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Diphosphazane supported platinum(II) triflate, amine, and amido complexes: synthesis and X-ray crystal structures

Aibing Xia, Paul R. Sharp *

125 Chemistry, University of Missouri, Columbia, MO 65211, USA

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Abstract

Treatment of L_2PtCl_2 ($L_2 = MeN[P(OPh_2)]_2$) with $AgSO_3CF_3$ gives the triflate complex $L_2Pt(SO_3CF_3)_2$ (**1**). Addition of 2,6-dimethylaniline to **1** in CH_2Cl_2 gives the monomeric diamine complex $[L_2Pt(NH_2Ar)_2](SO_3CF_3)_2$ (**2**, Ar = 2,6-$Me_2C_6H_3$), while reaction of **1** with lithium 2,6-dimethylanilide gives the dimeric bridging amido complex $[L_2Pt(\mu\text{-}NHAr)]_2(SO_3CF_3)_2$ (**3** Ar = 2,6-$Me_2C_6H_3$). Cyclometalation is observed when **1** is treated with lithium 2,4,6-triphenylanilide yielding the neutral complex $L_2Pt\{NH[2\text{-}(3,5\text{-}Ph_2C_6H_2)C_6H_4]\}$ (**4**). The structures of all four complexes were determined by X-ray diffraction methods. All display the expected four-coordinate square planar Pt geometry. The amine (**2**) and amido (**3**) complexes show N–H hydrogen bonding to the triflate anions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Amido; Amine; Triflate; Platinum; Diphosphazane; Cyclometalation

1. Introduction

Late transition metal amido complexes [1] have attracted considerable interest for their potential in organic synthesis [2] and for their usefulness as synthetic precursors [1,3,4]. Platinum(II) and palladium(II) amido complexes have been widely studied and their structural features and reactivities found to be influenced by differences in the supporting ligands [2,5,6]. A common feature of amido complexes is a relatively high amido ligand electron density. Since one of our major interests is deprotonation of amido ligands to imido ligands we are interested in factors that reduce amido ligand electron density and enhance acidity. Diphosphazanes ($RN(PX_2)_2$) are versatile supporting ligands that can be easily modified on both nitrogen and phosphorus centers to tune steric and electronic properties [7]. Here we report the synthesis and structures of several platinum(II) complexes, including amido complexes, employing the supporting diphosphazane ligand $MeN[P(OPh)_2]_2$.

2. Results and discussion

The high lability of the triflate ligand makes metal triflate complexes excellent synthetic precursors [8]. The triflate complex $L_2Pt(SO_3CF_3)_2$ (**1**) is readily obtained from the reaction of L_2PtCl_2 ($L_2 = MeN[P(OPh)_2]_2$) [9] with $AgSO_3CF_3$ in CH_2Cl_2 at ambient temperatures (Scheme 1). The ^{31}P NMR signal of the diphosphazane ligand shifts upfield by about 36 ppm (from 43.5 ppm for the dichloride to 7.5 ppm for the triflate). Along with this upfield shift, the Pt–P coupling constant increases almost 1000 Hz (from 5036 to 6008 Hz). These data imply a stronger P–Pt interaction consistent with the expected weaker *trans*-influence of the triflate ligand [10]. An X-ray crystal structure analysis of **1** (Fig. 1, Table 1) shows the expected square planar Pt center with a *cis*-disposition of the triflate ligands. Selected distances and angles are given in Table 2. There are two known structures of Pt(II) triflate complexes with a phosphorus ligand *trans* to the triflate ligand. The most closely related to **1** is the diphosphine complex $\{1,2\text{-}(PMePh)_2C_6H_4\}Pt(OTf)_2$ [11]. The Pt–O bond lengths in this complex are 2.142(9) and 2.091(8) Å, similar to those in **1** (2.080(3) and 2.096(3) Å). The Pt–O–S angles of 136.1(5)° and 131.1(6)° are slightly greater than those in **1** (130.19(17)° and 128.06(16)°). The more open Pt–

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* Corresponding author. Tel.: +1-573-882-7715; fax: +1-573-882-2754.

E-mail address: sharpp@missouri.edu (P.R. Sharp).

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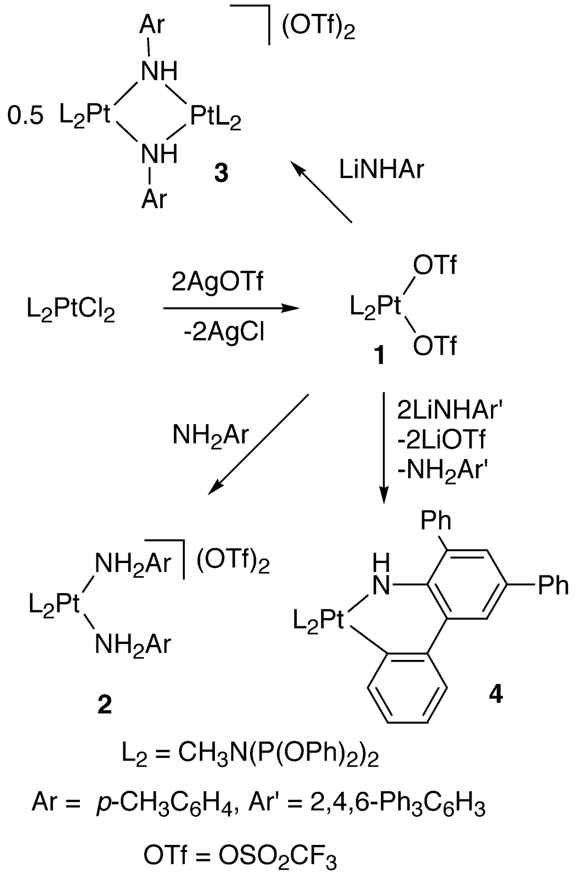


Scheme 1.

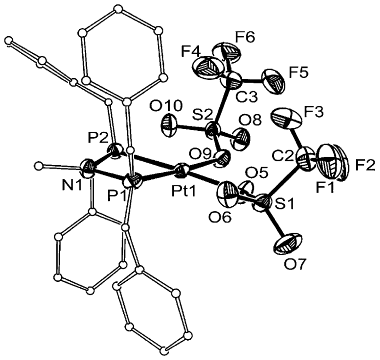


Fig. 1. ORTEP drawing of $L_2Pt(SO_3CF_3)_2$ (**1**). Hydrogen atoms are omitted for clarity. Atoms, except phenoxide atoms and the N–Me carbon (arbitrary spheres), are represented by 50% probability thermal ellipsoids.

O–S angle of $\{1,2\text{-}(PMePh)_2C_6H_4\}Pt(OTf)_2$ may result from steric crowding. Such factors are absent in **1** with its smaller bite angle diphosphazane and less sterically demanding OPh phosphorus substituents. The second complex for comparison is the diphosphine complex $\{(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2\}Pt(Me)(OTf)$ [12]. The Pt–O distance (2.090(6) Å) and the Pt–O–S angle (130.2(3)°) in this complex are almost identical to those of **1** suggesting minimal steric congestion, as in **1**.

As expected, the triflate ligands of **1** are labile and **1** reacts readily with 2,6-dimethylaniline at ambient temperature to afford the diamine complex $[L_2Pt(NH_2Ar)_2](SO_3CF_3)_2$ (**2**, Ar = 2,6-$Me_2C_6H_3$). Complex **2** gives a ^{31}P NMR signal at 16.5 ppm with a Pt–P coupling constant of 4900 Hz. This decrease in the Pt–P coupling constant from that of **1** and L_2PtCl_2 is indicative of the stronger *trans*-influence of the amine ligand relative to the triflate and chloride ligands [10]. The NH peak is observed in the ^1H NMR spectrum of **2** at 7.04 ppm (CD_2Cl_2), shifted downfield by about 2 ppm from that of the free ligand in the same solvent. An X-ray crystal structure analysis of **2** (Fig. 2, Table 1) shows the expected square planar Pt center with a *cis*-disposition of the amine ligands. The amine ligands interact with the two triflate anions through bifurcated hydrogen bonds. Metrical parameters are given in Table 3. Comparison structures with mononuclear *cis*-P_2PtN_2 cores are mostly limited to complexes incorporating the amine nitrogen in a chelate ring. An exception is the simple ammonia complex *cis*-$[(Ph_3P)_2Pt(NH_3)_2](NO_3)_2$ [13]. This complex shows a similar hydrogen bonding pattern of the coordinated amine to the counter anion, and an average Pt–N distance of 2.098(9) Å. Structures incorporating the amine into a chelate ring have average Pt–N distances ranging from 2.07(11) to 2.110(8) Å [14]. The Pt–N distances of **2** are in this range (2.118(4) and 2.129(4) Å).

Attempts to deprotonate **2** with $LiN(SiMe_3)_2$ to obtain an amido complex were not successful. ^1H NMR spectra of the reaction mixtures showed the loss of the diphosphazane N–Me triplet signal indicating disruption of the diphosphazane ligand, probably through nucleophilic attack on the phosphorus center.

As an alternative to the formation of an amido complex by deprotonation of **2**, **1** was treated with lithium 2,6-dimethylanilide in THF at −30 °C. The amido-bridged dimer $[L_2Pt(\mu\text{-}NHAr)]_2(SO_3CF_3)_2$ (**3**, Ar = 2,6-$Me_2C_6H_3$) was obtained as the only isolated product with anilide to Pt ratios of 1:1–2:1 (Scheme 1). Complex **3** gives a ^{31}P signal at 29.9 ppm with a Pt–P coupling constant of 4628 Hz. The ^1H NMR spectrum shows an N–H peak at 4.93 ppm, an upfield shift compared with the monomeric diamine complex **2** and suggestive of greater electron density on the nitrogen centers in the anilido dimer **3**. However, this shift is lower than that observed for analogous diphosphine complexes (4.6–2.6 ppm) [6] suggesting that the reduced donor properties of the diphosphazane ligand result in less electron density at the amido ligand. An X-ray crystal structure analysis of **3** (Figs. 3 and 4, Table 1) shows the expected edge-shared dimer with a *syn*-orientation of the amido aryl groups. One triflate anion is hydrogen-bonded to the amido groups. The Pt_2N_2 core is slightly bent at the N–N hinge. Factors involved in the bending of di-bridged d^8-square-planar dimers of

Table 1
Crystallographic and data collection parameters at 173 K [a]

Formula	$C_{27}H_{23}F_6NO_{10}P_2PtS_2$ (**1**)	$C_{43}H_{45}F_6N_3O_{10}P_2PtS_2$ (**2**)	$C_{68}H_{66}F_6N_4O_{14}P_4Pt_2S_2$ (**3**)·DME [d]	$C_{49}H_{40}N_2O_4P_2Pt$ (**4**)·1.5DME [d]
Color/habit	colorless/block	colorless/needle	yellow/prism	yellow/plate
Size (mm)	0.5 × 0.2 × 0.2	0.5 × 0.05 × 0.05	0.2 × 0.15 × 0.15	0.2 × 0.2 × 0.05
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group (Z)	$P\bar{1}$ (2)	Cc (4)	$P2_1/n$ (4)	$P\bar{1}$ (2)
a (Å)	10.7182(6)	13.185(2)	19.809(3)	13.3686(6)
b (Å)	11.2575(6)	17.330(2)	20.117(3)	13.3859(6)
c (Å)	15.7721(9)	21.515(3)	21.242(3)	15.9724(7)
α (°)	82.078(1)	90	90	91.497(1)
β (°)	83.812(1)	101.394(7)	112.780(2)	108.834(1)
γ (°)	64.575(1)	90	90	112.315(1)
Total reflections	13 552	14 825	48 486	19 793
Unique/R_{int}	7337/0.026	8833/0.028	17 226/0.056	10 675/0.029
Observed ($>2\sigma(I)$)	6501	8157	11 169	9391
θ_{max}/%measured	27.13/97.3	27.13/98.9	27.19/99.2	27.15/97.7
R_1 [b]	0.0249	0.0292	0.0381	0.0300
wR_2 [c]/No. var.	0.0582/443	0.0709/604	0.0780/963	0.0691/608

[a] Siemens CCD system (omega scans), SADABS absorption correction, λ (Mo Kα) = 0.71073 Å, refined on F_o^2, H atoms riding/refined.

[b] $R_1 = (\Sigma||F_o| - |F_c|)/\Sigma|F_o|$.

[c] $wR_2 = [(\Sigma(F_o^2 - F_c^2)^2)/\Sigma\, w(F_c^2)^2]^{1/2}$ with weight $= 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$; $x = 0.0333$, $y = 0$ for **1**; $x = 0.0420$, $y = 4.7556$ for **2**; $x = 0.0299$, $y = 0$ for **3**; $x = 0.0379$, $y = 0$ for **4**; $P = (F_o^{\ 2} + 2F_c^2)/3$.

[d] Solvent of crystallization, DME = $MeOCH_2CH_2OMe$ ($C_4H_{10}O_2$).

Table 2
Selected distances (Å) and angles (°) for $L_2Pt(OTf)_2$ (**1**)

Bond distances			
Pt1–O5	2.080(3)	S2–O10	1.430(3)
Pt1–O9	2.096(3)	S2–O9	1.487(3)
Pt1–P2	2.182(1)	S2–C3	1.819(5)
Pt1–P1	2.190(1)	F5–C3	1.327(5)
S1–O7	1.416(3)	F1–C2	1.325(5)
O5–S1	1.485(3)	F6–C3	1.333(6)
S1–C2	1.814(5)	F3–C2	1.326(6)
S1–O6	1.422(3)	F4–C3	1.325(6)
S2–O8	1.419(3)	F2–C2	1.311(5)
Bond angles			
O5–Pt1–P2	176.53(8)	P2–Pt1–P1	71.21(3)
O5–Pt1–O9	78.21(11)	O9–Pt1–P1	176.03(7)
O5–Pt1–P1	105.65(8)	S1–O5–Pt1	130.19(17)
O9–Pt1–P2	104.96(8)	S2–O9–Pt1	128.06(16)

this type have been studied [15]. Selected bond distances and angles are given in Table 4 and are similar to those of related structurally characterized amido complexes with $P_2Pt(\mu\text{-}N)_2PtP_2$ cores [6,16].

Previous work has shown that $[L_2Pt(\mu\text{-}NHAr)]_2^{2+}$ complexes can be converted to imido complexes by deprotonation if L_2 is the small bite-angle ligand $(Ph_2P)_2NMe$ [3]. We, therefore, anticipated that **3**, with its more weakly donating $[(PhO)_2P]_2NMe$ ligand, would deprotonate even more readily to produce an imido complex. However, treatment of **3** with $LiN(SiMe_3)_2$ does not give an imido complex but rather appears to lead to disruption of the diphosphazane ligand. As in the attempted deprotonation of **2** (see above), this is indicated by the loss of the N–Me triplet signal in the ^1H NMR spectrum of the reaction mixture.

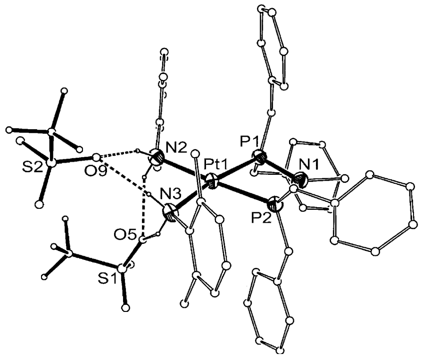


Fig. 2. ORTEP drawing of $[L_2Pt(NH_2Ar)_2](SO_3CF_3)_2$ (**2**, Ar = 2,6-$Me_2C_6H_3$). Hydrogen atoms, except the amine hydrogen atoms, are omitted for clarity. Arbitrary spheres represent the atoms except for the Pt, P, and N atoms, which are represented by 50% probability thermal ellipsoids.

Table 3
Selected distances (Å) and angles (°) for $[L_2Pt(NH_2Ar)_2](SO_3CF_3)_2$ (**2**, Ar = 2,6-$Me_2C_6H_3$)

Bond lengths			
Pt1–P1	2.211(4)	Pt1–P2	2.209(1)
Pt1–N2	2.118(4)	Pt1–N3	2.129(4)
P1–N1	1.664(4)	P2–N1	1.684(4)
N3–C1n	1.472(6)	N2–C1n2	1.475(6)
Bond angles			
P1–Pt1–P2	70.85(5)	N2–Pt1–N3	86.24(16)
Pt1–P1–N1	94.49(17)	Pt1–P2–N1	94.97(16)
P1–N1–P2	99.69(25)		

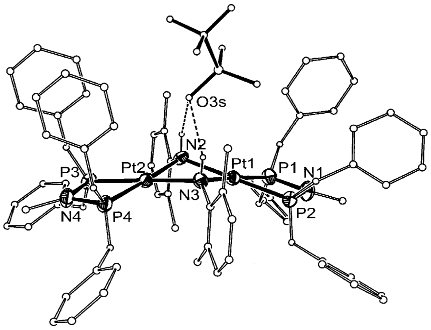


Fig. 3. ORTEP drawing of the cationic portion of $[L_2Pt(\mu\text{-}NHAr)]_2(SO_3CF_3)_2$ (**3**, Ar = 2,6-$Me_2C_6H_3$). Hydrogen atoms, except the N–H hydrogen atoms, are omitted for clarity. All atoms, except phenoxide atoms and the N–Me carbon (arbitrary spheres), are represented by 50% probability thermal ellipsoids.

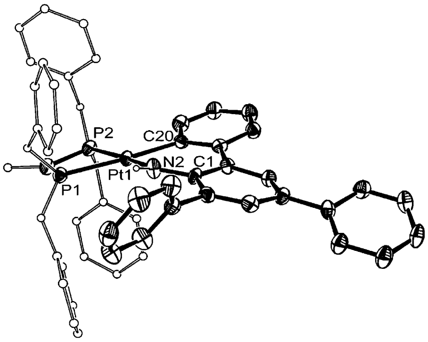


Fig. 4. ORTEP drawing of the cationic portion of $L_2Pt\{NH[2\text{-}(3,5\text{-}Ph_2C_6H_2)C_6H_4]\}$ (**4**). Hydrogen atoms, except the amine hydrogen atoms, are omitted for clarity. Atoms, except phenoxide atoms and the N–Me carbon (arbitrary spheres), are represented by 50% probability thermal ellipsoids.

Table 4
Selected distances (Å) and angles (°) for $[L_2Pt(\mu\text{-}NHAr)]_2(SO_3CF_3)_2$ (**3**, Ar = 2,6-$Me_2C_6H_3$)

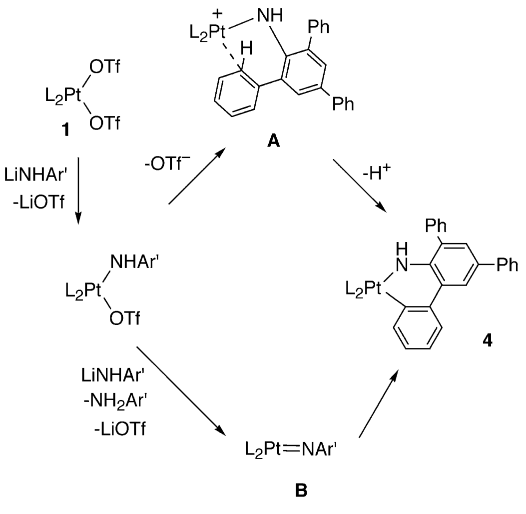
Bond lengths			
Pt1–Pt2	3.1732(5)	Pt1–N2	2.115(4)
Pt1–N3	2.104(4)	Pt1–P1	2.210(2)
Pt1–P2	2.206(1)	Pt2–N2	2.113(4)
Pt2–N3	2.104(4)	Pt2–P3	2.220(2)
Pt2–P4	2.208(2)		
Bond angles			
P1–Pt1–P2	70.54(5)	P3–Pt2–P4	70.77(5)
P1–Pt1–N2	106.3(1)	P3–Pt2–N2	105.7(1)
P1–Pt1–N3	175.2(1)	P3–Pt2–N3	175.7(1)
P2–Pt1–N2	176.8(1)	P4–Pt2–N2	176.4(1)
P2–Pt1–N3	104.7(1)	P4–Pt2–N3	105.7(1)
N2–Pt1–N3	78.53(15)	N2–Pt2–N3	78.58(15)
P1–N1–P2	99.53(25)	P3–N4–P4	100.6(3)
Pt1–N2–Pt2	97.26(15)	Pt1–N3–Pt2	97.90(16)

Table 5
Selected distances (Å) and angles (°) for $L_2Pt\{NH[2\text{-}(3,5\text{-}Ph_2C_6H_2)C_6H_4]\}$ (**4**)

Bond lengths			
Pt1–P1	2.284(2)	Pt1–P2	2.209(2)
Pt1–N2	1.995(5)	Pt1–C20	2.049(6)
P1–N1	1.673(6)	P2–N1	1.678(6)
Bond angles			
P1–Pt1–P2	69.48(6)	N2–Pt1–C20	89.9(2)
Pt1–P1–N1	96.4(2)	Pt1–P2–N1	93.6(2)
P1–N1–P2	99.7(3)		

In an effort to block dimer formation as observed in **3**, **1** was treated with 2 equiv. of the bulky anilide LiNH(2,4,6-$Ph_3C_6H_2$). Instead of the expected mononuclear diamido complex, cyclometalation product $L_2Pt\{NH[2\text{-}(3,5\text{-}Ph_2C_6H_2)C_6H_4]\}$ (**4**) was obtained (Scheme 1). The ^{31}P NMR spectrum of **4** shows two doublets ($J_{P-P} = 49.1$ Hz) at 70.8 ppm ($J_{P-Pt} = 3920$ Hz) and 95.9 ppm ($J_{P-Pt} = 1959$ Hz). The high-shift doublet with the small Pt–P coupling constant is assigned to the phosphorus atom *trans* to the carbon atom consistent with the strong *trans*-influence of a carbon anion [10]. An X-ray crystal structure analysis of **4** (Fig. 4, Table 1) confirms the cyclometalation of the amido ligand. Selected distances and angles are given in Table 5. Remarkably, despite the commercial availability of the aniline, this is apparently only the second report of a transition metal complex formed from this aniline [17]. This is in sharp contrast to other terphenyl ligands, [18] the related phenol, 2,6-$Ph_2C_6H_3OH$, [19] and other substituted anilines, [20] which have been used for the preparation of a number of metal complexes. Cyclometalations, like that observed here, have been reported with the phenoxo ligand 2,6-$Ph_2C_6H_3O$ for a number of early transition metals [19] and for Sn [21] and Ge [22].

Two possible pathways to cyclometalation product **4** are considered in Scheme 2. Both begin by formation of the amido triflate complex $L_2Pt(NHAr')(OTf)$. This species may loose a triflate anion to generate the three-coordinate species $[L_2Pt(NHAr')]^+$ (**A**). (A



Scheme 2.

Ni(II) analog of **A** has been isolated [23]). Three-coordinate species are thought to be required for significant cyclometalation rates in Pt(II) systems [24]. The second pathway requires formation of the terminal imido complex $L_2Pt{=}NAr'$ (**B**) either by deprotonation of $L_2Pt(NHAr')(OTf)$ (or **A**) or formation of $L_2Pt(NHAr')_2$ followed by elimination of H_2NAr'. Addition of the C–H bond across the Pt–N double bond, a process known for terminal early transition metal imido complexes, [25] would then yield **4**. Although never observed, terminal Pt(II) oxo complexes analogous to **B** have been postulated [26] and a Ni(II) analog of **B** has been recently reported [23]. Given the lack of evidence for imido complex **B**, we favor the well-established [24] electrophilic cyclometalation through three-coordinate **A**. However, future work will be directed at establishing the possible existence of **A** with aryl groups that are less susceptible to cyclometalation and supporting ligands (L_2) that discourage approach of the aryl group to the Pt center.

3. Experimental

3.1. General procedures

Experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres Corp. drybox. Solvents were dried by standard techniques and stored under nitrogen over 4 Å molecular sieves. The compounds 2,6-dimethylaniline, 2,4,6-triphenylaniline, and $AgSO_3CF_3$ were purchased from Aldrich or Acros Chemicals and were used as received. The lithium anilides were prepared from the anilines and $LiBu^n$ (2.5 M) in hexane. $L_2 = MeN[P(OPh)_2]_2$ and L_2PtCl_2 were prepared by literature procedures [9]. NMR spectra were recorded on a Bruker AMX-250 spectrometer. ^1H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) spectra are referenced to TMS or to solvent impurities referenced back to TMS. ^{31}P NMR (101 MHz) spectra are referenced to external 85% H_3PO_4. All NMR shifts are in ppm with negative shift upfield from the reference. Spectra were recorded at ambient temperatures (22 °C) unless otherwise indicated. Melting points are uncorrected.

*3.2. Preparation of $L_2Pt(OTf)_2$ (**1**)*

Silver trifluoromethane sulfonate (0.257 g, 1.00 mmol) was added to a suspension of L_2PtCl_2 (0.365 g, 0.500 mmol) in 2.0 ml of CH_2Cl_2. The mixture was stirred at ambient temperature overnight and then filtered. Addition of Et_2O (10 ml) to the filtrate afforded a white precipitate of the product. This was collected by filtration, washed twice with Et_2O (3 ml), and dried in vacuo to give 0.400 g (83.5%) of white solid. Colorless single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2–Et_2O. *Anal*. Calc. (Found): C 33.90 (34.12), H 2.42 (2.41), N 1.46 (1.49)%. M.p.: 180–182 °C. ^1H NMR (CD_2Cl_2): 2.91 (t, $^3J_{H-P} = 13.3$ Hz, 3H, Me), 7.20–7.41 (m, 20H, phenyl). ^{13}C NMR (CD_2Cl_2): 31.71 (s, Me), 120.92 (t, $J_{C-P} = 2.4$ Hz, C_{ortho} of Ph), 127.85 (s, C_{para} of Ph), 131.15 (s, C_{meta} of Ph), 149.39 (t, $J_{C-P} = 4.0$ Hz, C_{ipso} of Ph). ^{31}P (CD_2Cl_2): 7.49 ($J_{P-Pt} = 6008$ Hz).

*3.3. $[L_2Pt(NH_2Ar)_2](SO_3CF_3)_2$ (**2**, Ar = 2,6-$Me_2C_6H_3$)*

2,6-dimethylaniline (0.032 g, 0.260 mmol) was added to a solution of $(L_2Pt)(OTf)_2$ (0.126 g, 0.132 mmol) in CH_2Cl_2 (2 ml). The solution was stirred for 2 h at ambient temperature. Addition of Et_2O (10 ml) afforded a white precipitate of the product. This was collected by filtration, washed twice with Et_2O (3 ml), and dired in vacuo (0.135 g, 85.4%). Colorless single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2–Et_2O. *Anal*. Calc. (Found): C 43.08 (42.87), H 3.78 (3.87), N 3.50 (3.50)%. M.p.: 196–200 °C. ^1H NMR (CD_2Cl_2): 1.75 (t, $^3J_{H-P} = 12.0$ Hz, 3H, Me), 2.67 (s, 12H, Me), 7.04 (s, overlapped with Ph, NH), 6.87–7.49 (m, 30H, Ph). ^{13}C NMR (CD_2Cl_2): 15.00, 18.11, 110.09, 119.63, 124.53, 126.95, 127.62. ^{31}P (CD_2Cl_2): 16.47 ($J = 4909$ Hz).

*3.4. $[L_2Pt(\mu\text{-}NHAr)]_2(OTf)_2$ (**3**, Ar = 2,6-$Me_2C_6H_3$)*

A solution of lithium 2,6-dimethylanilide (0.010 g, 0.079 mmol) in THF (1 ml) was added to a solution of $(L_2Pt)(OTf)_2$ (0.039 g, 0.040 mmol) in THF (1 ml) at −30 °C. The mixture was kept at −30 °C overnight then warmed to ambient temperatures and the volume reduced in vacuo. Et_2O (10 ml) was added and the resulting precipitate was filtered and washed with Et_2O (3 ml) to afford the pale yellow solid product (0.020 g, 50%). Yellow crystals for the X-ray analysis were obtained from DME–$^iPr_2O$. M.p.: 205–208 °C. ^1H NMR (CD_2Cl_2): 2.13 (t, $^3J_{H-P} = 12.0$ Hz, 6H, Me), 2.42 (s, 6H, Me), 3.52 (s, Me), 4.93 (bs, 2H, NH), 6.73–7.45 (m, 26H, Ph). ^{13}C NMR (CD_2Cl_2): 19.18, 22.97, 120.14, 120.21, 127.34, 129.10, 130.80, 130.99, 131.44, 149.49. ^{31}P (CD_2Cl_2): 29.93 ($J_{P-Pt} = 4628$ Hz).

*3.5. $L_2Pt\{NH[2\text{-}(3,5\text{-}Ph_2C_6H_2)C_6H_4]\}$ (**4**)*

A solution of lithium 2,4,6-triphenylanilide (0.013 g, 0.040 mmol) in THF (1 ml) was added to a solution of $(L_2Pt)(OTf)_2$ (0.020 g, 0.020 mmol) in THF (1 ml) at −30 °C. The mixture was kept at −30 °C overnight and the volume was reduced under reduced pressure. Et_2O (10 ml) was added and the precipitate was filtered and washed with Et_2O (3 ml) to afford a pale yellow solid

(0.010 g, 50%). Yellow crystals for the X-ray analysis were obtained from DME–^{i}Pr$_2$O. M.p.: 196–200 °C. ^{1}H NMR (CD$_2$Cl$_2$): 3.00 (t, $^{3}J_{\mathrm{H-P}} = 8.0$ Hz, 3H, Me of L$_2$), 6.60 (1H, NH), 6.64–7.74 (38H, Phenyl). ^{13}C NMR (CD$_2$Cl$_2$): 14.27, 126.62, 126.72, 127.28, 127.77, 128.33, 128.62, 128.66, 129.10, 129.38, 131.10, 140.18, 140.95, 141.25. ^{31}P (CD$_2$Cl$_2$): 70.80 ($^{2}J_{\mathrm{P-P}} = 49.1$ Hz, $J_{\mathrm{P-Pt}} = 3920$ Hz, *trans* to N), 95.86 ($^{2}J_{\mathrm{PP}} = 49.1$ Hz, $J_{\mathrm{P-Pt}} = 1959$ Hz, *trans* to C).

4. Supplementary data

Full crystal structure information has been deposited with the Cambridge Crystallographic Data Center (deposition numbers CCDC 178035-CCDC 178038). Copies of this information are available upon request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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