and XIX with inserted isocyanides have their  $C_6F_5$  band ( $\sim 950 \text{ cm}^{-1}$ ) at wavelengths very similar to that observed for complexes with Pd–Pt bonds (I–V), indicating that the insertion of the isocyanide into the  $\text{Pd}^{\text{I}}\text{–Pt}^{\text{I}}$  bond does not appreciably change the electron density around the metal center [4a,20] (see Table 2). The IR spectra of complexes XVII–XX show absorptions at 1580 and 610  $\text{cm}^{-1}$  due to the anion  $\text{BPh}_4^-$ . Bands assigned to the dpmm ligand in the 600–400  $\text{cm}^{-1}$  region are listed in Table 2.

Table 1 lists the conductivities of acetone solutions ( $c$ ,  $\sim 5 \times 10^{-4} M$ ) of these complexes, which are as expected. The low but definite conductivity of the solution of complex XIV arises from the elimination-coordination (eq. 7) equilibrium in this solvent:



The existence of this equilibrium is confirmed by IR spectroscopy, the IR spectrum of the acetone solution showing an absorption at 2140  $\text{cm}^{-1}$  corresponding to coordinated isocyanide [4c].

TABLE 3

CRYSTAL DATA FOR  $\text{ClPt}(\mu\text{-dpmm})_2\text{Pd}(\text{C}_6\text{F}_5)$ 

Formula	$\text{C}_{56}\text{H}_{44}\text{ClF}_5\text{P}_4\text{PdPt}$
$M$	1272.8
Crystal system	Monoclinic
Space group	$P2_1/c$
$a$ (Å)	16.280(4)
$b$ (Å)	12.959(4)
$c$ (Å)	25.033(10)
$\beta$ (°)	91.42(3)
$V$ (Å <sup>3</sup> )	5279.7
Diffractometer	Enraf–Nonius CAD4
$T$ (K)	$293 \pm 1$
Radiation	Mo- $K_\alpha$
$\lambda$ (Å)	0.71069
$\mu$ (Mo- $K_\alpha$ ) ( $\text{cm}^{-1}$ )	30.5. Empirical absorption correction was applied (28)
$\theta$ -range (°)	1–22°
Mode	$\theta$ -2 $\theta$ scans
Data measured	6438
Data used	4436 ( $F > 6\sigma(F)$ )
Solution	Patterson; $\Delta F$ syntheses
Refinement	Block-diagonal least-squares
Model	C and H isotropic, all other atoms anisotropic. Rigid planar hexagons. H atoms in calculated positions. Group $U$ 's for H atoms (0.08).
Weighting scheme	$w^{-1} = [\sigma^2(F) + 0.0006F^2]$
$R_w$	0.0553
$R$	0.0587
Variables	237

TABLE 4  
 FRACTIONAL COORDINATES IN  $\text{ClPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)$

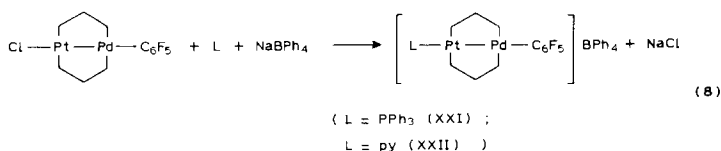
Atom	x	y	z
Pt	0.22581(4)	0.26558(4)	0.35196(2)
Pd	0.23783(6)	0.40994(7)	0.42630(3)
Cl	0.2172(3)	0.1297(4)	0.28430(16)
P(1)	0.09561(23)	0.22884(27)	0.37507(13)
P(2)	0.35724(22)	0.29894(27)	0.32956(13)
P(3)	0.31349(23)	0.50349(26)	0.36864(14)
P(4)	0.16306(22)	0.30326(26)	0.47744(13)
F(1)	0.1463(8)	0.6204(9)	0.4581(6)
F(2)	0.1594(13)	0.7558(9)	0.5351(9)
F(3)	0.2836(14)	0.7276(15)	0.6100(8)
F(4)	0.3843(12)	0.5559(19)	0.6056(6)
F(5)	0.3660(7)	0.4286(10)	0.5235(4)
C(1)	0.4016(8)	0.4243(10)	0.3521(5)
C(2)	0.0650(8)	0.2775(10)	0.4417(5)
C(3)	0.2540(9)	0.5172(11)	0.4872(6)
C(4)	0.2063(12)	0.6004(14)	0.4928(7)
C(5)	0.2120(14)	0.6771(17)	0.5355(9)
C(6)	0.2698(16)	0.6534(20)	0.5694(10)
C(7)	0.3216(17)	0.5783(20)	0.5700(11)
C(8)	0.3119(12)	0.5101(14)	0.5243(7)
C(10)	0.1355(5)	0.0209(8)	0.3919(4)
C(11)	0.1176(5)	0.0832(8)	0.3998(4)
C(12)	0.0364(5)	0.1174(8)	0.3968(4)
C(13)	-0.0269(5)	-0.0475(8)	0.3857(4)
C(14)	0.0091(4)	0.0565(8)	0.3778(4)
C(9)	0.0721(5)	0.0907(8)	0.3809(4)
H(10)	0.1983(5)	0.0474(8)	0.3943(4)
H(11)	0.1667(5)	0.1373(8)	0.4084(4)
H(12)	0.0226(5)	-0.1980(8)	0.4029(4)
H(13)	-0.0898(5)	0.0740(8)	0.3833(4)
H(14)	-0.0581(5)	0.1106(8)	0.3693(4)
C(16)	0.0356(7)	0.2743(9)	0.2763(5)
C(17)	-0.0215(7)	0.3104(9)	0.2382(5)
C(18)	-0.0960(6)	0.3517(9)	0.2544(4)
C(19)	-0.1134(6)	0.3569(9)	0.3086(5)
C(20)	-0.0563(6)	0.3208(9)	0.3467(5)
C(15)	0.0182(6)	0.2795(9)	0.3305(4)
H(16)	0.0933(6)	0.2423(9)	0.2637(5)
H(17)	0.0080(7)	0.3063(9)	0.1962(5)
H(18)	0.1402(6)	0.3796(9)	0.2250(5)
H(19)	0.1710(7)	0.3889(9)	0.3212(5)
H(20)	-0.0697(6)	0.3249(9)	0.3886(5)
C(22)	0.4476(5)	0.2682(8)	0.2366(4)
C(23)	0.4575(5)	0.2662(8)	0.1814(4)
C(24)	0.3932(5)	0.2970(8)	0.1472(4)
C(25)	0.3189(5)	0.3297(8)	0.1681(4)
C(26)	0.3090(5)	0.3317(8)	0.2233(4)
C(21)	0.3733(5)	0.3009(8)	0.2575(4)
H(22)	0.4973(5)	0.2444(8)	0.2631(4)
H(23)	0.5150(5)	0.2409(8)	0.1652(4)
H(24)	0.4009(5)	0.2954(8)	0.1044(4)
H(25)	0.2692(5)	0.3535(8)	0.1415(4)
H(26)	0.2515(5)	0.3570(8)	0.2394(4)

TABLE 4 (continued)

Atom	x	y	z
C(28)	0.4190(7)	0.1034(9)	0.3354(4)
C(29)	0.4726(7)	0.0254(10)	0.3525(4)
C(30)	0.5364(7)	0.0478(9)	0.3889(4)
C(31)	0.5465(7)	0.1481(9)	0.4082(4)
C(32)	0.4929(7)	0.2260(9)	0.3911(4)
C(27)	0.4291(7)	0.2037(9)	0.3547(4)
H(28)	0.3696(7)	0.0860(9)	0.3072(4)
H(29)	0.4647(7)	-0.0522(9)	0.3376(5)
H(30)	0.5779(7)	-0.0125(9)	0.4021(5)
H(31)	0.5959(7)	0.1654(9)	0.4364(4)
H(31)	0.5008(7)	0.3037(9)	0.4060(5)
C(34)	0.3206(5)	0.7167(8)	0.3845(4)
C(35)	0.3519(6)	0.8069(8)	0.4081(4)
C(36)	0.4213(6)	0.8015(8)	0.4418(4)
C(37)	0.4596(6)	0.7068(8)	0.4518(4)
C(38)	0.4283(6)	0.6172(8)	0.4281(4)
C(33)	0.3588(6)	0.6220(8)	0.3945(4)
H(34)	0.2668(6)	0.7205(8)	0.3584(4)
H(35)	0.3223(6)	0.8796(8)	0.4004(4)
H(36)	0.4455(6)	0.8709(8)	0.4601(4)
H(37)	0.5134(6)	0.7030(8)	0.4778(4)
H(38)	0.4579(6)	0.5439(8)	0.4359(4)
C(40)	0.3181(5)	0.5875(8)	0.2678(5)
C(41)	0.2851(5)	0.6157(8)	0.2179(4)
C(42)	0.2020(5)	0.5988(8)	0.2060(4)
C(43)	0.1519(5)	0.5538(8)	0.2439(5)
C(44)	0.1849(5)	0.5256(8)	0.2938(4)
C(39)	0.2680(5)	0.5424(8)	0.3057(4)
H(40)	0.3824(5)	0.6005(8)	0.2770(5)
H(41)	0.3239(5)	0.6505(8)	0.1885(4)
H(42)	0.1765(5)	0.6206(8)	0.1674(4)
H(43)	0.0876(5)	0.5407(8)	0.2347(4)
H(44)	0.1462(5)	0.4907(8)	0.3232(4)
C(46)	0.0522(5)	0.3858(8)	0.5511(3)
C(47)	0.0285(5)	0.4124(8)	0.6025(4)
C(48)	0.0830(5)	0.3985(8)	0.6458(3)
C(49)	0.1611(5)	0.3580(8)	0.6377(4)
C(50)	0.1847(6)	0.3314(8)	0.5864(4)
C(45)	0.1303(5)	0.3453(8)	0.5430(4)

Synthesis of the cationic complexes  $[LPt(\mu\text{-dppm})_2Pd(C_6F_5)]BPh_4$  ( $L = PPh_3$  (XXI),  $py$  (XXII))

Addition of neutral ligands L to complex I suspended in methanol induces complete dissolution and subsequent addition of  $NaBPh_4$  permits the isolation of  $[LPt(\mu\text{-dppm})_2Pd(C_6F_5)]BPh_4$  (see eq. 8).



Complexes XXI and XXII behaves as 1/1 electrolytes in  $5 \times 10^{-4}$  M acetone solution.

Their IR spectra show the presence of  $\text{BPh}_4^-$ ,  $\text{C}_6\text{F}_5$  and dppm. Complex XXII shows a band at 1595 due to the py ligand [21], (see Table 2).

*Structure of  $\text{ClPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)$*

The structure of complex I was determined by single crystal X-ray diffraction. General crystallographic information is presented in Table 3. Positional parameters and selected bond distances and angles are given in Tables 4 and 5, respectively, and lists of hydrogen atom coordinates, thermal parameters, and structure factors are available from the authors. Figure 1 shows the molecular structure of the complex which is similar to other analogous  $\text{Pd}^{\text{I}}$  or  $\text{Pt}^{\text{I}}$  derivatives [6,22,23] and consists of Pt-Cl and Pd- $\text{C}_6\text{F}_5$  fragments linked by a Pd-Pt bond and two bridging bis(diphenylphosphino)methane ligands. The distance Pd-Pt is 2.643(1) Å, in the same range or somewhat shorter than the distances found in analogous  $\text{Pd}^{\text{I}}$  (2.644(2) Å in  $\text{ClPd}(\mu\text{-dppm})_2\text{PdSnCl}_3$  [6], 2.699 Å in  $\text{BrPd}(\mu\text{-dppm})_2\text{PdBr}$  [22], or  $\text{Pt}^{\text{I}}$  (2.651(1) Å in  $\text{ClPt}(\mu\text{-dppm})_2\text{PtCl}$  [23]), species. The coordination geometries about the Pd and Pt centers are approximately planar (the dihedral angles between the planes Pd-Pt-P(1), P(2)-Pt-Cl and Pd-Pt-P(4), Pd-P(3)-C(3) are 178.23 and 175.85°.

TABLE 5

SELECTED MOLECULAR GEOMETRY PARAMETERS FOR  $\text{ClPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)$

<i>Bond lengths (Å)</i>	
Pt-Pd	2.643(1)
Pt-Cl	2.444(4)
Pd-C(3)	2.076(14)
Pt-P(1)	2.262(4)
Pt-P(2)	2.267(4)
Pd-P(3)	2.271(4)
Pd-P(4)	2.260(3)
C(1)-P(2)	1.859(13)
C(1)-P(3)	1.820(13)
C(2)-P(1)	1.862(12)
C(2)-P(4)	1.841(13)
<i>Bond angles (°)</i>	
Pt-Pd-P(4)	86.2(1)
Pt <sub>1</sub> Pd-P(3)	87.8(1)
Pt-Pd-C(3)	175.9(4)
P(3)-Pd-P(4)	174.0(1)
P(3)-Pd-C(3)	92.8(4)
P(4)-Pd-C(3)	93.1(4)
Pd-Pt-P(1)	91.3(1)
Pd-Pt-P(2)	89.2(1)
Pd-Pt-Cl	178.7(1)
P(1)-Pt-P(2)	178.7(1)
P(1)-Pt-Cl	89.3(1)
P(2)-Pt-Cl	90.2(1)
P(1)-C(2)-P(4)	104.4(6)
P(2)-C(1)-P(3)	105.1(6)

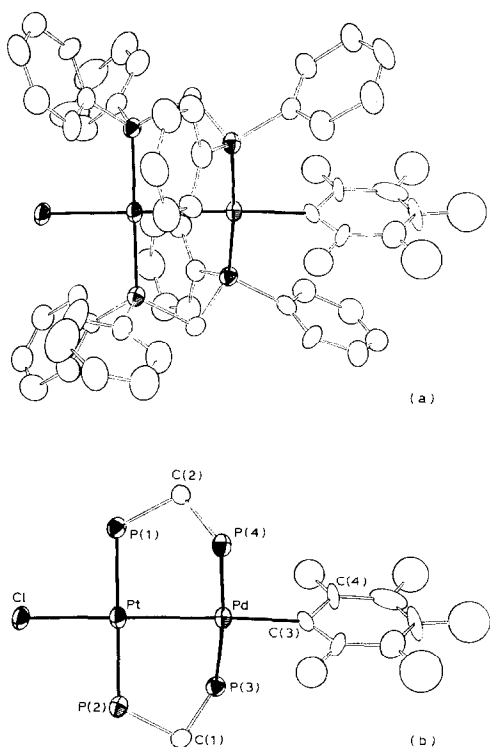


Fig. 1. Perspective views of  $\text{ClPt}(\mu\text{-dppm})_2\text{Pd}(\text{C}_6\text{F}_5)$ : (a) Complete molecule. (b) Central section with Ph rings removed, showing numbering of key atoms.

respectively). The  $\text{Cl-Pt-Pd-C(3)}$  chain is almost linear, and the angles  $\text{Cl-Pt-Pd}$  or  $\text{Pt-Pd-C(3)}$  are  $178.7(1)$  and  $175.9(4)^\circ$ , respectively.

The angles between mutually *cis*-palladium or platinum-ligand bonds are in the range  $86.2\text{--}93.1^\circ$  and the corresponding angles between mutually *trans*-palladium or platinum-ligands bonds are in the range  $174.0\text{--}178.7^\circ$  (see Table 5). The  $\text{Pt-Cl}$  distance ( $2.444(4)$  Å) is longer than that for other binuclear  $\text{Pt}^{\text{I}}$  derivatives ( $2.401(5)$  and  $2.408(5)$  Å in  $\text{ClPt}(\mu\text{-dppm})_2\text{PtCl}$  [23],  $2.382(10)$  and  $2.426(9)$  Å in  $[\text{PtCOCl}_2]_2^{2-}$  [24], suggesting a rather high *trans*-influence of the  $\text{Pd-Pt}$  bond. In accord with such a *trans*-influence the  $\text{Pd-C(3)}$  distance is ( $2.076(14)$  Å) longer than that found for other pentafluorophenyl palladium(II) derivatives ( $2.029(4)$  and  $2.012(6)$  Å in *cis*- $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{S}_2\text{CPCy}_3)$  [25]). The distances  $\text{Pd-P}$  or  $\text{Pt-P}$  are in the same range as those in other similar  $\text{Pd}^{\text{I}}$  [5,6,22] or  $\text{Pt}^{\text{I}}$  [23] derivatives.

The coordination planes around the palladium and platinum atoms are twisted about the  $\text{Pt-Pd}$  bond and the dihedral angle between them is  $37.57^\circ$ , similar to those in  $\text{BrPd}(\mu\text{-dppm})_2\text{PdBr}$  ( $39^\circ$ ) [22] and  $\text{ClPt}(\mu\text{-dppm})_2\text{PtCl}$  ( $38.6^\circ$ ) [23].

## Experimental

C, H and N analyses were carried out on a Perkin-Elmer 240 microanalyzer. Melting points were determined with a Buchi apparatus and are uncorrected.

Conductivities were measured in approx.  $5 \times 10^{-4}$  M solutions with a Philips PW 9501/01 conductimeter. The IR spectra were recorded (in the 4000–200  $\text{cm}^{-1}$  range) on a Perkin-Elmer spectrophotometer using Nujol mulls between polyethylene sheets.  $^{19}\text{F}$  NMR spectra were recorded with  $\text{CDCl}_3$  solutions on a Varian XL-200;  $\delta$  is relative to  $\text{CFCl}_3$ .

The complexes  $\text{Pt}(\text{COD})_2$  [26],  $\text{Pt}(\text{PPh}_3)_4$  [27],  $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{dppm})_2$  [4a],  $\text{PdCl}(\text{C}_6\text{F}_5)(\text{dppm})_2$  [4a],  $\text{PdBr}(\text{C}_6\text{F}_5)(\text{dppm})_2$  [4a], were prepared as described elsewhere.

*XPt( $\mu$ -dppm) $_2$ Pd(C $_6$ F $_5$ ) (X = Cl (I), Br (II), C $_6$ F $_5$  (III)) from Pt(COD) $_2$*

To a solution of 0.137 g (0.33 mmol) of  $\text{Pt}(\text{COD})_2$  in 20 ml of benzene (deoxygenated) under nitrogen was added 0.33 mmol of  $\text{PdX}(\text{C}_6\text{F}_5)(\text{dppm})_2$  (X = Cl, Br,  $\text{C}_6\text{F}_5$ ). The initially colourless solution turned orange, and was stirred for 1 h at room temperature, then concentrated to  $\sim 5$  ml. Addition of  $\text{Et}_2\text{O}$  or n-hexane then gave the product as a deep yellow (I, III) or orange (II) precipitate. Yields: I: 80%, II: 65%, III: 40%.

*(C $_6$ F $_5$ )Pt( $\mu$ -dppm) $_2$ Pd(C $_6$ F $_5$ ) (III) from Pt(PPh $_3$ ) $_4$*

To a solution of 0.300 g (0.24 mmol) of  $\text{Pt}(\text{PPh}_3)_4$  in 30 ml of deoxygenated benzene under nitrogen, was added 0.291 g (0.24 mmol) of  $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{dppm})_2$ . The mixture was refluxed for 30 min then evaporated almost to dryness. Addition of 10 ml of  $\text{Et}_2\text{O}$  produced a deep yellow precipitate (III). Yield 77%.

*(SCN)Pt( $\mu$ -dppm) $_2$ Pd(C $_6$ F $_5$ ) (IV)*

To a suspension of 0.100 g (0.07 mmol) of I in 20 ml of methanol, was added 0.007 g (0.07 mmol) of KSCN. The mixture was stirred for 5 h at room temperature then evaporated to  $\approx 10$  ml, and the resulting solid was filtered off, washed with  $4 \times 10$  ml of water, and dried under vacuum. Yield 70%.

*(Cl $_3$ Sn)Pt( $\mu$ -dppm) $_2$ Pd(C $_6$ F $_5$ ) (V)*

To a solution of 0.1 g (0.07 mmol) of I in 30 ml of  $\text{CH}_2\text{Cl}_2$  was added 0.014 g (0.07 mmol) of  $\text{SnCl}_4$ . The yellow solution turned orange. The mixture was stirred for 90 min at room temperature, then evaporated to  $\sim 10$  ml and i-PrOH/hexane (1/1, 30 ml) was added to precipitate complex V in 65% yield.

*[XPt( $\mu$ -dppm) $_2$ ( $\mu$ -N $_2$ R)Pd(C $_6$ F $_5$ )]BF $_4$ ; (X = Cl, R = *p*-CH $_3$ C $_6$ H $_4$  (VI); X = C $_6$ F $_5$ , R = *p*-CH $_3$ C $_6$ H $_4$  (VII); X = Cl, R = *o*-NO $_2$ C $_6$ H $_4$  (VIII); X = C $_6$ F $_5$ , R = *o*-NO $_2$ C $_6$ H $_4$  (IX))*

To a cooled ( $-25^\circ\text{C}$ ) solution of I (0.11 g, 0.07 mmol) in acetone (40 ml) was added 0.016 g (0.07 mmol) of (*p*-CH $_3$ C $_6$ H $_4$ N $_2$ )BF $_4$ . The solution was stirred at  $-25^\circ\text{C}$  for 15 min and then allowed to reach room temperature during ca. 30 min. Evaporation to ca. 5 ml and addition of  $\text{Et}_2\text{O}$  (20 ml) afforded VI, which was recrystallized from acetone/ $\text{Et}_2\text{O}$ . Yield: 70%.

Similar procedures gave: VII: 60% yield; VIII: 66% yield; IX: 61% yield.

*[XPt( $\mu$ -dppm) $_2$ ( $\mu$ -C $_2$ (CO $_2$ Me) $_2$ )Pt(C $_6$ F $_5$ )]*; (X = Cl (X); X = C $_6$ F $_5$  (XI))

To a solution of I (0.100 g, 0.078 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 ml) were added 9.6  $\mu\text{l}$  (0.078 mmol) of  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ . The mixture, protected from the light, was stirred at room temperature for 6 d, then evaporated to ca. 3 ml. Addition of  $\text{Et}_2\text{O}$  (40 ml) afforded X in 45% yield. XI was obtained similarly in 50% yield.

$[XPt(\mu-dppm)_2(\mu-SO_2)Pt(C_6F_5)]$  ( $X = Cl$  (XII);  $X = C_6F_5$  (XIII))

SO<sub>2</sub> was bubbled for 1 h at room temperature through a solution of I (0.142 g, 0.100 mmol) in 4 ml of CH<sub>2</sub>Cl<sub>2</sub>. The initial yellow solution turned orange. Et<sub>2</sub>O (50 ml) was added to precipitate XII, which separated with one molecule of CH<sub>2</sub>Cl<sub>2</sub> of crystallization. Yield: 90%.

A similar procedure gave complex XIII; 92% yield.

$XPt(\mu-dppm)_2(\mu-p-TolNC)Pd(C_6F_5)$  ( $X = Cl$  (XIV);  $X = C_6F_5$  (XV))

To a solution of 0.178 g (0.138 mmol) of I in 40 ml of benzene was added *p*-TolNC (17.4 μl, 0.138 mmol). After 2 h stirring at room temperature the solution was concentrated to ca. 5 ml and hexane (ca. 30 ml) was added to precipitate XIV, which recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane. Yield 69%.

XV was obtained similarly from III in 81% yield.

$[(RNC)Pt(\mu-dppm)_2Pd(C_6F_5)]BPh_4$  ( $R = p-TolNC$  (XVI);  $R = CyCN$  (XVIII))

(a) From I. To a suspension of 0.100 g (0.07 mmol) of I in 10 ml of NCMe was added *p*-TolNC (9.8 μl, 0.07 mmol). The suspension was stirred for 5 min at room temperature, then 0.026 g (0.07 mmol) of NaBPh<sub>4</sub> was added to the resulting yellow-orange solution and the mixture was stirred for 1 h. The solution was filtered and evaporated, and the residual oil was stirred with *i*-PrOH/n-hexane to give crystalline XVI, which was dried at 80°C. Yield 65%.

XVIII was obtained similarly; 62% yield.

(b) Synthesis of XVI from XIV. A solution of 0.070 g (0.01 mmol) of XIV in 15 ml of NCMe was stirred 1 h at room temperature, then a solution of 0.017 g (0.05 mmol) of NaBPh<sub>4</sub> in 20 ml of *i*-PrOH was added. Evaporation to dryness left a pale yellow residue, which was washed with 2 × 10 ml of water and dried. Yield 80%.

$[(RNC)Pt(\mu-dppm)_2(\mu-RNC)Pd(C_6F_5)]BPh_4$  ( $R = p-TolNC$  (XVII);  $R = CyNC$  (XIX))

To a suspension of 0.100 g (0.07 mmol) of I in 10 ml of NCMe, was added *p*-TolNC (21 μl, 0.16 mmol). The suspension was stirred for 5 min at room temperature, then 0.026 g (0.07 mmol) of NaBPh<sub>4</sub> was added and the mixture was stirred for 1 h then evaporated. The residual oil was stirred with *i*-PrOH/hexane to give crystalline XVII. Yield 70%.

XIX was obtained similarly. In this case, the product was recrystallized from NCMe/*i*-PrOH in the presence of ~ 5 μl of CyNC. Yield 63%.

$[(t-BuNC)Pt(\mu-dppm)_2Pd(C_6F_5)]BPh_4$  (XX)

Complex XX is obtained by the method described for the preparation of complex XVIII using a 2.5/1 molar ratio of *t*-BuNC to I. Yield 60%.

$[(L)Pt(\mu-dppm)_2Pd(C_6F_5)]BPh_4$  ( $L = PPh_3$  (XXI);  $L = py$  (XXII))

PPh<sub>3</sub> (0.041 g, 0.155 mmol) was added to a suspension of I (0.100 g, 0.078 mmol) in 15 ml of MeOH. Stirring at room temperature for 10 min resulted in complete dissolution. After addition of NaBPh<sub>4</sub> (0.030 g, 0.087 mmol) the stirring was continued for 15 min. The solution was evaporated to dryness and the residue recrystallized from acetone/*i*-PrOH. Yield 80%.

A similar procedure gave XXII; Yield 75%.

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