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SYNTHESIS AND REACTIVITY OF MIXED PENTAFLUOROPHENYLPALLADIUM(I)-PLATINUM(I) DERIVATIVES. MOLECULAR STRUCTURE OF $ClPt(\mu\text{-dppm})_2Pd(C_6F_5)$ *

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Summary

$XPt(\mu\text{-dppm})_2Pd(C_6F_5)$ (X = Cl (I), Br (II), C_6F_5 (III)) have been prepared by treating $PdX(C_6F_5)(\eta^1\text{-dppm})_2$ with $Pt(COD)_2$ or $Pt(PPh_3)_4$. Substitution reactions of I yield neutral (SCN) or cationic (PPh_3, py) derivatives. The species R_2N^+, SO_2 or RC≡CR (R = COOMe) insert into the Pd–Pt bond of I to give A-frame Pd^{II}-Pt^{II} complexes, but reaction with $SnCl_2$ gives the $SnCl_3^-$ derivative. The reactions of $X\text{-}Pt(\mu\text{-dppm})_2Pd(C_6F_5)$ (X = Cl (I), C_6F_5 (III)) with isonitriles RNC (R = *p*-Tol, Cy, t-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 $ClPt(\mu\text{-dppm})_2Pd(C_6F_5)$ has been established by a single crystal X-ray study.

Introduction

The ability of 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 Pd–Pd or Pt–Pt bond and two bridging dppm ligands have been much studied recently [2], but hetero-binuclear Pd^I-Pt^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 dppm as

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

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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≡CR into the Pd–Pt bond have also been studied.

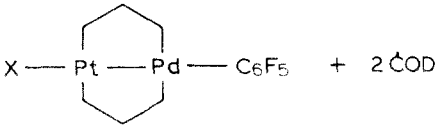
The molecular structure of $[ClPt(\mu\text{-dppm})_2Pd(C_6F_5)]$ has been established by an X-ray diffraction study.

Results and discussion

Synthesis of hetero-binuclear palladium(I)-platinum(I) complexes [XPt(μ-dppm)$_2$Pd-(C$_6$F$_5$)] (X = Cl, Br, SnCl$_3$, C$_6$F$_5$)

Reactions of complexes *trans*-$Pd(X)(C_6F_5)(\eta^1\text{-dppm})_2$ (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-Pt^I complexes $[XPt(\mu\text{-dppm})_2Pd(C_6F_5)]$ (X = Cl, Br, C_6F_5), according to eqn. 1:

trans-$Pd(X)(C_6F_5)(\eta^1\text{-dppm})_2$ + $Pt(COD)_2$ ⟶



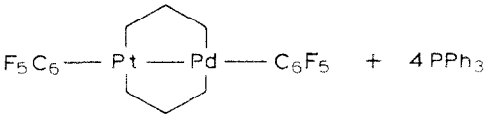
+ 2 COD (1)

= dppm

(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:

trans-$Pd(C_6F_5)_2(\eta^1\text{-dppm})_2$ + $Pt(PPh_3)_4$ ⟶ (2)



+ 4 PPh_3

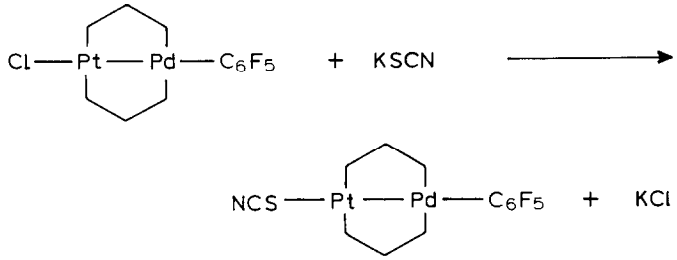
The X-ray structure and ^{19}F NMR spectrum of complex I (see below) show that the redox condensation process (eq. 1) takes place through the migration of the X group from the Pd^{II} to Pt^0 center.

In the ^{19}F NMR spectrum of complex I, the signal, F_o, from the *ortho*-fluorines at δ −117.9 ppm, is basically a doublet (owing to coupling with the neighbouring *meta*-fluorines), with platinum satellites, the $^4J(Pt\text{–}F_o)$, 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 (δ −116.4 ppm), and the other to the two *ortho*-fluorines of the C_6F_5 group bonded to Pd (δ −109.7 ppm); both signals are basically doublets, owing to coupling to the neighbouring *meta*-fluorines; the first signal shows platinum satellites with $^3J(Pt-F_o)$ 229 Hz and the other shows platinum satellites with $^4J(Pt-F_o)$ 56 Hz.

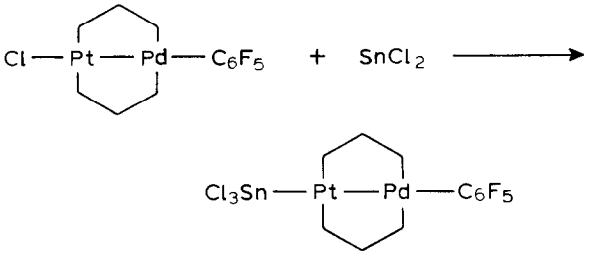
Reaction 2 gives a better yield (77%) of complex III than does reaction 1 (40%); on the other hand, samples of complex III made by reaction 1 contain small amounts of an impurity, which was identified by ^{19}F NMR spectroscopy as the homo-binuclear complex of Pd^I: $[(C_6F_5)Pd(\mu\text{-dppm})_2Pd(C_6F_5)]$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

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



(3)

Treatment of complex I with an equimolar amount of $SnCl_2$ leads to insertion of $SnCl_2$ into the Pt–Cl bond according to eq. 4, as previously observed for other Pd^I and Pt^I complexes [4c,5–7]:



(4)

(V)

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 cm^{-1} region) along wit those of the C_6F_5 group at ~ 1500, ~ 950 cm^{-1} [8]. It is noteworthy that the band at ca. 950 cm^{-1} is shifted to lower wavelengths 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 cm^{-1}) in this IR region owing to the presence of two different C_6F_5 groups, one attached to Pd^I and the other to Pt^I. Complex I shows ν(Pt–Cl) at 247m,w cm^{-1}, (compare 249 cm^{-1} for [ClPt(μ-dppm)PdCl] [3]). Complex IV exhibits an absorption at 2085 cm^{-1} assignable to $\nu(C\equiv N)$ of the SCN group [9]. Complex V shows IR bands in the 320–260 region due to ν(Sn–Cl) [10]. (see Table 2).

Insertion reactions

Insertions of a variety of small molecules into the Pd–Pt bond in the complexes $[XPt(\mu\text{-dppm})_2Pd(C_6F_5)]$ (X = Cl (I), C_6F_5 (III)) give new asymmetric "A-frame"

TABLE 1

ANALYTICAL DATA, CONDUCTIVITIES AND MELTING POINTS

Complex	Analysis (Found (calcd.) (%))			Λ_M[a] (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)
	C	H	N		
$ClPt(\mu\text{-dppm})_2Pd(C_6F_5)$ (I)	52.85	3.46	–	0.80	190d
	(52.85)	(3.48)			
$BrPt(\mu\text{-dppm})_2Pd(C_6F_5)$ (II)	50.67	3.35	–	0.67	180d
	(51.06)	(3.37)			
$(C_6F_5)Pt(\mu\text{-dppm})_2Pd(C_6F_5)$ (III)	53.03	3.30	–	0.08	198d
	(53.05)	(3.16)			
$(SCN)Pt(\mu\text{-dppm})_2Pd(C_6F_5)$ (IV)	52.09	3.04	1.19	nc	212d
	(52.84)	(3.42)	(1.08)		
$(Cl_3Sn)Pt(\mu\text{-dppm})_2Pd(C_6F_5)$ (V)	45.70	3.35	–	nc	225d
	(45.99)	(3.03)			
$[ClPt(\mu\text{-dppm})_2(\mu\text{-}N_2\text{-}p\text{-Tol})Pd(C_6F_5)]BF_4$ (VI)	50.55	3.55	1.96	114	230d
	(51.17)	(3.47)	(1.89)		
$[(C_6F_5)Pt(\mu\text{-dppm})_2(\mu\text{-}N_2\text{-}p\text{-Tol})Pd(C_6F_5)]BF_4$ (VII)	51.58	3.28	1.74	124	267d
	(51.46)	(3.00)	(2.02)		
$[ClPt(\mu\text{-dppm})_2(\mu\text{-}N_2C_6H_4\text{-}o\text{-}NO_2)Pd(C_6F_5)]BF_4$ (VIII)	49.17	3.03	3.20	117	230d
	(49.23)	(3.20)	(2.78)		
$[(C_6F_5)Pt(\mu\text{-dppm})_2(\mu\text{-}N_2C_6H_4\text{-}o\text{-}NO_2)Pd(C_6F_5)]BF_4$ (IX)	49.27	2.82	2.56	110	248d
	(49.76)	(2.94)	(2.56)		
$[ClPt(\mu\text{-dppm})_2(\mu\text{-}C_2(CO_2Me)_2)Pd(C_6F_5)]$ (X)	51.71	3.56	–	nc	245d
	(52.63)	(3.56)			
$[(C_6F_5)Pt(\mu\text{-dppm})_2(\mu\text{-}C_2(CO)_2Me)_2)Pd(C_6F_5)]$ (XI)	52.49	3.67	–	nc	270d
	(52.81)	(3.25)			
$[ClPt(\mu\text{-dppm})_2(\mu\text{-}SO_2)Pd(C_6F_5)]\cdot CH_2Cl_2$ (XII)	48.19	3.28	–	nc	182d
	(48.15)	(3.26)			
$[(C_6F_5)Pt(\mu\text{-dppm})_2(\mu\text{-}SO_2)Pd(C_6F_5)]$ (XIII)	50.21	3.35	–	nc	170d
	(50.71)	(3.02)			
$[ClPt(\mu\text{-dppm})_2(\mu\text{-}p\text{-TolNC})Pd(C_6F_5)]$ (XIV)	54.78	3.76	1.01	9.5	160d
	(55.30)	(3.69)	(1.00)		
$[(C_6F_5)Pt(\mu\text{-dppm})_2(\mu\text{-}p\text{-TolNC})Pd(C_6F_5)]$ (XV)	55.71	3.50	0.81	nc	156d
	(55.26)	(3.79)	(0.92)		
$[(p\text{-TolNC})Pt(\mu\text{-dppm})_2Pd(C_6F_5)]BPh_4$ (XVI)	63.26	4.27	0.84	72.9	132d
	(63.15)	(4.27)	(0.83)		
$[(p\text{-TolNC})Pt(\mu\text{-dppm})_2(\mu\text{-}p\text{-TolNC})Pd(C_6F_5)]BPh_4$ (XVII)	64.01	4.57	1.33	72.5	140d
	(64.38)	(4.38)	(1.56)		
$[(CyNC)Pt(\mu\text{-dppm})_2Pd(C_6F_5)]BPh_4$ (XVIII)	62.14	4.62	0.91	86.7	132d
	(62.73)	(4.53)	(0.84)		
$[(CyNC)Pt(\mu\text{-dppm})_2(\mu\text{-}CyNC)Pd(C_6F_5)]BPh_4$ (XIX)	63.50	4.91	1.48	94.4	126d
	(63.61)	(4.88)	(1.57)		
$[(t\text{-BuNC})Pt(\mu\text{-dppm})_2Pd(C_6F_5)]BPh_4$ (XX)	62.61	4.85	0.81	87.0	136d
	(62.26)	(4.48)	(0.85)		
$[(Ph_3P)Pt(\mu\text{-dppm})_2Pd(C_6F_5)]BPh_4$ (XXI)	64.83	4.68	–	64.0	152d
	(64.71)	(4.37)			
$[(py)Pt(\mu\text{-dppm})_2Pd(C_6F_5)]BPh_4$ (XXII)	62.92	4.30	1.00	82.3	134d
	(62.41)	(4.25)	(0.85)		

[a] nc = non-conducting.

hetero-bimetallic Pd-Pt compounds. Thus, treatment of I and III with the diazonium salts $(N_2R)BF_4$ (R = p-$CH_3C_6H_4$, or o-$NO_2C_6H_4$) gives complexes VI–IX. MeOOCC≡CCOOMe reacts slowly with complexes I and III to give complexes X

TABLE 2

SOME RELEVANT IR ABSORPTIONS

Complex	$\nu(cm^{-1})$			
	C_6F_5	$\nu(C\equiv N)$ or $\nu(C=N)$	600–400 region	Others
I	1493s,945s		512s,498m,478s,450m,425m	247m [a]
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 [b]
V	1495s,946s		520s,505m,483s,445m,425w	318s,298m,292m [c]
VI	1502s,951s		513s,479s	1060s,br [d]
VII	1500s,954s		515s,483s	1060s,br [d]
VIII	1500s,958s		514s,482s	1060s,br [d],1525m [e]
IX	1500s,955s		515s,485s	1060s,br [d],1525m [e]
X	1500s,950s		516s,490s	1702s [f]
XI	1498s,948s		510s493m,478m	1720s [f]
XII	1498s,951s		512s,496s,470m,423m	1140s,1025m [g]
XIII	1498s,951s		511s,497s,476m,428m	1145s,1025s [g]
XIV	1492s,947s	1620(s,br)	512s,507s,480m,472m	
XV	1490s,946s	1620s,br	510s,500s,485m,475m	1580m,610m [h]
XVI	1495s,948s	2160s	515s,502m,482s	1580m,610m [h]
XVII	1497s,948s	2170s,1620s,br	518s,509s,485s	1580m,610m [h]
XVIII	1490s,947s	2165s	513s,498m,480s	1580m,610m [h]
XIX	1490s,945s	2167s,1620s,br	505s,475m	1580m,610m [h]
XX	1490s,947s	2150s	517s,500m,482s	1580m,610m [h]
XXI	1490s,943s		515s,505m,487s	1580m,610m [h]
XXII	1487s,942s		512s,503m,485s	1595m [i],1580m,610m [h]

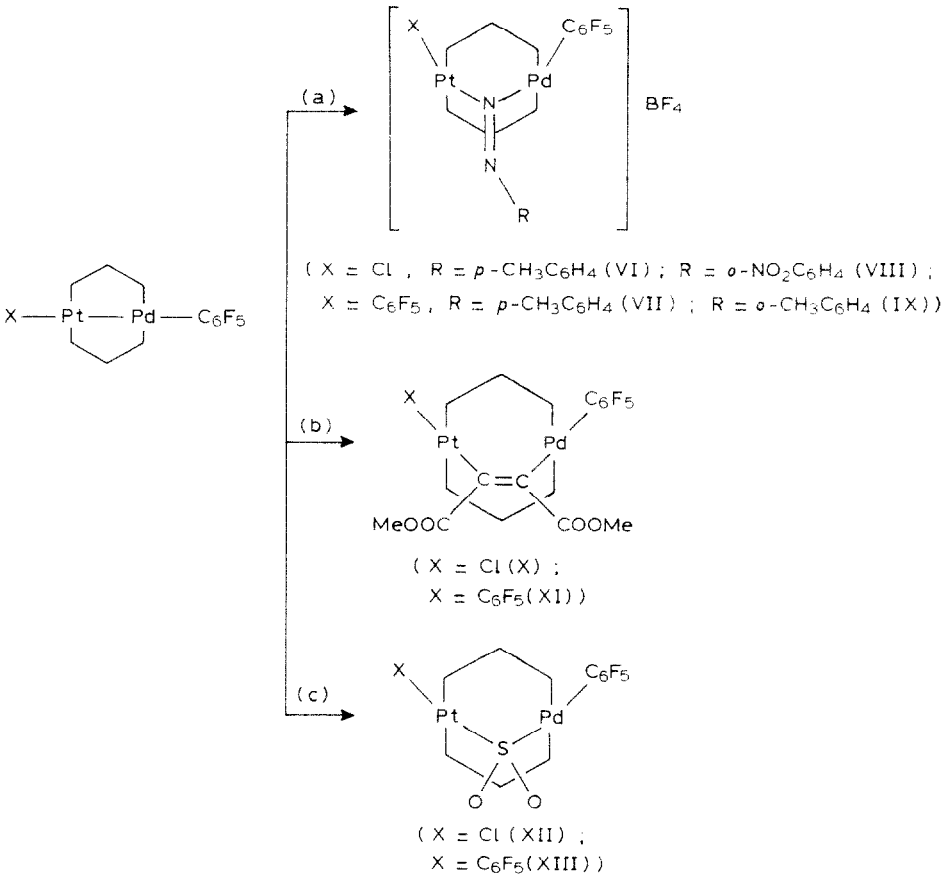
[a] ν(Pt–Cl). [b] $\nu(C\equiv N)$, SCN group. [c] ν(Sn–Cl). [d] BF_4. [e] $\nu_{as}(NO_2)$. [f] $\nu_s(C=O)$. [g] $\nu(SO_2)$. [h] BPh_4. [i] py.

and XI, respectively. Bubbling of SO_2 through a CH_2Cl_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 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.

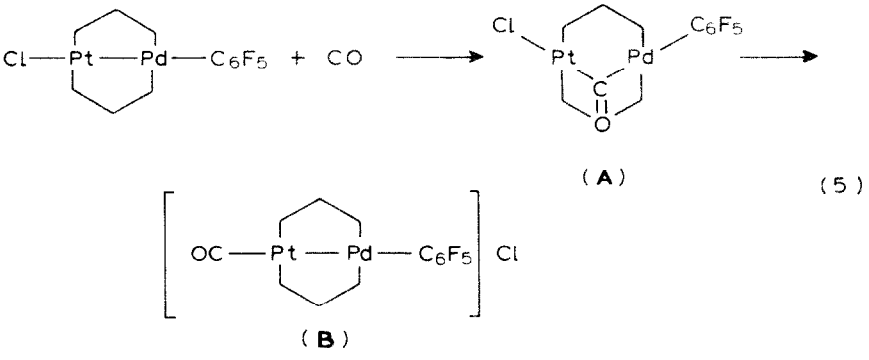
The IR spectra of the complexes show the characteristic absorptions of the dppm ligand (600–400 cm^{-1} region) along with those of C_6F_5 group (see above). The change in the formal oxidation state of the metal (Pd, Pt) was expected to increase the frequencies of the C_6F_5 absorption near 950 cm^{-1} 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 cm^{-1} due to the counterion BF_4^- [12]. Complexes VIII–IX exhibit a band at 1525 cm^{-1} due to $\nu_{as}(NO_2)$ of the N_2R^+ group [13]. Complexes X and XI show a strong absorption at $\sim$ 1700 cm^{-1} due to $\nu_s(C=O)$ of the inserted group, shifted to lower energies compared with that for free acetylene ligand (1740 cm^{-1}). Complexes XII and XIII show absorptions at $\sim$ 1145 and $\sim$ 1125 cm^{-1} due to the symmetric and asymmetric ν(S–O) stretching frequencies, respectively [14].



SCHEME 1. (a) $[N_2R]BF_4$; (b) MeOOCC≡CCOOMe; (c) SO_2.

Reaction with CO

As observed for $[(C_6F_5)Pd(\mu\text{-dppm})_2Pd(C_6F_5)]$ and $[(C_6F_5)Pt(\mu\text{-dppm})_2Pt(C_6F_5)]$ [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^{-1} indicated the presence of a mixture of complexes, one of which contains inserted CO (**A**) and the other coordinated CO (**B**) (eq. 5).

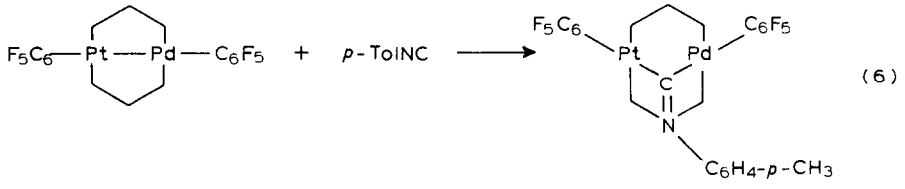


After the CO has been passed for 1 h, the IR spectrum of the dichloromethane solution shows only the absorption at 2055s cm^{-1} indicating the exclusive presence of the coordinated species **B**, suggesting that the reaction initially gives the insertion product **A** (eq. 5). All attempts to isolate compound **B** gave only the starting complex I. The addition of $NaBPh_4$ to the dichloromethane solution and partial evaporation yielded a solid which showed absorptions assignable to ν(C=O) (2045 cm^{-1}) and to the BPh_4^- (610 cm^{-1}), but the analytical results indicate that this solid is not a single species and may be a mixture of the carbonyl derivative $[(OC)Pt(\mu\text{-dppm})_2Pd(C_6F_5)]BPh_4$ and the starting material $[ClPt(\mu\text{-dppm})_2Pd(C_6F_5)]$. 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 $[ClPt(\mu\text{-dppm})_2Pt(C_6F_5)]$ gives rise to an IR spectrum with a strong absorption at 2052 but none near 1700 cm^{-1}, indicating the presence of $[COPt(\mu\text{-dppm})_2Pt(C_6F_5)]Cl$, but attempts to isolate this compound gave only starting material; however when the reaction was carried out in the presence of $NaBPh_4$, $[(CO)Pt(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$ was obtained [5]. Bubbling of CO for 30 min through a dichloromethane solution of $[ClPd(\mu\text{-dppm})_2Pd(C_6F_5)]$ gives rise to absorption at 1715 but none at ~ 2100 cm^{-1}, indicating the exclusive presence of $[ClPd(\mu\text{-dppm})_2(\mu\text{-CO})Pd(C_6F_5)]$ however, only the starting material $[ClPd(\mu\text{-dppm})_2Pd(C_6F_5)]$ was isolated from the solution.

In view of the reactions of $[XM(\mu\text{-dppm})_2M'X']$ (X' = X = Cl, M = M' = Pd [16], Pt [17]; X = Cl, X' = C_6F_5, M = M' = Pd [15], Pt [5]; X = X' = C_6F_5, M = M' = Pd [15], Pt [15]; X' = X = Cl, M = Pd, M' = Pt [3]; X = Cl, X' = C_6F_5, M = Pt, M' = Pd and X = X' = C_6F_5, M = Pt, M' = 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 C_6F_5 groups, and that $[(OC)M(\mu\text{-dppm})M'X]X'$ formation is only possible if the CO group can be coordinated to a platinum center.

Reaction with isonitriles RNC

The complex $[(C_6F_5)Pt(\mu\text{-dppm})_2Pd(C_6F_5)]$ (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.



(6)

(XV)

The reaction of $[ClPt(\mu\text{-dppm})_2Pd(C_6F_5)]$ (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.

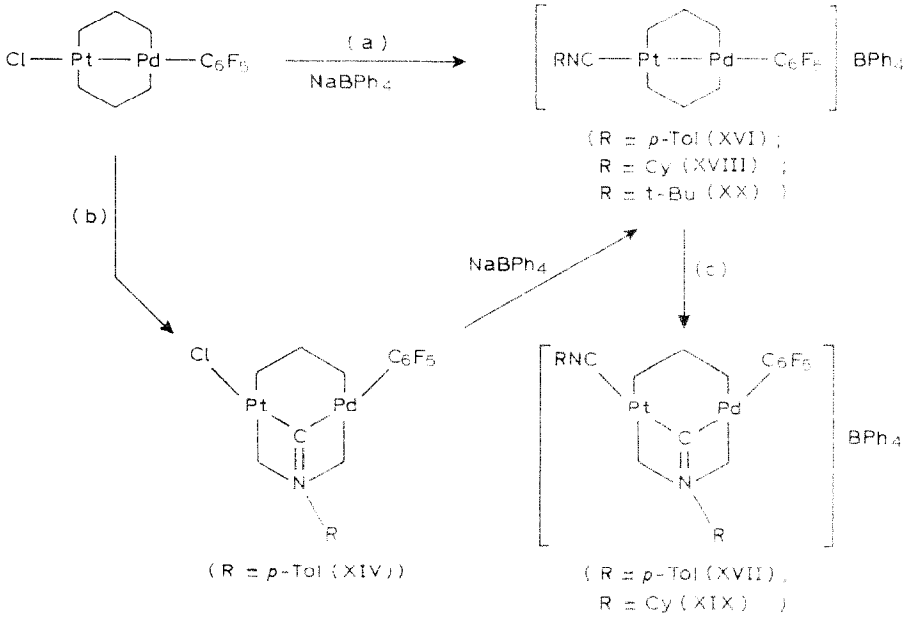
Complex I reacts in benzene with a stoicheiometric amount of *p*-TolNC to give the insertion product XIV. On the other hand, when CyNC is added to a solution of complex I in benzene (1/1 molar ratio) the IR spectrum of the solution shows an

absorption due to ν(C=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 ν(C≡N) and ν(C=N) that reveal that this solid is a mixture of two isomers [ClPt(μ-dppm)$_2$(μ-CNCy)Pd(C_6F_5)] and [CyNCPt(μ-dppm)$_2$Pd(C_6F_5)]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 [t-BuNCPt(μ-dppm)$_2$Pd(C_6F_5)]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 $NaBPh_4$ (See Scheme 2). When an excess of RNC (R = *p*-TolNC, CyNC) is used, the corresponding cationic complexes [RNCPt(μ-dppm)$_2$(μ-RNC)Pd(C_6F_5)]BPh_4 (R = *p*-Tol (XVII), 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, [t-BuNCPt(μ-dppm)$_2$Pd(C_6F_5)]BPh_4 (XX).

Addition of $NaBPh_4$ to an acetonitrile solution of [ClPt(μ-dppm)$_2$(μ-*p*-TolNC)Pd(C_6F_5)] (XIV) results, as expected, in bridging-to-terminal migration of the isonitrile and formation of the cationic derivative [(*p*-TolNC)Pt(μ-dppm)$_2$Pd(C_6F_5)]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*-TolNC > CyNC > 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≡N, with ν 2100–2200 cm^{-1}, and/or inserted C=N, with ν 1500–1650 cm^{-1} (see Table 2). It is noteworthy that complexes XIV, XV, XVII and XIX with inserted isonitriles have their C_6F_5 band (~ 950 cm^{-1}) at wavelengths very similar to that observed for complexes with Pd–Pt bonds (I–V), indicating that the insertion of the isonitrile into the Pd^I–Pt^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 cm^{-1} due to the anion BPh_4^-. Bands assigned to the dppm ligand in the 600–400 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:

$$ClPt(\mu\text{-dppm})_2(\mu\text{-}p\text{-TolNC})Pd(C_6F_5) \rightleftharpoons [(p\text{-TolNC})Pt(\mu\text{-dppm})_2Pd(C_6F_5)]Cl \qquad (7)$$

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

TABLE 3

CRYSTAL DATA FOR $ClPt(\mu\text{-dppm})_2Pd(C_6F_5)$

Formula	$C_{56}H_{44}ClF_5P_4PdPt$
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)
β (°)	91.42(3)
V (Å^3)	5279.7
Diffractometer	Enraf–Nonius CAD4
T (K)	293 ± 1
Radiation	Mo-K_α
λ (Å)	0.71069
μ(Mo-K_α) (cm^{-1})	30.5. Empirical absorption correction was applied (28)
θ-range (°)	1–22°
Mode	θ–2θ scans
Data measured	6438
Data used	4436 ($F > 6\sigma(F)$)
Solution	Patterson; ΔF 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 $ClPt(\mu\text{-dppm})_2Pd(C_6F_5)$

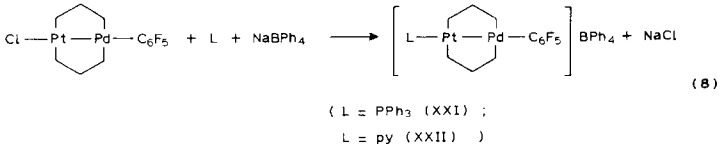
Atom	*x*	*y*	*z*
Pt	0.22581(4)	0.26558(4)	0.35196(2)
Pd	0.23783(6)	0.40994(7)	0.42630(3)
Cl	0.2172(3)	0.1297(4)	0.28430(16)
P(1)	0.09561(23)	0.22884(27)	0.37507(13)
P(2)	0.35724(22)	0.29894(27)	0.32956(13)
P(3)	0.31349(23)	0.50349(26)	0.36864(14)
P(4)	0.16306(22)	0.30326(26)	0.47744(13)
F(1)	0.1463(8)	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(μ-dppm)$_2$Pd(C$_6$F$_5$)]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(μ-dppm)$_2$Pd(C$_6$F$_5$)] BPh_4 (see eq. 8).



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

Their IR spectra show the presence of BPh_4^-, C_6F_5 and dppm. Complex XXII shows a band at 1595 due to the py ligand [21], (see Table 2).

Structure of $ClPt(\mu\text{-dppm})_2Pd(C_6F_5)$

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 Pd^I or Pt^I derivatives [6,22,23] and constists of Pt–Cl and Pd–C_6F_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 Pd^I (2.644(2) Å in $ClPd(\mu\text{-dppm})_2PdSnCl_3$ [6], 2.699 Å in $BrPd(\mu\text{-dppm})_2PdBr$ [22], or Pt^I (2.651(1) Å in $ClPt(\mu\text{-dppm})_2PtCl$ [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 $ClPt(\mu\text{-dppm})_2Pd(C_6F_5)$

Bond lenghts (Å)	
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)
Bond angles (°)	
Pt–Pd–P(4)	86.2(1)
Pt–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)

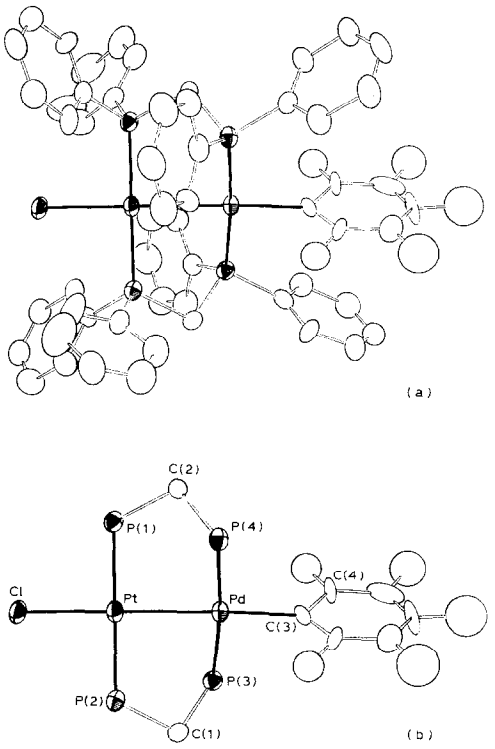


Fig. 1. Perspective views of $ClPt(\mu\text{-dppm})_2Pd(C_6F_5)$: (a) Complete molecule. (b) Central section with Ph rings removed, showing numbering of key atoms.

respectively). The Cl–Pt–Pd–C(3) chain is almost linear, and the angles Cl–Pt–Pd or Pt–Pd–C(3) are 178.7(1) and 175.9(4)°, respectively.

The angles between mutually *cis*-palladium or platinum–ligand bonds are in the range 86.2–93.1° and the corresponding angles between mutually *trans*-palladium or platinum–ligands bonds are in the range 174.0–178.7° (see Table 5). The Pt–Cl distance (2.444(4) Å) is longer than that for other binuclear Pt^I derivatives (2.401(5) and 2.408(5) Å in $ClPt(\mu\text{-dppm})_2PtCl$ [23], 2.382(10) and 2.426(9) Å in $[PtCOCl_2]_2^{2-}$ [24], suggesting a rather high *trans*-influence of the Pd–Pt bond. In accord with such a *trans*-influence the 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*-$Pd(C_6F_5)_2(S_2CPCy_3)$ [25]). The distances Pd–P or Pt–P are in the same range as those in other similar Pd^I [5,6,22] or Pt^I [23] derivatives.

The coordination planes around the palladium and platinum atoms are twisted about the Pt–Pd bond and the dihedral angle between them is 37.57°, similar to those in $BrPd(\mu\text{-dppm})_2PdBr$ (39°) [22] and $ClPt(\mu\text{-dppm})_2PtCl$ (38.6°) [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. 5×10^{-4} *M* solutions with a Philips PW 9501/01 conductimeter. The IR spectra were recorded (in the 4000–200 cm^{-1} range) on a Perkin–Elmer spectrophotometer using Nujol mulls between polyethylene sheets. ^{19}F NMR spectra were recorded with $CDCl_3$ solutions on a Varian XL-200; δ is relative to $CFCl_3$.

The complexes $Pt(COD)_2$ [26], $Pt(PPh_3)_4$ [27], $Pd(C_6F_5)_2(dppm)_2$ [4a] $PdCl(C_6F_5)(dppm)_2$ [4a], $PdBr(C_6F_5)(dppm)_2$ [4a], were prepared as described elsewhere.

$XPt(\mu\text{-}dppm)_2Pd(C_6F_5)$ (X = Cl (I), Br (II), C_6F_5 (III)) from $Pt(COD)_2$

To a solution of 0.137 g (0.33 mmol) of $Pt(COD)_2$ in 20 ml of benzene (deoxygenated) under nitrogen was added 0.33 mmol of $PdX(C_6F_5)(dppm)_2$ (X = Cl, Br, C_6F_5). The initially colourless solution turned orange, and was stirred for 1 h at room temperature, then concentrated to ~ 5 ml. Addition of Et_2O or n-hexane then gave the product as a deep yellow (I, III) or orange (II) precipitate. Yields. I: 80%, II: 65%, III: 40%.

$(C_6F_5)Pt(\mu\text{-}dppm)_2Pd(C_6F_5)$ (III) from $Pt(PPh_3)_4$

To a solution of 0.300 g (0.24 mmol) of $Pt(PPh_3)_4$ in 30 ml of deoxygenated benzene under nitrogen, was added 0.291 g (0.24 mmol) of $Pd(C_6F_5)_2(dppm)_2$. The mixture was refluxed for 30 min then evaporated almost to dryness. Addition of 10 ml of Et_2O produced a deep yellow precipitate (III). Yield 77%.

$(SCN)Pt(\mu\text{-}dppm)_2Pd(C_6F_5)$ (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 ≈ 10 ml, and the resulting solid was filtered off, washed with 4×10 ml of water, and dried under vacuum. Yield 70%.

$(Cl_3Sn)Pt(\mu\text{-}dppm)_2Pd(C_6F_5)$ (V)

To a solution of 0.1 g (0.07 mmol) of I in 30 ml of CH_2Cl_2 was added 0.014 g (0.07 mmol) of $SnCl_2$. The yellow solution turned orange. The mixture was stirred for 90 min at room temperature, then evaporated to ~ 10 ml and i-PrOH/hexane (1/1, 30 ml) was added to precipitate complex V in 65% yield.

$[XPt(\mu\text{-}dppm)_2(\mu\text{-}N_2R)Pd(C_6F_5)]BF_4$; (X = Cl, R = p-$CH_3C_6H_4$ (VI); X = C_6F_5, R = p-$CH_3C_6H_4$ (VII); X = Cl, R = o-$NO_2C_6H_4$ (VIII); X = C_6F_5, R = o-$NO_2C_6H_4$ (IX))

To a cooled (−25°C) solution of I (0.11 g, 0.07 mmol) in acetone (40 ml) was added 0.016 g (0.07 mmol) of (p-$CH_3C_6H_4N_2$)BF_4. The solution was stirred at −25°C for 15 min and then allowed to reach room temperature during ca. 30 min. Evaporation to ca. 5 ml and addition of Et_2O (20 ml) afforded VI, which was recrystallized from acetone/Et_2O. Yield: 70%.

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

$[XPt(\mu\text{-}dppm)_2(\mu\text{-}C_2(CO_2Me)_2)Pt(C_6F_5)]$; (X = Cl (X); X = C_6F_5 (XI))

To a solution of I (0.100 g, 0.078 mmol) in CH_2Cl_2 (30 ml) were added 9.6 µl (0.078 mmol) of $MeO_2CC{\equiv}CCO_2Me$. The mixture, protected from the light, was stirred at room temperature for 6 d, then evaporated to ca. 3 ml. Addition of Et_2O (40 ml) afforded X in 45% yield. XI was obtained similarly in 50% yield.

[XPt(μ-dppm)$_2$(μ-SO$_2$)Pt(C$_6$F$_5$)] (X = Cl (XII); X = C$_6$F$_5$ (XIII))

SO_2 was bubbled for 1 h at room temperature through a solution of I (0.142 g, 0.100 mmol) in 4 ml of CH_2Cl_2. The initial yellow solution turned orange. Et_2O (50 ml) was added to precipitate XII, which separated with one molecule of CH_2Cl_2 of crystallization. Yield: 90%.

A similar procedure gave complex XIII; 92% yield.

XPt(μ-dppm)$_2$(μ-p-TolNC)Pd(C$_6$F$_5$) (X = Cl (XIV); X = C$_6$F$_5$ (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_2Cl_2/n-hexane. Yield 69%.

XV was obtained similarly from III in 81% yield.

[(RNC)Pt(μ-dppm)$_2$Pd(C$_6$F$_5$)]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 $NaBPh_4$ 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 $NaBPh_4$ 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(μ-dppm)$_2$(μ-RNC)Pd(C$_6$F$_5$)]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 $NaBPh_4$ 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(μ-dppm)$_2$Pd(C$_6$F$_5$)]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(μ-dppm)$_2$Pd(C$_6$F$_5$)] BPh$_4$ (L = PPh$_3$ (XXI); L = py (XXII))

PPh_3 (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 $NaBPh_4$ (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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