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PALLADIUM(II) AND PLATINUM(II)-C₍₃₎-SUBSTITUTED 2,2'-BIPYRIDINES

Reaction of Pd(OAc)₂ with HL¹ and HL² (HL¹=6-*iso*-propyl-2,2'-bipyridine; HL²=6-*neo*-pentyl-2,2'-bipyridine), followed by treatment with LiCl or KI gives [PdCl(L¹)₂] (1), [PdCl(L²)₂] (2), [PdI(L²)₂] (3), respectively. The chloride bridge in complexes 1 and 2 is split by PPh³ to give the mononuclear species PdCl(L¹)(PPh₃) (4), and PdCl(L²)(PPh₃) (5). Spectroscopic data provide evidence for coordination of the deprotonated ligands through a nitrogen and the C₍₃₎ atom of the 6-substituted pyridine. An analogous platinum complex PtCl(L³)(SMe₂) (6), (HL³=6-*tert*-butyl-2,2'-bipyridine) was obtained from *trans*-PtClMe(SMe₂)₂ and HL³. The crystal structures of compounds 1 and 6 have been solved by X-ray diffraction analysis.

INTRODUCTION

2,2'-bipyridines are traditional ligands in the coordination chemistry of transition metals, and their complexes have been known ago, many years [1]. Recently they have received a growing and widespread interest, as applications of their derivatives were widening to encompass different fields: a) assembly of supramolecular networks [2–3]; b) molecular devices of photochemical interest [4]; c) materials with non-linear optical properties [5]; d) liquid crystals [6]; e) intermediates in synthesis, even asymmetric, [6]; f) catalytic precursors in polymerization and copolymerization processes [8, 9].

As a consequence, much attention has been devoted to the synthesis of substituted 2,2'-bipyridines, bearing substituents with widely ranging electronic and steric properties to evaluate their influence on the behavior of the ligands.

In recent years we have studied the coordination of a series of 6-substituted-2,2'-bipyridines with R = Ph, CH₂Ph, alkyl etc, and isolated and characterized adducts with different metals (Pd(II), Pt(II), Au(III), Rh(III)). In addition, much work has been directed to achieve activation of C-H bond on the substituent [10] to give cyclometallated N,N,C derivatives: new species have been obtained arising both from C(sp³)-H and C(sp²)-H activation with the formation of 5- and 6-membered rings [11–14].

In contrast, up to now, in no case we observed activation of C-H bond of pyridine ring. Examples of transition metal C-substituted 2,2'-bipyridines are really rare: as far as we know, only a few species have been unambiguously characterized. The first one is [Ir(2,2'-bipyridinyl-C³,N')(2,2'-bipyridine-N,N')]₂⁺⁺ the nature of which has been confirmed after a long and controversial debate [15–17]. Activation of C-H bond has been also invoked to explain the formation of ArH in a process of thermal rearrangement of (Ar)₂(biPy)platinum(II) complexes: no simple mononuclear species were isolated but the metallation was confirmed by the X-ray structure of a more complex dinuclear species [18].

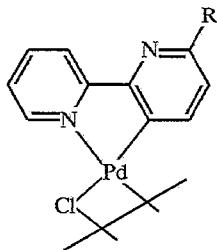
Finally Wimmer and coworkers reported the $C_{(3)}$ metallation of N-methylbipyridine [19].

Here we describe some palladium and platinum derivatives with 6-alkyl-2,2'-bipyridines containing a M-C(sp^2) bond, isolated in the course of an investigation of the reactivity of $Pd(OAc)_2$ and $PtClMe(SMe)_2$.

The new compounds have been fully characterized, including X-ray determination, as unusual examples of "roll-over" metallation of the heterocyclic bipyridine system.

DISCUSSION

The unsymmetric 6-R-2,2'-bipyridine (HL^1 , $R=CHMe_2$; HL^2 , $R=CH_2CMe_3$; HL^3 , $R=CMe_3$) were obtained according to a procedure previously described [20–21]. The reaction of $Pd(OAc)_2$ with HL^1 and HL^2 in benzene at reflux, gives crude products which were treated with LiCl in acetone/water solution. After crystallization complexes **1** and **2**, $[PdCl(L)]_2$, $L=L^1$, **1**, and $L=L^2$, **2**, were isolated in moderate yields, as yellow solids. In the case of HL^2 , treatment of the crude product with KI instead of LiCl, allowed to isolate $[Pd(L^2)]_3$, **3**.



1 $R = CHMe_2$; **2** $R = CH_2CMe_3$

Surprisingly, in the 1H NMR spectra of compounds **1** and **2** (Table 1) only six resonances are observed in the aromatic region. The analysis of the spectra reveals the presence of an AB system formed by the $H_{(4)}$ and $H_{(5)}$ protons (δ 6.85 d, 7.63 d, $J_{AB} = 8.0$ Hz, **1**; 6.77 d, 7.61 d, $J_{AB} = 8.0$ Hz, **2**) giving evidence for existence of trisubstituted pyridine ring. This implies that metallation has occurred to give a Pd- $C_{(3)}$ bond. Taken together with analytical data and molecular weight determinations, a dimeric species with chloride bridges can be envisaged. The X-ray analysis of complex **2** has been solved and the nature of compound **2** as 3-metallated dinuclear complex confirmed.

The structure of **1** consists of the packing of $[PdCl(L^1)]_2$ molecules with no unusual van der Waals contacts. The molecule lies on crystallographic inversion centre, so that the Pd-Cl-Pd'-Cl' rhombus is strictly planar. An ORTEP [22] view of the molecule is shown in Fig. 1. Principal bond lengths and angles are listed in Table 2. The Pd atom is in a square-planar coordination with a very slight tetrahedral distortion, maximum distances from the best plane being +0.066(6) Å for $C_{(7)}$ and -0.052(5) Å for $N_{(1)}$. The dihedral angle between this best plane and the plane of the Pd-Cl-Pd'-Cl' moiety is 1.8(1.3)°. The dihedral angle between the Cl-Pd-Cl' and $N_{(1)}$ -Pd- $C_{(7)}$ planes is 4.6(1.2)°.

Proton and $^{31}\text{P}\{^1\text{H}\}$ NMR data for the ligands and compounds 1-6

$\delta^1\text{H}$	HL ¹	HL ²	HL ³	[PdCl(L ¹) ₂], 1	[PdCl(L ²) ₂], 2	[Pd(L ²) ₂], 3	[PdCl(L ¹)(PPh ₃)], 4	[PdCl(L ²)(PPh ₃)], 5	[PtCl(L ³)(SMe ₂)], 6
CH ₃	1.35 d	1.05 s	1.43 s	1.30 [6H, d] (7.1)	0.96 [9H, s]	0.96 [9H, s]	1.22 [6H, d] (6.8)	0.90 [9H, s]	1.37 [9H, s] 2.78 [6H, s] [53.7]
CH ₂ CH	3.10 m	2.80 s		3.00 [1H, m] (7.1)	2.62 [2H, s]	2.60 [2H, s]	2.85 [1H, m] (6.8)	2.48 [2H, s]	
H _{(6'})	8.65 ddd	8.66 ddd	8.66 ddd	8.74 [1H, br]	8.75 [1H, br]	9.08 [1H, br]	9.58 [1H, m]	9.58 [1H, m]	9.61 [dd, 1H] [38.4]
H _(5')	7.26 ddd	7.27 ddd	7.29 ddd	7.26 [1H, ddd]	7.27 [1H, ddd]	7.29 [1H, ddd]	7.33 [1H, m]	7.34 [1H, m]	7.33 [m, 1H]
H _(4')	7.78 td	7.79 ddd	7.81 ddd	7.91 [1H, td]	7.89 [1H, td]	7.92 [1H, td]	7.91 [1H, td]	7.90 [1H, td]	7.91 [td, 1H]
H ₍₃₎	8.50 dt	8.42 dt	8.55 dt						
H _(3')	8.20 dd	8.22 dd	8.21 dd	8.01 [1H, dd]	8.07 [1H, dd]	8.17 [1H, dd]	8.29 [1H, dd]	8.24 [1H, dd]	8.21 [dd, 1H]
H ₍₄₎	7.71 t	7.69 t	7.74 t	7.63 [1H, d] (8.0)	7.61 [1H, d] (8.0)	8.06 [1H, br]	6.62 [1H, dd] (8.1) [6.1]	6.58 [1H, dd] (8.0) [6.3]	7.78 [d, 1H] [45.7] (8.1)
H ₍₅₎	7.17 dd	7.11 dd	7.35 dd	6.85 [1H, d] (8.0)	6.1 [1H, d] (8.0)	6.73 [1H, d] (8.0)	6.31 [1H, d] (8.1)	6.23 [1H, d] 6.24 (8.0)	7.08 [d, 1H] [12.7] (8.1)
<i>o</i> -H							7.77 [6H, m]	7.78 [6H, m]	
<i>m</i> -H							7.38 [6H, m]	7.39 [6H, m]	
<i>p</i> -H							7.46 [3H, m]	7.46 [3H, m]	
$\delta^{31}\text{P}$							43.99	43.80	

Note: Spectra recorded at room temperature in CDCl₃, chemical shifts in ppm from internal TMS (^1H) and external 85% H₃PO₄ (^{31}P); coupling constants are given in Hz, $J_{(\text{H-H})}$ in parentheses, $J_{(\text{Pt-H})}$ in square brackets.

Table 2.
Selected bond distances (Å) and angles (deg.) with estimated standard deviations (e.s.d.'s) in parentheses for $[\text{PdCl}(\text{L}^1)]_2$, **1** and $[\text{PtCl}(\text{L}^3)(\text{SMe}_2)]$, **6**

$[\text{PdCl}(\text{L}^1)]_2$, (1)		$[\text{PtCl}(\text{L}^3)(\text{SMe}_2)]$, (6)	
Pd–Cl	2.458(2)	Pt–Cl	2.395(2)
Pd–N ₍₁₎	2.039(4)	Pt–N ₍₁₎	2.042(4)
Pd···Pd'	3.481(1)	S–C ₍₁₅₎	1.777(10)
Cl–Pd–Cl'	86.9(1)	Cl–Pt–S	92.6(1)
Cl–Pd–C ₍₇₎	175.7(2)	Cl–Pt–C ₍₇₎	172.6(2)
Cl'–Pd–C ₍₇₎	94.5(2)	S–Pt–C ₍₇₎	92.2(2)
Pd–Cl–Pd'	93.1(1)	Pt–S–C ₍₁₅₎	108.5(4)
Pd–Cl'	2.335(2)	C ₍₁₅₎ –S–C ₍₁₆₎	97.9(5)
Pd–C ₍₇₎	1.970(5)	Pt–S	2.263(2)
Cl–Pd–N ₍₁₎	97.4(1)	Pt–C ₍₇₎	1.990(5)
Cl'–Pd–N ₍₁₎	175.5(2)	S–C ₍₁₆₎	1.759(11)
N ₍₁₎ –Pd–C ₍₇₎	81.4(2)	Cl–Pt–N ₍₁₎	94.3(1)
		S–Pt–N ₍₁₎	173.0(1)
		N ₍₁₎ –Pt–C ₍₇₎	81.1(2)
		Pt–S–C ₍₁₆₎	110.1(3)

The Pd···Pd' distance, 3.481(1) Å, is nonbonding. Bond lengths involving palladium in the present molecule can be compared with those found in $[\{\text{LPd}(\mu\text{-Cl})_2 \text{PdL}_2\}_2 (\text{HL} = 2\text{-phenylpyridine})]$, compound **7** [23], where two dimeric units similar to that observed in the present molecule are weakly connected through crystallographic centre of symmetry. The Pd–Cl' distance found here, 2.335(2) Å, is similar to the average Pd–Cl bond length *trans* to nitrogen atom in **7**, 2.355 Å, whereas the present Pd–Cl bond length, 2.458(2) Å, which is elongated by the *trans* influence of the aryl C₍₇₎ atom, is similar

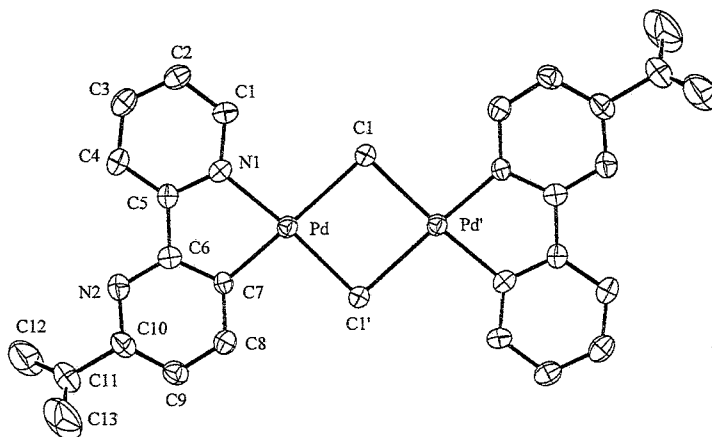


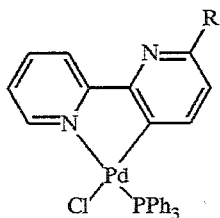
Fig 1. ORTEP view of $[\text{PdCl}(\text{L}^1)]_2$, **1**. Primed atoms are related to unprimed ones by the symmetry operation $-x, -y, 1-z$. Ellipsoids are drawn at the 30% probability level

to the average Pd–Cl bond length *trans* to carbon atom in **7**, 2.423 Å. The Pd–N₍₁₎ distance here, 2.039(4) Å, is close to the average Pd–N bond length in **7**, 2.009 Å, and the present Pd–C₍₇₎ bond length, 1.970(5) Å, is statistically coincident with the average Pd–C distance in **7**, 1.975 Å. The N_{(1)...}C₍₅₎ and N_{(2)...}C₍₁₀₎ rings in the present molecule are strictly planar.

As usually observed, the halide bridges in dinuclear species such as **1** and **2** are easily cleaved by two electron donors as PPh₃, to give the mononuclear complexes [PdCl(L¹)(PPh₃)], **4**, and [PdCl(L²)(PPh₃)], **5**.

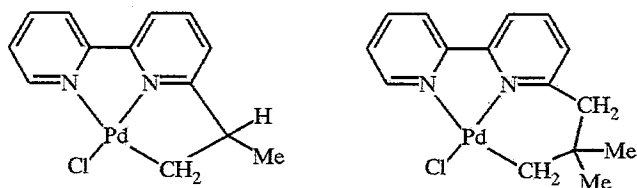
The splitting of the chloride bridge by PPh₃ can afford two isomers having a P–Pd–N and a P–Pd–C *trans* arrangement, respectively. In agreement with the strong *trans* influence of carbon ligand, the NMR data suggest that phosphorus atom is bonded *trans* to the nitrogen atom, as indicated by the resonance of the H_(6') proton. Previous observations have shown that in mononuclear systems with similar geometries the chemical shift of the H_(6') proton is strongly dependent on the nature of the ligand coordinated in its proximity: triphenylphosphine exerts usually a shielding effect, compared to the free ligand, whereas coordinated chlorine or iodine atom possess a strongly deshielding effect [24].

In compounds **4** and **5**, the H_(6') protons are strongly deshielded (δ 9.58), and the H₍₄₎ protons are strongly shielded (δ 6.62, **4**; 6.58, **5**) confirming the P–Pd–N arrangement. In the aromatic region an ABX spin system can be observed for H₍₄₎ and H₍₅₎ (X = P, $4J_{(P-H)}$ ca. 6 Hz). This formulation was supported by NOE difference experiments on complex **4** (CDCl₃ solution). Irradiation of the H₍₄₎ at δ 6.62 gives enhancement of signals at δ 6.31 (H₍₅₎) and 7.77 (*o*-H of PPh₃), whereas irradiation of H₍₅₎ at δ 6.31 results in enhancement of the H₍₄₎ proton and of CH and CH₃ of the *iso*-propyl substituent at δ 2.85 and 1.22, respectively.



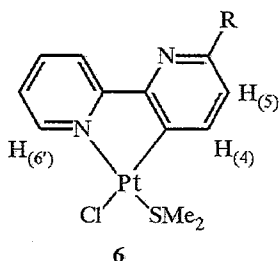
4 R = CHMe₂, **5** R = CH₂CMe₃

Complexes **1-5** are unusual examples of C₍₃₎-metallated 2,2'-bipyridine. It is worth to note that complexes **1-2** are not the only ones which are formed in the reaction between Pd(OAc)₂, the ligands and LiCl. Indeed in the crude products, after isolation of **1** or **2**, several other products are present, as shown by ¹H NMR spectra. Among them are simple 1:1 adducts, which can be obtained also by reaction with Na₂[PdCl₄] and cyclometallated species arising from activation of C(sp³)-H bond in the substituent. It seems therefore that the transfer of H from the aromatic ring to give C₍₃₎-metal bonds is not related to the bulky nature of the substituents. The accompanying activation of a methyl group to give the cyclometallated derivatives similar to those previously reported in the case of 6-*tert*-butyl-2,2'-bipyridine [25], is likely to be favoured by the formation of a second ring to give N,N,C terdentate ligand.



Quite recently in the course of an investigation on the reactivity of some 6-substituted-2,2'-bipyridines with organometallic derivatives of platinum(II), we met with another example of a $C_{(3)}$ -metallated complex. The reaction of *trans*-[PtCl(Me)(SMe₂)₂] with HL³ in mild conditions (CH₂Cl₂, r.t.) is very slow: after two weeks under stirring we were able to isolate, with low yield, complex **6**, [PtCl(L³)(SMe₂)]. In this case the reaction seems to be selective: in the reaction mixture, in addition to **6**, only the reagents were identified.

The ¹H NMR spectra, besides the signals of the coordinated SMe₂ (δ 2.78 s, ³J_(Pt-H) ca. 54 Hz), show six aromatic protons only. The AB system formed by H₍₄₎ and H₍₅₎ is accompanied by the satellites due to coupling to ¹⁹⁵Pt (³J_(Pt-H) = 46 Hz and ⁴J_(Pt-H) = 13 Hz) confirming coordination of platinum with the C₍₃₎ atom. The H_(6') proton is strongly deshielded (δ 9.61), supporting the presence of chlorine atom in its proximity and showing coupling, ³J_(Pt-H) = 38 Hz, indicative of the coordination of the nitrogen atom.



The X-ray study confirmed the proposed structure.

The crystal structure of **6** consists of the packing of [PtCl(L³)(SMe₂)] molecules with no unusual van der Waals contacts. An ORTEP [22] view of the molecule is shown in Fig. 2. Principal bond lengths and angles are shown in Table 2. The Pt atom is in a square-planar coordination with very slight tetrahedral distortion, maximum distances from the best plane being +0.063(4) Å for N₍₁₎ and -0.084(5) Å for C₍₇₎. The dihedral angle between the Cl-Pt-S and the N₍₁₎-Pt-C₍₇₎ planes is 6.0(9)°. The Pt-Cl distance, 2.395(2) Å, is normal for a terminal interaction *trans* to aryl carbon atom, and is statistically coincident with the Pt-Cl bond length, 2.393(1) Å, found in chloro(diethylsulfido)-{(2'-thienyl)pyridinato-N,C₍₃₎}platinum(II), compound **8** [26]. The Pt-S bond length, 2.263(2) Å, is also coincident with the Pt-S distance, 2.263(1) Å, found in **8**. The Pt-N₍₁₎ and Pt-C₍₇₎ bond lengths, 2.042(4) and 1.990(5) Å, respectively, are very similar to the corresponding values found in compound **1** (Table 2), and to the Pt-N and Pt-C distances, 2.055(3) and 1.974(4) Å, respectively, found in **8**. The N₍₁₎...C₍₆₎ and N₍₂₎...C₍₁₀₎ rings are strictly planar.

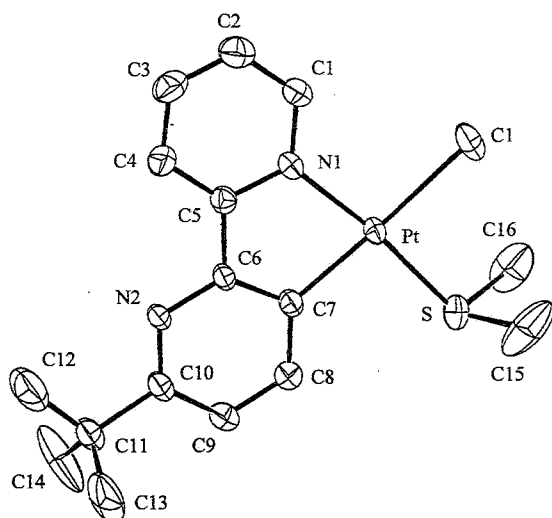


Fig. 2. ORTEP view of $[\text{PtCl}(\text{L}^3)(\text{SMe}_2)]$, **6**. Ellipsoids as in Fig. 1.

The synthesis of compound **6** reminds that described by Skapsi *et al.* [18]: in that case the “roll-over” metallation was postulated to explain formation of ArH in the thermal rearrangement of diaryl(bipyridyl)platinum(II) complexes. No mononuclear species were observed but the molecular structure of dimeric species provided evidence for the metallation. In our case, the $\text{C}_{(3)}$ metallation likely involves hydrogen transfer from the ligand with elimination of methane.

EXPERIMENTAL

The ligands were prepared according to the known methods [20–21]. $\text{Pd}(\text{CH}_3\text{COO})_2$ and K_2PtCl_4 were obtained from Janssen and Engelhard, respectively. All the solvents were purified before use according to standard methods.

Elemental analyses were performed with a Perkin-Elmer Elemental Analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductometer. Infrared spectra were recorded with a Perkin-Elmer 983 using Nujol mulls or in CH_2Cl_2 solution. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ 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 I. Chemical shifts are given in ppm downfield to internal standard TMS (^1H , ^{13}C) or external standard 85% H_3PO_4 (^{31}P).

Mass spectra were obtained with a VG 7070EQ, instrument operating under FAB conditions with 3-nitrobenzyl alcohol (NBA) as supporting matrix.

Synthesis

Preparation of compounds 1-2. General procedure. Solution of HL (1.50 mmol) and $\text{Pd}(\text{CH}_3\text{COO})_2$ (1.50 mmol) in benzene (40 ml) was refluxed for *ca.* 7 h, then filtered and evaporated to dryness. The residue was treated with a mixture of water/acetone 1:3 (40 ml) containing LiCl (excess) and stirred for *ca.* 1 week. The precipitate formed was filtered and recrystallized from CH_2Cl_2 to give the analytical sample as a yellow solid.

$[\text{PdCl}(\text{L}^1)]_2$ (**1**). Yield 25 %, m. p. 265 °C. MW (CHCl_3): found 693, calculated 678.2. IR (nujol) ν_{max} , cm^{-1} : 1605 m, 1551 s, 344 w. Found, %: C 46.30; H 3.77; N 8.15. $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{N}_4\text{Pd}_2$. Calculated, %: C 46.04; H 3.83; N 8.26.

[PdCl(L²)]₂ (2). Yield: 35 %, m. p. 293 °C (dec.). IR (nujol) ν_{\max} , cm⁻¹: 1605 s, 1535 w, 740 s, 338 s, 295 s, 258 s; MS (FAB), *m/z*: 697 ([M-Cl]⁺). Found, %: C 48.92; H 4.60; N 7.29. C₃₀H₃₄Cl₂N₄Pd₂. Calculated, %: C 49.07; H 4.67; N 7.63.

[PdI(L²)]₂ (3). The procedure described for compound 2 was followed, using KI in place of LiCl. Yield 40%, m. p. 267°C (dec). Found, %: C 37.78; H 3.85; N 5.62. C₃₀H₃₄I₂N₄Pd₂·H₂O. Calculated, %: C 38.53; H 3.88; N 5.99.

[PdCl(L¹(PPh₃))] (4). To a suspension of complex 1 (46.8 mg, 0.069 mmol) in CH₂Cl₂ 36.2 mg of PPh₃ (0.138 mmol) were added. The mixture was stirred for 5 h at room temperature, then evaporated to dryness. The crude product was crystallized from CH₂Cl₂/hexane to give the analytical sample as a cream solid. Yield 86%, m. p. 145°C (dec). IR (nujol) ν_{\max} , cm⁻¹: 1604 m, 1100s. Found, %: C 61.44; H 4.49; N 4.55. C₃₁H₂₈ClN₂PPd. Calculated, %: C 61.91; H 4.69; N 4.66%

[PdCl(L²(PPh₃))] (5). The procedure described for complex 4 was followed, using complex 2 instead of 1. Yield 82%, m. p. 205...216 °C (dec.). IR (nujol) ν_{\max} , cm⁻¹: 1600 s, 1100 s, 530 s. MS (FAB), *m/z*: 628 ([M]⁺), 593 ([M-Cl]⁺), 366 ([M-PPh₃]⁺). Found, %: C 62.48; H 5.30; N 4.53. C₃₃H₃₂ClN₂PPd. Calculated, %: C 62.97; H 5.12; N 4.45.

[PtCl(L³(SMe₂))] (6). To a solution of *trans*-[PtClMe(SMe₂)₂] (0.060 g, 0.16 mmol) in CH₂Cl₂ (20 ml) a solution of HL³ (0.037 g, 0.17 mmol) in the same solvent (5 ml) was added. The mixture was stirred at room temperature until a pale yellow color was formed (12 days). Then it was concentrated to small volume. Pure 6 was obtained by column chromatography on silica gel, using dichloromethane as eluent. Yield 10%. m.p. 206...208° C. FAB mass spectrum: *m/z* 503 ([M]⁺), 468 ([M-Cl]⁺), 441 ([M-SMe₂]⁺), 406 ([M-Cl-SMe₂]⁺). IR (nujol) ν_{\max} /cm⁻¹: 1608 m, 1562 mw, 1551 mw, 1526 mw, 392 m, 275 s. Found, %: C 37.89; H 3.87; N 5.26. C₁₆H₂₁ClN₂PtS. Calculated, %: C 38.13; H 4.20; N 5.56. ¹³C NMR data (CDCl₃) δ : 23.3 (S(CH₃)₂, *J*_{Pt-C} = 24 Hz); 30.1 (CH₃); 37.0 (C(CH₃)₃); 119.9 (*J*_{Pt-C} = 50.5 Hz), 121.2 (*J*_{Pt-C} = 43.4 Hz), 123.6 (*J*_{Pt-C} = 32.4 Hz) (C₍₃₎); C₍₅₎, C₍₅₎; 131.7, C₍₃₎; 137.9 (C₍₄₎, *J*_{Pt-C} = 64 Hz); 149.3, (C₍₆₎), *J*_{Pt-C} = 19.8 Hz); 164.25, 164.4, 161.4 (C₍₂₎, C₍₂₎, C₍₆₎). ¹³C NMR data for HL³ (given for comparison, solvent CDCl₃, assignments accomplished by 2D ¹H-¹³C heteronuclear correlation experiments (HETCOR)) δ : 30.1 (CH₃); 37.5 (CMe₃); 117.4 (C₍₃₎); 118.9 (C₍₅₎); 121.0 (C₍₃₎); 123.3 (C₍₅₎); 136.6 (C₍₄₎); 136.9 (C₍₄₎); 148.8 (C₍₆₎); 154.3, 156.3 (C₍₂₎, C₍₂₎); 168.3 (C₍₆₎).

X-ray Data Collection and Structure Determination

Crystal data and other experimental details are summarized in Table 3. The diffraction experiment concerning 1 was carried out on a Enraf-Nonius CAD-4 diffractometer at room temperature using MoK α radiation ($\lambda=0.71073$ Å) with a graphite crystal monochromator in the incident beam. A periodic monitoring of three standard reflections revealed a crystal decay which was of about 2.7% (on intensities) at the end of data collection. The intensities were corrected for Lorentz, polarization, decay and absorption effects (empirical correction) [27].

The diffraction experiment concerning 6 was carried out on a Siemens SMART CCD area-detector diffractometer at room temperature using MoK α radiation ($\lambda=0.71073$ Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from the least-squares refinement of 164 reflections measured in three different sets of 15 frames each, in the range $3 < \theta < 23^\circ$. At the end of data collection the first 45 frames, containing 555 reflections, were recollected to have a monitoring of crystal decay, which was not observed, so that no time-decay correction was needed. The 1937 collected frames were processed with the software SAINT [28], and an empirical absorption correction was applied (SADABS) [29] to the 40804 collected reflections, 4468 of which are unique with $R_{\text{int}} = 0.055$ ($R_{\text{int}} = \sum |F_0^2 - F_{\text{mean}}^2| / \sum F_0^2$). Scattering factors and anomalous dispersion corrections were taken from ref. [30].

The calculations were performed on an AST Power Premium 486/33 computer using the Personal Structure Determination Package [31–32] and the physical constants tabulated therein. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\sum w (F_0 - k |F_c|)^2$. In compound 1 the Me groups of the isopropyl moiety are disordered, and the two methylic group carbon atoms have been treated as four “half” carbon atoms with an occupancy factor of 0.50 each (atoms C₍₁₂₎–C₍₁₅₎). In Fig. 1 only two of these disordered carbon atoms have been depicted [C₍₁₂₎ and C₍₁₃₎]. Anisotropic thermal factors were refined for all the non-hydrogen atoms.

Table 3.

Crystallographic experimental details

	Compound 1	Compound 6
Empirical formula	C ₂₆ H ₂₆ Cl ₂ N ₄ Pd ₂	C ₁₆ H ₂₁ ClN ₂ PtS
M	678.2	504.0
Colour	pale yellow	yellow
Crystal system	monoclinic	tetragonal
Space group	C2/c (no. 15)	I4 ₁ cd (no. 110)
Unit cell parameters		
<i>a</i> , Å	39.567 (9)	12.121 (1)
<i>b</i> , Å	5.168 (1)	
<i>c</i> , Å	12.989 (4)	48.147 (5)
β, deg.	99.87 (2)	
<i>V</i> , Å ³	2617 (2)	7074 (2)
<i>Z</i>	4	16
<i>F</i> (000)	1344	3872
<i>T</i> , K	298	298
<i>D</i> _c , g cm ⁻³	1.72	1.89
Crystal dimension (mm)	0.11x0.34x0.39	0.084x0.48x0.53
μ (MoK _α), cm ⁻¹	15.8	82.8
Min. and max. transmiss.factors	0.89-1.00	0.52-1.00
Scan mode	ω	ω
ω-scan width, deg.	1.80 + 0.35 tgθ	
Frame width, deg.		0.38
Time per frame, sec		30
No. of frames		1937
Detector/sample distance/cm		5.00
θ-range, deg.	3 - 25	3 - 26
Reciprocal space explored	+ <i>h</i> , + <i>k</i> , ± <i>l</i>	± <i>h</i> , ± <i>k</i> , ± <i>l</i>
Measured reflections (total, independent)	2279, 2279	40804, 4468
<i>R</i> _{int}		0.055
Unique observed reflections with <i>I</i> > 3σ(<i>I</i>)	1551	3890
Final <i>R</i> and <i>R</i> ' ^a	0.035, 0.045	0.028, 0.029
No. of variables	172	189
Goodness of fit ^b	1.21	1.04

^(a) $R = [\sum (|F_0 - k|F_c|) / \sum F_0]$, $R' = [\sum w(F_0 - k|F_c|)^2 / \sum wF_0^2]^{1/2}$

^(b) $[\sum w(F_0 - k|F_c|)^2 / (N_0 - N_v)]^{1/2}$, where $w = 1/[\sigma(F_0)]^2$,

$\sigma(F_0) = [\sigma^2(F_0^2) + (0.04F_0^2)^2]^{1/2} / 2F_0$,

*N*₀ is the number of observations, *N* - the number of variables.

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). For noncentrosymmetric compound **6**, full refinement of the correct structure model led to $R = 0.028$ and $R' = 0.029$, whereas full refinement of the inverted structure led to $R = 0.038$ and $R' = 0.044$. The final Fourier maps showed maximum residuals of $1.32(9) \text{ e}/\text{Å}^3$ at 1.20 Å from Cl in compound **1** and $1.51(12) \text{ e}/\text{Å}^3$ at 1.04 Å from Pt in compound **6**.

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