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Six-membered cyclometallated derivatives of platinum(II) derived from 2-benzylpyridines. Crystal and molecular structure of [Pt(L)(Ph_3P)Cl] (HL = 2-(1-methylbenzyl)pyridine)

Giovanni Minghetti, Antonio Zucca, Sergio Stoccoro and Maria Agostina Cinellu

Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari (Italy)

Mario Manassero and Mirella Sansoni

Istituto di Chimica Strutturistica Inorganica, Università di Milano, Centro CNR, via Venezian 21, I-20133 Milano (Italy)

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Abstract

The reaction of $K_2[PtCl_4]$ with 2-(1-methylbenzyl)pyridine, HL, and 2-benzylpyridine, HL′, affords the cyclometallated species [{Pt(L)Cl}$_2$] (**1**) and [{Pt(L′)Cl}$_2$] (**2**), respectively. The chloride bridge in complex **1** can be split by neutral or anionic species to give the monomeric, [Pt(L)(Ph_3P)Cl], as two isomers, *trans*-P–Pt–C (**3**) and *trans*-P–Pt–N, (**4**), [Pt(L)(py)Cl] (**5**), [Pt(L)(CO)Cl] (**6**), [Pt(L)($CNCH_2SO_2C_6H_4CH_3$-4)Cl} (**7**), [Pt(L)(acac)] (Hacac = 2,4-pentanedione) (**8**), [Pt(L)(dppm)][BF_4] (dppm = bis(diphenylphosphino)methane) (**9**), [Pt(L)(dppe)][BF_4] (dppe = bis(diphenylphosphino)ethane) (**10**) and [Pt(L)(dipy)][BF_4](dipy = 2,2′-dipyridine) (**11**). Similarly, compound **2**, by reaction with Ph_3P, affords [Pt(L′)(Ph_3P)Cl], as two isomers, *trans*-P–Pt–C (**12**) and *trans*-P–Pt–N (**13**). Reaction of compounds **1** or **4** with $AgBF_4$ in acetonitrile affords [Pt(L)(CH_3CN)$_2$][BF_4] (**14**) or [Pt(L)(Ph_3P)(CH_3CN)][BF_4] (**15**). From these, [Pt(L)(Ph_3P)$_2$][BF_4] (**16**), [Pt(L)(Ph_3P)(CO)][BF_4] (**17**) and [Pt(L)(Ph_3P)(py)][BF_4] (**18**), can be obtained by displacement of the coordinated acetonitrile. The new complexes were characterized by IR, ^1H and ^{31}P NMR and FAB–MS spectroscopic techniques. The NMR spectra at room temperature of most of the species derived from HL give evidence for the presence in solution of two diastereomers **a** and **b**. The structure of one diastereomer of complex **4** has been solved by single crystal X-ray diffraction, **4b**. The platinum atom is in an almost square planar geometry with a P–Pt–N *trans* arrangement: Pt–N = 2.095(3), Pt–C = 1.998(4), Pt–P = 2.226(1) and Pt–Cl = 2.400(1) Å. The six-membered cyclometallated ring is in a boat conformation, with the CH_3 group in an equatorial position, *i.e* pointing away from the metal. Attempts to obtain [{Pt(L″)Cl}$_2$] (HL″ = 2-(dimethylbenzyl)pyridine), afforded an insoluble product heavily contaminated by platinum metal; treatment of this crude material with Ph_3P gave [Pt(L″)(Ph_3P)Cl] (**19**).

Key words: Platinum; Cyclometallation; X-ray structure

1. Introduction

Among the many cyclometallated derivatives of palladium(II) and platinum(II) stabilized by nitrogen donors [1], palladium(II) complexes derived from 2-benzyl- or 2(substituted benzyl)pyridines have been described previously by others [2] as well as by us [3]. Aspects of their reactivity with multiply bonded molecules such as CO and olefins have been also investigated [2,3]. In contrast, to our knowledge the reactions of such molecules with platinum(II) have not been reported. Here we describe a series of cyclometallated platinum(II) derivatives, neutral and cationic, **1**–**19**, which contain a six-membered ring, arising from direct activation of an aromatic C–H bond (Scheme 1).

As reported for 6-(1-methylbenzyl)-2,2′-dipyridine [4] only *ortho*-metallation occurs. Under our experimental conditions, there is no evidence for the activation of the CH_3 substituents to give five-membered cyclometallated species, in spite of the belief that the five-membered C–N ring is distinctly favoured [5]. Many factors can drive a reaction towards the formation of either five- or six-membered rings [6]. This has been the

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Correspondence to: Prof. G. Minghetti

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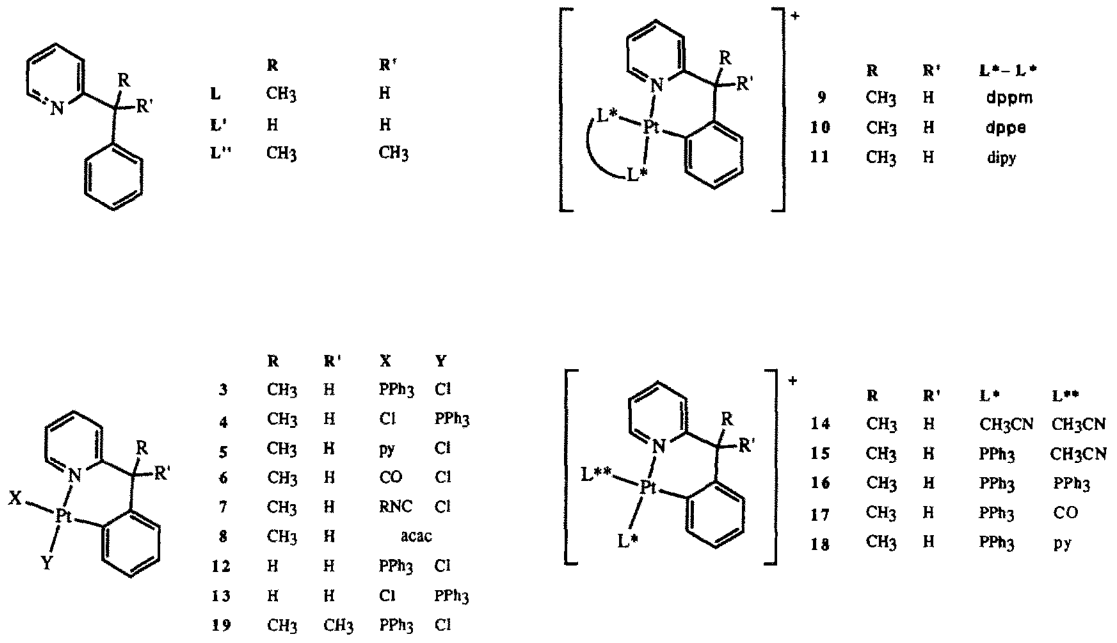


	R	R'
L	CH_3	H
L'	H	H
L''	CH_3	CH_3

	R	R'	L*–L*
9	CH_3	H	dppm
10	CH_3	H	dppe
11	CH_3	H	dipy

	R	R'	X	Y
3	CH_3	H	PPh_3	Cl
4	CH_3	H	Cl	PPh_3
5	CH_3	H	py	Cl
6	CH_3	H	CO	Cl
7	CH_3	H	RNC	Cl
8	CH_3	H	acac	
12	H	H	PPh_3	Cl
13	H	H	Cl	PPh_3
19	CH_3	CH_3	PPh_3	Cl

	R	R'	L*	L**
14	CH_3	H	CH_3CN	CH_3CN
15	CH_3	H	PPh_3	CH_3CN
16	CH_3	H	PPh_3	PPh_3
17	CH_3	H	PPh_3	CO
18	CH_3	H	PPh_3	py

Scheme 1.

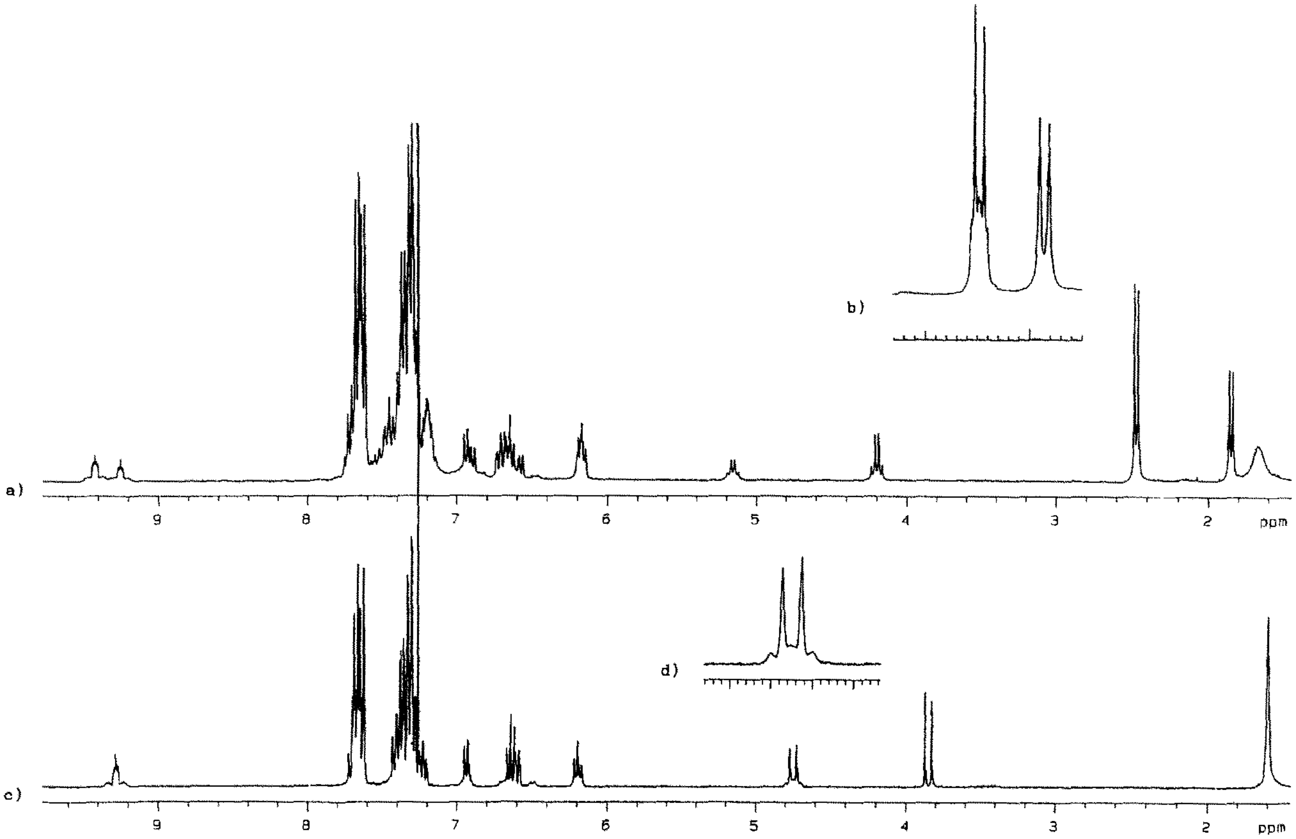


Fig. 1. (a) ^1H NMR spectrum of complex **4** (**4a** + **4b**) ($CDCl_3$, 300 MHz); (b) detail of the CH_3 region, at 80 MHz, showing the $^{195}Pt-^1H$ coupling in conformer **4a**, see text; (c) ^1H NMR spectrum of complex **13** ($CDCl_3$, 300 MHz); (d) expansion of the low field part of the AB system (CH_2) showing the coupling to ^{195}Pt, see text.

subject of many investigations, especially in palladium chemistry [7], often being associated with the relative ease of activation of an aromatic C–H compared to activation of a methyl C–H bond. A preliminary account of this work has appeared [8].

2. Results and discussion

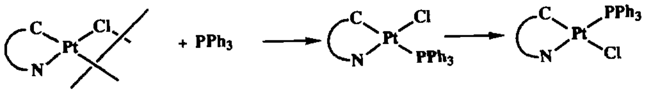
The complexes [{Pt(L)Cl}$_2$], (**1**) and [{Pt(L′)Cl}$_2$] (**2**) (HL = 2-(1-methylbenzyl)pyridine; HL′ = 2-benzylpyridine) were obtained by reaction of $K_2[PtCl_4]$ with the pyridines,

$$K_2[PtCl_4] + HL \rightarrow 1/2[\{Pt(L)Cl\}_2] + 2KCl + HCl$$

Under the experimental conditions, the metallated species **1** and **2** were the only products isolated and identified, albeit in *ca.* 50% yield. At variance with previous results in palladium chemistry [2,3], no adduct $[Pt(HL)_2Cl_2]$, was isolated. However, ^{1}H NMR spectra and TLC gave evidence that after recovery of the insoluble compounds **1** or **2**, several species are present in the mother solution. Attempts to separate them by crystallization or chromatography failed, so that their identity was not further investigated.

Pure adducts were also not obtained by reaction of *cis*- or *trans*-$[Pt(PhCN)_2Cl_2]$ with the pyridines. Even in this case, mixtures of products including metallated species were formed. The characterization of compounds **1** and **2** in solution was hampered by their insolubility. Their formulation rests on elemental analyses, and MS-FAB and IR spectra. In particular, the disappearence from the IR spectra of the absorption at 700 cm^{-1}, assigned in the free pyridines to an out-of-plane skeletal mode typical of a mono-substituted phenyl ring [9] is taken to be diagnostic of metallation. As a rule, the chloride bridge in complexes **1** and **2** is easily split by a variety of neutral or anionic donors to give mononuclear species amenable to characterization in solution. In all cases but one the bridge splitting reaction afforded only one of the two possible geometrical isomers.

The reaction of compound **1** with Ph_3P proceeds to the thermodynamic product, **4**, *trans*-N–Pt–P, *via* the isomer *trans*-C–Pt–P, **3**.



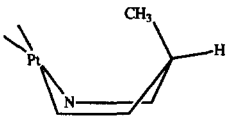
(1) (3) (4)

Complex **3** can be isolated in pure form by stopping the reaction a few minutes after the addition of Ph_3P. An excess of Ph_3P promotes isomerization of **3** to **4**. Similarly, two isomers are also observed in the reaction of [{Pt(L′)Cl}$_2$] with Ph_3P, but in this case isomerization to the stable P–Pt–N derivative, **13**, is very fast and the P–Pt–C isomer, **12**, can be detected only in solution (^{31}P NMR spectrum). In contrast, only the P–Pt–C isomer is obtained from [Pt(L″)(Ph$_3$P)Cl], (**19**). Steric effects may affect the stability of the 5-coordinate species which is likely to be the intermediate in the isomerization process.

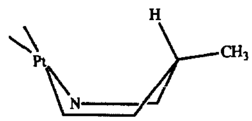
Both IR (ν(Pt–Cl), 339 (**3**), 282 (**4**), 282 (**13**) cm^{-1} [10]) and ^{31}P NMR spectra (^1J(Pt–P) < 1900 Hz (**3**, **12**, **19**), ^1J(Pt–P) > 4300 Hz (**4**, **13**) [11]) support the proposed geometries.

The six-membered cyclometallated ring adopts a boat-like conformation, as shown in the solid state by complex **4** (see later) and in solution by the ^{1}H NMR spectra. For instance, in complex **13** the CH$_2$ resonance displays an AB pattern. Such a pattern persists up to room temperature, inconsistent with the dynamic behaviour, involving rapid inversion of the metallacycle and observed for the analogous palladium(II) species. The last compound becomes rigid at low temperature [2a].

Consistent with a boat-like conformation, in most of the species derived from HL, two diastereomers (**a** and **b**) are observed in solution at ambient temperature.



a



b

The ^{31}P and ^{1}H (aromatic region) NMR spectra of the two diastereomers of complex **3** and **4** are very similar. In particular, both diastereomers of complex **4** exhibit the H(6) resonance at very low field (δ 9.42 (**a**) and 9.25 (**b**), ^3J(Pt–H) *ca.* 30 Hz) as expected for species having a chlorine near the proton H6 [12].

There are striking differences between the resonances of the two diastereomers of the substituents at the asymmetric benzylic carbon. The $\Delta\delta$ values are *ca.* 0.6 and 0.9 ppm for the CH$_3$ and the CH protons, respectively. The CH$_3$ resonance at lower field (doublet, δ 2.40 (**3**), 2.49 (**4**)) assigned to diastereomer **a**, which has the CH$_3$ group in a pseudo-axial position [13], shows at 80 MHz [14], a definite, albeit small, coupling to ^{195}Pt (J(Pt–H) 5–6 Hz), whereas no coupling (^4J(Pt–H)) is resolved for the corresponding CH resonance (quartet). This indicates some kind of long-range interaction between the CH$_3$ group and the metal atom [15].

In the other diastereomer, **4b**, the CH proton is more deshielded than in **4a**, but no Pt–H coupling is observed, suggesting at most, a very weak, metal–hydrogen interaction (see X-ray solid structure, complex **4b**). A possible interaction even with the CH group is supported by the ^1H NMR spectrum of complex **13** (HL′ = 2-benzylpyridine). This is rigid on the NMR time-scale at room temperature, and the resonance at lower field of the AB system due to the CH_2 protons, shows a significant coupling to ^{195}Pt ($J(Pt-H) = 16$ Hz).

Only one isomer is observed for the complexes **5–7**, [Pt(L)(L*)Cl] (L* = py, **5**; CO, **6**, RNC, **7**). Judged by the IR spectra, this is likely to be the *trans*-C–Pt–L* isomer. The carbonyl derivative, **6**, which contains a terminally bonded CO ($\nu(CO) = 2095$ cm^{-1}) [16] can be isolated in the solid state, unlike the palladium analogue described previously [3]. In that case, a species with a terminal CO group was detected in solution and supposed to be an intermediate in the reaction which leads to the eventual formation of a benzo[*b*]quinolizin-6-one, with extrusion of the metal. Reaction of compound **1** with thallium(I) acetylacetonate gives [Pt(L)(acac)], **8**, fluxional at room temperature. However, even in this case, two diastereomers are observed at −40°C (see ^1H NMR spectrum, Table 2).

Displacement of the chloride from **1** can also be achieved by reaction with bidentate donors in the presence of a poorly coordinating anion, such as BF_4. Thus, complexes [Pt(L)(L*-L*)][BF_4] (**9–11**) (L*-L* = dppm, bis(diphenylphosphino)methane (**9**), dppe, 1,2-bis(diphenylphosphino)ethane (**10**); dipy, 2,2′-dipyridine (**11**)) can be isolated in good yields. The FAB-MS spectra (positive ions) give evidence of the mononuclearity of the cations. The ^1H and ^{31}P NMR spectra of **10** and **11** indicate the existence of diastereomers. The J(Pt–P) values allow the assignment of the ^{31}P resonances to the ^{31}P atoms *trans* to N ($J(Pt-P) > 3500$ Hz) and to C ($J(Pt-P) < 1800$ Hz), respectively. The value (1305 Hz) of J(Pt–P) relative to the ^{31}P atom *trans* to C in complex **9** is very small. Cationic species with two-electron donors, $[Pt(L)(L^*)(L^{**})]^+$ ($L^* = L^{**} = CH_3CN$, **14**; $L^* = Ph_3P$, $L^{**} = CH_3CN$, **15**; $L^* = L^{**} = PPh_3$, **16**; $L^* = Ph_3P$, $L^{**} = CO$, **17** and $L^* = Ph_3P$, $L^{**} = py$, **18**) can be obtained by eqns. (1)–(4).

$$1/2[\{Pt(L)Cl\}_2] + AgBF_4 \xrightarrow{CH_3CN} [Pt(L)(CH_3CN)_2][BF_4] + AgCl \quad (1)$$

$$[Pt(L)(Ph_3P)Cl] + AgBF_4 \xrightarrow{CH_3CN} [Pt(L)(Ph_3P)(CH_3CN)][BF_4] + AgCl \quad (2)$$

$$[Pt(L)(Ph_3P)(CH_3CN)][BF_4] + L^{**} \rightarrow [Pt(L)(Ph_3P)(L^{**})][BF_4] \quad (3)$$

$$[Pt(L)(CH_3CN)_2][BF_4] + 2Ph_3P \rightarrow [Pt(L)(Ph_3P)_2][BF_4] \quad (4)$$

The species **15**, **17** and **18**, as obtained from isomer **4**, have a *trans* P–Pt–N arrangement ($J(Pt-P) > 4000$ Hz) and give rise to two diastereomers. Complex **16**, [Pt(L)($Ph_3P)_2$][BF_4], can be isolated from the reaction of either **3** or **4**. However, the ratios between the two diastereomers are not the same.

The bis(acetonitrile) complex [Pt(L)($CH_3CN)_2$][BF_4] (**14**) is remarkable. Two distinct resonances for the methyl protons of the CH_3CN are observed in the ^1H NMR spectra. One of them shows long-range coupling to ^{195}Pt ($^4J(Pt-H) = 11.5$ Hz) suggesting that one acetonitrile is more tightly bonded to the metal than the other. The former is likely to be the nitrile *trans* to the N atom. Investigations on the reactivity of this and related species are currently in progress.

2.1. Structure of compound 4b in the solid state

The structure consists of [Pt(L)(Ph_3P)Cl] molecules with no unusual Van der Waals contacts. An ORTEP view of the molecule is shown in Fig. 2. Principal bond parameters are listed in Table 4.

The coordination around the platinum atom is essentially square planar, with maximum deviations from the best plane of +0.085 (N1) and −0.095 (C9) Å. The dihedral angle between the Pt–Cl–P and Pt–N1–C9 planes is 6.6°. The N1–Pt–C9 angle is 85.1°. The Pt–P and Pt–C9 distances are normal (2.226(1) and 1.998(4) Å, respectively). The Pt–Cl bond, 2.400(1) Å, is rather long but well in keeping with the *trans*-influence of the aryl carbon atom. The Pt–N1 distance, 2.095(3) Å, is long if compared with those found in $C_{18}H_{15}ClN_2Pd$ [4] (Pd–N = 2.008(4) Å) and in $C_{24}H_{28}N_2O_8Pt$ [17] (Pt–N = 2.013(3) and 2.021(3) Å). In the first of these compounds, the pyridine nitrogen atom is *trans* to a chloride, and in the second two substituted pyridines are *trans* to each other. The observed lengthening is probably due to the *trans* influence of the phosphine, as suggested by a comparison with other M–N(sp^2) bonds *trans* to a phosphine (M = Pd or Pt). See, for instance, Pd–N 2.103(5) Å in [PdCl(C(O)-C_9H_6N)-(PPh_3)] [18] where the *trans* ligand is triphenylphosphine and Pt–N 2.160(2) Å in *trans*-[$PtCl_2L(PEt_3)$] (L = quinoline-8-carbaldehyde) where the *trans* ligand is triethylphosphine.

The six-membered metallacycle is in a boat conformation: the N1–C2–C8–C9 atoms are coplanar (maximum deviations from the best plane +0.024 and −0.024 Å), with the Pt and C7 atoms 0.950 and 0.716 Å above their plane, respectively. The observed Pt ··· H7 distance, 2.95(4) Å, is at the upper end of the accepted range (2.3–2.9 Å) reported for weak Pt ··· H long-range interactions [15c]

Bond parameters within the two aromatic rings are normal (see Table 4). The dihedral angle between their

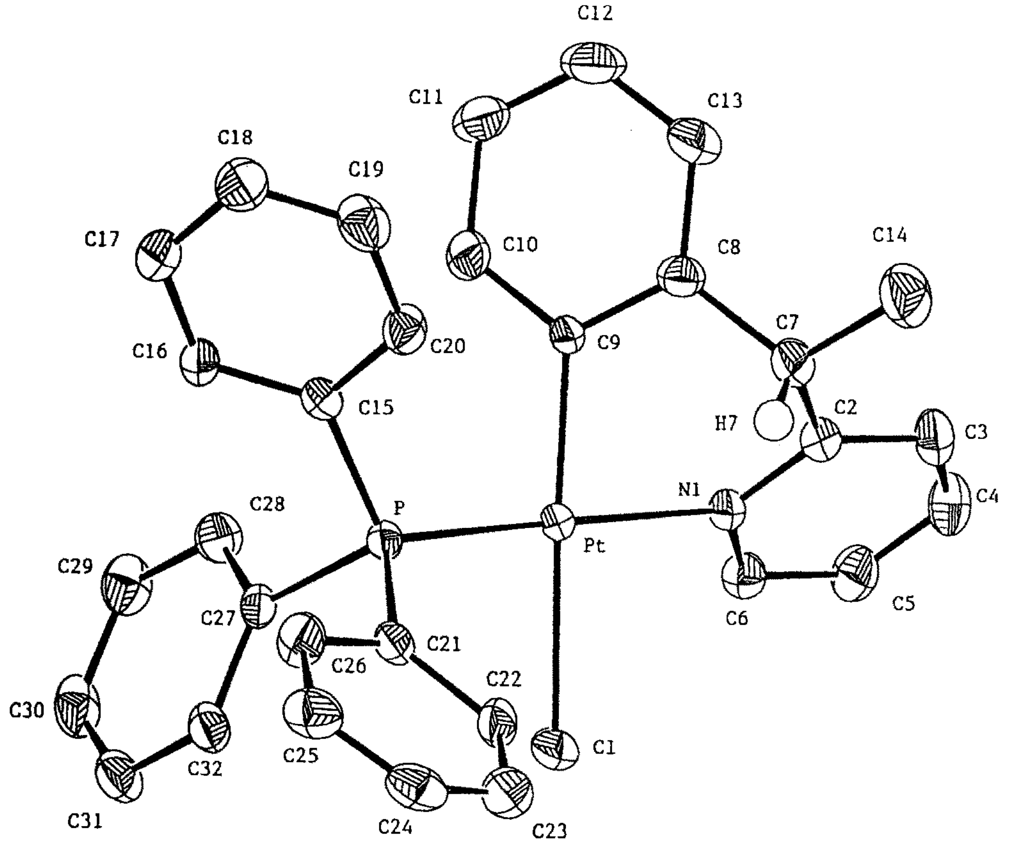


Fig. 2. ORTEP view of [Pt(L)(Ph$_3$P)Cl] **4b**.

TABLE 1. Analytical and other data

Compound		m.p. (°C)	Analytical data (found (calc) %)			IR (cm^{-1})
			C	H	N	
[Pt(L)(Cl)]$_2$ [a]	**1**	> 270	37.99 (37.81)	3.25 (2.91)	3.32 (3.39)	
[Pt(L')(Cl)]$_2$	**2**	> 270	35.55 (36.13)	2.57 (2.51)	3.05 (3.51)	
[Pt(L)(Ph$_3$P)Cl] (*trans*-P–Pt–C)	**3**	205–210	54.81 (55.15)	3.86 (4.00)	2.16 (2.07)	339 ν(Pt–Cl)
[Pt(L)(Ph$_3$P)Cl] (*trans*-P–Pt–N)	**4**	250–255	55.56 (55.15)	3.99 (4.00)	1.97 (2.07)	282 ν(Pt–Cl)
[Pt(L)(py)Cl]	**5**	186–189	43.30 (43.94)	3.43 (3.46)	5.51 (5.70)	331 ν(Pt–Cl)
[Pt(L)(CO)Cl]	**6**	> 270	38.20 (38.13)	2.98 (2.72)	3.10 (3.18)	341 ν(Pt–Cl); 2095 ν(CO)
[Pt(L)(RNC)Cl]	**7**	140–145	43.28 (43.45)	3.52 (3.46)	4.41 (4.61)	334 ν(Pt–Cl); 2190 ν(NC)
[Pt(L)(acac)]	**8**	128–130 (dec > 80)	44.67 (45.37)	4.15 (3.99)	3.00 (2.94)	
[Pt(L)(dppm)][BF$_4$]	**9**	196	53.12 (53.78)	3.94 (4.01)	1.91 (1.65)	1050b ν(BF$_4$)
[Pt(L)(dppe)][BF$_4$]	**10**	161	54.06 (54.30)	3.90 (4.18)	1.65 (1.62)	1050b ν(BF$_4$)
[Pt(L)(dipy)][BF$_4$]	**11**	208	44.90 (44.52)	3.22 (3.23)	6.57 (6.78)	1050b ν(BF$_4$)
[Pt(L')(Ph$_3$P)Cl] (*trans*-P–Pt–N)	**13**	204–205 (dec)	55.26 (54.50)	4.27 (3.78)	1.97 (2.12)	282 ν(Pt–Cl)
[Pt(L)(CH$_3$CN)$_2$][BF$_4$]	**14**	240–241	36.83 (37.37)	3.25 (3.30)	7.27 (7.69)	1050b ν(BF$_4$); 2290, 2310 ν(CN)
[Pt(L)(Ph$_3$P)(CH$_3$CN)][BF$_4$]	**15**	180–185	51.60 (51.64)	3.98 (3.91)	3.49 (3.65)	1050b ν(BF$_4$); 2300, 2320 ν(CN)
[Pt(L)(Ph$_3$P)$_2$][BF$_4$]	**16**	156–157 (dec)	58.80 (59.52)	4.47 (4.25)	1.46 (1.42)	1050b ν(BF$_4$)
[Pt(L)(Ph$_3$P)(CO)][BF$_4$]	**17**	162 (dec)	50.67 (50.94)	3.70 (3.58)	1.97 (1.86)	1050b ν(BF$_4$); 2112 ν(CO)
[Pt(L)(Ph$_3$P)(py)][BF$_4$]	**18**	151–152 (dec)	54.15 (53.67)	4.24 (3.98)	3.04 (3.48)	1050b ν(BF$_4$)
[Pt(L'')(Ph$_3$P)Cl] (*trans*-P–Pt–C)	**19**	200–202	55.10 (55.77)	4.10 (4.21)	1.89 (2.03)	333 ν(Pt–Cl)

[a] %Cl 8.50(8.60).

best planes is 68.5°. The phosphine does not show any unusual features.

3. Experimental details

Analytical and other data are reported in Table 1. ^{1}H and ^{31}P NMR data are collected in Tables 2 and 3, respectively.

HL was obtained as described previously [19], and HL′ was supplied by Aldrich. HL″ was prepared as described in Section 3.16. Thallium(I) acetylacetonate and toluene-4-sulfonylmethyl isocyanide were purchased from Strem and Fluka, respectively. Elemental analyses were performed (with a Perkin-Elmer Elemental Analyzer 240B) by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari) or by Pascher Mikroanalytisches Laboratorium, Remagen, Germany. Conductivities were measured with a Philips PW 9505 conductimeter. IR spectra were recorded with Perkin-Elmer 1310 and 983 spectrophotometers using Nujol mulls. The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9 (^{1}H) and 121.4 (^{31}P) MHz, or with a Bruker instrument operating at 80 and 32.4 MHz, respectively. Chemical shifts are given in ppm relative to internal tetramethylsilane (^{1}H) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained with a VG 7070 instrument operating under FAB conditions (positive ions) with 3-nitrobenzyl alcohol (NBA) as supporting matrix.

TABLE 2. ^{1}H NMR data [a]

Compound		Integral ratio	CH_3	CH	H(6) [b]	Aromatics	Other
HL			1.73 d (7.2)	4.31 q (7.2)	8.55	7.05–8.60	
HL				4.12 s	8.52	7.05–8.55	
HL′			1.74 s		8.57	7.05–8.60	
[Pt(L″)(Ph$_3$P)Cl] (*trans*-P–Pt–C)	**3a**	3	2.40 d (7.2) [c]	4.21 q (7.2)	8.07 (n.r.)	6.1–8.2	
	3b	2	1.82 d (7.2)	4.99 q (7.2)	8.17 (n.r.)		
[Pt(L)(Ph$_3$P)Cl] (*trans*-P–Pt–N)	**4a**	3	2.49 d (7.2) [d]	4.22 q (7.2)	9.42 (30–32)	6.1–9.5	
	4b	2	1.86 d (7.2)	5.18 q (7.2)	9.25 (28–30)		
[Pt(L)(py)Cl]	**5a**	5	2.51 d (7.1)	4.28 q (7.1)		6.8–8.9	
	5b	2	1.86 d (7.1)	5.00 q (7.1)			
[Pt(L)(CO)Cl]	**6a**	1	2.25 d (7.2)	4.30 br	8.95 (n.r.)	6.9–9.1	
	6b	1	1.87 d (7.2)	4.85 br	9.05 (n.r.)		
[Pt(L)(RNC)Cl] [e]	**7**		2.23 d (6.8)	4.45 q (6.8)	9.09 (52–54)	6.9–9.2	4.80 CH_2 (RNC), 2.47 CH_3 (RNC)
[Pt(L)(acac)]	**8**		2.12 br	4.36 br	8.95 (50–52)	6.9–9.1	1.98 CH_3 acac; 5.51 CH acac
T = 55°C			2.10 d (7.3)	4.35 q (7.3)	8.95 (50–52)	6.9–9.1	1.97 s, 1.96 s, CH_3 acac; 5.48 s CH acac
T = −40°C			2.21 d (7.0)	4.28 q (7.0)	8.91 (n.r.)	7.0–9.0	2.00 CH_3 acac; 5.56 CH acac
			1.80 d (7.0)	4.77 q (7.0)	8.83 (n.r.)		
[Pt(L)(dppm)][BF$_4$]	**9**		2.13 br	4.41 br	8.65 (35–40)	6.6–8.7	4.6–4.9 m CH_2 dppm
[Pt(L)(dppe)][BF$_4$]	**10**	3	1.81 d (7.2) [f]	4.22 q (7.2)	8.39 (35–36)	6.5–8.4	2.3–2.9 m CH_2 dppe
		1	1.88 d (7.1)	4.62 q (7.1)	8.07 (30–35)		
[Pt(L)(dipy)][BF$_4$]	**11a**	1	2.38 d (7.2) [g]	4.35 q (7.2)		7.0–9.0	
	11b	1	1.82 d (7.2)	4.88 q (7.2)			
[Pt(L′)(Ph$_3$P)Cl] (*trans*-P–Pt–N)	**13**			4.74 (13.7) [h] 3.84 (13.7)	9.28 (32)	6.15–9.3	
[Pt(L)(CH$_3$CN)$_2$][BF$_4$] [i]	**14**		2.20 br	4.29 br	8.81 (50)	6.9–8.9	2.58 [l] CH_3, 2.48 CH_3
[Pt(L)(Ph$_3$P)(CH$_3$CN)][BF$_4$] [i]	**15a**	2	2.48 d (7.3)	4.40 q (7.3)	8.97 (30–32)	6.3–9.1	1.85 CH_3CN
	15b	1	1.98 d (7.3)	5.10 q (7.3)	8.89 (30–35)		1.87 CH_3CN
[Pt(L)(Ph$_3$P)$_2$][BF$_4$] [i]	**16a**	1 [m]	2.72 d (7.3)	4.40 q (7.3)	8.22 (40)	6.1–8.3	
	16b	1	2.04 d (7.1)	5.31 q (7.1)	8.05 (35)		
[Pt(L)(Ph$_3$P)(CO)][BF$_4$]	**17a**	3	2.32 d (7.2)	4.42 q (7.2)	8.82 (n.r.)	6.3–9.0	
	17b	2	1.95 d (7.2)	4.99 q (7.2)	8.76 (n.r.)		
[Pt(L)(Ph$_3$P)(py)][BF$_4$] [i]	**18a**	2	2.72 d (7.1)	4.50 q (7.1)		6.3–8.7	
	18b	1	2.06 d (7.1)	n			
[Pt(L″)(Ph$_3$P)Cl] (*trans*-P–Pt–C)	**19**		2.73 s 1.95 s		8.21 (56–58)	6.05–8.3	

[a] Chemical shifts in ppm downfield from internal TMS, solvent $CDCl_3$ (unless otherwise stated), room temperature, coupling constants in Hz, n.r. = not resolved. [b] J(Pt–H) in parentheses. [c] J(Pt–H) = 5.5 Hz, see text. [d] J(Pt–H) = 5.7 Hz, see text. [e] RNC = toluene-4-sulfonylmethyl isocyanide. [f] J(Pt–H) = 4.4 Hz, see text. [g] J(Pt–H) = 5.9 Hz, see text. [h] J(Pt–H) = 16 Hz, see text. [i] Solvent CD_2Cl_2; [l] J(Pt–H) = 11.5 Hz. [m] Obtained according to eqn. (4). [n] Obscured by solvent (CD_2Cl_2).

TABLE 3. ^{31}P NMR data [a]

Compound		δ (J(Pt–P))		Integral ratio
[Pt(L)(PPh$_3$)Cl] (*trans*-P–Pt–C)	**3a**	24.18 (1895)		3
	3b	23.58 (1873)		2
[Pt(L)(PPh$_3$)Cl] (*trans*-P–Pt–N)	**4a**	17.11 (4430)		3
	4b	17.21 (4377)		2
[Pt(L)(dppm)][BF$_4$]	**9**	−30.36 (1305) [b]	−39.79 (3508)	
[Pt(L)(dppe)][BF$_4$]	**10**	46.63 (1727)	33.61 (3822)	3
		47.61 (1728)	34.31 (3786)	1
[Pt(L′)(PPh$_3$)Cl] (*trans*-P–Pt–C)	**12**	24.06 (1885)		
[Pt(L′)(PPh$_3$)Cl] (*trans*-P–Pt–N)	**13**	16.80 (4381)		
[Pt(L)(PPh$_3$)(CH$_3$CN)][BF$_4$] [c]	**15a**	14.58 (4234)		2
	15b	14.39 (4186)		1
[Pt(L)(PPh$_3$)$_2$][BF$_4$] [c]	**16a**	24.77 (1760) [d]	13.06 (4005)	1 [f]
	16b	23.94 (1767) [e]	11.73 (3958)	1
[Pt(L)(PPh$_3$)(CO)][BF$_4$] [c]	**17a**	17.14 (4394)		3
	17b	16.93 (4346)		2
[Pt(L)(PPh$_3$)(py)][BF$_4$] [c]	**18a**	16.56 (4306)		2
	18b	15.86 (4257)		1
[Pt(L″)(PPh$_3$)Cl] (*trans*-P–Pt–C)	**19**	24.85 (1902)		

[a] Chemical shifts in ppm downfield from external 85% H_3PO_4, room temperature, $CDCl_3$ (unless otherwise stated); coupling constants in Hz. [b] J(P–P) = 33 Hz. [c] Solvent CD_2Cl_2. [d] J(P–P) = 16 Hz. [e] J(P–P) = 16 Hz. [f] Obtained according to eqn. (4).

TABLE 4. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for compound **4b**

Pt–Cl	2.400(1)	Pt–P	2.226(1)
Pt–N1	2.095(3)	Pt–C9	1.998(4)
P–C15	1.832(4)	P–C21	1.832(4)
P–C27	1.826(4)	N1–C2	1.353(5)
N1–C6	1.339(5)	C2–C3	1.398(6)
C2–C7	1.528(6)	C3–C4	1.371(7)
C4–C5	1.352(7)	C5–C6	1.379(6)
C7–C8	1.541(6)	C7–C14	1.517(7)
C7–H7	0.99(4)	C8–C9	1.398(6)
C8–C13	1.388(6)	C9–C10	1.407(6)
C10–C11	1.390(6)	C11–C12	1.372(7)
C12–C13	1.405(7)		
C–C(phosphine, average)	1.379		
Pt···H7	2.95(4)		
Cl–Pt–P	89.80(4)	Cl–Pt–N1	89.29(9)
Cl–Pt–C9	171.9(1)	P–Pt–N1	176.6(1)
P–Pt–C9	96.2(1)	N1–Pt–C9	85.1(1)
Pt–P–C15	117.6(1)	Pt–P–C21	115.9(1)
Pt–P–C27	110.7(1)	C15–P–C21	99.9(2)
C15–P–C27	106.2(2)	C21–P–C27	105.2(2)
Pt–N1–C2	119.8(3)	Pt–N1–C6	119.8(3)
C2–N1–C6	120.3(4)	N1–C2–C3	118.5(4)
N1–C2–C7	116.8(4)	C3–C2–C7	124.6(4)
C2–C3–C4	120.3(5)	C3–C4–C5	120.2(5)
C4–C5–C6	118.5(4)	N1–C6–C5	122.2(4)
C2–C7–C8	106.6(4)	C2–C7–C14	114.1(4)
C2–C7–H7	110 (2)	C8–C7–C14	115.5(4)
C8–C7–H7	112 (2)	C14–C7–H7	99 (2)
C7–C8–C9	118.0(4)	C7–C8–C13	121.1(4)
C9–C8–C13	120.9(4)	Pt–C9–C8	119.2(3)
Pt–C9–C10	122.8(3)	C8–C9–C10	117.6(4)
C9–C10–C12	121.6(4)	C10–C11–C12	120.1(5)
C11–C12–C13	119.6(4)	C8–C13–C12	120.3(5)

3.1. Preparation of [{Pt(L)Cl}$_2$] (1)

To a solution of $K_2[PtCl_4]$ (871 mg, 2.1 mmol) in water (30 ml) was added 384 mg of racemic LH (2.1 mmol) and 6 ml of 2N HCl. The mixture was heated on a water bath for 8 days, then cooled. The pale yellow precipitate was filtered off and washed with water, ethanol, dichloromethane and diethyl ether to give the analytical sample (cream). Yield 50%. Mass spectrum (FAB): m/z 824 (M^+), 789 (M − Cl).

3.2. Preparation of [{Pt(L′)Cl}$_2$] (2)

The procedure described for complex **1** was followed, using L′ instead of L. Yield 50%. Mass spectrum (FAB): m/z 796 (M^+)

3.3. Preparation of [Pt(L)(Ph$_3$P)Cl] (3) (*trans*-P–Pt–C)

A chloroform suspension containing **1** (235 mg, 0.285 mmol) and Ph_3P (150 mg, 0.57 mmol) was stirred for 15 min at room temperature. The solution obtained was filtered and the filtrate concentrated to small volume. The cream precipitate formed by addition of diethyl ether was filtered off and recrystallized from chloroform/diethyl ether. Yield 75%. Mass spectrum (FAB): m/z 674 (M^+), 639 (M − Cl), 457 [M − L − Cl], 377 (M − Cl − Ph_3P).

3.4. Preparation of [Pt(L)(Ph$_3$P)Cl] (4) (*trans*-P–Pt–N)

A chloroform suspension of **1** (235 mg, 0.285 mmol) and Ph_3P (298 mg, 1.14 mmol) was stirred for 5 h at room temperature. The resulting solution was filtered and the filtrate concentrated to small volume. The cream precipitate formed by addition of diethyl ether was filtered off and recrystallized from chloroform/diethyl ether. Yield 80%. Mass spectrum (FAB): 674 (M^+), 639 (M − Cl), 457 (M − L − Cl), 377 (M − Cl − Ph_3P).

3.5. *Preparation of [Pt(L)(py)Cl] (5)*

To a suspension of complex **1** (67 mg, 0.08 mmol) in chloroform (20 ml) was added a solution of pyridine (63 mg, 0.8 mmol) in the same solvent (10 ml). The mixture was stirred at room temperature for 24 h, then filtered and the filtrate concentrated to small volume. The cream precipitate formed by addition of diethyl ether was filtered off and recrystallized from chloroform/diethyl ether. Yield 70–75%.

3.6. *Preparation of [Pt(L)(CO)Cl] (6)*

Carbon monoxide was bubbled for 3 h into a dichloromethane suspension of **1** (309 mg, 0.375 mmol) and stirred vigorously. The resulting solution was filtered and the filtrate concentrated to small volume. The white precipitate formed by addition of hexane was filtered off and washed with hexane. Yield 75%.

3.7. *Preparation of [Pt(L)(toluene-4-sulfonylmethyl isocyanide)Cl] (7)*

To a suspension of **1** (167 mg, 0.20 mmol) in dichloromethane (20 ml) was added a solution of toluene-4-sulfonylmethyl isocyanide (87 mg, 0.445 mmol) in the same solvent (10 ml). The mixture was stirred under reflux for 3 h. After cooling, the pale yellow precipitate obtained was collected and recrystallized from dichloromethane/diethyl ether. Yield 40%. Mass spectrum (FAB): m/z 607 (M^+), 572 (M − Cl), 377 (M − Cl − RNC).

3.8. *Preparation of [Pt(L)(acac)] (8)*

To a chloroform (20 ml) suspension of **1** (82.5 mg, 0.10 mmol) was added a chloroform solution containing 61 mg (0.20 mmol) of thallium(I) acetylacetonate. The mixture was stirred at room temperature for 90 min, then filtered and evaporated to dryness. The residue was extracted with diethyl ether. The extract was filtered and evaporated to dryness to give the analytical sample as a yellow solid. Yield 45%. Mass spectrum (FAB): 476 (M^+), 377 (M − acac), 294 (M − L).

3.9. *Preparation of [Pt(L)(dppm)][BF$_4$] (9), [Pt(L)(dppe)][BF$_4$] (10), [Pt(L)(dipy)][BF$_4$] (11)*

To a suspension of **1** (165.0 mg, 0.20 mmol) in acetone (30 ml) were added 0.40 mmol of the appropriate donor and 66 mg of $NaBF_4$ (0.6 mmol). The mixture was stirred at room temperature for 2 h, then filtered. The solution was concentrated to small volume and diethyl ether was added to give a crude product which was filtered and recrystallized from dichloromethane/diethyl ether. Compound **9**: yield 86% (cream) Λ_M (acetone, 5×10^{-4} M); 152 ohm^{-1} cm^2 mol^{-1}. Mass spectrum (FAB): m/z 761 (M^+), 579 [M − L], 377 [M − dppm]. Compound **10**: yield 83% (cream). Λ_M (acetone, 5×10^{-4} M); 122 ohm^{-1} cm^2 mol^{-1}. Mass spectrum (FAB): m/z 775 (M^+), 593 [M − L], 377 (M − dppe). Compound **11**: yield 84% (yellow) Λ_M (acetone, 5×10^{-4} M); 148 ohm^{-1} cm^2 mol^{-1}. Mass spectrum (FAB): m/z 533 (M^+), 351 (M − L).

3.10. *Preparation of [Pt(L′)(Ph$_3$P)Cl] (13)*

The procedure described for complex **4** was followed, using [{(L′)PtCl}$_2$] instead of [(L)PtCl]$_2$. Yield 80%. Mass spectrum (FAB): m/z 660 (M^+), 625 (M − Cl), 457 [M − L′ − Cl].

3.11. *Preparation of [Pt(L)(CH$_3$CN)$_2$][BF$_4$] (14)*

To a suspension of complex **1** (412 mg, 0.50 mmol) in CH_3CN (30 ml) was added a solution of $AgBF_4$ (195 mg, 1.00 mmol) in the same solvent. The mixture was stirred at room temperature for 2 h, then filtered to remove AgCl, and concentrated to small volume. The cream precipitate formed by addition of diethyl ether was filtered and washed with diethyl ether. Yield 90–95%. Λ_M (acetonitrile, 5×10^{-4} M); 148 ohm^{-1} cm^2 mol^{-1}. Mass spectrum (FAB): 459 (M^+), 418 (M − CH_3CN), 377 (M − 2CH_3CN).

3.12. *Preparation of [Pt(L)(Ph$_3$P)(CH$_3$CN)][BF$_4$] (15)*

To a solution of **4** (237 mg, 0.35 mmol) in CH_3CN (20 ml) was added a solution of $AgBF_4$ (0.35 mmol) in the same solvent. The mixture was stirred for 3 h, then filtered and the filtrate evaporated to dryness. The crude product was crystallized from dichloromethane/diethyl ether to give the analytical sample (cream). Yield 80%. Λ_M (acetone, 5×10^{-4} M); 144 ohm^{-1} cm^2 mol^{-1}. Mass spectrum (FAB): m/z 639 (M − CH_3CN), 457 [M − L − CH_3CN], 377 (M − Ph_3P − CH_3CN).

3.13. *Preparation of [Pt(L)(PPh$_3$)$_2$][BF$_4$] (16)*

(I) To a solution of compound **14** (54 mg, 0.10 mmol) in $CHCl_3$ (20 ml) was added a solution of Ph_3P (53 mg, 0.20 mmol) in the same solvent. The mixture was stirred for 5 h at room temperature, then filtered and the filtrate concentrated to small volume. The white precipitate formed by addition of diethyl ether was filtered and recrystallized from chloroform/diethyl ether. Yield 80–85%, Λ_M (acetone, 5×10^{-4} M); 131 ohm^{-1} cm^2 mol^{-1}.

(II) To a solution of compound **15** (55 mg, 0.07

mmol) in $CHCl_3$ (20 ml) was added a solution of Ph_3P (18.5 mg, 0.07 mmol) in the same solvent. The mixture was stirred for 6 h at room temperature, then concentrated to small volume. The precipitate formed after addition of diethyl ether was filtered off and recrystallized from dichloromethane/diethyl ether. Yield 85–90%.

3.14. Preparation of $[Pt(L)(Ph_3P)(CO)][BF_4]$ (17)

Carbon monoxide was bubbled for 2 h into a stirred solution of compound **15** (50 mg, 0.065 mmol) in dichloromethane (10 ml). From the filtered solution a precipitate was obtained by addition of diethyl ether. The crude product was filtered off washed with diethyl ether and recrystallized from dichloromethane/diethyl ether to give the analytical sample (cream). Yield 88%. Λ_M (acetone, 5×10^{-4} M); 140 ohm^{-1} cm^2 mol^{-1}. Mass spectrum (FAB): m/z 667 (M^+), 639 (M – CO), 457 (M – L – CO).

3.15. Preparation of $[Pt(L)(Ph_3P)(py)][BF_4]$ (18)

To a solution of compound **15** (76 mg, 0.10 mmol) in chloroform (20 ml) was added a solution of pyridine (7.9 mg, 0.10 mmol) in the same solvent. The mixture was stirred for 4 h at room temperature, then filtered and the filtrate concentrated to small volume. The white precipitate formed after addition of diethyl ether was filtered off and recrystallized from dichloromethane/diethyl ether. Yield 90–95%. Λ_M (acetone, 5×10^{-4} M); 137 ohm^{-1} cm^2 mol^{-1}.

3.16. Preparation of 2-(dimethylbenzylpyridine), HL″

To a solution containing 0.16 mol of lithium diisopropylamide in THF (200 ml) at −78°C was added 18.90 g of 2-(1-methylbenzyl)nitrile (0.144 mol). After stirring at −78°C for 1 h, CH_3I (1 : 1) was added. The solution was allowed to warm slowly to room temperature, treated with water and extracted with petroleum ether. The extract was filtered and the solvent was removed under reduced pressure. The residue was distilled in vacuo (110°C, 10^{-2} mbar) to give a colourless oil, $PhC(CH_3)_2CN$. Yield 70%. From the nitrile, HL″ was obtained as described in ref. 19.

3.17. Preparation of $[Pt(L'')(Ph_3P)Cl]$ (19)

Attempts to obtain complex $[\{Pt(L'')Cl\}_2]$ by reaction of $K_2[PtCl_4]$ and HL″ in water/HCl, as described for HL and HL′, failed. The reaction was carried out by adding to a solution of $K_2[PtCl_4]$ (536 mg, 1.29 mmol) in water (20 ml) the base (247.5 mg, 1.26 mmol) dissolved in THF (20 ml); the solution was stirred at 40°C for 2 h.

The precipitate which formed (180 mg), almost black due to the presence of platinum metal and insoluble in the most common solvents, was filtered off and washed with water, ethanol and diethyl ether. The crude material was added to a solution of Ph_3P (121 mg, 0.46 mmol) in chloroform (30 ml) and the mixture was stirred for 24 h. After filtration, the solution was concentrated to small volume. Addition of diethyl ether gave a dirty-white precipitate which was filtered off, washed with diethyl ether, and recrystallized from chloroform/diethyl ether. Yield 16%.

TABLE 5. Crystallographic data for compound **4b**

Compound	$Pt(L)(Ph_3P)Cl$
Formula	$C_{31}H_{27}Cl_1N_1P_1Pt_1$
F.W. (amu)	675.1
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	17.141(8)
b (Å)	9.318(2)
c (Å)	17.569(9)
β (°)	107.99(4)
V (Å^3)	2669(3)
Z	4
$D_{calc.}$ (g cm^{-3})	1.680
Crystal dimensions (mm^3)	$0.25 \times 0.33 \times 0.45$
Colour	Pale yellow
μ (Mo–Kα) (cm^{-1})	54.9
Min. transmission factor	0.85
Scan mode	ω
ω-scan width (°)	$1.4 + 0.35 \tan \theta$
θ-range (°)	3–27
Reciprocal space explored	+h, +k, ±1
Measured reflections	6140
Unique observed reflections with $I > 3\sigma(I)$	3450
Final R and R_W indices [a]	0.021, 0.024
No. of variables	320
GOF [b]	1.21

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $R_W = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}$. [b] GOF $= [\Sigma w(F_o - k|F_c|)^2/(N_{observations} - N_{variables})]^{1/2}$ $w = 1/(\sigma(F_o))^2$, $\sigma(F_o) = [\sigma^2(I) + (0.025I)^2]^{1/2}/2F_oL_P$.

3.18. X-ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 5. The diffraction experiment was carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo-Kα radiation (λ = 0.71073 Å) with a graphite crystal monochromator in the incident beam. The calculations were performed on a PDP 11/73 computer using the SDP Structure Determination Package [20] and the physical constants tabulated therein. No crystal decay was observed during data collection. The diffracted intensities were corrected for Lorentz, polarization and absorption effects (empirical correction) [21]. Scattering factors and anomalous dispersion corrections were taken from ref. 22. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, mini-

TABLE 6. Fractional atomic coordinates (with e.s.d.s in parentheses) for the refined atoms of compound **4b**

Atom	x	y	z	B (Å^2)
Pt	−0.16000(1)	0.25520(2)	0.02154(1)	2.452(2)
Cl	−0.13456(7)	0.3478(1)	−0.09606(6)	3.87(2)
P	−0.29253(6)	0.3075(1)	−0.03119(6)	2.45(2)
N1	−0.0363(2)	0.1957(4)	0.0664(2)	2.84(7)
C2	−0.0159(3)	0.0663(5)	0.1019(3)	3.4(1)
C3	0.0668(3)	0.0269(6)	0.1281(3)	4.6(1)
C4	0.1256(3)	0.1187(6)	0.1186(3)	5.1(1)
C5	0.1039(3)	0.2481(6)	0.0836(3)	4.2(1)
C6	0.0219(3)	0.2838(5)	0.0573(3)	3.5(1)
C7	−0.0859(3)	−0.0253(5)	0.1123(3)	3.9(1)
C8	−0.1281(3)	0.0649(5)	0.1617(3)	3.4(1)
C9	−0.1667(2)	0.1924(5)	0.1281(2)	2.69(8)
C10	−0.2003(3)	0.2787(5)	0.1757(3)	3.7(1)
C11	−0.1973(3)	0.2381(6)	0.2527(3)	4.7(1)
C12	−0.1598(3)	0.1121(7)	0.2845(3)	5.7(1)
C13	−0.1257(3)	0.0235(6)	0.2383(3)	5.0(1)
C14	−0.0602(4)	−0.1752(6)	0.1438(4)	5.6(1)
C15	−0.3610(2)	0.2610(5)	0.0271(2)	2.62(8)
C16	−0.4179(2)	0.3524(5)	0.0408(3)	3.2(1)
C17	−0.4711(3)	0.3047(6)	0.0810(3)	4.2(1)
C18	−0.4676(3)	0.1632(6)	0.1064(3)	4.8(1)
C19	−0.4107(3)	0.0726(5)	0.0928(3)	4.6(1)
C20	−0.3578(3)	0.1201(5)	0.0529(3)	3.7(1)
C21	−0.3459(3)	0.2177(4)	−0.1257(2)	2.86(9)
C22	−0.3027(3)	0.1411(5)	−0.1674(3)	3.4(1)
C23	−0.3446(3)	0.0650(5)	−0.2354(3)	4.4(1)
C24	−0.4284(3)	0.0651(6)	−0.2623(3)	4.5(1)
C25	−0.4716(3)	0.1416(6)	−0.2226(3)	4.5(1)
C26	−0.4303(3)	0.2187(5)	−0.1540(3)	4.1(1)
C27	−0.3067(2)	0.4992(4)	−0.0526(2)	2.70(9)
C28	−0.2819(3)	0.5943(5)	0.0110(3)	3.8(1)
C29	−0.2881(3)	0.7405(5)	−0.0019(3)	4.5(1)
C30	−0.3179(3)	0.7919(5)	−0.0794(3)	4.6(1)
C31	−0.3407(3)	0.6984(5)	−0.1425(3)	4.4(1)
C32	−0.3357(3)	0.5515(5)	−0.1293(3)	3.6(1)
H7	−0.124(2)	−0.051(4)	0.059(2)	2.5(8) *

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)\ [a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ab(\cos\gamma)\beta_{1,2} + ac(\cos\beta)\beta_{1,3} + bc(\cos\alpha)\beta_{2,3}]$.

* Atom was refined isotropically.

mizing the function $\Sigma w(F_o - k\,|\,F_c\,|)^2$. Anisotropic thermal factors were refined for all the non-hydrogen atoms. Atom H7 (see Fig. 2) was included in the last cycles of refinement. The other hydrogen atoms were placed in their ideal positions (C–H = 0.98 Å, B = 1.0 Å^2 higher than that of the C atom to which each of them is bonded) and not refined. The final Fourier map showed maximum residuals of 0.78 e Å^{-3} in the proximity of the metal atom. The atomic coordinates of the structure model are listed in Table 6. Full lists of data have been deposited with the Cambridge Crystallographic Data Centre.

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