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Synthesis and Reactivity of Mixed Pentafluorophenyl Platinum(I)–Palladium(I) Derivatives

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Abstract

$XPd(\mu\text{-dppm})_2Pt(C_6F_5)$ (X = Cl (I), Br (II)) have been prepared by reacting $Pd_2(dba)_3 \cdot CHCl_3$ and $PtX(C_6F_5)(\eta^1\text{-dppm})_2$. Reaction of complex I with $SnCl_2$ gives the $SnCl_3^-$ derivative, whilst ligands L (PPh_3, $P(OPh)_3$, $SbPh_3$) render the cationic complexes. The species R_2N^+, SO_2 or MeOOC–C≡C–COOMe insert into the Pd–Pt bond of I to give A-frame Pd(II)–Pt(II) complexes. The reactions of $ClPd(\mu\text{-dppm})_2Pt(C_6F_5)$ with isonitriles CNR (R = *p*-Tol, Cy) lead to products containing either terminal or inserted isocyanide or both.

Introduction

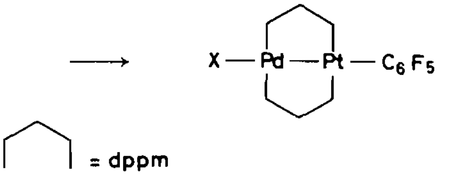
Bis(diphenylphoshino)methane (dppm) has been the subject of much recent work [1] in part because of its ability to form binuclear bridged complexes with transition metals in a low oxidation state. Of particular interest has been the chemistry of homobinuclear metal–metal bonded palladium(I) (or platinum(I)) complexes and the study of their reactivity [1, 2]. In contrast, hetero-binuclear Pd(I)–Pt(I) complexes of this type have received only very little attention [2, 3].

This paper deals with the synthesis of some heterobinuclear pentafluorophenyl Pd(I)–Pt(I) derivatives with dppm as bridging ligand and with the study of their reactivity. Recently we have described another set of heterobinuclear Pd(I)–Pt(I) derivatives [2], which are coordination isomers of the here described complexes, the isomerism arising from a different distribution of ligands between the two metal centers. This paper follows our previous work on perhalophenyl palladium(I) [4] and platinum(I) [5] derivatives with dppm as bridging ligand.

Results and Discussion

Reaction of complexes *trans*-$Pt(X)(C_6F_5)(\eta^1\text{-dppm})_2$ (X = Cl, Br) with $Pd_2(dba)_3 \cdot CHCl_3$, carried out in oxygen-free benzene gives the corresponding hetero-binuclear metal–metal bonded Pd(I)–Pt(I) complexes $[(X)Pd(\mu\text{-dppm})_2Pt(C_6F_5)]$ (X = Cl, Br) according to eqn. (1)

trans-$Pt(X)(C_6F_5)(\eta^1\text{-dppm})_2$ + ½$Pd_2(dba)_3 \cdot CHCl_3$



$$\longrightarrow X{-}Pd{-}Pt{-}C_6F_5 \qquad (1)$$

X = Cl (I), Br (II)

The migration of the X group from the Pt^{II} to the Pd^0 center in the redox condensation process (eqn. (1)) has been confirmed by the ^{19}F NMR spectrum of complex I. The F_o (*ortho*-fluorines) signal is basically a doublet, $\delta = -121.0$ ppm (due to the neighbour *meta*-fluorine atoms) showing platinum satellites with the value for $^3J(Pt{-}F_o) = 303$ Hz commonly found in similar systems [5], in agreement with the presence of a C_6F_5 group attached to the Pt^I center. The ^1H NMR spectrum of I shows a broad band (the fine structure is blurred) at δ = 4.26 ppm, with Pt satellites ($^3J(Pt{-}H) = 61$ Hz) [5, 6], corresponding to the equivalence of the protons in methylene groups.

The reaction between $Pd(Cl)(C_6F_5)(\eta^1\text{-dppm})_2$ and $Pt(PPh_3)_4$ (or $Pt(COD)_2$) leads to the isomer $(C_6F_5)Pd(\mu\text{-dppm})_2Pt(Cl)$ [2], whilst $Pt(Cl)(C_6F_5)(\eta^1\text{-dppm})_2$ reacts with $Pd_2(dba)_3 \cdot CH_3Cl$ to give the isomer $(Cl)Pd(\mu\text{-dppm})_2Pt(C_6F_5)$; thus, the Cl group moves from the M^{II} to the M^0 center readier than the C_6F_5 group does. Although $(C_6F_5)Pd(\mu\text{-dppm})_2Pt(C_6F_5)$ can be obtained by the redox condensation between $Pd(C_6F_5)_2(\eta^1\text{-dppm})_2$ and $Pt(PPh_3)_4$ [2], the reaction between $Pt(C_6F_5)_2(\eta^1\text{-dppm})_2$ and $Pd_2(dba)_3 \cdot CHCl_3$ also gives the same compound but in lower yields and some decomposition takes place, thus suggesting the reactivity of $Pt(C_6F_5)_2(\eta^1\text{-dppm})_2$ is lower than that of $Pd(C_6F_5)_2(\eta^1\text{-dppm})_2$.

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TABLE I. Analytical Data, Conductivities and Melting Points

Complex		Analysis (found(calc.) (%))			Λ_M (ohm^{-1} cm^2 mol^{-1})	Melting point
		C	H	N		
$[ClPd(\mu\text{-dppm})_2Pt(C_6F_5)]$	(I)	52.69 (52.84)	3.45 (3.48)		n.c.	215(d)
$[BrPd(\mu\text{-dppm})_2Pt(C_6F_5)]$	(II)	50.74 (51.06)	3.51 (3.36)		n.c.	185(d)
$[Cl_3SnPd(\mu\text{-dppm})_2Pt(C_6F_5)]$	(III)	45.81 (45.99)	2.91 (3.07)		n.c.	228(d)
$[ClPd(\mu\text{-dppm})_2(\mu\text{-}N_2C_6H_4\text{-}o\text{-}NO_2)Pt(C_6F_5)]BF_4$	(IV)	49.37 (49.33)	3.09 (3.18)	2.66 (2.78)	117.5	208(d)
$[ClPd(\mu\text{-dppm})_2(\mu\text{-}C_2(CO_2Me)_2)Pt(C_6F_5)]$	(V)	51.86 (52.63)	3.66 (3.53)		n.c.	267(d)
$[ClPd(\mu\text{-dppm})_2(\mu\text{-}SO_2)Pt(C_6F_5)]$	(VI)	50.07 (50.33)	3.29 (3.29)		n.c.	140(d)
$[(Ph_3P)Pd(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$	(VII)	64.51 (64.73)	4.35 (4.37)		68.2	120(d)
$[((PhO)_3P)Pd(\mu\text{-dpm})_2Pt(C_6F_5)]BPh$	(VIII)	62.77 (63.05)	4.50 (4.23)		109.54	108(d)
$[(Ph_3Sb)Pd(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$	(IX)	61.22 (61.63)	4.12 (4.14)		79.94	200(d)
$[ClPd(\mu\text{-dppm})_2(\mu\text{-CyNC})Pt(C_6F_5)]$	(X)	53.81 (54.75)	3.95 (4.01)	1.08 (1.01)	51.44	140(d)
$[(CyNC)Pd(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$	(XI)	62.59 (62.73)	4.31 (4.53)	0.88 (0.84)	78.61	126(d)
$[(CyNC)Pd(\mu\text{-dppm})_2(\mu\text{-CyNC})Pt(C_6F_5)]BPh_4$	(XII)	63.52 (63.61)	4.56 (4.88)	1.26 (1.57)	116.12	110(d)
$[ClPd(\mu\text{-dppm})_2(\mu\text{-p-TolNC})Pt(C_6F_5)]$	(XIII)	55.06 (55.30)	3.61 (3.69)	0.98 (1.00)	3.0	175(d)
$[(p\text{-TolNC})Pd(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$	(XIV)	62.68 (63.15)	4.31 (4.27)	0.86 (0.83)	81.93	136(d)
$[(p\text{-TolNC})Pd(\mu\text{-dppm})_2(\mu\text{-p-TolNC})Pt(C_6F_5)]BPh_4$	(XV)	65.18 (64.38)	4.41 (4.38)	1.22 (1.56)	100.0	115(d)

The chemistry derived from I is summarized in Schemes 1 and 2. The analytical data, conductivites and melting points for the complexes are collected in Table I.

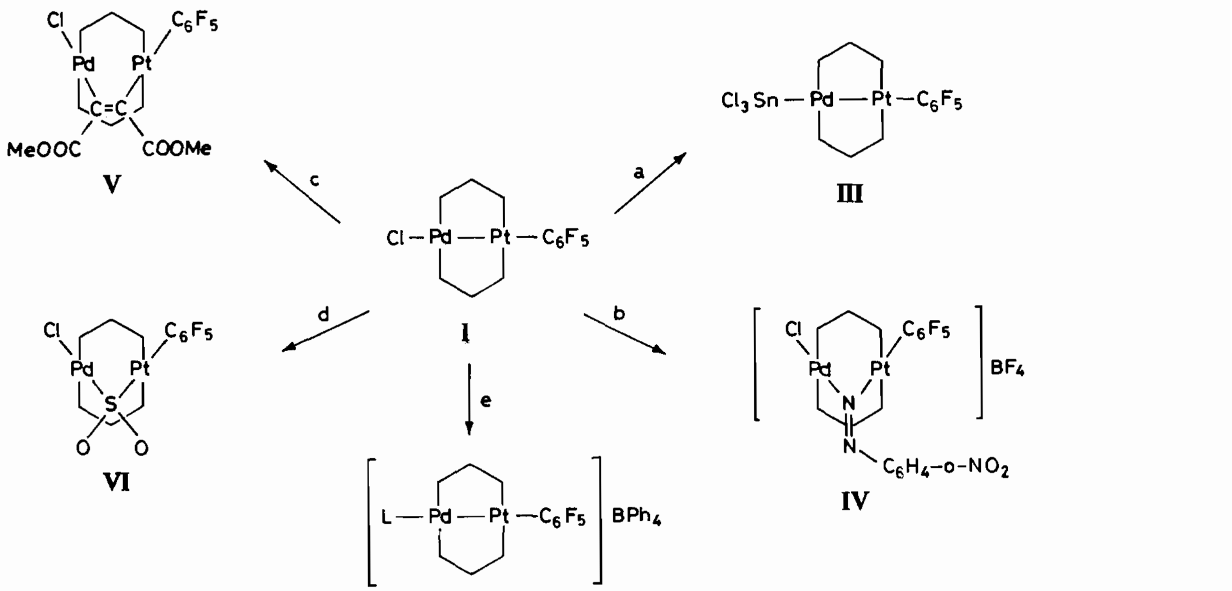
Several reactions of I lead to the synthesis of new Pd(I)–Pt(I) complexes, without the breaking of the metal–metal bond. Thus, treatment of I with $SnCl_2$ (1:1 ratio) leads to the insertion of $SnCl_2$ into the Pd–Cl bond (complex III) and not into the Pd–Pt one, similarly to other reactions described before for Pd(I) and Pt(I) complexes [4c, 7, 8].

Cationic complexes of the type $[(L)Pd(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$ ($L = PPh_3$ (VII), $P(OPh)_3$ (VIII), $SbPh_3$ (IX)) have been obtained by the addition of neutral ligands L to methanol suspensions of I followed by addition of $NaBPh_4$. The neutral ligand L displaces the Cl anion bonded to the Pd(I) center and the large BPh_4^- anion facilitates the crystallization of the cationic complexes.

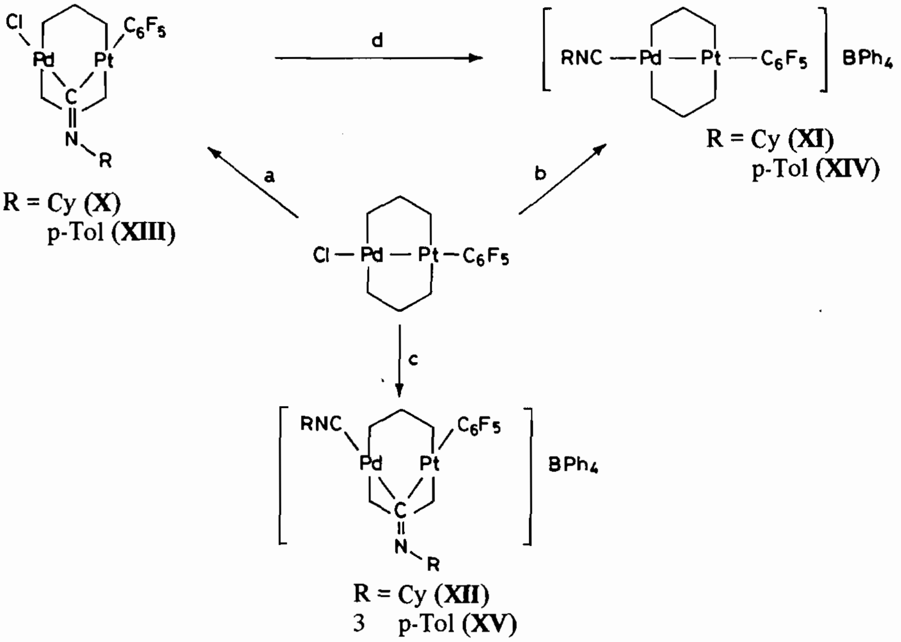
On the other hand, several reactions of I lead to the breaking of the Pd(I)–Pt(I) bond and to the insertion of a variety of small groups into the M–M bond to give new assymmetric A-frame hetero-binuclear complexes of Pd(II) and Pt(II). Thus the treatment of I with the diazonium salt $(N_2C_6H_4\text{-}o\text{-}NO_2)BF_4$ gives complex $[(Cl)Pd(\mu\text{-dppm})_2(\mu\text{-}N_2C_6H_4\text{-}o\text{-}NO_2)Pt(C_6F_5)]BF_4$ (IV). $MeOOCC{\equiv}CCOOMe$ reacts slowly with I to give complex $[(Cl)Pd(\mu\text{-dppm})_2(\mu\text{-}C_2(COOMe)_2)Pt(C_6F_5)]$ (V). By bubbling SO_2 through a CH_2Cl_2 solution of I, complex $[(Cl)Pd(\mu\text{-dppm})_2(\mu\text{-}SO_2)Pt(C_6F_5)]$ (VI) is formed (Scheme 1).

Complex I does not react with CO (NTP) in benzene or dichloromethane solution. We have previously concluded [2] that the insertion of CO into the M–M′ bond (in systems of the type $(X)M\text{-}\mu\text{-dppm})_2M'(X')$, $X,X' = Cl$, C_6F_5, $M,M' = Pd$, Pt) is hindered by the presence of C_6F_5 groups and that the formation of $[(OC)M(\mu\text{-dppm})_2M'(X')]X$ is only possible if the CO group can be coordinated to a platinum center. This general behaviour is in agreement with our results in the case of I.

An interesting behaviour has been observed in the reactivity of complexes of the type $[(X)M(\mu\text{-dppm})_2\text{-}$



Scheme 1. L = PPh_3 (**VII**), $P(OPh)_3$ (**VIII**), $SbPh_3$ (**IX**). (a) $SnCl_2$, (b) $[N_2C_6H_4\text{-}o\text{-}NO_2]BF_4$, (c) MeOOC–C≡C–COOMe, (d) SO_2, (e) L, $NaBPh_4$.



Scheme 2. (a) RNC in benzene; (b) RNC in acetonitrile, $NaBPh_4$; (c) RNC in an excess in acetonitrile, $NaBPh_4$; (d) $NaBPh_4$ in acetonitrile.

M′(X′)] X,X′ = Cl, C_6F_5, C_6Cl_5; M,M′ = Pd, Pt towards isonitriles. Our studies of the reactions of the pentafluorophenyl M(I)–M′(I) derivatives with different isonitriles have shown that the precursor, solvents and the isonitrile used all influence the nature of the products; the resulting complexes can present coordinated-terminal-isonitrile, or inserted-isonitrile into the M–M′ bond or both coordinated and inserted-isonitrile [2, 4, 5].

The reactivity of CNR (R = Cy, *p*-Tol) with **I** is summarized in Scheme 2.

Complex **I** reacts in benzene with stoichiometric amounts (1:1) of CNR (R = Cy, *p*-Tol) to afford the insertion products (**X**) and (**XIII**) respectively.

TABLE II. Some Relevant IR Absorption

Complex	C_6F_5 [9]	ν(C≡N) or ν(C=N)	600–400 region	Others
I	1495(s), 946(s)		515(s), 502(m), 490(s), 478(m), 427(s)	245(m)[a]
II	1490(s), 945(s)		515(s), 500(m), 485(s), 418(m)	
III	1499(s), 946(s)		512(s), 502(m), 495(s), 423(s)	305(s), 287(s), 280(s)[b]
IV	1496(s), 955(s)		512(s), 480(s)	1100(s,br)[c], 1525(s)[d]
V	1499(s), 952(s)		510(s), 485(s)	1688(s)[e]
VI	1507(s), 953(s)		510(s), 483(s), 435(s)	1150(s), 1025(s)[f]
VII	1492(s), 950(s)		535(s), 515(s), 500(s), 485(s)	610(m)[g]
VIII	1481(s), 950(s)		585(s), 537(m), 515(s), 498(s), 475(s)	880(s)[h], 610(m)[g]
IX	1502(s), 950(s)		513(s), 500(m), 485(s), 475(m), 460(m)	610(m)[g]
X	1490(s), 948(s)	1625(s,br)	512(s), 483(s)	
XI	1490(s), 949(s)	2160(s)	515(s), 500(m), 480(s)	610(m)[g]
XII	1490(s), 948(s)	2160(s), 1620(s,br)	512(s), 501(s), 482(s)	610(m)[g]
XIII	1490(s), 948(s)	1612(s)	510(s), 505(s), 483(s)	
XIV	1490(s), 950(s)	2140(s)	512(s), 503(s), 480(s)	610(m)[g]
XV	1492(s), 950(s)	2140(s), 1260(s,br)	510(s), 502(s), 485(s)	610(m)[g]

[a] ν(Pd–Cl). [b] ν(Sn–Cl). [c] BF_4. [d] $\nu_{as}(NO_2)$. [e] ν(CO). [f] $\nu(SO_2)$. [g] BPh_4. [h] $P(OPh)_3$.

Addition of $NaBPh_4$ to acetonitrile solutions of **X** or **XIII** yields the cationic complexes $[(RNC)Pd(\mu\text{-dppm})_2Pt(C_6F_5)]BPh_4$ (**XI**, R = Cy. **XIV**, R = *p*-Tol) by deinsertion of the bridging CNR, which coordinate to the Pd(I) center as a terminal ligand. The cationic complexes **XI** and **XIV** can also be obtained by the reaction of **I** with CNR (molar ratio 1:1) in acetonitrile and in the presence of $NaBPh_4$.

Addition of an excess of isonitrile (CyNC or *p*-TolNC) to a solution of **I** gives rise to the formation of cationic complexes with both coordinated and inserted isonitrile $[(RNC)Pd(\mu\text{-dppm})_2(\mu\text{-CNR})Pt(C_6F_5)]^+$ which can be isolated with BPh_4^- as counterion upon addition of $NaBPh_4$ (complexes **XII** and **XV**).

Relevant IR absorptions for the complexes are collected in Table II.

The IR spectra of these complexes (**I–XV**) show the characteristic absorptions of the dppm ligand (600–400 cm^{-1} region) along with those of the C_6F_5 group [9] at ~1500 and ~950 cm^{-1}.

The band at *ca.* 950 cm^{-1} in the platinum(II) precursor, *trans*-$PtCl(C_6F_5)(\eta^1\text{-dppm})_2$ appears at 958 cm^{-1}. It is noteworthy that this absorption in the Pd^I–Pt^I complexes is shifted (8–13 cm^{-1}) towards lower wavelengths relative to its position in the M(II) precursor [2, 4, 5].

The insertion of small groups into the Pd(I)–Pt(I) bonds leads to a change in the formal oxidation state of the metal atoms and, consequently, to an increase in the wavenumber of C_6F_5 absorption near 950 cm^{-1} (complexes **IV**, **V**, **VI**). In the isonitrile derivatives (**X–XV**) the complexes with the Pd(I)–Pt(I) bond, as well as those resulting from the isonitrile insertion, exhibit this C_6F_5 band at very similar wavelengths; which indicates that the insertion process does not modify the electron density around the metal [2, 4a, 10].

Complex **I** shows a weak absorption at 245 cm^{-1}, assigned to ν(Pd–Cl) in the same range found for ν(M–Cl) (M = Pd, Pt) in $[(Cl)Pd(\mu\text{-dppm})M(Cl)]$ (M = Pd, Pt) [3, 11], the ν(Pt–Cl) in the precursor complex $PtCl(C_6F_5)(\eta^1\text{-dppm})_2$ appears at higher wavenumber (312 cm^{-1}).

Complex **III** shows IR bands in the 320–260 cm^{-1} region due to ν(Sn–Cl) [12]. Complex **IV** shows a strong and broad absorption at ~1100 cm^{-1} due to the counterion BF_4^- [13] and a band at 1525 cm^{-1} due to $\nu_{as}(NO_2)$ of the N_2R^+ group [14]. Complex **V** shows a strong absorption at 1700 cm^{-1} due to ν_s(C=O) of the inserted group, shifted towards lower energies relative to the free acetylene-ligand (1740 cm^{-1}). Complex **VI** exhibits two absorptions located at 1145 and 1125 cm^{-1} which are due to the symmetric and asymmetric ν(S–O) stretching frequencies respectively [15].

The IR spectra of the isonitrile complexes were very valuable to confirm the presence of coordinated ν(C≡N) in 2100–2200 cm^{-1} and/or inserted ν(C=N) in 1500–1650 cm^{-1}. In the cationic complexes with BPh_4^- as counter ion, an absorption appears at 610 cm^{-1}.

We have recorded the $^{31}P\{^1H\}$ NMR spectra of some representative complexes; the following parameters are relevant: **I**: δP_A: 3.60 ppm (P_A: P on Pt), δP_B: −6.22 (P_B: P on Pd) ^1J(Pt–P): 2739 Hz, N = $^2J(P_AP_B) + {^4J}(P_AP_{B'})$ = 89 Hz; **III** : δP_A: 2.55 ppm, δP_B: −5.14 ppm, ^1J(Pt–P): 2651 Hz. N: 73 Hz; **V**: δP_A: 6.10 ppm, δP_B: 1.61 ppm, ^1J(Pt–P) = 3042 Hz, ^3J(Pt–P): 174 Hz, N: 27 Hz. The $^{31}P\{^1H\}$ NMR spectra are very characteristic. They are all examples of AA′BB′ spin systems with satellites due to ^{195}Pt coupling. Values of $^1J(\mathrm{PtP_A})$ can be measured directly from the spectra; however, for **I** and **III** $^3J(\mathrm{PtP_B})$ cannot be inequivocally derived from their $^{31}\mathrm{P}\{^1\mathrm{H}\}$ spectra.

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 approximately 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 599 spectrophotometer using Nujol mulls between polyethylene sheets. ^{19}F and ^{31}P NMR spectra were recorded on a Varian XL-200 (referred to $CFCl_3$ and to H_3PO_4 respectively, solvent $CDCl_3$).

The complexes $\mathrm{PtX(C_6F_5)(dppm)_2}$ [5] and $\mathrm{Pd_2(dba)_3 \cdot CHCl_3}$ [16] were prepared as described elsewhere.

[ClPd(μ-dppm)₂Pt(C₆F₅)] (I)

To a solution of 0.176 g, (0.16 mmol) of $\mathrm{Pd_2(dba)_3 \cdot CHCl_3}$ in 20 ml of $CHCl_3$ (deoxygenated) under nitrogen were added 0.375 g (0.32 mmol) of $\mathrm{PtCl(C_6F_5)(\eta^1\text{-}dppm)_2}$. The mixture was stirred for 30 min at 40–50 °C. The filtered solution was evaporated to dryness. The addition of 15 ml of Et_2O gave a deep yellow solid, **I**. Yield: 68%.

[BrPd(μ-dppm)₂Pt(C₆F₅)] (II)

To a solution of 0.176 g (0.16 mmol) of $\mathrm{Pd_2(dba)_3 \cdot CHCl_3}$ in 25 ml of CH_2Cl_2 (deoxygenated) under nitrogen were added 0.400 g (0.32 mmol) of $\mathrm{PtBr(C_6F_5)(\eta^1\text{-}dppm)_2}$. The mixture was stirred for 1 h at room temperature. The filtered solution was evaporated to dryness. The addition of 15 ml of Et_2O gave a deep yellow solid, **II**. Yield: 70%.

[(Cl₃Sn)Pd(μ-dppm)₂Pt(C₆F₅)] (III)

To a solution of 0.1 g (0.07 mmol) of **I** in 10 ml of CH_2Cl_2 was added a solution of 0.014 g (0.07 mmol) of $SnCl_2$ in 5 ml of methanol. The yellow solution turned orange. The mixture was stirred for 90 min at room temperature; the filtered solution was evaporated to ~5 ml and Et_2O (~10 ml) was added to precipitate **III** in 65% yield.

[ClPd(μ-dppm)₂(μ-N₂C₆H₄-o-NO₂)Pt(C₆F₅)]BF₄ (IV)

To a cooled (–20 °C) suspension of **I** (0.1 g, 0.07 mmol) in acetone (40 ml), were added 0.016 g (0.07 mmol) of $(o\text{-}NO_2\text{-}C_6H_4N_2)BF_4$. The solution was stirred at –20 °C for 10 min and then allowed to reach room temperature over a period of ~30 min. The solution was evaporated almost to dryness and the addition of Et_2O (20 ml) afforded **IV** which was recrystallized from acetone/Et_2O. Yield: 79%.

[ClPd(μ-dppm)₂(μ-C₂(CO₂Me)₂)Pt(C₆F₅)] (V)

To a solution of **I** (0.1 g, 0.07 mmol) in 5 ml of CH_2Cl_2, were added 10.12 μl (0.08 mmol) of MeOOC–C≡C–C–COOMe and the mixture, protected from the light, was stirred at room temperature for 50 days. Evaporation to *ca.* 1 ml and addition of Et_2O (10 ml) afforded **V** in 58% yield.

[ClPd(μ-dppm)₂(μ-SO₂)Pt(C₆F₅)] (VI)

SO_2 was bubbled for 30 min at room temperature through a solution of **I** (0.150 g, 0.11 mmol) in 5 ml of CH_2Cl_2. The initial yellow solution turned orange. Afterwards, n-hexane (50 ml) was added to precipitate **VI**. Yield: 95%.

[(L)Pd(μ-dppm)₂Pt(C₆F₅)]BPh₄ (L = PPh₃ (VII), P(OPh)₃ (VIII), SbPh₃ (IX))

To a suspension of 0.1 g (0.785 mmol) of **I** in 20 ml of methanol, was added PPh_3 (0.024 g, 0.094 mmol). The mixture was stirred at reflux temperature for 1 h. To the filtered solution, was added a solution of $NaBPh_4$ (0.026 g, 0.078 mmol) in 10 ml of ^{i}PrOH. The resulting solution was evaporated almost to dryness. Addition of ~10 ml of ^{i}PrOH precipitated an orange solid, which was identified as **VII**. Yield: 77%.

VIII and **IX** were obtained similarly. Yield: 61%, 33% respectively.

[ClPd(μ-dppm)₂(μ-CNR)Pt(C₆F₅)] (R = CyNC (X), p-TolNC (XIII))

To a solution of 0.100 g (0.078 mmol) of **I** in 15 ml of benzene, were added 10.5 μl (0.078 mmol) of CyNC. After 30 min stirring at room temperature the solution was concentrated to a small volume (~5 ml) and n-hexane (~30 ml) was added to precipitate **X**. Yield: 72%.

XIII was similarly obtained. Yield: 68%.

[(RNC)Pd(μ-dppm)₂Pt(C₆F₅)](BPh₄) (R = CyNC (XI), p-TolNC (XIV))

(a) From I

To a solution of 0.069 g (0.05 mmol) of **I** in 15 ml of NCMe, was added CyNC (6.5 μl, 0.05 mmol). The solution was stirred for 5 min at room temperature; afterwards were added 0.018 g (0.05 mmol of $NaBPh_4$; then further stirred for 60 min. The filtered solution was evaporated to dryness, the resulting oil was stirred with ^{i}PrOH/n-hexane to crystallize **XI**. Yield: 65%.

XIV was similarly obtained. Yield: 68%.

(b) Synthesis of XI and XIV from X and XIII respectively

To a solution of 0.040 g (0.029 mmol) of **X** in 10 ml of $NCCH_3$, were added 0.010 g (0.029 mmol) of $NaBPh_4$. The mixture was stirred for 30 min at room temperature; the resulting solution was evaporated to dryness; the residue was stirred with ^iPrOH/n-hexane to obtain a solid, which was washed with 3 X 5 ml of water and dried. Yield: 62%.

XIV was similarly obtained from **XIII**.

$[(RNC)Pd(\mu\text{-dppm})_2(\mu\text{-RNC})Pt(C_6F_5)]BPh_4$ (R = CyNC (XII), p-TolNC (XV))

To a solution of 0.075 g (0.05 mmol) of **I** in 10 ml of $NCCH_3$, were added CyNC (20 μl, 0.165 mmol) and $NaBPh_4$ (0.020 g, 0.05 mmol). The mixture was stirred for 1 h at room temperature, then evaporated almost to dryness. The addition of ^iPrOH/n-hexane gave an orange solid, which was washed with H_2O and dried. Yield: 58%.

XV was similarly obtained. Yield: 60%.

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