Cyclometallated Derivatives of Platinum(II) derived from 6-(*tert*-Butyl)-2,2'-bipyridine (HL). Crystal and Molecular Structure of [Pt(L)Cl]†

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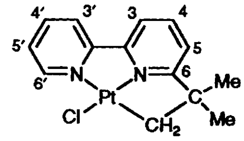
The reaction of $K_2[PtCl_4]$ with 6-(*tert*-butyl)-2,2'-bipyridine (HL) gave [Pt(L)Cl] **1a** a cyclometallated species resulting from direct activation of a methyl C–H bond. The structure has been determined by X-ray diffraction. The crystals contain two independent molecules: average values for the principal parameters are Pt–Cl 2.300, Pt–C 2.003, Pt–N (*trans* to C) 2.114 and Pt–N (*trans* to Cl) 1.948 Å. The chlorine atom in **1a** can easily be displaced by neutral ligands (L'); in the presence of $NaBF_4$ the cationic species $[Pt(L)(L')][BF_4]$ (L' = PPh_3 **2**, CO **3** or 3,5-dimethylpyridine **4**) were isolated in good yields. With potentially bidentate neutral ligands, L"–L" [$Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_2AsPh_2$ (dadpe) or $Ph_2PC{\equiv}CPPh_2$ (dppa)], $[LPt(\mu\text{-L}''\text{–L}'')PtL]^{2+}$ (L"–L" = dppe **5**, dadpe **6** or dppa **7**) or $[PtL(L''\text{–L}'')]^+$ species (L"–L" = dppe **8** or dadpe **9**) can be obtained by adequate choice of the L"–L": Pt molar ratio (1 : 2 or 1 : 1, respectively). The new complexes **1**–**9** were characterized in solution by ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR spectra.

6-Substituted-2,2'-bipyridines have been used as precursors of cyclometallated complexes containing terdentate N,N,C anionic ligands.[1] Cycloplatinated derivatives arising from direct activation of C–H aromatic bonds have been described both for five-[2] and six-membered metallated rings.[3] We have shown previously that, even with 6-(α-methylbenzyl)-2,2'-bipyridine, metallation involves the phenyl rather than the methyl substituent,[3] in spite of the extra stability often ascribed to five-membered rings.[4,5] Cycloplatinated species with Pt–C(sp^3) bonds are rare: examples derived from 2,2'-bipyridine (and related molecules) 6- (and 6,6'-) functionalized with $(CH_2)_n$-$CH(CO_2R)_2$ groups (*n* = 1 or 2, R = Me or Et) have been described by Newkome *et al.*[6] In the presence of alkali, the acidic hydrogen of the methinic group generates an intermediate carbanion from which the Pt–C(sp^3) bond is easily formed.

Here we report a series of platinum(II) complexes containing an N,N,C(sp^3) ligand obtained directly by reaction with 6-(*tert*-butyl)-2,2'-bipyridine, HL: the crystal structure of [Pt(L)Cl] **1a** determined by X-ray diffraction, is described in detail. The chloride ligand in complex **1a** is rather substitution labile: it can easily be substituted by anionic and neutral ligands such as I^-, PPh_3, CO, or 3,5-dimethylpyridine. The [5,5] fused bicyclic ring is robust: attempts to displace the external nitrogen atom from the metal, taking advantage of chelating ligands, were successful in one case only. A preliminary report of part of this work has been given.[7]

Results and Discussion

The ligand 6-(*tert*-butyl)-2,2'-bipyridine (HL) was synthesized from *tert*-butyl cyanide according to a general procedure described previously.[8] Complex **1a**, [Pt(L)Cl], was obtained by reaction of $K_2[PtCl_4]$ with HL in aqueous HCl at reflux temperature: yield *ca.* 80%. Adducts, $[Pt(HL)_nCl_2]$ (*n* = 1 or 2), were not isolated from the reaction mixture. In solution, complex **1a** was identified as a cyclometallated species mainly on the basis of NMR data. The ^1H and ^{13}C-{^1H} NMR spectra (see Tables 1 and 2) give clear evidence for a CH_2 group directly bonded to the platinum atom [^2J(Pt–H) = 84, ^1J(Pt–C) = 741 Hz]. In addition, in the ^1H NMR spectrum H(6') is strongly deshielded (δ 9.21, $CDCl_3$) with respect to the free bipyridine (δ 8.66), as often observed when a chlorine atom is in the proximity of the heterocyclic ring.[9]



1a

The assignment of the resonances in the ^1H and ^{13}C NMR spectra has been accomplished by two-dimensional ^1H–^1H correlation spectroscopy (COSY) and ^1H–^{13}C heteronuclear correlation (HETCOR) experiments, respectively. The ^{13}C spectrum deserves comment. In CD_2Cl_2 there are 12 of the expected 13 lines: the missing one is that of the quaternary carbon of the *tert*-butyl substituent, likely hidden under the methyl resonance. The CH_2 resonance, at higher field than the methyl, is strongly coupled to ^{195}Pt: the ^1J(Pt–C) value, 741 Hz, although comparable to that reported for five-membered cyclometallated species having a *trans* C(sp^3)–Pt–Cl arrangement,[10] 745 and 751 Hz, is rather large if the different *trans* influences of the two ligands (Cl and N) are taken into account. The value is large even when compared with those reported for methyl derivatives with pyridines *trans* to the C(sp^3) atom.[11]

In addition, the ^{195}Pt–^{13}C coupling constants relevant to the carbon atoms of the inner ring are much larger than those of the corresponding atoms of the other ring, *e.g.*

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Proton NMR data[a]

Compound	Solvent	Aromatics	CH$_2$[b]			CH$_3$	H(6′)	Other
1a [Pt(L)Cl]	CDCl$_3$	7.2–9.2	2.83	[84]		1.44	9.21	
1b [Pt(L)I]	CDCl$_3$	7.3–9.6	2.80	[77]		1.44	9.54	
2 [PtL(PPh$_3$)][BF$_4$]	CDCl$_3$	7.15–8.75	2.14	[68]	(3.0)	1.34		
3 [PtL(CO)][BF$_4$]	CDCl$_3$	7.6–8.9	2.96	[58]		1.53	8.86	
4 [PtL(3,5Me$_2$-py)][BF$_4$]	CDCl$_3$	7.3–8.5	2.59	[82]		1.46		2.45 CH$_3$ (3,5Me$_2$-py)
5 [Pt$_2$L$_2$(μ-dppe)][BF$_4$]$_2$	CD$_2$Cl$_2$	7.2–8.4	2.10	[63]	*c*	1.30		2.65–2.85 CH$_2$ (dppe)
6 [Pt$_2$L$_2$(μ-dadpe)][BF$_4$]$_2$	CD$_2$Cl$_2$	7.2–8.5	2.27[d]	[61]		1.35		2.7–2.9 CH$_2$ (dadpe)
			2.23[e]	[62]	(2.9)	1.37		
7 [Pt$_2$L$_2$(μ-(dppa)][BF$_4$]$_2$	CD$_2$Cl$_2$	7.0–8.5	2.36	[62]	(3.7)	1.34		
8 [PtL(dppe)][BF$_4$]	CDCl$_3$	6.8–8.15	2.15	[27]	*c*	1.28		2.2–2.4 CH$_2$ (dppe)
9 [PtL(dadpe)][BF$_4$]	CDCl$_3$	7.1–8.7	2.26	[63]	(2.9)	1.37		2.2–2.6 CH$_2$(dadpe)

[a] Room temperature, chemical shifts in ppm from internal SiMe$_4$, coupling constants in Hz. [b] ^2J(Pt–H) in square brackets, ^3J(P–H) in parentheses. [c] Not observed. [d] CH$_2$PtAs. [e] CH$_2$PtP.

Table 2 Proton and ^{13}C-{^{1}H} NMR data[a] for HL, **1a** and **3**

	HL	[Pt(L)Cl] **1a**		[PtL(CO)][BF$_4$] **3**	
	δ	δ	J^b/Hz	δ	J/Hz
(*a*) ^{1}H					
CH$_3$	1.43	1.44		1.53	
CH$_2$		2.83	84	2.96	58
H(6′)	8.66	9.21	10	8.86	17
H(5′)	7.28	7.69		7.83	
H(4′)	7.81	8.11		8.41	
H(3′)	8.54	8.00		8.73	
H(3)	8.21	7.72	11	8.59	8
H(4)	7.74	8.04		8.39	
H(5)	7.36	7.23	10	7.64	8
(*b*) ^{13}C					
CH$_3$	30.2	31.3	26	31.8	25
CH$_2$		19.0	741	24.3	573
C(6′)	148.8	147.7	19	151.9	29
C(5′)	123.3	127.3		129.6	14
C(4′)	136.6	138.1		142.2[c]	
C(3′)	121.1	121.8	12	125.6	12
C(3)	117.5	119.9	37	122.7	25
C(4)	136.9	135.8		143.9[c]	
C(5)	118.9	124.1	64	124.4	50
C(6)	168.3	178.0	104	175.9	105
C(2), C(2′)	154.3	152.8	25	154.6	23
	156.8	156.0	54	155.4	36
CO				169.9	1840

[a] Assignments based on COSY and HETCOR experiments, room temperature, CDCl$_3$, chemical shifts in ppm from internal SiMe$_4$. [b] J(Pt–H) or J(Pt–C). [c] Assignments of C(4) and C(4′) may be reversed.

^2J[Pt–C(6)] 104 *vs.* ^2J[Pt–C(6′)] 19 Hz. In agreement, the crystal structure of compound **1a** (see later) indicates that (*i*) the N–Pt–C angle [83.8(4)°] is closer to the ideal value than is the N–Pt–N angle [79.9(3)°], allowing a profitable Pt–C orbital overlap and hence a large J(Pt–CH$_2$) value, (*ii*) the pyridine ring involved in the cyclometallation is more tightly bonded than the other one.

The FAB mass spectrum (3-nitrobenzyl alcohol as matrix) of compound **1a** shows the molecular ion, M^+, at *m*/*z* 441. A peak with very low intensity at *m*/*z* 847, corresponding to $[M_2 - \text{Cl}]^+$, is likely to arise from interaction in the vapour phase between [Pt(L)Cl] and the [Pt(L)]$^{\cdot +}$ fragment.

Reaction of compound **1a** with an excess of sodium iodide in acetone solution neatly renders the analogous iodide, [Pt(L)I] **1b**. The isolation of **1b** allows us to assign the strong absorption observed at 337 cm^{-1} in the IR spectrum of **1a** to the Pt–Cl stretching vibration.[12]

Reaction of compound **1a** with neutral ligands L′ to give cationic species, [Pt(L)L′]$^+$, does not require displacement of the chloride ion by means of silver salts. This contrasts with the behaviour observed previously for cyclometallated species derived from 6-benzyl-substituted 2,2′-bipyridines.[13] In the presence of BF$_4^-$, complexes **2**–**4** (L′ = PPh$_3$ **2**, CO **3** or 3,5-dimethylpyridine **4**) were isolated in fairly good yields and characterized by elemental analyses, conductivity measurements and FAB mass, IR and NMR spectra. Complex **2**, [PtL(PPh$_3$)][BF$_4$], is obtained regardless of the ligand to Pt ratio (1 : 1 or 2 : 1), showing that the terdentate anionic ligand is rather robust. The carbonyl derivative, [PtL(CO)][BF$_4$] **3**, which contains a terminal CO [IR: ν(CO) 2101 cm^{-1}],[13,14] can be obtained under mild conditions, *i.e.* bubbling CO into an acetone solution of **1a**: it is fairly stable and can be isolated in the solid state. The ^{1}H and ^{13}C-{^{1}H} resonances are collected in Table 2. The ^1J[Pt–C(sp^3)] value, 573 Hz, is smaller than for complex **1a**, as expected owing to the substitution of a strong π-acceptor ligand (CO) for the Cl donor *cis* to the metal–carbon bond.[15]

The reactivity of compound **1a** with potentially bidentate ligands, L″–L″ [Ph$_2$P(CH$_2$)$_2$PPh$_2$ (dppe), Ph$_2$P(CH$_2$)$_2$AsPh$_2$ (dadpe) or Ph$_2$PC≡CPPh$_2$ (dppa)] has been investigated in order to establish whether square-planar mononuclear (with the N,N,C or the L″–L″ ligand acting as bi- or mono-dentate, respectively) or five-co-ordinated species were formed. The reaction can be driven toward two different types of products by an adequate choice of the ligand to platinum ratio. A 1 : 1 molar ratio gives mononuclear derivatives [PtL(L″–L″)]$^+$, while a 1 : 2 molar ratio renders dinuclear species containing L″–L″ as bridging ligands.[16]

The dinuclear species [LPt(μ-L″–L″)PtL][BF$_4$]$_2$ (L″–L″ = dppe **5**, dadpe **6** or dppa **7**) were characterized by elemental analyses and FAB mass spectra; the latter show both the $[M + \text{BF}_4]^+$ and $[M]^+$ ions. The NMR spectra (^{1}H and ^{31}P-{^{1}H}) at room temperature indicate highly symmetric systems. In particular the ^{31}P-{^{1}H} spectra (Table 3) show only one resonance with a pattern consistent with a dinuclear species.[18] Of the mono- and di-nuclear species, we believe the latter to be the more favoured. The mononuclear complexes [PtL(L″–L″)]$^+$ may be formed through substitution of one PtL(L″–L″) fragment brought about by an L″–L″ ligand [equation (1)]. Indeed, addition of dppe to complex **5** (1 : 1) gave

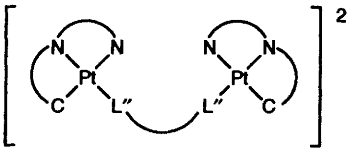
$$[\text{LPt(L}''\text{–L}'')\rightarrow\text{PtL}]^{2+} + \text{L}''\text{–L}'' \longrightarrow 2[\text{Pt(L)(L}''\text{–L}'')]^+ \quad (1)$$

8 quantitatively (^{31}P NMR criterion). We feel confident that **8** is a square-planar species resulting from chelation of the dppe ligand and displacement of the external pyridine ring. The ^{31}P-{^{1}H} NMR spectrum shows two resonances, rather broad at room temperature, both coupled to ^{195}Pt. On cooling, the spectrum sharpens: at −30 °C two resonances are observed with coupling constants ^1J(Pt–P) 4053 and 1787 Hz, consistent with phosphorus nuclei *trans* to N and C atoms, respectively.[19] The chemical shifts and ^1J(Pt–P) values are comparable with

Table 3 Phosphorus-31 NMR spectral data[a]

Compound	δ	J(Pt–P)/Hz	J(P–P)/Hz
2	20.6	4086	
5[b]	14.5	4041	52
6[b]	14.7	4039	
7[b]	−0.2	4200	*c*
8[d]	37.1	4053	6
	44.5	1787	6
9	15.0	4021	
10[e]	−3.1	4169	*c*
	−32.1		

[a] Room temperature, chemical shifts in ppm downfield from external 85% H_3PO_4, solvent $CDCl_3$ unless otherwise indicated. [b] Solvent CD_2Cl_2. [c] Not observed. For comments see ref. 17. [d] −30 °C. [e] Not isolated.



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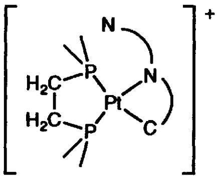

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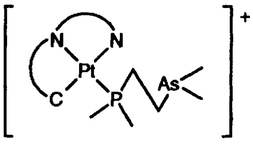

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those reported previously for [PtL′(dppe)]$^+$ [HL′ = 2-(α-methylbenzyl)pyridine].[20]

In contrast, in complex **9**, [PtL(dadpe)][BF_4], the potentially bidentate dadpe is likely to act as a monodentate ligand. The geometrical isomers which might be anticipated in the case of chelating behaviour (P *trans* to N or *trans* to C) are not observed. The $^{31}P-\{^1H\}$ NMR spectrum shows only one signal at δ 15.0, ^1J(Pt–P) 4021 Hz: both the chemical shift and the coupling constant are very similar to those observed for the dinuclear species **6**. In addition, in the ^1H NMR spectrum, the resonances assigned to the protons of the pyridine rings are almost superimposable on those of compound **2**, [PtL(PPh_3)]$^+$, suggesting that the external pyridine ring is still co-ordinated. Although a long-range interaction between the As and Pt atoms cannot be completely ruled out, on the whole the spectroscopic data are consistent with the proposed structure. Species like **8** are crowded molecules as suggested among other things by the broadness of the signals in the ^{31}P NMR spectrum at room temperature: thus, even small differences in steric hindrance could dictate a different behaviour of the ligands.

Finally we note that in the case of $Ph_2PC{\equiv}CPPh_2$ the mononuclear species [PtL($Ph_2PC{\equiv}CPPh_2$)]$^+$ **10** was not isolated. Even with a Pt : L″–L″ molar ratio of 1 : 1 a mixture (*ca.* 3 : 2) of di- and mono-nuclear species was formed, as inferred from the $^{31}P-\{^1H\}$ NMR spectrum.

Structure of Compound **1a**.—The structure consists of the packing of two crystallographically independent [Pt(L)Cl] molecules A and B separated by normal van der Waals interactions. An ORTEP[21] view of molecule A is shown in Fig. 1. Principal bond parameters for both molecules are listed in Table 4. Corresponding bond lengths in the two molecules are all equal within three standard deviations, whereas corresponding angles differ in only four cases for more than three but are all coincident within four standard deviations.

The co-ordination around the platinum atom is essentially square planar. The average N(2)–Pt–C(12) angle, 83.7°, is smaller than the ideal value of 90° as usually observed in five-membered metallacycles.[2a] The Pt–C(12) distances 2.000(11) in A and 2.006(11) Å in B are in good agreement with the Pd^{II}–C(sp^3) bond lengths, 2.026(3) and 2.029(3) Å, found in dimethyl(*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)-palladium(II),[22] where the Pd–C bonds are *trans* to sp^3 nitrogen atoms, but are significantly shorter than a number of Pd^{II}–C(sp^3) bond lengths *trans* to an sp^2 nitrogen atom reported by Newkome *et al.*[23] [see for instance Pd–C 2.090(6), 2.108(5) and 2.090(5),[23] 2.083 Å[1b]]. However, in all the latter molecules the aliphatic carbon atom bonded to palladium bears bulky substituents, and steric overcrowding may play a role in the observed lengthening of the Pd–C distances. The Pt–N(1) bond lengths, 2.117(7) in A and 2.112(7) Å in B, are long but well in keeping with the *trans* influence of the alkyl carbon atom [compare for instance Pd–N(1) 2.119(4) Å in ref. 3], whereas the Pt–N(2) bonds, 1.959(7) in A and 1.937(7) Å in B, are rather short but not unprecedented.[2a] The pentaatomic ring Pt–N(1)–C(5)–C(6)–N(2) is essentially planar in both molecules, whereas in the pentaatomic metallacycle the quasi planarity is limited to atoms Pt, N(2), C(10) and C(12), with C(11) lying above their best plane [0.24(1) in A and 0.38(1) Å in B]. The two pyridine rings are each strictly planar, and are twisted by 7.6 in A and 8.7° in B with respect to each other. Bond lengths within these rings are normal.

Experimental

Elemental analyses, conductance measurements, instrumentation and acquisition of spectroscopic data (IR, NMR and FAB mass) were as described elsewhere.[20]

Preparations.—[Pt(L)Cl] **1a**. To a solution of $K_2[PtCl_4]$ (0.415 g, 1.000 mmol) in water (50 cm^3) were added 6-(*tert*-butyl)-2,2′-bipyridine (0.212 g, 1.000 mmol) and 2 mol dm^{-3} HCl (5 cm^3). The mixture was heated on a water-bath until the solution was colourless; after cooling, the orange-yellow precipitate was filtered off, washed with water, ethanol and diethyl ether. The crude product was recrystallized from CH_2Cl_2–Et_2O, yield 81%, m.p. 210 °C (Found: C, 38.50; H, 3.45; N, 6.15. Calc. for $C_{14}H_{15}ClN_2Pt$: C, 38.05; H, 3.45; N, 6.35%). IR (Nujol): 1598s, 1564m and 337s cm^{-1}. FAB mass spectrum: m/z 441 ([M]$^+$) and 406 ([M − Cl]$^+$).

[Pt(L)I] **1b**. To an orange-yellow solution of complex **1a** (0.090 g, 0.200 mmol) in acetone (30 cm^3) was added KI (0.067 g, 0.225 mmol) with stirring. The mixture was stirred for 23 h at room temperature. The resulting solution was evaporated to dryness and the residue dissolved in CH_2Cl_2, filtered and evaporated to small volume. Addition of pentane gave the orange analytical sample, yield 65%, m.p. 164 °C (decomp.) (Found: C, 31.20; H, 2.85; N, 5.10. Calc. for $C_{14}H_{15}IN_2Pt$: C, 31.50; H, 2.80; N, 5.25%). IR (Nujol): 1596s and 1555m cm^{-1}.

[Pt(L)(PPh_3)][BF_4] **2**. To a solution of complex **1a** (0.099 g, 0.225 mmol) in acetone (25 cm^3) was added PPh_3 (0.059 g, 0.225 mmol) with stirring. To the resulting pale yellow solution solid $NaBF_4$ (0.100 g, 0.911 mmol) was added and the mixture stirred at room temperature. The solution was evaporated to dryness and the residue taken up with CH_2Cl_2. The solution was filtered and evaporated to small volume. Addition of diethyl ether gave the pale yellow analytical sample, yield 76%, m.p. 238 °C

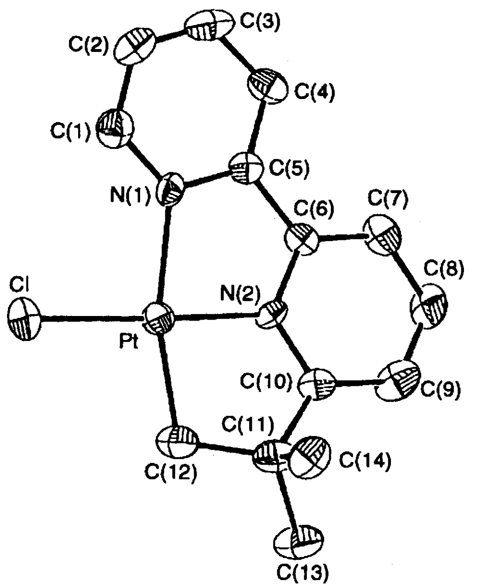

Fig. 1 An ORTEP view of molecule A of compound **1a**. Ellipsoids are drawn at the 30% probability level

Table 4 Principal bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for the two independent molecules of compound **1a**

	Molecule A	Molecule B
Pt–Cl	2.303(3)	2.298(3)
Pt–N(1)	2.117(7)	2.112(7)
Pt–N(2)	1.959(7)	1.937(7)
Pt–C(12)	2.000(11)	2.006(11)
Cl–Pt–N(1)	99.0(2)	98.2(2)
Cl–Pt–N(2)	178.6(2)	178.0(2)
Cl–Pt–C(12)	97.2(3)	98.4(3)
N(1)–Pt–N(2)	79.9(3)	80.0(3)
N(1)–Pt–C(12)	163.6(4)	163.2(4)
N(2)–Pt–C(12)	83.8(4)	83.5(4)

Table 5 Crystallographic data for compound **1a**

Formula	$C_{14}H_{15}ClN_2Pt$
M	441.8
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.392(3)
b/Å	16.188(7)
c/Å	14.047(4)
β/°	97.51(2)
U	2794(2)
Z	8
D_c/g cm^{-3}	2.101
Crystal dimensions/mm	0.31 × 0.38 × 0.43
Colour	Orange
μ(Mo-Kα)/cm^{-1}	103.3
Minimum transmission factor	0.44
Scan mode	ω
ω-Scan width/°	1.20 + 0.35 tan θ
θ range/°	3–25
Reciprocal space explored	$+h, +k, \pm l$
Measured reflections	5305
Unique observed reflections with $I > 3\sigma(I)$	2470
Final *R* and *R'* indices[a]	0.028, 0.030
No. of variables	325
Goodness of fit[b]	1.14

[a] $R = \Sigma(F_o - k|F_c|)/\Sigma F_o$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [b] $[\Sigma w(F_o - k|F_c|)^2/(N_{observations} - N_{variables})]^{\frac{1}{2}}$, $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = [\sigma^2\text{-}(I) + (0.03I)^2]^{\frac{1}{2}}/2F_oL_p$, L_p = Lorentz polarization.

(decomp.) (Found: C, 50.45; H, 3.95; N, 3.70. Calc. for $C_{32}H_{30}BF_4N_2PPt$: C, 50.85; H, 3.95; N, 3.80%). IR (Nujol): 1598s, 1564m and 1060vs (br) cm^{-1}. FAB mass spectrum: *m/z* 668 ([*M*]$^+$). Λ_M (5×10^{-4} mol dm^{-3}, acetone) = 134 Ω^{-1} cm^2 mol^{-1}.

[PtL(CO)][BF$_4$] **3**. Carbon monoxide was bubbled through a solution of complex **1a** (0.153 g, 0.350 mmol) in acetone (25 cm^3), with stirring and NaBF$_4$ (0.100 g, 0.911 mmol) was added. The mixture was kept at room temperature until a yellow solution was obtained. This was evaporated to dryness and the residue dissolved in CH_2Cl_2, filtered and evaporated to small volume. Addition of diethyl ether gave the yellow analytical sample, yield 76%, m.p. 183 °C (decomp.) (Found: C, 34.25; H, 2.90; N, 5.65. Calc. for $C_{15}H_{15}BF_4N_2OPt$: C, 34.55; H, 2.90; N, 5.40%). IR (Nujol): 2101vs, 1599s, 1558m and 1033vs (br) cm^{-1}. FAB mass spectrum: *m/z* 433 ([*M*]$^+$). Λ_M (5×10^{-4} mol dm^{-3}, acetone) = 160 Ω^{-1} cm^2 mol^{-1}.

[PtL(3,5Me$_2$-py)][BF$_4$] **4**. (3,5Me$_2$-py = 3,5-*dimethylpyridine*). To a solution of complex **1a** (0.101 g, 0.228 mmol) in acetone (25 cm^3) was added 3,5Me$_2$-py (0.025 g, 0.233 mmol) with stirring. Solid NaBF$_4$ (0.100 g, 0.911 mmol) was added and the mixture was refluxed for 3 d. The resulting solution was evaporated to dryness and the residue dissolved in CH_2Cl_2, filtered and evaporated to small volume. Addition of diethyl ether gave the yellow analytical sample, yield 77%, m.p. 208–210 °C (Found: C, 42.35; H, 4.10; N, 6.80. Calc. for $C_{21}H_{24}BF_4N_3Pt$: C, 42.00; H, 4.00; N, 7.00%). IR (Nujol): 1599s, 1558m and 1056vs (br) cm^{-1}. FAB mass spectrum: *m/z* 513 ([*M*]$^+$). Λ_M (5×10^{-4} mol dm^{-3}, acetone) = 154 Ω^{-1} cm^2 mol^{-1}.

[Pt$_2$L$_2$(μ-L″–L″)][BF$_4$]$_2$ (L″–L″ = dppe **5**, dadpe **6** *or* dppa **7**). To a solution of complex **1a** (0.150 g, 0.340 mmol) in acetone (30 cm^3), was added L″–L″ (molar ratio 2 : 1) with stirring. Solid NaBF$_4$ (0.150 g, 1.366 mmol) was added to the pale yellow solution and the mixture stirred for 3 h at room temperature. After evaporation to dryness the residue was dissolved in CH_2Cl_2, filtered and concentrated to small volume. Addition of diethyl ether gave the pale yellow analytical sample. Compound **5**: yield 82%, no decomposition up to 290 °C (Found: C, 47.15; H, 3.95; N, 4.05. Calc. for $C_{54}H_{54}B_2F_8N_4P_2Pt_2$: C, 46.85; H, 3.90; N, 4.05%); IR (Nujol) 1599s, 1567m and 1058vs (br) cm^{-1}; Λ_M (5×10^{-4} mol dm^{-3}, acetone) = 250 Ω^{-1} cm^2 mol^{-1}. Compound **6**: yield 76%, no decomposition up to 290 °C (Found: C, 45.00; H, 3.50; N, 4.10. Calc. for $C_{54}H_{54}AsB_2F_8N_4Pt_2$: C, 45.40; H, 3.80; N, 3.90%); IR (Nujol) 1599s, 1563m and 1056vs (br) cm^{-1}; FAB mass spectrum *m/z* 1254 ([*M*]$^+$) and 1340 ([*M* + BF$_4$]$^+$); Λ_M (5×10^{-4} mol dm^{-3}, acetone) = 240 Ω^{-1} cm^2 mol^{-1}. Compound **7**: yield 78%, m.p.: 138 °C according to ^{1}H NMR evidence contains 2 molecules of CH_2Cl_2 (Found: C, 43.00; H, 3.20; N, 3.90. Calc. for $C_{56}H_{54}B_2Cl_4F_8N_4P_2Pt_2$: C, 43.35; H, 3.50; N, 3.60%). IR (Nujol): 1599s, 1564m and 1056vs (br) cm^{-1}; FAB mass spectrum *m/z* 1206 ([*M*]$^+$) and 1292 ([*M* + BF$_4$]$^+$); Λ_M (5×10^{-4} mol dm^{-3}, acetone) = 234 Ω^{-1} cm^2 mol^{-1}.

[PtL(L″–L″)][BF$_4$] (L″–L″ = dppe **8** *or* dadpe **9**). To a solution of complex **1a** (0.0904 g, 0.205 mmol) in acetone (25 cm^3), was added L″–L″ (molar ratio 1 : 1) with stirring. To the resulting pale yellow solution solid NaBF$_4$ (0.110 g, 1.002 mmol) was added and the mixture stirred at room temperature. The solution was evaporated to dryness and the residue taken up with CH_2Cl_2, filtered and evaporated to small volume. Addition of diethyl ether gave the pale yellow analytical sample. Compound **8**: yield 75%, m.p. 265 °C (decomp.) (Found: C, 53.35; H, 4.10; N, 3.10. Calc. for $C_{40}H_{39}BF_4N_2P_2Pt$: C, 53.90; H, 4.40; N, 3.15%); IR (Nujol) 1599s, 1562s and 1056vs (br) cm^{-1}; FAB mass spectrum *m/z* 804 ([*M*]$^+$); Λ_M (5×10^{-4} mol dm^{-3}, acetone) = 126 Ω^{-1} cm^2 mol^{-1}. Compound **9**: yield

Table 6 Fractional atomic coordinates (with e.s.d.s in parentheses) for compound **1a**

Atom	*x*	*y*	*z*
Pt(A)	0.470 59(3)	0.105 77(3)	0.347 33(3)
Pt(B)	−0.007 99(3)	0.102 78(3)	−0.178 69(3)
Cl(A)	0.419 7(3)	0.048 0(2)	0.198 4(2)
Cl(B)	−0.035 1(3)	0.076 0(2)	−0.340 7(2)
N(1A)	0.598 2(5)	0.023 7(5)	0.398 3(6)
N(1B)	0.123 1(5)	0.020 8(5)	−0.140 3(6)
N(2B)	0.020 2(5)	0.124 1(5)	−0.042 0(5)
N(2A)	0.514 4(6)	0.152 2(5)	0.475 3(5)
C(1A)	0.637 6(8)	−0.035 3(7)	0.349 3(9)
C(1B)	0.173 5(8)	−0.026 1(7)	−0.199 3(8)
C(2A)	0.729(1)	−0.080 1(8)	0.388(1)
C(2B)	0.263 1(9)	−0.072 4(7)	−0.164 0(9)
C(3A)	0.776 4(9)	−0.060 6(9)	0.477(1)
C(3B)	0.298 5(8)	−0.072 6(7)	−0.070(1)
C(4B)	0.245 4(8)	−0.024 3(7)	−0.005 9(8)
C(4A)	0.733 6(8)	−0.000 4(8)	0.530 7(9)
C(5A)	0.642 5(7)	0.043 1(6)	0.488 3(7)
C(5B)	0.157 3(7)	0.021 3(6)	−0.044 5(7)
C(6B)	0.099 9(7)	0.078 2(6)	0.011 1(7)
C(6A)	0.595 9(7)	0.113 4(6)	0.532 6(7)
C(7A)	0.622 6(9)	0.142 1(8)	0.624 5(8)
C(7B)	0.120 1(8)	0.091 4(7)	0.108 7(7)
C(8B)	0.060 8(9)	0.152 4(8)	0.147 6(7)
C(8A)	0.573(1)	0.210 5(8)	0.655 7(8)
C(9A)	0.494 0(9)	0.248 2(7)	0.594 4(8)
C(9B)	−0.014 6(9)	0.199 7(8)	0.092 4(8)
C(10B)	−0.033 8(7)	0.186 2(7)	−0.006 1(7)
C(10A)	0.462 8(8)	0.220 2(6)	0.500 3(7)
C(11A)	0.384 2(8)	0.257 8(7)	0.424 7(8)
C(11B)	−0.104 0(8)	0.234 9(8)	−0.080 5(9)
C(12B)	−0.130 5(8)	0.183 0(8)	−0.173 3(8)
C(12A)	0.357 1(8)	0.194 3(8)	0.338 2(8)
C(13A)	0.280 1(9)	0.285 8(8)	0.464(1)
C(13B)	−0.208 9(9)	0.268 3(8)	−0.042(1)
C(14B)	−0.034 2(9)	0.312 0(8)	−0.100 2(9)
C(14A)	0.440(1)	0.334 6(9)	0.388(1)

81.4%, m.p. 165 °C (Found: C, 51.35; H, 4.10; N, 3.30. Calc. for $C_{40}H_{39}AsBF_4N_2PPt$: C, 51.35; H, 4.15; N, 3.00%); IR (Nujol) 1599s, 1567m and 1058vs (br) cm^{-1}; FAB mass spectrum *m*/*z* 848 ($[M]^+$); Λ_M (5×10^{-4} mol dm^{-3}, acetone) = 133 Ω^{-1} cm^2 mol^{-1}.

X-Ray Data Collection and Structure Determination of [Pt(L)Cl] **1a**.—Crystal data and other experimental details are summarized in Table 5. An Enraf-Nonius CAD-4 diffractometer was employed at room temperature with Mo-Kα radiation (λ = 0.710 73 Å) and a graphite-crystal monochromator in the incident beam. The calculations were performed on a PDP 11/73 computer using the SDP Structure Determination Package[24] 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).[25] Scattering factors and anomalous dispersion corrections were taken from ref. 26. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions (C–H 0.97 Å, B = 1.20 times that of the C atom to which the atom is bonded) and not refined. The final Fourier map showed maximum residuals of 0.80 e $Å^{-3}$ in the proximity of the metal atoms. The atomic coordinates are listed in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 (*a*) G. R. Newkome, M. Onishi, W. E. Puckett and W. A. Deutsch, *J. Am. Chem. Soc.*, 1980, **102**, 4557; (*b*) G. R. Newkome, W. E. Puckett, G. E. Kiefer, V. K. Gupta, F. R. Fronczek, D. C. Pantaleo, G. L. McClure, J. B. Simpson and W. A. Deutsch, *Inorg. Chem.*, 1985, **24**, 811; (*c*) G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kiefer, *Chem. Rev.*, 1986, **86**, 451.

2 E. C. Constable, R. P. G. Henney, T. A. Leese and D. A. Tocher, (*a*) *J. Chem. Soc., Chem. Commun.*, 1990, 513; (*b*) *J. Chem. Soc., Dalton Trans.*, 1990 443.

3 G. Minghetti, M. A. Cinellu, G. Chelucci, S. Gladiali, F. Demartin and M. Manassero, *J. Organomet. Chem.*, 1986, **307**, 107.

4 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.

5 I. Omae, *Organometallic Intramolecular-Coordination Compounds*, Elsevier, Amsterdam, 1986, p. 9.

6 G. R. Newkome, D. W. Evans, G. E. Kiefer and K. J. Theriot, *Organometallics*, 1988, **7**, 2537; G. R. Newkome, K. J. Theriot, F. R. Fronczek and B. Villar, *Organometallics*, 1989, **8**, 2513.

7 S. Stoccoro, G. Chelucci, M. A. Cinellu, A. Zucca and G. Minghetti, *J. Organomet. Chem.*, 1993, **450**, C15.

8 U. Azzena, G. Chelucci, G. Delogu, S. Gladiali, M. Marchetti, F. Soccolini and C. Botteghi, *Gazz. Chim. Ital.*, 1986, **116**, 307; C. Botteghi, G. Chelucci, G. Chessa, G. Delogu, S. Gladiali and F. Soccolini, *J. Organomet. Chem.*, 1986, **304**, 217.

9 P. K. Byers and A. J. Canty, *Organometallics*, 1990, **9**, 210.

10 P. S. Pregosin, F. Wombacher, A. Albinati and F. Lianza, *J. Organomet. Chem.*, 1991, **418**, 249.

11 B. E. Mann and B. F. Taylor, *^{13}C NMR Data for Organometallic Compounds*, Academic Press, London, 1981, pp. 47–50.

12 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley-Interscience, New York, 1986; T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.

13 M. A. Cinellu, S. Gladiali and G. Minghetti, *J. Organomet. Chem.*, 1989, **363**, 401.

14 F. Calderazzo and D. Belli Dell'Amico, *Inorg. Chem.*, 1981, **20**, 1310.

15 A. Albinati, U. von Gunten, P. S. Pregosin and H. Ruegg, *J. Organomet. Chem.*, 1985, **295**, 239.

16 J. Dehand, M. Pfeffer and M. Zinsius, *Inorg. Chim. Acta*, 1975, **13**, 229; G. R. Newkome, D. K. Kohli and F. R. Fronczek, *J. Am. Chem. Soc.*, 1982, **104**, 994; J. M. Vila, M. Gayoso, A. Fernandez, N. A. Bailey and H. Adams, *J. Organomet. Chem.*, 1993, **448**, 233.

17 I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1982, 1915.

18 A. A. Kiffen, C. Masters and J. P. Visser, *J. Chem. Soc., Dalton Trans.*, 1975, 1311; I. J. Colquhoun, H. C. E. McFarlane, W. McFarlane, J. A. Nash, R. Keat, D. S. Rycroft and D. G. Thompson, *Org. Magn. Reson.*, 1979, **12**, 473.

19 P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, 1979.

20 G. Minghetti, A. Zucca, S. Stoccoro, M. A. Cinellu, M. Manassero and M. Sansoni, *J. Organomet. Chem.*, 1994, **481**, 195.

21 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

22 W. de Graaf, J. Boersma, W. J. J. Smeets, A. L. Spek and G. van Koten, *Organometallics*, 1989, **8**, 2907.

23 G. R. Newkome, Y. A. Frere, M. Onishi, V. K. Gupta and F. R. Fronczek, *Organometallics*, 1986, **5**, 348.

24 B. A. Frenz and Associates, SDP PLUS, Version 1.0, Enraf-Nonius, Delft, 1980.

25 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

26 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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