Metallation of Unactivated Methyl Groups − Platinum(II) Derivatives with 6-Alkyl-2,2′-bipyridines

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The reaction of $K_2[PtCl_4]$ with three 6-alkyl-2,2′-bipyridines HL, ($N_2C_{10}H_7R$; R = CH_2Me, HL^{et}; $CHMe_2$, HL^{ip}; CH_2CMe_3, HL^{np}) affords five- and six-membered cyclometallated complexes [Pt(L)Cl] where L is a terdentate *N*,*N*,*C* anionic ligand which originates from HL through direct activation of a $C(sp^3)$–H bond. In the case of HL^{ip}, metallation generates a stereogenic carbon atom β to the metal. Complex **5**, $[Pt(L^{np})Cl]$, having an uncommon six-membered ring containing a Pt–$C(sp^3)$ bond, was studied in depth in solution, by means of 1- and 2- dimensional NMR spectroscopy, and in the solid state by X-ray diffraction. Differences are observed in the behaviour of these ligands: thus with HL^{et} an adduct, $[Pt(HL^{et})Cl_2]$, was also isolated and its structure was determined by X-ray diffraction. In the metallated species, the fourth ligand, Cl, can easily be substituted by neutral or anionic ligands (CO, PPh_3, CN^-). The metallated species react with potentially bidentate ligands L′–L′′ [$Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_2AsPh_2$ (dppae)] to give, with different Pt:L ratios, mononuclear $[Pt(L)(L'–L'')]^+$ or dinuclear $[(L)Pt(\mu–L'–L'')Pt(L)]^{++}$ cationic species. In the second case an uncommon unsupported L′–L′′ bridge is present. The cyclometallated species are stable in air and moisture, and the *N*,*N*,*C* system is rather robust.

Introduction

Cyclometallated compounds, in particular those derived from nitrogen ligands, have attracted considerable interest as a consequence of the wide range of their potential applications in many areas including organic synthesis,[1] homogeneous catalysis[2] (even asymmetric), photochemistry[3], and the design of new metallomesogens[4], sensors[5] and antitumour drugs.[6]

In recent years, in addition to the classical bidentate N,C systems, attention has also been devoted towards potentially terdentate-bound anionic ligands able to coordinate through different sets of donor atoms (e.g. *N*,*N*,*C*,[7] *N*,*C*,*N*,[8] *C*,*N*,*C*[9]). The sequence of coordinating atoms, the size of the metallacycles and the type of metallated carbon atom can be tuned to obtain complexes with different properties.

Although cyclometallation reactions, especially those concerning metals of the platinum group, have been extensively studied, the factors that control the process are not completely understood. Whereas for Pd^{II} the most common mechanism is electrophilic, in the case of Pt^{II} both electrophilic and nucleophilic behaviour has been ascertained.[10] The reaction, besides the obvious electronic and steric factors, seems to be affected by a number of factors: we have shown in previous papers that even subtle differences in the substituents of the ligands can drive the cyclometallation reactions towards unpredictable results.[7a]

In general, nitrogen donor ligands show a strong tendency to form five-membered rings, although a few six-membered rings are known. The great majority of papers in this field concern $C(sp^2)-H$ bond activation, in spite of the present interest in activation of alkyl groups. Only few cyclometallated species containing nitrogen ligands and $C(sp^3)-Pt$ bonds are known and, to the best of our knowledge, only two six-membered cyclometallated species with a $Pt-C(sp^3)$ bond have been described,[11] but none of them derives from a true C−H activation.

Here we describe a series of platinum(II) complexes containing terdentate bound anionic ligands with an *N*,*N*,*C*(sp^3) sequence of donor atoms obtained by the direct activation of a methyl group of 6-alkyl-2,2′-bipyridines. The substituents on the bipyridines have been chosen in order to compare five and six-membered rings. In addition, one of the ligands (HL^{ip}, $N_2C_{10}H_7CHMe_{2}$–6), is potentially able to give a stereogenic carbon atom directly by metallation.

Depending on the ligand and the reaction conditions both adducts $[Pt(HL)Cl_2]$ and five- or six-membered cyclo-

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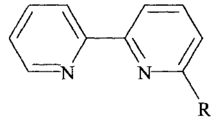
metallated species, [Pt(L)Cl], can be obtained from $K_2[PtCl_4]$. The chloride ligand in the metallated species has been found to be rather substitution labile, so that its replacement by anionic or neutral ligands as CN^-, CO or PPh_3 has been studied. We also report on the reaction with the potentially chelating ligands L′−L′′ [$Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_2AsPh_2$ (dppae)] with 1:1 and 2:1 Pt/L′−L′′ molar ratios.

The behaviour of $[PtCl_4]^{2-}$ is compared with that of $[PdCl_4]^{2-}$, which is previously described.[7a]

Results and Discussion

The ligands 6-ethyl-2,2′-bipyridine (HL^{et}), 6-isopropyl-2,2′-bipyridine (HL^{ip}) and 6-neopentyl-2,2′-bipyridine (HL^{np}) were obtained as previously described.[12]



R	
CH_2CH_3	HL^{et}
$CH(CH_3)_2$	HL^{ip}
$CH_2C(CH_3)_3$	HL^{np}

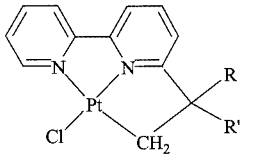
The activation of one $C(sp^3)-H$ bond was achieved with HL^{ip} and HL^{np}, in high yields (ca. 90%), by reacting the ligand with $K_2[PtCl_4]$ in aqueous HCl under refluxing conditions. In the case of HL^{et} the metallation, possibly owing to the presence of only one methyl group, is more difficult and a mixture of the metallated complex $[Pt(L^{et})Cl]$ (**2**) and the adduct $[Pt(HL^{et})Cl_2]$ (**1**), is obtained. We recently reported[7a] that the analogous reactions of these ligands with $Na_2[PdCl_4]$ give only the adducts $[Pd(HL)Cl_2]$: C−H activation however can be easily obtained from $[Pd(OAc)_2]$. A peculiar behaviour is observed with a forth ligand HL^{tb} (R = $C(CH_3)_3$]: activation of a methyl group by reaction with $[PdCl_4]^{2-}$ occurs even at room temperature, whereas refluxing conditions are needed with $[PtCl_4]^{2-}$.

The adduct $[Pt(HL^{et})Cl_2]$, **1**, can also be synthesised from *cis*-$[Pt(DMSO)_2Cl_2]$ (see the Exp. Sect.) in fairly good yields. The ^1H NMR spectrum (see Table 1) shows all the expected resonances: in particular the 6′-H and the CH_2 protons are strongly deshielded with respect to the free ligand ($\Delta\delta = 0.95$ and 0.83 ppm, respectively) as is often observed when a chlorine atom is coordinated in their proximity. In addition the 6′-H is strongly coupled to platinum ($^3J_{Pt-H} = 40$ Hz), providing evidence for the coordination of the nitrogen atom of the unsubstituted pyridine ring. Complex **1** was characterised in the solid state by X-ray diffraction.

The structure consists of the packing of $[Pt(HL^{et})Cl_2]$ molecules with no unusual van der Waals contacts. There are two crystallographically independent molecules, A and B, in the asymmetric unit. Selected bond lengths and angles for the two molecules are reported in Table 4. An ORTEP view of molecule A is shown in Figure 1. The platinum atom displays a square-planar coordination with a slight square-pyramidal distortion. The displacement of the metal atom from the best plane of atoms Cl(1), Cl(2), N(1), and N(2) is 0.090(1) Å in molecule A and 0.111(1) Å in molecule B. Corresponding bond lengths and angles in the two molecules are all very similar (see Table 4). The Pt−Cl(1) and Pt−Cl(2) distances, (average 2.298 and 2.284 Å, respectively) are both in good agreement with the Pt−Cl bond length, 2.299(2) Å, found in $[PtCl(Me)(HL^{et})]$, compound **19**.[13] The Pt−N(2) distance, average 2.050 Å, is longer than the Pt−N(1) one, average 1.996 Å, and the Cl(1)−Pt−N(2) angle, average 100.5°, is much larger than the Cl(2)−Pt−N(1) angle, average 92.7°. Both effects are probably due to the steric hindrance of the ethyl substituent on atom C(10). An even larger Cl−Pt−N(2) angle, 103.1(1)°, had been found in **19**. It must be observed that in compound **19** a clear intramolecular hydrogen bond was found between a CH_2 hydrogen atom and the Cl ligand (Cl···H 2.28 Å, C(11)−H···Cl angle 160.4°, see ref.[13]). There is no such hydrogen bond in either of the two present independent molecules, which exhibit different conformations of the ethyl substituent, with a shortest Cl(1)···H distance of 2.52 Å and a C(11)−H···Cl(1) angle of 126.6° in molecule B.

Metallated Compounds

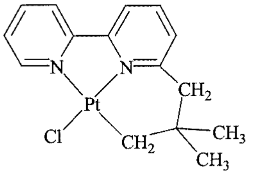
From $K_2[PtCl_4]$ the metallated compounds $[Pt(L^{ip})Cl]$ (**3**) and $[Pt(L^{np})Cl]$ (**5**) have been obtained in pure form, whereas isolation of complex **2** requires separation from adduct **1** by column chromatography. The synthesis of complex **4** has been previously reported.[7b]



2 R = R' = H

3 R = H, R' = CH_3

4 R = R' = CH_3



5

Metallation entails a $C(sp^3)-H$ activation to give a five-membered cycle in the case of compounds **2**, **3** and **4**, and a less common six-membered ring in the case of complex **5.** To the best of our knowledge this is the first six-membered cyclometallated species of platinum(II) with nitrogen donors originating directly from an unactivated $C(sp^3)-H$ bond: two precedent reports involved a benzylic C−H bond[11a] and an acidic C−H group in the presence of alkali.[11b]

The metallated species were fully characterised by analytical and spectroscopic methods. In particular NMR spectroscopy (^1H and $^{13}C\{^1H\}$) gives evidence for a methylenic

Table 1. Proton NMR spectroscopic data[a]

		CH_3	CH_2-Pt	CH_2-C, CH_2-P/As	CH	H(6′)	other aromatics
$Pt(HL^{et})Cl_2$	**1**	1.43 (t, 3 H) (7.5)		3.73 (q, 2 H) (7.5)		9.65 (dd, 1 H) [40]	7.4−8.2 (m, 6 H)
$Pt(L^{et})Cl$	**2**		2.96 (t, 2 H) (6.4)[85]	3.92 (t, 2 H) (6.4) [31]		9.23 (ddd, 1 H) [10]	7.4−8.35 (m, 6 H)
$Pt(L^{ip})Cl$	**3**	1.46 (d, 3 H) (7.2)	2.66 (dd 1 H) (12.0, 5.6) [89] 3.07 (dd 1 H) (12.0, 7.5) [79]		3.45 (m, 1 H)	9.21 (ddd, 1 H) [12]	7.25−8.25 (m, 6 H)
$Pt(L^{np})Cl$	**5**	1.09 (s, 6 H)	2.43 (s, 2 H) [87]	2.82 (s, 2 H)		9.56 (ddd, 1 H) 10]	7.28−8.10 (m, 6 H)
$[Pt(L^{ip})(CN)$	**6**	1.42 (d, 3 H) (7.1)	2.57 (dd, 1 H) (12.9, 5.5) [78] 3.01 (dd, 1 H) (12.9, 7.2) [64]		3.54 (m, 1 H)	9.08 (dd, 1 H) [15]	7.40−8.18 (m, 6 H)
$[Pt(L^{ip})(CO)][BF_4]$	**7**	1.54 (d, 3 H) (7.0)	2.83 (dd,1 H) (12.2, 5.6) [66] 3.25 (dd, 1 H) (12.2, 6.6) [52]		3.88 (m, 1 H)	8.85 (ddd, 1 H) [15]	7.68−8.55 (m, 6 H)
$[Pt(L^{np})(CO)][BF_4]$	**8**	1.17 (s, 6 H)	2.50 (s, 2 H) [52]	3.14 (s, 2 H)		8.76 (dd, 1 H) [n.r]	7.58−8.82 (m, 6 H)
$[Pt(L^{et})(PPh_3)][BF_4]$	**9**		2.21 (td, 2 H) (6.2) [71]{2.7}	3.97 (t, 2 H) (6.2) [35]		[c]	7.14−8.71 (m, 7 H)
$[Pt(L^{ip})(PPh_3)][BF_4]$	**10**	1.43 (d, 3 H) (7.1)	2.08 (ddd, 1 H) (12.4, 6.8){3.4}[n.r.] 2.24 (ddd, 1 H) (12.4, 5.6){2.2}[n.r.]		3.52 (m, 1 H)	[c]	7.14−8.69 (m, 22 H)
$[Pt(L^{np})(PPh_3)][BF_4]$	**11**	0.86 (s, 6 H)	1.60 (d, 2 H) {7.1} [67]	2.91 (s, 2 H)		[c]	6.94−8.72 (m, 22 H)
$[Pt_2(L^{np})_2(\mu\text{-dppm})][BF_4]_2$	**12**	0.93 (s, 12 H)	1.52 (d, 4 H) {6.5} [60]	2.65 (s, 4 H) (bipy) 3.71 (t, 2 H) {12.2} (dppm)		[c]	6.97−8.35 (m, 34 H)
$[Pt_2(L^{ip})_2(\mu\text{-dppe})][BF_4]_2$	**13**	1.33 (d, 6 H) (7.2)	2.12 (m, 2 H) 2.28 (m, 2 H)	2.81 (m, 4 H)	3.53 (m, 2 H)	[c]	7.24−8.42 (m, 34 H)
$[Pt_2(L^{np})_2(\mu\text{-dppe})][BF_4]_2$	**14**	0.81 (s, 12 H)	1.61 (d, H) [60] {ca 5.0}	2.94 (s, 4 H) (bipy) 2.72 (m, 4 H) (dppe)		[c]	6.94−8.42 (m, 34 H)
$[Pt_2(L^{np})_2(\mu\text{-dppae})][BF_4]_2$	**15**[b]	0.87 (s, 6 H) 0.88 (s, 6 H)	1.73 (d, 2 H) {6.9} [ca 65] 1.84 (s, 2 H) [ca 65][d]	2.97 (s, 2 H) (bipy) 2.99 (s, 2 H) (bipy) 2.73 (m, 4 H) (dppae)		[c]	6.96−8.42 (m, 34 H)
$[Pt(L^{np})(dppm)][BF_4]$	**16**	0.85 s, 6H	1.69 (d, 2 H) {7.3} [65]	2.84 (s, 2 H) (bipy) 3.43 d {10.5} [49] 2H (dppm)		[c]	6.97−8.56 (m, 27 H)
$[Pt(L^{np})(dppe)][BF_4]$	**17**	0.31 (s, 3 H) 0.76 (s, 3 H)	1.18−2.84 (m, 8 H)[d]			[c]	6.43−8.19 (m, 27 H)
$[Pt(L^{np})(dppae)][BF_4]$	**18**	0.91 (s 6 H)	1.79 (d, 2 H) {6.8} [62]	2.96 (s, 2 H) (bipy) 2.25 (m, 2 H) (dppae) 2.42 (m, 2 H) (dppae)		[c]	6.92−8.64 (m, 27 H)

[a] Room temperature, solvent $CDCl_3$, chemical shifts in ppm from internal $SiMe_4$, coupling constants in, $J_{Pt,H}$ in square brackets, $J_{P,H}$ in braces; n.r. = not resolved. [b] Solvent: CD_2Cl_2. [c] In all the phosphane complexes the 6′-H is strongly shielded. [d] Complex pattern from δ = 1.18 to 2.84 ppm, due CH_2-Pt, CH_2 (dppe), CH_2(bipy), 8 H.

group strongly coupled to the metal ($^2J_{Pt,H}$ = 80−90, $^1J_{Pt,C}$ = 668−743 Hz, see Table 1 and 2).

In complexes **2−5** the signals of the 6′-H protons are strongly deshielded and coupled to the metal ($^3J_{Pt,H}$ = ca. 10 Hz). In the series of palladium(II) and platinum(II) *N,N,C* cyclometallated compounds derived from 6-substituted 2,2′-bipyridines[7a−7g] (see Scheme 1) the chemical shifts of 6′-H appear to be strongly dependent on the nature of the metal and of the fourth ligand as well as on the size of the metallated cycle.

Coordinated halides exert a strong deshielding effect. At variance, the chemical shifts are not remarkably affected by the nature of the carbon atom, C(sp^3) or C(sp^2), bonded to the metal.

For platinum(II) compounds, in the case of 5,5 fused rings, values of ca. δ = 9.20 ppm are typical, whereas for 5,6 fused rings more deshielded resonances (ca. 9.60 ppm) are usually observed. In the analogous palladium species the same trend is observed, but all the signals are less deshielded (ca. 0.4 ppm) than in the corresponding platinum

Table 2. ^{13}C NMR spectroscopic data (room temperature, $CDCl_3$, chemical shifts in ppm from TMS, coupling constants in Hz, $J_{Pt,C}$ in square brackets

	[Pt(L^{et})Cl], **2**	[Pt(L^{ip})Cl], **3**	[Pt(L^{np})Cl], **5**	[Pt(L^{ip})(CO)][BF$_4$], **7**
CH_2-Pt	- 1.2 [743]	10.1 [736]	18.2 [668]	16.2 [567]
CH_3		21.8 [44]	29.6 [28]	22.4 [39]
CH_2	44.0		55.5 [68]	
CH		49.3 [10]		49.4 [5]
C			32.2 [28]	
C3, C3′	127.7, 124.1 [51]	127.3, 124.2 [59]	120.2 [33], 121.3	129.8 [15], 125.3 [14]
C5, C5′	123.4 [11], 119.8 [35]	121.8 [12], 119.7 [36]	128.7 [45], 126.8	125.1 [47], 122.1 [25]
C4, C4′	138.5, 135.6	138.1, 135.4	136.6 (C4) 137.8 (C4′)	143.5, 142.3
C2, C2′		156.2, 152.6	157.6, 154.6	
C6		172.5	164.2	
C6′	147.9 [19]	147.8 [19]	148.0 [25]	152.3 [30]

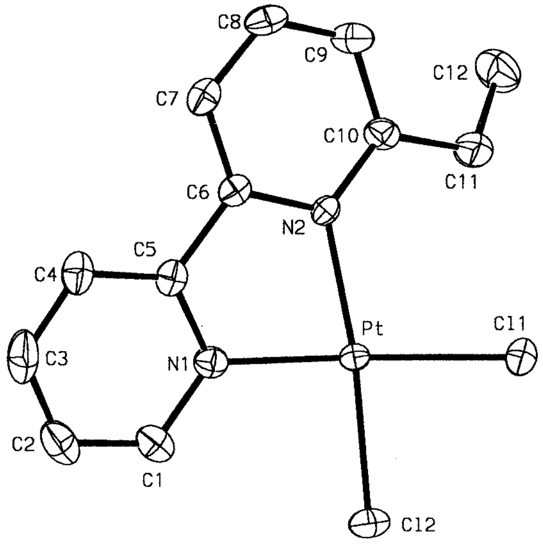
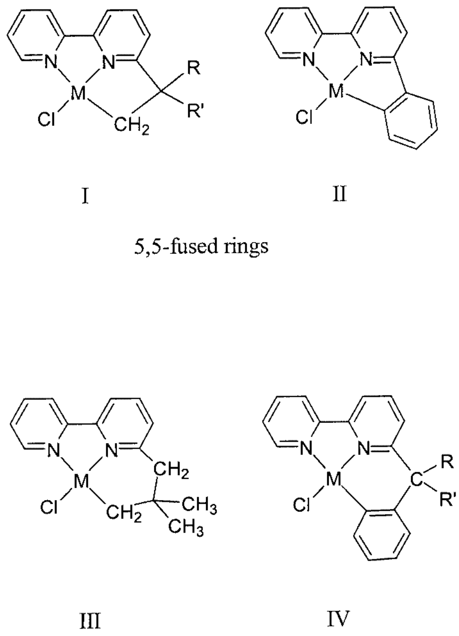


Figure 1. ORTEP view of molecule A in compound **1**; thermal ellipsoids are drawn at the 30% probability level



M = Pd, Pt

Scheme 1

complexes. Similar trends have also been recently observed for analogous gold(III) cationic species $[Au(N,N,C)Cl]^+$ [7g] for which, however, less experimental data are available.

The $^{13}C\{^1H\}$ spectra of **2−5** deserve comments: the chemical shifts of the CH_2-Pt resonances depend mainly on the degree of substitution on the carbon β to the metal, irrespective of the cycle [e.g. $Pt-CH_2-C(CH_3)_2-$, ca. 18−19 ppm (**4** and **5**), $Pt-CH_2-CH(CH_3)-$, ca. δ = 10 ppm (**3**), and $Pt-CH_2-CH_2$-, −1.2 ppm (**2**)] reflecting only electronic effects. At variance, the $^1J_{Pt,C}$ values are higher for the five-membered rings (ca 740 Hz, **2−4**) than for the six-membered one (668 Hz in **5**).

In the analogous palladium compounds the CH_2-Pd resonances are shifted downfield (e.g. Pd(L^{tb})Cl, δ = 32.8 ppm; Pd(L^{np})Cl, δ = 34.9 ppm).[7a]

In the case of compound **5**, taking into account the rarity of six-membered cyclometallated rings containing C(sp^3)−Pt bonds, complete assignment of ^1H and ^{13}C signals was accomplished by 2D NMR studies (COSY and HETCOR experiments, see experimental). The coupling constants $J_{Pt,C}$ in the inner pyridine ring are much larger than those of the outer one [e.g.: ^3J(Pt−C(3) = 33 Hz, ^3J(Pt−C(3′)] not observed, ^4J(Pt−C(4) = 45 Hz, ^4J(Pt−C(4′) not observed] indicating that the pyridine involved in the cyclometallation is more tightly bonded than the other one, in agreement with the X-ray data.

The crystal structure of **5**·$CHCl_3$ consists of the packing of [Pt(L^{np})Cl] and $CHCl_3$ molecules in a 1:1 molar ratio with no unusual van der Waals contacts. Selected bond parameters are listed in Table 5. An ORTEP view of **5** is shown in Figure 2. The Pt atom is in a square-planar coordination with a very slight square-pyramidal distortion. It is displaced by only 0.026(1) Å from the best plane of atoms Cl(1), N(1), N(2), and C(13). A comparison can be made between compound **5** and the corresponding Pd derivative,

Table 3. ^{31}P NMR spectroscopic data (room temperature, solvent $CDCl_3$, chemical shifts in ppm downfield from external 85% H_3PO_4)

		solvent	δ	$^1J_{Pt,P}$ /Hz	$J_{P,P}$ /Hz	$^3J_{Pt,P}$ /Hz
$[Pt(L^{et})(PPh_3)][BF_4]$	**9**		20.27	4038		
$[Pt(L^{ip})(PPh_3)][BF_4]$	**10**		20.36	4066		
$[Pt(L^{np})(PPh_3)][BF_4]$	**11**		22.59	4453		
$[Pt_2(L^{np})_2(\mu\text{-dppm})][BF_4]_2$	**12**	CD_2Cl_2	8.86	4581		32
$[Pt_2(L^{ip})_2(\mu\text{-dppe})][BF_4]_2$	**13**	CD_2Cl_2	14.49	4020	52	
$[Pt_2(L^{np})_2(\mu\text{-dppe})][BF_4]_2$	**14**	CD_2Cl_2	15.28	4412	52	
$[Pt_2(L^{np})_2(\mu\text{-dppae})][BF_4]_2$	**15**	CD_2Cl_2	15.14	4414		
$[Pt(L^{np})(dppm)][BF_4]$	**16**		7.69	4421	83	
			−25.09			94
$[Pt(L^{np})(dppe)][BF_4]$	**17**		44.84	1912		
			32.37	4138		
$[Pt(L^{np})(dppae)][BF_4]$	**18**		15.22	4382		

Table 4. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound **1**

	molecule A	molecule B
Pt−Cl(1)	2.295(2)	2.300(2)
Pt−Cl(2)	2.286(2)	2.282(2)
Pt−N(1)	1.998(6)	1.994(5)
Pt−N(2)	2.045(5)	2.054(5)
Cl(1)−Pt−Cl(2)	84.9(1)	87.1(2)
Cl(1)−Pt−N(1)	170.8(2)	170.9(2)
Cl(1)−Pt−N(2)	101.3(2)	99.7(2)
Cl(2)−Pt−N(1)	93.0(2)	92.4(2)
Cl(2)−Pt−N(2)	173.6(2)	172.5(2)
N(1)−Pt−N(2)	80.6(2)	80.3(2)

Table 5. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound **5**

Pt−Cl(1)	2.309(1)	Pt−N(1)	2.116(3)
Pt−N(2)	2.020(3)	Pt−C(13)	2.040(4)
Cl(1)−Pt−N(1)	95.5(1)	Cl(1)−Pt−N(2)	175.0(1)
Cl(1)−Pt−C(13)	88.1(1)	N(1)−Pt−N(2)	79.8(1)
N(1)−Pt−C(13)	176.1(1)	N(2)−Pt−C(13)	96.7(1)

$[PdL^{np}Cl]$, compound **20**.[7a] The Pt−Cl, Pt−N(1), and Pt−N(2) distances, 2.309(1), 2.116(3), and 2.020(3) Å, respectively, are slightly shorter than the corresponding ones involving palladium, 2.314(1), 2.138(2), and 2.046(2) Å, respectively. This is in keeping with the recent observation that platinum is slightly smaller than palladium.[7a,14] On the contrary, the Pt−C(13) bond, 2.040(4) Å, is slightly longer than the Pd−C(13) one, 2.022(3) Å. As pointed out in ref.[7a], this can be due to the different packing forces in the two nonisomorphous crystals. The conformation of the Pd−N(2)−C(10)−C(11)−C(12)−C(13) six-membered ring is irregular, as previously found in **20**, ref.[7a]. Atoms Pt, N(2), C(10), and C(13) are approximately planar (maximum distances from their best plane are +0.033(3) Å for N(2) and −0.023(4) Å for C(10)], with atoms C(11) and C(12) lying at −0.336(4) and +0.471(4) Å from this best plane.

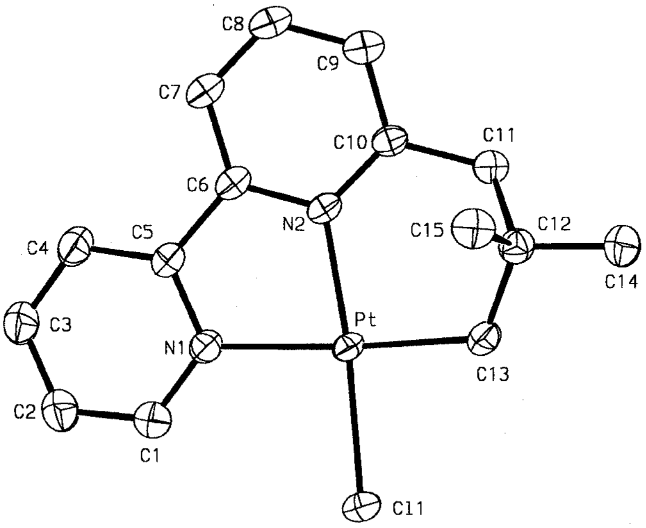


Figure 2. ORTEP view of compound **5**. Thermal ellipsoids as in Figure 1.

In the case of compound **3**, the activation of the methyl group directly generates a stereogenic carbon atom β to the metal atom, a result still rare,[7a] even if not unprecedented. In agreement, the ^1H NMR spectrum shows two diastereotopic hydrogens α to the metal atom ($\delta_A = 2.66$, dd; $\delta_B = 3.07$, dd).

Reactivity of the Metallated Species

In contrast with the behaviour of the analogous cyclometallated species containing Pt−C(sp^2) bonds,[7d] displacement of the chloride ligand in complexes **2**−**5** is easily accomplished in mild conditions by both neutral (e.g. CO, PPh_3) and anionic ligands (e.g. CN^-)

Derivatives **7**−**12** were obtained in good yields in the presence of $[BF_4]^-$ and characterised by analytical and spectroscopic methods. In particular the carbonyl derivatives $[Pt(L)CO][BF_4]$, **7** and **8**, show strong IR absorptions in the region around 2100 cm^{-1} [$\tilde{\nu}_{max}$ (cm^{-1}) = 2107, **7**; 2100, **8**)].

In the ^{1}H and ^{13}C{^{1}H} NMR spectra of **7**, the $^2J_{Pt-H}$ and $^1J_{Pt-C}$ values relevant to the metallated methylene group are small ($J_{Pt,H}$ = 66 and 52 Hz; J_{Pt-C} = 567 Hz) in comparison with those of the chloride species **5** (J = 89, 79 and 736 Hz, respectively), as previously observed when a strong π acceptor ligand is *cis* to the metal−carbon bond.[7b]

Compounds **9−11**, [Pt(L)(PPh$_3$)][BF$_4$], can be obtained both with a Pt/P 1:1 or 1:2 molar ratio, showing that the terdentate *N,N,C* system is rather robust. The ^{31}P NMR spectra (see Table 3) are in agreement with a phosphorus *trans* to a nitrogen atom: the $^1J_{Pt,P}$ values in the five-membered compounds **9** and **10**, as well as in [Pt(L^{tb})(PPh$_3$)][BF$_4$],[7b] are in the range 4000−4100 Hz, whereas in the six-membered species **11** a greater value, 4453 Hz is found. Similar values (4400−4471 Hz) have been observed in the case of the *N,N,C*(sp^2) six-membered compounds derived from substituted benzylbipyridines[7d] (see Scheme 1, compounds of type IV, M = Pt).

The reactivity of compound **5** with the potentially bidentate ligands L′−L″ (Ph$_2$P(CH$_2$)PPh$_2$, dppm, Ph$_2$P(CH$_2$)$_2$PPh$_2$, dppe, and Ph$_2$P(CH$_2$)$_2$AsPh$_2$, dppae) was studied with the aim of establishing whether square-planar (mono- or dinuclear) or five-coordinated complexes were formed.

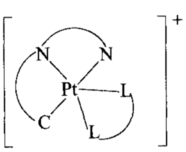
The reaction was investigated both with a 1:1 and a 2:1 Pt/L′−L″ molar ratio: in the first case mononuclear cationic species of the general formula [Pt(L)(L′−L″)]$^+$ were formed, whereas dinuclear species containing a not so common unsupported L′−L″ bridging unit were isolated in the second case.

The dinuclear species [(L)Pt(μ-L′−L″)Pt(L)]$^{2+}$, **12−15**, were characterised mainly on the basis of ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. In particular the ^{31}P{^{1}H} NMR spectra of **12−15** deserve comments: the chemical shifts rule out a chelating behaviour of the ligands L′−L″ and support a bridging coordination.[15] In the analysis of the ^{31}P NMR spectra, due to the presence of ^{31}P (100% natural abundance) and ^{195}Pt (33.8% natural abundance) nuclei, four isotopomers have to be considered.

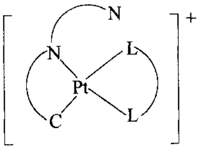
I	Pt_A-$P_A \frown P_B$-Pt_B	43.8%
II	$^{195}Pt_A$-$P_A \frown P_B$-Pt_B	22.4%
III	Pt_A-$P_A \frown P_B$-$^{195}Pt_B$	22.4%
IV	$^{195}Pt_A$-$P_A \frown P_B$-$^{195}Pt_B$	11.4%

In symmetric species, such as **12** and **14**, the ^{31}P NMR spectra should consist of a singlet due to isotopomer I located in the centre of a satellite system. If the complex pattern due to IV is ignored owing to its low natural abundance, the satellite system is governed by species II−III, which in symmetric species, are equivalent. Isotopomers II and III give rise to an ABX spin system (X = ^{195}Pt) and the ^{31}P spectrum can be described as being formed by two AB subspectra.[16] Two different situations are shown by the dppm and dppe bridging systems, respectively: in the former case no $^2J_{P-P}$ has been resolved, but a $^3J_{Pt-P}$ (32 Hz) is observed, whereas in the latter case a $^3J_{P-P}$ = 52 Hz is present but the $^4J_{Pt,P}$ is negligible. The reaction with dppe has also been carried out on complex **3**, [Pt(L^{ip})Cl]: in this case, due to the presence of a couple of stereogenic centres two diastereomers are expected, and this is reflected by the complex pattern of the ^{1}H NMR spectrum,. It is also worth noting that in these dinuclear complexes the $^1J_{Pt,P}$ is very different in the six- and five-membered species ($^1J_{Pt,P}$ = 4020 Hz, **13**, and $^1J_{Pt,P}$ = 4412 Hz, **14**). Compound **15**, [(L^{np})Pt(μ-dppae)Pt(L^{np})][BF$_4$]$_2$, at variance with compounds **12−14**, is no longer symmetric so that resonances relevant to two different bipy units are present in the ^{1}H NMR spectrum (Table 1).

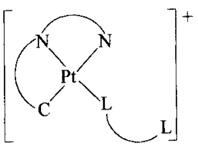
When the reaction is carried out with a Pt/L′−L″ 1:1 molar ratio at least three different species should be considered: a pentacoordinated, (A), and two square-planar compounds (B and C).



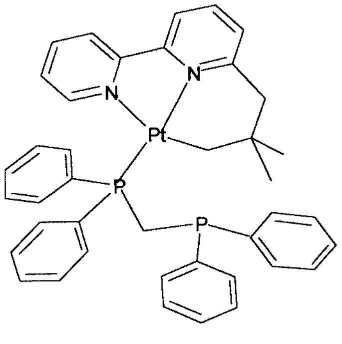
A



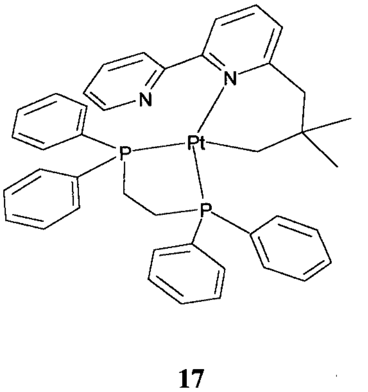
B



C



16



17

In the case of dppm a type C species, **16**, is formed as indicated, inter alia, by the $^{31}P\{^1H\}$ NMR spectrum which shows two different signals, corresponding to a coordinated (δ = 7.69 ppm, doublet, $^1J_{Pt,P}$ = 4421, $^2J_{P,P}$ = 83 Hz), and to an uncoordinated phosphorus atom (δ = −25.9 ppm doublet, $^3J_{Pt,P}$ = 94, $^2J_{P,P}$ = 83 Hz). The ^1H NMR spectrum, as expected, is almost coincident with that of $[Pt(L^{np})(PPh_3)]^+$ (e.g. CH_2-Pt, δ = 1.60 ppm, **11**; 1.69, **16**). At variance, with dppe a type-B complex is obtained, **17**: in the $^{31}P\{^1H\}$ NMR spectrum two sets of signals, centred at δ = 44.84 ppm ($^1J_{Pt\text{-}P}$ = 1912 Hz) and 32.37 ppm, ($^1J_{Pt\text{-}P}$ = 4138 Hz), are consistent with phosphorus atoms *trans* to a carbon and a nitrogen nucleus, respectively. The ^1H NMR spectrum is complex, which is likely due to the crowded environment, all the protons of the four CH_2 groups are not equivalent anymore.

The nature of complex **17** has been confirmed by the resolution of the structure.

The crystal consists of the packing of $[Pt(L^{np})(dppe)]^+$ cations, $[BF_4]^-$ anions and CH_2Cl_2 molecules in the molar ratio 1:1:1 with no unusual van der Waals contacts. Principal bond parameters are listed in Table 6. An ORTEP view of the cation is shown in Figure 3. The Pt atom displays a square-planar coordination with a slight tetrahedral distortion, with maximum distances from the best plane of −0.084(2) and +0.1035(3) Å for atoms C(13) and N(2), respectively. The Pt−P(1) distance, 2.314(1) Å, is markedly longer than the Pt−P(2) one, 2.209(1) Å, because of the strong *trans* influence of the C(13) alkyl atom. Also the Pt−C(13), 2.115(3) Å, and Pt−N(2), 2.127(2) Å, bond lengths are elongated by the *trans* influence of atoms P(1) and P(2), respectively. The Pt−N(2)−C(10)−C(11)−C(12)−C(13) ring is in a boat conformation, with atoms N(2), C(11), C(12), and C(13) approximately planar [maximum distances from their best plane are −0.068(2) Å for N(2) and +0.074(3) Å for C(10)] and atoms Pt and C(11) lying at −1.289(1) and −0.615(3) Å from the best plane, respectively. The P(1)−Pt−N(2) angle, 100.9(1)°, is larger than the P(2)−Pt−C(13) one, 92.4(1)°, probably as a result of the steric hindrance of the noncoordinated pyridine ring. The two pyridine rings are planar and form a dihedral angle of 29.2(2)°.

Table 6. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for cation **17**

Pt−P(1)	2.314(1)	Pt−P(2)	2.209(1)
Pt−N(2)	2.127(2)	Pt−C(13)	2.115(3)
P(1)−Pt−P(2)	85.5(1)	P(1)−Pt−N(2)	100.9(1)
P(1)−Pt−C(13)	173.5(1)	P(2)−Pt−N(2)	173.0(1)
P(2)−Pt−C(13)	92.4(1)	N(2)−Pt−C(13)	81.6(1)

The spectroscopic evidences for **18**, $[Pt(L^{np})(dppae)][BF_4]$, indicate a monodentate P coordination of dppae, as for dppm, so that the *N,N,C* coordination environment is retained. The $^{31}P\{^1H\}$ NMR resonance at δ = 15.22 ppm, is indicative of a nonchelating behaviour of dppae and the $^1J_{Pt,P}$ = 4382 Hz is typical for a P nucleus *trans* to a pyridinic nitrogen atom. In the ^1H NMR spectrum the signals of the pyridine rings as well as those of the CH_2-Pt groups are almost superimposable to those of compounds **11** and **16**, providing further evidence for the terdentate behaviour of the *N,N,C* ligand. In crowded species such as **16−18**, it is reasonable to deem that either the different size or the coordinating ability of the As atom with respect to P can direct the reaction towards a different outcome.

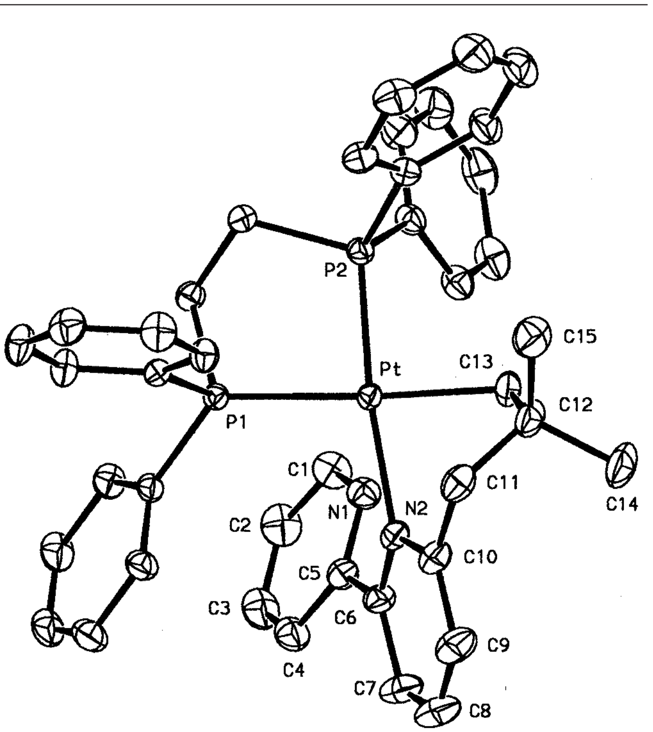


Figure 3. ORTEP view of compound **17**; thermal ellipsoids as in Figure 1

Conclusions

In this paper we have shown that organoplatinum(II) compounds containing an *N,N,C*(sp^3) terdentate ligand are readily formed from $K_2[PtCl_4]$ through a direct C(sp^3)−H bond activation of an unactivated aliphatic chain. Among the species obtained, $[Pt(L^{np})Cl]$, having a rare six-membered cyclometallated N,C(sp^3) cycle, and $[Pt(L^{ip})Cl]$, where a stereogenic centre has been directly formed through metallation, are of particular interest. The ligands studied have different reactivities: with HL^{et} the metallation can be achieved with difficulty and an adduct species, which can be regarded as an intermediate in the cyclometallation, has been isolated in the solid state and studied by X-ray diffraction. Also the structure of $[Pt(L^{np})Cl]$ has been solved, allowing comparisons to be made with the analogous Pd^{II} six-membered N,C(sp^3) metallacyle. NMR spectroscopic data seem to indicate that in the six-membered $[Pt(N,N,C)L]^{n+}$ species (L = neutral, n = 1; or anionic ligand, n = 0) the Pt−C bond is weaker and the Pt−L (L = PR_3) bond is stronger than in the five-membered ones, as indicated by $^1J_{Pt,C}$ in **2−5** and by $^1J_{Pt,P}$ in **9−18**.

In the course of the study on the reactivity of these species the chloride ligand has been shown to be rather labile whereas the *N,N,C* system is rather robust. The chloride ligand can easily be removed by anionic and neutral ligands: in the case of neutral bidentate ligands both mono- and binuclear species can be obtained. Only in one case (with dppe) has the external nitrogen atom of the terdentate *N,N,C* ligand been displaced from the metal to give a crowded $[Pt(N,C)(P,P)]^+$ compound whose structure has been resolved in the solid state.

All the new species are remarkably stable towards air and moisture, even in solution, and so all the reactions can be performed in air.

Experimental Section

The ligands HL were prepared according to literature methods.[12] $K_2[PtCl_4]$ (43.035% Pt) was obtained from Engelhard S.r.l. and $[(DMSO)_2PtCl_2]$ was synthesised as described in ref[17]. All the solvents were purified before use according to standard methods.[18] Elemental analyses were performed with a Perkin−Elmer Elemental Analyser 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. Infrared Spectra were recorded with a Perkin−Elmer 983 using Nujol mulls. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9, 75.4 and 121.4 MHz respectively, and are collected in Table 1−3.

Chemical shifts are given in ppm relative to internal TMS (^1H, ^{13}C) and external 85% H_3PO_4 (^{31}P). The 2D experiments were performed by means of standard pulse sequences.

The mass spectrometric measurements were performed on a VG 7070EQ instrument, equipped with a PDP 11−250 J data system and operating under positive ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix.

Preparations

$[Pt(HL^{et})Cl_2]$ (1): a) *cis*-$[(DMSO)_2PtCl_2]$ (215 mg, 0.51 mmol) was added to a solution of HL^{et} (92 mg, 0.50 mmol) in $CHCl_3$ (50 mL). The yellow solution was stirred for 36 h, then evaporated to dryness. The resulting solid was crystallised from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid. Yield 85% (191 mg). The reaction can also be carried out in other solvents (e.g. EtOH).

b) $K_2[PtCl_4]$ (43.035% Pt, 1.297 g, 2.86 mmol) was dissolved in H_2O (30 mL) and filtered. HL^{et} (523.7 mg, 2.85 mmol) and of 2 M HCl (5 mL) were added to the solution. The mixture was stirred at room temperature until the solution became colourless. The precipitate that formed was filtered, washed with H_2O, EtOH and Et_2O and recrystallised from CH_2Cl_2/Et_2O to give the analytical sample. Yield 30% (384 mg). M.p. 220 °C. $C_{12}H_{12}Cl_2N_2Pt$ (450.2): calcd. C 32.01; H 2.69; N 6.22 ; found C 31.97; H 2.65; N 6.11%. IR (Nujol): $\tilde{\nu}$ = 1600 s 1558 w, 1375 s, 335 w cm^{-1}.

$[Pt(L^{et})Cl]$ (2): HL^{et} (184 mg, 1.00 mmol) and 2 M HCl (3.5 mL) were added to an aqueous solution (30 mL) containing $K_2[PtCl_4]$ (1.00 mmol) in water. The mixture was heated in a water bath for 1 d: the precipitate that formed was filtered, washed with water, EtOH and Et_2O and recrystallised from CH_2Cl_2/Et_2O. The crude obtained (362 mg) was a mixture ca. 1:1 of compounds **1** and **2** (NMR criterion). The products were separated by column chromatography on silica gel, using a mixture of CH_2Cl_2/acetone 20:1 as eluent. Complex **2** was obtained with a 30% yield. M.p. 258−260 °C (dec). $C_{12}H_{11}ClN_2Pt$ (413.8): calcd. C 34.83, H 2.68, N 6.77; found C 35.44, H 2.80, N 6.50%. IR (Nujol): $\tilde{\nu}$ = 1597 s 1556 w, 328 s cm^{-1}. FAB$^+$: *m/z* = 413 [M$^+$], 378 [M − Cl], 791 [M_2−Cl].

$[Pt(L)Cl]$ (L = L^{ip}, 3; L = L^{np}, 5): HL (1.00 mmol) and 2 M HCl (3.0 mL) were added to an aqueous solution (30 mL) containing K_2PtCl_4 (1.00 mmol). The mixture was heated in a water bath until a colourless solution was obtained and an orange precipitate formed. The suspension was filtered off, washed with water, ethanol and diethyl ether and recrystallised from CH_2Cl_2/Et_2O

3: Yield 91% (389 mg), m.p. 245 °C. $C_{13}H_{13}ClN_2Pt$ (427.8): calcd. C 36.50, H 3.06, N 6.55; found C 36.50, H 3.05, N 6.25%. IR (Nujol): $\tilde{\nu}$ = 1596 s, 1552 w, 332 s cm^{-1}. FAB$^+$: *m/z* = 427 [M$^+$], 392 [M − Cl], 819[M_2−Cl].

5: Yield 90% (410 mg), m.p.: 233 °C (dec). $C_{15}H_{17}ClN_2Pt$ (455.8) calcd. C 39.52, H 3.76, N 6.15; found C 39.27, H 3.84, N 6.04%. IR (Nujol): $\tilde{\nu}$ = 1600 s, 1564 w, 328 s cm^{-1}. FAB$^+$: *m/z* = 455 [M$^+$].

$[Pt(L^{ip})(CN)]$ (6): Complex **3** (175 mg, 0.41 mmol) was added to a methanolic solution (25 mL) of KCN (27 mg, 0.41 mmol) whilst stirring. The mixture was stirred for 1 day, then evaporated to dryness and the solid residue recrystallised from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid. Yield 56% (96 mg), m.p. 115 °C. $C_{14}H_{13}N_3Pt$ (418.3) calcd. C 40.19, H 3.13, N 10.04; found C 39.67, H 3.06, N 9.62%. IR (Nujol): $\tilde{\nu}$ = 2105 m, 1595 s, 1557 w cm^{-1}.

$[Pt(L)(CO)]$ $[BF_4]$ (L = L^{ip}, 7; L = L^{np}, 8): $NaBF_4$ (121 mg, 1.00 mmol) was added to a solution of the relevant $[Pt(L)Cl]$ (0.25 mmol) in acetone (20 mL) whilst stirring and carbon monoxide, at atmospheric pressure, was bubbled through the solution. After 6 h the solvent was evaporated to dryness and the solid residue was crystallised from CH_2Cl_2/Et_2O.

7 Yield 70% (89 mg), m.p.: 235 °C. Λ_M ($5{\cdot}10^{-4}$ M, acetone) = 138 ohm^{-1} cm^2 mol^{-1}. $C_{14}H_{13}BF_4N_2OPt$ (507.2): calcd. C 33.16, H 2.58, N 5.52; found C 33.28, H 2.60, N 5.30%. IR (Nujol): $\tilde{\nu}$ = 2107 s 1598 s 1563 s 1050 b. FAB$^+$: *m/z* = 420 [M$^+$], 392 [M − CO].

8: Yield: 76% (102 mg), m.p.182−184 °C. Λ_M (5.10^{-4} M, acetone) = 157 ohm^{-1} cm^2 mol^{-1}. $C_{16}H_{17}BF_4N_2OPt$ (535.2): calcd. C 35.91, H 3.20, N 5.23; found C 35.40, H 3.06, N 5.11%. IR (Nujol): $\tilde{\nu}$ = 2100 s, 1600 s, 1560 w, 1050 s cm^{-1}.

$[Pt(L)(PPh_3)][BF_4]$ (L = L^{et}, 9; L = L^{ip}, 10; L = L^{np}, 11): PPh_3 (0.22 mmol) and $NaBF_4$ (100 mg, 0.900 mmol) were added to a solution of the relevant $[Pt(L)Cl]$ (0.20 mmol) in acetone (30 mL) whilst stirring. The mixture was stirred at room temperature, then evaporated to dryness and crystallised from CH_2Cl_2/Et_2O.

9: Yield 90% (131 mg), m.p. 253 °C. Λ_M ($5{\cdot}10^{-4}$ M acetone) = 150 ohm^{-1} cm^2 mol^{-1}. $C_{30}H_{26}BF_4N_2PPt$ (727.4): calcd. C 49.54, H 3.60, N 3.85; found C 48.93, H 3.55, N 3.71%. FAB$^+$: *m/z* = 640 [M$^+$], 378 [M − PPh_3].

10: Yield 76% (113 mg), m.p. 275 °C. Λ_M ($5{\cdot}10^{-4}$ M, acetone) = 130 ohm^{-1} cm^2 mol^{-1}. $C_{31}H_{28}BF_4$ N_2PPt (741.4): calcd. C 50.22, H 3.81, N 3.78; found C 50.34, H 3.91, N 3.63%. IR (Nujol): $\tilde{\nu}$ = 1598 s, 1564 w, 1102 s, 1050br, s. FAB$^+$: *m/z* = 654 [M$^+$] 392 [M − PPh_3].

11: Yield: 77% (118 mg), m.p. 263 °C. Λ_M ($5{\cdot}10^{-4}$ M, acetone) = 150 ohm^{-1} cm^2 mol^{-1}. $C_{33}H_{32}BF_4N_2PPt$ (769.5): calcd. C 51.51, H 4.19, N 3.64%; found C 51.26, H 4.09, N 3.65%. IR (Nujol): ṽ = 1602 s, 1568 w, 1050 s, 540 w. FAB$^+$: m/z = 682 [M$^+$].

$[Pt_2(L^{np})_2(\mu\text{-dppm})]$ $[BF_4]_2$ (12): A mixture containing **5** (42 mg, 0.092 mmol), dppm (17.4 mg, 0.046 mmol) and $NaBF_4$ (43 mg) in acetone (30 mL) was stirred at room temperature for 4 days, then evaporated to dryness and recrystallised from CH_2Cl_2/Et_2O, to give the analytical sample as a yellow solid. Yield: 59% (34 mg), m.p 168 °C (dec.). Λ_M (5 10^{-4} M, acetone) = 260 ohm^{-1} cm^2 mol^{-1}. $C_{55}H_{56}B_2F_8N_4P_2Pt_2\cdot 0.5CH_2Cl_2$ (1441.2): calcd. C 46.25, H 3.99, N 3.89 ; found C 46.37, H 4.03, N 3.96%. IR (Nujol): ṽ = 2100 s, 1600 s, 1560 w, 1050 br s cm^{-1}. FAB$^+$: m/z = 1224 [M$^+$], 1311 [M$^+$ + BF_4].

$[Pt_2(L)_2(\mu\text{-dppe})]$ $[BF_4]_2$ (L = L^{ip}, 13; L = L^{np}, 14): dppe (0.20 mmol) and $NaBF_4$ (150 mg) were added to a suspension of the relevant [Pt(L)Cl] (0.40 mmol) in acetone (25 mL) whilst stirring. The mixture was stirred for a few hours, then evaporated to dryness and crystallised by CH_2Cl_2/Et_2O to give the analytical sample.

13: Yield 75% (203 mg); m.p. 280 °C. Λ_M (5.10^{-4} M, acetone) = 202 ohm^{-1} cm^2 mol^{-1}. $C_{52}H_{50}B_2F_8N_4PPt_2$ (1356.7): calcd. C 46.04, H 3.71, N 4.13; found C 45.74, H 3.74, N 4.01%. (IR (Nujol): ṽ = 1598 s 1564 w, 1050 broad cm^{-1}.

14: (yellow) Yield 93% (279 mg); m.p. 184 °C (dec). Λ_M (5 10−4 M, acetone) = 248 ohm^{-1} cm^2 mol^{-1}. $C_{56}H_{58}B_2F_8N_4P_2Pt_2\cdot CH_2Cl_2$ (1497.7): calcd. C 45.71, H 4.04, N 3.74 ; found C 46.26, H 4.18, N 3.71%. IR (Nujol): ṽ = 1602 s, 1569 w, 1050 br s cm^{-1}.

$[Pt_2(L^{np})_2(\mu\text{-dppae})]$ $[BF_4]_2$ (15): A mixture containing **5** (39 mg, 0.085 mmol), dppae (18.8 mg, 0.0425 mmol) and $NaBF_4$ (50 mg) in acetone (30 mL) was stirred at room temperature for 1 day, then evaporated to dryness and crystallised from CH_2Cl_2/Et_2O, to give the analytical sample as a yellow solid. Yield 80% (51 mg), m.p. 250−255 °C. $C_{56}H_{58}AsB_2F_8N_4Pt_2P\cdot 0.5CH_2Cl_2$ (1499.2): calcd. C 45.26, H 3.97, N 3.74; found C 45.02, H 3.98, N 3.68%.

$[Pt(L^{np})(L'-L'')][BF_4]$ (L′−L′′ = dppm, 16, L′−L′′ = dppe, 17, L′−L′′ = dppae, 18): $NaBF_4$ (120 mg) was added to an acetone solution (30 mL) of **5** (103 mg, 0.25 mmol) and L′−L′′ (0.25 mmol) whilst stirring. The mixture was stirred for 4 h, then evaporated to dryness. The solid obtained was crystallised from CH_2Cl_2/Et_2O to give the analytical sample as a yellow solid.

L′−L′′ = dppm, **16**, pale-yellow. Yield: 90% (201 mg); m.p. 238−240 °C. $C_{40}H_{39}BF_4N_2P_2Pt$ (891.6): calcd. C 53.88, H 4.41, N 3.14; found C 53.40, H 4.53, N 3.07%.

L′−L′′ = dppe, **17**, yellow. Yield: 88% (199 mg). M.p. 182−5 °C (dec). Λ_M (5 10^{-4} M, acetone) = 133 ohm^{-1} cm^2 mol^{-1}. $C_{41}H_{41}BF_4N_2P_2Pt$ (905.6): calcd. C 54.38, H 4.56, N 3.09; found C 54.42, H 4.56, N 3.11%. IR (Nujol): ṽ = 1600, 1580 w, 1050 s, 540 s cm^{-1}.

Table 7. Crystallographic experimental details

Compound	**1**	**5**·$CHCl_3$	**17**$[BF_4]\cdot CH_2Cl_2$
Formula	$C_{12}H_{12}Cl_2N_2Pt$	$C_{16}H_{18}Cl_4N_2Pt$	$C_{42}H_{43}BCl_2F_4N_2P_2Pt$
M	450.24	575.24	990.57
Colour	yellow	yellow-orange	pale yellow
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	14.909(2)	9.209(1)	11.969(1)
b/Å	9.503(1)	10.813(1)	13.307(1)
c/Å	17.732(2)	10.980(1)	13.659(1)
α/°	90	78.77(1)	75.97(1)
β/°	99.87(2)	65.60(1)	83.35(1)
γ/°	90	82.07(1)	89.67(1)
V/Å^3	2511.2(6)	974.6(2)	2095.8(3)
Z	8	2	2
F(000)	1680	548	984
T/K	296	296	296
D_c/g cm^{-3}	2.38	1.96	1.57
Crystal dimensions (mm)	0.33 × 0.45 × 0.50	0.16 × 0.27 × 0.44	0.13 × 0.30 × 0.44
μ (Mo-K_α)/cm^{-1}	117.0	78.3	36.3
Min. and max.transmiss. factors	0.81−1.00	0.88−1.00	0.59−1.00
Scan mode	ω	ω	ω
ω-scan width/°	1.20 + 0.35 tan θ		
Frame width/°		0.30	0.30
Time per frame/s		20	20
No. of frames		2450	2450
Detector/sample distance/cm		5.00	5.00
θ-range/°	3−27	3−26	3−26
Reciprocal space explored	quadrant	full sphere	full sphere
Measured reflections (total, independent)	5444, 5444	12214, 4798	32505, 12183
R_{int}		0.029	0.026
Unique observed reflections with I>3σ(I)	4239	3965	10764
Final R and R'[a]	0.030, 0.037	0.023, 0.028	0.024, 0.033
No. of variables	308	209	496
Goodness of fit[b]	1.40	0.94	1.19

[a] $R = [\Sigma(|F_o - k|F_c||)/\Sigma F_o]$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}$. [b] $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = [\sigma^2(F_o^2) + (0.04F_o^2)^2]^{1/2}/2F_o$, N_o is the number of observations, N_v the number of variables.

L′−L′′ = dppae, **18**, yellow. Yield: 84% (199 mg), m.p. 205−213 °C (dec). Λ_M (5 10^{-4} M, acetone) = 147 ohm^{-1}cm^{2}mol^{-1}. $C_{41}H_{41}AsBF_4N_2PPt$ (949.6): calcd. C 51.86, H 4.35, N 2.95; found C 51.47, H 4.39, N 2.97%. IR (Nujol): $\tilde{\nu}$ = 1600 s, 1560 w, 1050 br, 530 s cm^{-1}.

X-ray Data Collection and Structure Determination: Crystal data and other experimental details are summarised in Table 7. The diffraction experiment concerning **1** was carried out on an Enraf−Nonius CAD-4 diffractometer at room temperature using Mo-K_α radiation (λ = 0.71073 Å) with a graphite crystal monochromator in the incident beam. A periodic monitoring of three standard reflections did not reveal any crystal decay. The diffracted intensities were corrected for Lorentz, polarisation, and absorption effects (empirical correction).[19]

The diffraction experiments concerning **5**·$CHCl_3$ and **17**[BF_4]·CH_2Cl_2 were carried out on a Bruker SMART CCD area-detector diffractometer at room temperature using Mo-K_α radiation (λ = 0.71073 Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from the least-squares refinement of 69 reflections (for **5**·$CHCl_3$) and of 148 reflections (for **17**[BF_4]·CH_2Cl_2) measured in three different sets of 15 frames each, in the range $3 < \theta < 23°$. At the end of data collections the first 50 frames, containing 171 and 362 reflections (for **5**·$CHCl_3$ and **17**[BF_4]·CH_2Cl_2, respectively) were recollected to have a monitoring of crystal decay, which was not observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[20] and an empirical absorption correction was applied (SADABS[21]) to the collected reflections. Scattering factors and anomalous dispersion corrections were taken from ref.[22].

The calculations were performed on a Pentium III PC using the Personal Structure Determination Package[23] and the physical constants tabulated therein.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimising the function $\Sigma\omega(F_o - k|F_c|)$ (refinement on F). In compound **17**[BF_4]·CH_2Cl_2 three fluorine atoms of the BF_4^- anion are disordered. Anisotropic thermal factors were refined for all the non-hydrogen atoms. Hydrogen atoms were placed in their ideal positions (C−H: 0.97 Å, B: 1.10 times that of the carbon atom to which they are attached) and not refined . The final Fourier maps showed maximum residuals of 1.34(19) e/Å^3 at 0.87 Å from Pt_A (in compound **1**), 1.22(11) e/Å^3 at 0.96 Å from Pt (in compound **5**·$CHCl_3$), and of 1.18(9) e/Å^3 at 0.83 Å from Pt (in compound **17**[BF_4]·CH_2Cl_2). The atomic coordinates of the structure models have been deposited with the Cambridge Data File.

CCDC-181834 (**1**), -181835 (**5**·$CHCl_3$) and -181836 (**17**-[BF_4]·CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] A. D. Ryabov, *Synthesis* **1985**, 233.

[2] [2a] D. M. Grove, G. van Koten and A. H. M. Verschuuren, *J. Mol. Catal.* **1988**, *45*, 169−174. [2b] M. Camargo, P. Dani, J. Dupont, R. F. De Souza, M. Pfeffer, I. Tkatchenko, *J. Mol. Catal.* **1996**, *109*, 127.

[3] [3a] Y. Wakatsuki, H. Yamazaki, P. A. Grutsch, M. Southanam, M. Kutal, *J. Am. Chem. Soc.* **1985**, *107*, 8153. [3b] C. Cornioley-Deuschel, T. Ward, A. von Zelewsky, *Helv. Chim. Acta* **1988**, *71*, 130. [3c] M. Maestri, D. Sandrini, V. Balzani, A. von Zelewsky, P. Jolliet, *Helv. Chim. Acta* **1988**, *71*, 134. [3d] R. Schwartz, G. Gliemann, P. Jolliet, A. von Zelevsky, *Inorg. Chem.* **1989**, *28*, 742. [3e] C. A. Craig, R. Watts, *Inorg. Chem.* **1989**, *28*, 309.

[4] [4a] D. P. Lydon, J. P. Rourke, *Chem. Commun.* **1997**, 1741−1742 and references therein. [4b] P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano, E. Sola, *Coord. Chem. Rev.* **1992**, *117*, 215.

[5] M. Albrecht, M. Lutz, A. M. M. Schreurs, E. T. H. Lutz, A. L. Spek, G. van Koten, *J. Chem. Soc., Dalton Trans.* **2000**, 3797−3805.

[6] [6a] G. Marcon, S. Carotti, M. Colonnello, L. Messori, E. Mini, P. Orioli, T. Mazzei, M. Cinellu, G. Minghetti, *J. Med. Chem.* **2002**, *45*, 1672−1677. [6b] C. Navarro-Ranninger, I. Lopez-Solera, J. M. Perez, J. R. Masaguer, C. Alonso, *Appl. Organomet. Chem.* **1993**, *7*, 57.

[7] e. g. [7a] A. Zucca, M. A. Cinellu, M. V. Pinna, S. Stoccoro, G. Minghetti, M. Manassero, M. Sansoni, *Organometallics* **2000**, *19*, 4295−4304. [7b] G. Minghetti, M. A. Cinellu, S. Stoccoro, A. Zucca, M. Manassero, *J. Chem. Soc., Dalton Trans.* **1995**, 777−781. [7c] G. Minghetti, M. A. Cinellu, G. Chelucci, S. Gladiali, F. Demartin, M. Manassero, *J. Organomet. Chem.* **1986**, *307*, 107. [7d] G. Sanna, G. Minghetti, A. Zucca, M. I. Pilo, R. Seeber, F. Laschi, *Inorg. Chim. Acta* **2000**, *305*, 189−205. [7e] E. C. Constable, R. P. G. Henney, T. A. Leese, T. A. Tocher, *J. Chem. Soc., Chem. Commun.* **1990**, 513. [7f] E. C. Constable, R. P. G. Henney, T. A. Leese, T. A. Tocher, *J. Chem. Soc., Dalton Trans.* **1990**, 443. [7g] M. A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero, M. Sansoni, *J. Chem. Soc., Dalton Trans.* **1996**, 4217−4225. [7h] M. A. Cinellu, G. Minghetti, M. V. Pinna, S. Stoccoro, A. Zucca, M. Manassero, *Chem. Commun.* **1998**, 2397−2398. [7i] S. W. Lai, M. C. W. Chan, K. K. Cheung, C. M. Che, *Organometallics* **1999**, *18*, 3327. [7j] A. Zucca, S. Stoccoro, M. A. Cinellu, G. Minghetti, M. Manassero, *J. Chem. Soc., Dalton Trans.* **1999**, 3431. [7k] F. Neve, A. Crispini, S. Campagna, S. Serroni, *Inorg. Chem.* **1999**, *38*, 2250. [7l] G. Garcìa-Herbosa, A. Munoz, D. Miguel, S. Garcìa-Granda, *Organometallics* **1994**, *13*, 1775−1780. [7m] M. Crespo, C. Grande, A. Klein, *J. Chem. Soc., Dalton Trans.* **1999**, 1629−1637. [7n] C. Anderson, M. Crespo, M. Font-Bardìa, A. Klein, X. Solans, *J. Organomet. Chem.* **2000**, *601*, 22−33. [7o] A. Fernández, P. Urìaa, J. J. Fernández, M. López-Torres, A. Suárez, D. Vázquez-García, M. T. Pereira, J. M. Vila, *J. Organomet. Chem.* **2001**, *620*, 8−19. [7p] J. M. Vila, M. Gayoso, M. T. Pereira, M. Lopez Torres, J. J. Fernandez, A. Fernandez, J. M. Ortigueira, *J. Organomet. Chem.* **1997**, *532*, 171. [7q] M. Crespo, M. Font-Bardia, S. Pérez, X. Solans, *J. Organomet. Chem.* **2002**, *642*, 171−178. [7r] P. L. Alsters, P. F. Engel, M. P. Hogerheide, M. Copijn, A. L. Spek, G. van Koten, *Organometallics* **1993**, *12*, 1831−1844.

[8] e. g. [8a] P. Steenwinkel, R. A Gossage,; G. van Koten, *Chem. Eur. J.* **1998**, *4*, 759. [8b] A. W. Kleij, H. Kleijn, J. T. B. H. Jastrzebski, A. L. Spek, G. van Koten, *Organometallics* **1999**, *18*, 277. [8c] P. Steenwinkel, R. A. Gossage, T. Maunula, D. M. Grove, G. van Koten, *Chem. Eur. J.* **1998**, *4*, 763. [8d] M. Albrecht, P. Dani, M. Lutz, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **2000**, *122*, 11822−11833. [8e] M.-C. Lagunas, R. A. Gossage, A. L. Spek, G. van Koten, *Organometallics* **1998**, *17*, 731−741. [8f] G. van Koten, J. Terhijeden, J. A. M. van Beek, I. C. M. Wehman-Ooyevaar, F. Muller, C. H. Stam, *Organometallics* **1990**, *9*, 903−912. [8g] M. Schmülling, D. M. Grove, G. van Koten, R. van Eldik, N. Veldman, A. L. Spek, *Organometallics* **1996**, *15*, 1384−1391. [8h] D. J. Cardenas, A. M. Echavarren, M. C. Ramirez de Arellano, *Organometallics* **1999**, *18*, 3337. [8i] M. H. P. Rietveld, D. M. Grove, G. van Koten, *New. J. Chem.* **1997**, *21*, 751. [8j] A. J. Canty, N. J. Minchin, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1987**, 1477. [8k] A. J. Canty, J. Patel,

B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2000**, *607*, 194.

[9] e. g. [9a] G. W. V. Cave, F. P. Fanizzi, R. J. Deeth, W. Errington, J. P. Rourke, *Organometallics* **2000**, *19*, 1355. [9b] G. W. V. Cave, N. W. Alcock, J. P. Rourke, *Organometallics* **1999**, *18*, 1801. [9c] W. Lu, M. C. W. Chan, K. K. Cheung, C. M. Che, *Organometallics* **2001**, *12*, 2477. [9d] C. Cornioley-Deutschel, T. Ward, A. von Zelewsky, *Helv. Chim. Acta* **1988**, *71*, 130. [9e] G. R. Newkome, T. Kawato, D. K. Kohli, W. E. Puckett, B. D. Olivier, G. Chiari, F. R. Fronczek, W. A. Deutsch, *J. Am. Chem. Soc.* **1981**, *103*, 3423. [9f] K. H. Wong, K. K. Cheung, M. C. W. Chan, C. M. Che, *Organometallics* **1998**, *17*, 3505. [9g] C. P. Newman, G. W. V. Cave, M. Wong, W. Errington, N. W. Alcock, J. P. Rourke, *J. Chem. Soc., Dalton Trans.* **2001**, 2678−2682.

[10] A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403−424.

[11] [11a] L. Calligaro, R. A. Michelin, P. Uguagliati, *Inorg. Chim. Acta* **1983**, *76*, L83. [11b] G. R. Newkome, K. J. Theriot, F. R. Fronczek, B. Villar, *Organometallics* **1989**, *8*, 2513.

[12] [12a] U. Azzena, G. Chelucci, G. Delogu, S. Gladiali, M. Marchetti, F. Soccolini, C. Botteghi, *Gazz. Chim. Ital.* **1986**, *116*, 307. [12b] C. Botteghi, G. Chelucci, G. Chessa, G. Delogu, S. Gladiali, F. Soccolini, *J. Organomet. Chem.* **1986**, *304*, 217.

[13] A. Doppiu, M. A. Cinellu, G. Minghetti, S. Stoccoro, A. Zucca, M. Manassero, M. Sansoni, *Eur. J. Inorg. Chem.* **2000**, 2555−2563.

[14] K. Herbst, B. Rink, L. Dahlenburg, M. Brorson, *Organometallics* **2001**, *20*, 3655−3660.

[15] P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}*C NMR of Transition Metal Phosphane Complexes, Springer-Verlag, Berlin, **1979**.

[16] J. B. Benson, E. A. Keiter, R. L. Keiter, *J. Organomet. Chem.* **1995**, *495*, 77−81.

[17] R. Romeo, L. Monsù Scolaro, *Inorg. Synth.* **1998**, *32*, 153.

[18] *Vogel's Textbook of Practical Organic Chemistry*, fifth edition, Longman Scientific and Technical Ed., Harlow, **1989**.

[19] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

[20] SAINT, *Reference manual*, Siemens Energy and Automation, Madison, WI, **1994− 1996**.

[21] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Gottingen, **1997**.

[22] *International Tables for X-ray Crystallography*, Vol.4, Kynoch Press, Birmingham, 1974.

[23] [23a] B. A. Frenz, *Comput. Phys.* **1988**, *2*, 42. [23b] B. A. Frenz, *Crystallographic Computing 5*, Oxford University Press: Oxford, U. K., **1991**; chapter 11, p. 126 .

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