N^N^C platinum(II) and palladium(II) cyclometallates of 6,6′-diphenyl-2,2′-bipyridine, L: Crystal and molecular structure of [Pd(L–H)Cl]

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ARTICLE INFO

ABSTRACT

Reaction of $K_2[PtCl_4]$ or $Na_2[PdCl_4]$ with 6,6′-diphenyl-2,2′-bipyridine, L, gives the cyclometallated species [Pt(L–H)Cl], **1**, and [Pd(L–H)Cl], **2**, respectively, where L–H is a terdentate N^N^C anionic ligand originated by direct activation of a $C(sp^2)$–H bond. The crystal structure of **2** has been solved by X-ray diffraction and compared to that of the analogous complex [Pd(L′–H)Cl] L′ = 6-phenyl-2,2′-bipyridine. The second phenyl ring in **2** entails a considerable distortion of the coordination around the metal. A similar distortion is also to be expected in the analogous compound **1,** due to the almost equal covalent radii of palladium(II) and platinum(II).

From the complexes **1** and **2** the chloride can be displaced with $AgBF_4$ and substituted by CO or PPh_3 to give the corresponding cationic species. By reaction of **1** with $Na[BH_4]$ substitution of H^- for Cl^- can be achieved: the rare hydrido complex [Pt(L–H)H], stabilized only by nitrogen ligands, was isolated in the solid state and fully characterized in solution. It is noteworthy that in the case of the 6-phenyl-2,2′-bipyridine the analogous terminal hydride [Pd(L′–H)H] is unstable. In platinum chemistry the reaction of 6-substituted 2,2′-bipyridines is known to give either N^N^C or N′^C(3) rollover cyclometallation, depending on the nature of the metal precursor. In the case of $6,6′-Ph_2-2,2′$-bipy cyclometallation was also shown to undergo multiple C–H activation giving the C^N^C pincer complex [Pt(L-2H)(DMSO)]. The latter species can be related to complex **1**: indeed its reaction with HCl produces complex **1** and [Pt(L–H)(DMSO)Cl], a rollover species with a pendant phenyl substituent.

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1. Introduction

Cyclometallated derivatives of late transition metals with heterocyclic nitrogen ligands [1] have attracted, and still attract, great attention due to the considerable range of their potential applications in many fields such as organic synthesis [2], homogeneous catalysis [3], novel materials [4] and medicinal chemistry [5].

In recent years interest in C^N cyclometallates has mostly been addressed to platinum(II) derivatives due to their potential applications as chemosensors [6], switches [7], metallomesogens [8] and luminescent devices [9e,15]. Besides the classical bidentate C^N ligands, as time went up more complex molecules have been used, potentially able to act as terdentate ligands, and many cyclometallates with different sequence of donor atoms, e.g., N^N^C [10], N^C^N [11], and C^N^C [12], have been synthesized. A particular interest was devoted to species with planar aromatic terden-

tate ligands, typically, e.g., those arising from 6-aryl-2,2′-bipyridines. This planar motif implies a delocalized π system which can give rise to peculiar photophysical and photochemical properties, involving, *inter alia*, weak non-covalent interactions such as d^8–d^8, π–π, or C–H···π interactions [13]. In this framework much studied ligands have been 6-phenyl-2,2′-bipyridine, (L′), able to act as an N^N^C donor [14], compounds **A** (Chart 1), 1,3-dipyridyl-benzene, an N^C^N pincer ligand [9], compounds **B**, and 2,6-diphenyl-pyridine [13a,16], which can give rise to C^N^C compounds **C.** On the whole compounds **A-C** remind those of the neutral ligand terpy, compounds **D**.

Recently it has been shown that ligands such as 6-phenyl-2,2′-bipyridine and 6,6′-diphenyl-2,2′-bipyridine have a rich organometallic chemistry depending on the nature of the platinum precursor. In the case of 6-Ph-2,2′-bipy two divergent behaviour have been reported: with an inorganic precursor, typically an alkaline salt of $[PtCl_4]^{2-}$, activation of an ortho C–H bond of the pendant phenyl substituent is achieved with loss of HCl: an N^N^C cyclometallate is obtained in good yields [14a] (compound **A**). At variance, by reaction with an organo precursor, e.g., the electron-rich
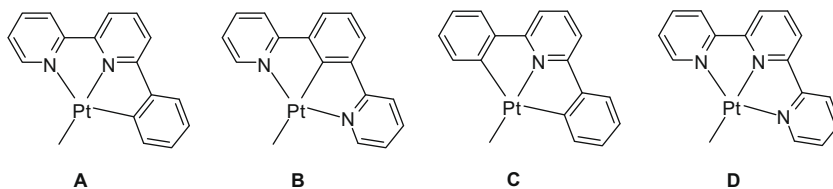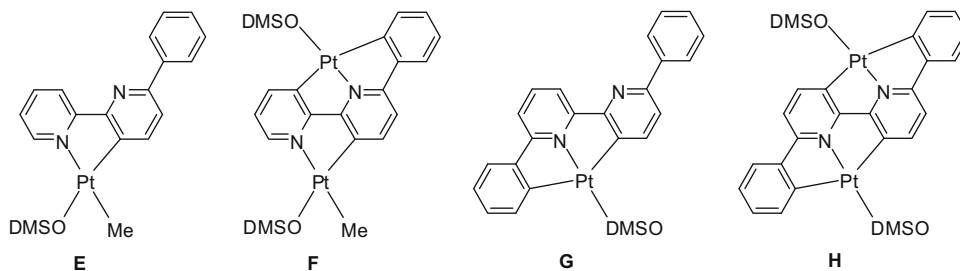
Chart 1.

Chart 2.

[Pt(Me)$_2$(DMSO)$_2$], activation of the C(3)–H(3) bond of the substituted pyridine ring occurs with loss of CH$_4$, and a C(3)–(N′) "roll-over" cyclometallate is formed [17] (Chart 2, compound **E**). With the same organo precursor an analogous behaviour has also been observed for the disubstituted 6,6′-Ph$_2$-2,2′-bipy, with activation both of a C(aryl)–H and a C(pyridyl)–H bond, to give compound **G** [18]. More complex dinuclear species, which imply multiple C–H activations have also been synthesized for both the ligands, compounds **F** and **H**, respectively. (Chart 2) [17,18]

Herein we describe the behaviour of the 6,6′-diphenyl-2,2′-bipyridine, **L**, in the reaction with the inorganic precursors [PtCl$_4$]$^{2-}$ and [PdCl$_4$]$^{2-}$, and compare it with that of the 6-phenyl-2,2′-bipyridine. The effect of the additional phenyl substituent on the stability and reactivity of some new cyclometallates is discussed. The X-ray structure of [Pd(L–H)Cl] is also reported.

2. Results and discussion

2.1. Synthesis of Pt(L–H)Cl (**1**) and Pd(L–H)Cl (**2**)

The ligand 6,6′-diphenyl-2,2′-bipyridine was synthesized from 2,2′-bipyridine and phenyl lithium, as previously described [18]. Throughout this paper **L** and **L′** indicate 6,6′-diphenyl-2,2′-bipyridine and 6-phenyl-2,2′-bipyridine, respectively.

6,6'-diphenyl-2,2'-bipyridine, L   6-phenyl-2,2'-bipyridine, L'
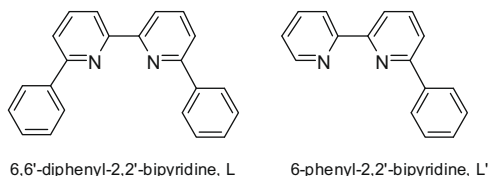
The cyclometallated compound [Pt(L′–H)Cl], a well-known N^N^C derivate of type **A** which has attracted great attention for its outstanding properties especially in photochemistry, can be obtained by reaction of K$_2$[PtCl$_4$] under classical conditions (water, HCl, reflux temperature, see Section 2). In order to compare the behaviour of the ligands **L** and **L′**, the reaction of **L** with K$_2$[PtCl$_4$] was carried out under the same experimental conditions. The outcome of the reaction, according to analytical data, is a cyclometallate [Pt(L–H)Cl], **1**. The ^{1}H NMR spectrum indicates a not symmetric ligand due to the absence of an aromatic proton with respect to the ligand.

Compared with [Pt(L′–H)Cl], the spectrum shows four spin systems of 4, 3, 3 and 5 aromatic protons, corresponding to a disubstituted phenyl, two disubstituted pyridines and a mono-substituted phenyl ring, respectively. The part of the spectrum relative to protons away from the second phenyl ring (e.g., H4″, H5″, H6″, and H5) is almost superimposable to that of [Pt(L′–H)Cl]. A ^{1}H 2D COSY spectrum allowed us to fully assign the proton resonances.
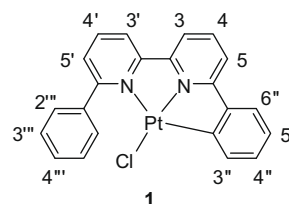
The appearance of the spectrum is dependent on the concentration of **1**, however we were unable to gain clear indication of intermolecular interactions.

The cyclopalladation reaction was performed under the same conditions, from Na$_2$[PdCl$_4$], to give compound **2**, [Pd(L–H)Cl]. Also in this case analytical and spectroscopic data are consistent with cyclometallation and a terdentate behaviour of the L–H ligand.

X-ray quality crystals of compound **1** were not obtained: at variance, suitable crystals of the palladium complex **2**, were collected by slow diffusion of di-isopropyl ether into a chloroform solution at room temperature.

2.2. X-ray crystal structure of compound **2**

The structure of **2** consists of the packing of [Pd(L–H)Cl] molecules (L = 6,6′-diphenyl-2,2′-bipyridine) in the triclinic space group P$\bar{1}$. The L–H anion behaves as a terdentate ligand, with the deprotonated phenyl ring bonded to the palladium atom, whereas the other phenyl ring remains pending (see Fig. 1).

The structure of **2** is unusual because there are four crystallographically independent molecules in the asymmetric unit. In order to favour the comparison between the four molecules, we have used the same labels and numbering for corresponding atoms of the molecules, adding three different markers to three of them. So, the four metal atoms are labeled Pd, Pd′, Pd*, and Pd#, and the molecules to which they belong carry the same markers, and will
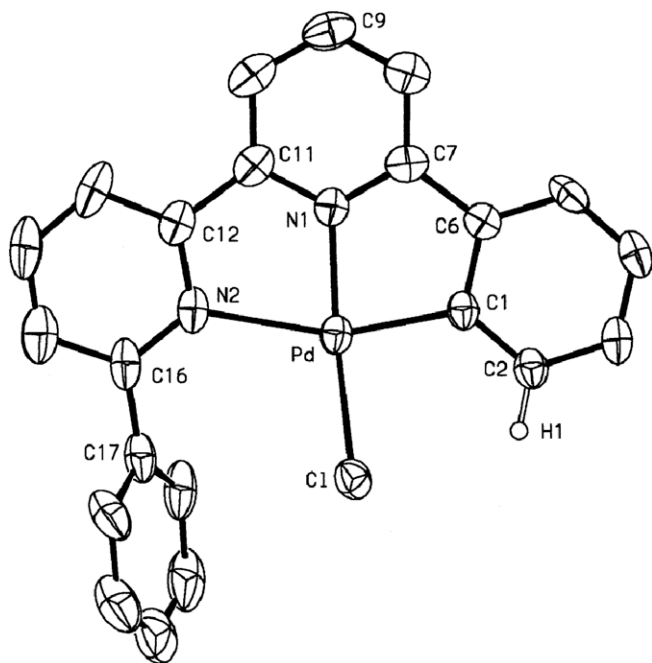
Fig. 1. ᴏʀᴛᴇᴘ view of molecule 1 of compound **2**. The other three crystallographically independent molecules differ only for the conformation of the pending phenyl ring. Atom H1 is shown because it forms a weak interaction with atom Cl (see text). Ellipsoids are drawn at the 30% probability level.

be called hereinafter molecule 1, 2, 3 and 4 (in the shown order). The four molecules are very similar to each other, differing only for the conformation of the pending phenyl ring (see later). Fig. 1 shows a view of molecule 1, and can represent also the other three molecules, with the exception of the pending phenyl ring. Selected bond distances and angles for corresponding interactions of the four molecules are listed in Table 1, together with the average value of each interaction. The metal atoms are all in a square planar

Table 1
Selected bond distances (Å) and angles (°) for the four independent molecules of **2**, with estimated standard deviations (esd's) on the last figure in parentheses.

	Mol. 1	Mol. 2	Mol. 3	Mol. 4	Average
Pd–Cl	2.300(1)	2.304(2)	2.293(1)	2.299(1)	2.299
Pd–N1	1.962(4)	1.979(4)	1.958(3)	1.977(4)	1.969
Pd–N2	2.233(3)	2.230(3)	2.262(4)	2.244(3)	2.242
Pd–C1	1.993(4)	1.983(3)	1.971(5)	1.950(4)	1.974
Cl–Pd–N1	167.5(1)	167.9(1)	169.1(1)	171.4(1)	169.0
Cl–Pd–N2	106.4(1)	106.7(1)	107.9(1)	107.5(1)	107.1
Cl–Pd–C1	94.6(1)	93.8(2)	93.4(1)	93.1(2)	93.7
N1–Pd–N2	78.2(1)	78.2(1)	77.0(1)	78.2(1)	77.9
N1–Pd–C1	81.1(2)	81.3(2)	82.2(2)	81.4(2)	81.5
N2–Pd–C1	159.0(2)	159.4(2)	158.7(2)	159.4(2)	159.1

coordination, with a more or less marked tetrahedral distortion. It may be useful to observe that if the Cl atoms are excluded by the calculation of the metal best planes, the planarity of the other four atoms becomes much more regular, and the Cl atoms are out of these best planes of 0.541(1), 0.487(1), 0.504(1), and 0.318(1) Å, for molecules 1, 2, 3 and 4, respectively. The crystal packing is characterized by the formation of isolate dimers between molecules 1 and 2 of the same unit cell (see Figs 2 and 3), whereas molecules 3 and 4 show only usual van der Waals contacts.

The dimer is not due to a short metal–metal interaction, as previously found in a number of similar molecules (see for instance, [Pd(L′–H)Cl] **3** (L′ = 6-phenyl-2,2′-bipyridine) [14a] [Pd(L″–H)Cl] **4** (L″ = 4-carboxy-6-phenyl-2,2′-bipyridine) [19], and [Pt(L‴–H)(CH₃CN)][ClO₄], **5** (L‴ = 2,9-diphenyl-1,10-phenanthroline) [20] where the Pd···Pd short distances are 3.28(1) and 3.27 Å (**3** and **4**) and the Pt···Pt short distance is 3.373(1) Å (**5**). Our intradimeric Pd···Pd′ distance is 3.920(1) Å. Moreover, in **3** and **4** there are infinite chains of stacked molecules, alternating short and long distances: in **3** it is reported as long distance the Pd···Pd interaction of 4.59(1) Å, whereas in **4** it is reported the distance between the centroids of the rings, 4.63 Å. Instead, in our case, the dimers are isolated (as in **5**), the shortest extradimeric Pd′···Pd distance being 8.638(1) Å. Our dimer is due to a typical π–π interaction between
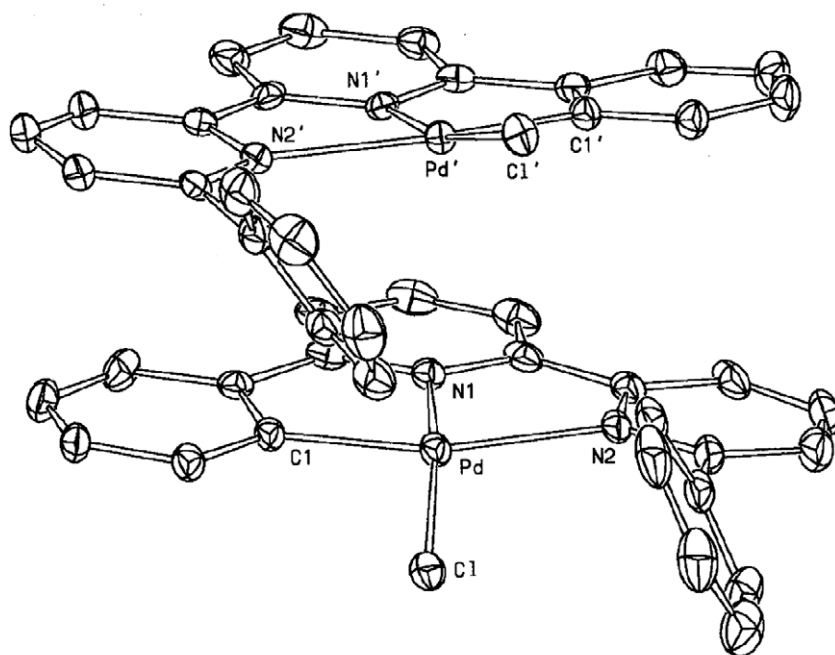

Fig. 2. Perspective view of the dimeric unit formed by molecules 1 and 2, due to π–π interaction between aromatic rings. Ellipsoids are drawn at the 20% probability level.
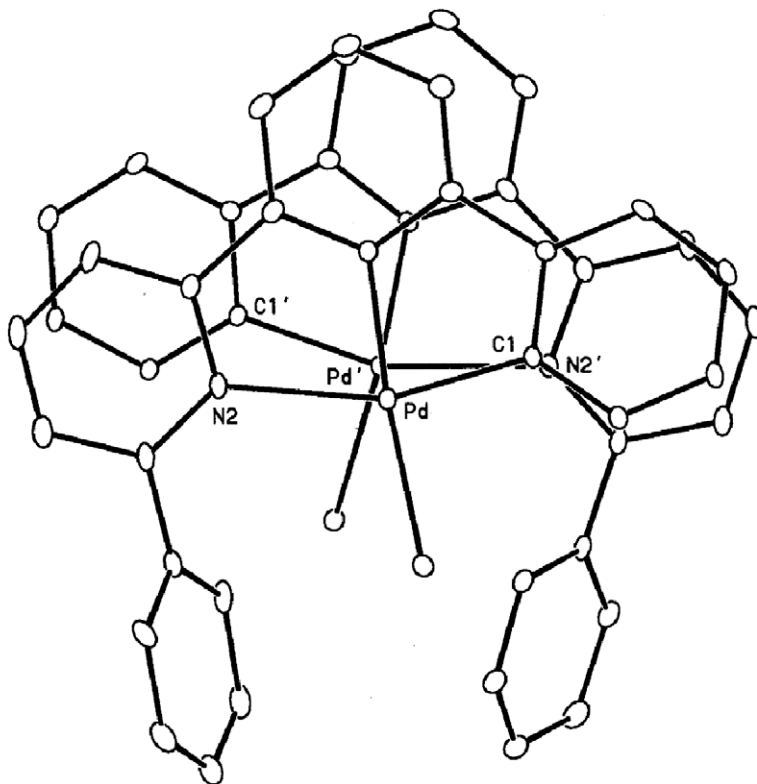
Fig. 3. Projection of the dimeric unit of Fig. 2 onto the best plane of the interacting aromatic rings. Ellipsoids are drawn at the 5% probability level.

the aromatic rings of the two almost flat (excluding the Cl atoms) molecules (see Figs 2 and 3). The interplanar distance in the dimeric unit is 3.614(6) Å and the interplanar angle is 4.4(1)°.

Distances and angles involving the metal atoms (see Table 1) can be compared with those reported in **3**, **4** and **5**. It is remarkably long, in our molecules, the Pd–N2 distance [average 2.242 Å, which to our knowledge is the longest interaction reported to date for M–N bond lengths in these molecules (M = Pd, Pt)]. The same distance is 2.067(3) Å in **3**, (where the molecule is identical to the present ones, with the exclusion of the pending phenyl ring, but there is a disorder N2/C1, due the fact that the molecule lies on a crystallographic twofold axis), 2.150(3) Å in **4**, where there is a carboxy moiety bonded to atom C9, and 2.212 (average of two) Å in **5** (M = Pt), where the flat ligand is 2,9-diphenyl-1,10-phenantroline. It is apparent that the presence of substituents on the flat parts of these molecules, particularly at their ends, induces an elongation of the M-N bond. The M–N1 bond lengths are in better agreement, being 1.969, 1.960(4), 1.964(3), and 1.927, respectively, in the four structures compared above. These distances are particularly short because they are the central bonds of bicycloterdentate ligands, and the shortening is usual [21]. The M–C bond lengths are 1.974, 2.067(3) (N2/C1), 1.997(4), and 1.98 Å, in the usual order. Also in this case, the bond length in compound **3** is markedly different from the others, but it is referred to a disordered C/N atom. The M–Cl distances are rather dispersed, being 2.299, 2.317(1), and 2.334 (1) Å (**5** does not carry a chlorine ligand, but an acetonitrile). These differences are probably due to packing forces. Listing them in the usual order (this work, **3**, **4** and **5**, respectively), the N1–M–N2 bite angles are 77.9, 80.2(1), 78.6(1), and 78.9°. The agreement is good, with the exception of the disordered molecule 3. The other bite angles, N1–M–C1, are 81.5, 80.2(1) (C/N), 81.4(1), and 81.5, respectively. They are statistically identical, with the usual exception of **3**. The N2–M–C1 angles are 159.1, not readable in **3**,

160.0(1) and 160.2°, respectively, showing a good agreement. The angles involving Cl are present in our molecules and in **3** and **4**. It is remarkable the deviation from linearity of our N1–Pd–Cl angle, 169.0°, whereas in **3** and **4** they are 180 (by crystallographic symmetry) and 177.5(1)°, respectively. Our four N1–Pd–Cl angles are all markedly non-linear (see Table 1), so that their non-linearity is likely due to steric repulsion of the pending phenyl rings. The average N2–Pt–N3 (acetonitrile) in **5** is 174.1°, much more close to linearity than our N1–Pd–Cl angles. It must be observed that in our molecules the average N2–Pd–Cl and C1–Pd–Cl are very different, being 107.1° and 93.7°, respectively. In 3 these two angles are equal by symmetry [99.7(1)°], and in 4 are not reported. In our case the difference between the two angles is ascribable to the phenyl ring that pushes the chlorine at a short distance from the cyclometallated phenyl producing weak interactions Cl···H1(C2) (2.625–2.70 Å).

As mentioned above, our four independent molecules differ for the conformation of the pending phenyl rings. The dihedral angles between these rings and those to which they are bonded are 57.8(2)°, 53.2(2)°, 39.7(3)°, and 133.7(1)° for molecules 1, 2, 3, and 4, respectively.

On the whole the effects of the pendant phenyl ring appear significant and likely affect both the reactivity and stability of the complexes. The distortion observed in compound **2** is also to be expected in the analogous compound **1**, taking account of the almost equal covalent radii of palladium and platinum.

2.3. Reactivity of compounds 1 and 2

Given the differences observed in the structures of the cyclometallates of the ligand **L** compared to those of the **L′** corresponding species, we have deemed worth to study also the effects of the additional phenyl substituent on some aspects of their reactivity.

Our attention has been focused on the fourth ligand, the chloride anion, and we investigated the feasibility of its substitution by neutral ligands to give cationic species, as well as by other anions.

Reaction of complex **1** with the silver salt of a poorly coordinating anion, $AgBF_4$, in acetone, leads to the displacement of Cl^-; after removal of AgCl, CO was bubbled into the acetone solution at room temperature. The cationic species $[Pt(L–H)(CO)][BF_4]$, **6**, similar to carbonyl complexes previously described, is isolated in good yields. In the IR spectra a very strong band at 2108 cm^{-1} (nujol mull), indicative of a terminal carbonyl, is shifted with respect to the analogous $[Pt(L'–H))(CO)][BF_4]$ derived from 6-phenyl-2,2'-bipyridine, 2094 cm^{-1} [10k].


M = Pt, Pd

M = Pt, L = CO, **6**

M = Pt, L = PPh$_3$, **7**

M = Pd, L = CO, **8**

M = Pd, L = PPh$_3$, **9**
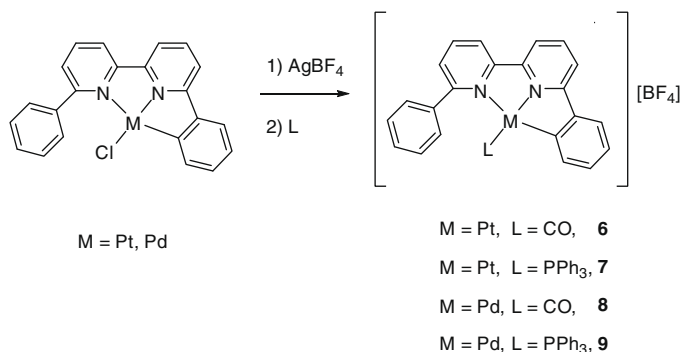
The complex $[Pt(L–H)(PPh_3)][BF_4]$, **7**, was likewise obtained by reaction of **1** with $AgBF_4$, removal of AgCl and addition of one equivalent of PPh$_3$. The $^{31}P\{^1H\}$ NMR spectrum is consistent with a P–Pt–N trans arrangement, δ 20.05 ppm (CDCl$_3$) and $^1J_{Pt–P}$ = 4262 Hz.

The reactivity of complex **2** is somehow similar to that of complex **1**, but the resulting products are generally less stable. So, treatment of **2** with $AgBF_4$ in acetone, followed by addition of CO or PPh$_3$, gave $[Pd(L–H)(CO)][BF_4]$, **8**, and $[Pd(L–H)(PPh_3)][BF_4]$, **9**, respectively. The former was characterized only in solution (^1H NMR and IR) because partial decomposition occurs during the workup procedures for crystallization. Its CO stretching (2130 cm^{-1}) is at higher wavenumber compared to that of the platinum species **6**, but in line with the difference showed by $[Pt(L'–H)(CO)][BF_4]$ and $[Pd(L'–H)(CO)][BF_4]$ (2094 vs 2130 cm^{-1}). The latter species, compound **10**, which is reported here for the first time, is more stable than **8** but almost insoluble in most organic solvents, maybe due to its assumed flatness. The CO stretching in **8** and **10** is almost coincident. The ^1H NMR spectra of **2**, **8** and **9** are similar to that of the corresponding platinum species **1**, **6** and **7**, even though with subtle differences, likely ascribable to the different influence of Pd(II) and Pt(II) on the chemical shift of aromatic protons, as usually observed.

As previously mentioned we also studied the replacement of the chloride with an anionic ligand. In particular our interest was focused on the substitution, in complex **1**, of the hydride, H$^-$, for the chloride, Cl$^-$. The rationale of our choice mainly rests on the knowledge that platinum(II) hydrides with nitrogen ligands are very rare [22], and among them, the cyclometallated ones are even rarer. In the case of complex **1**, reaction with NaBH$_4$ in THF yields the terminal hydride $[Pt(L–H)H]$, **11**, fairly stable in air both in solution and in the solid state. The corresponding terminal hydride $[Pt(L'–H)H]$, **12**, observed in solution together with a bridging dinuclear hydride, was not isolated in pure form [23].

The IR spectrum of complex **11** shows a medium band at 2114 cm^{-1} (nujol), in the region typical for the stretch of a terminal Pt–H bond. In the ^1H NMR spectrum, ((CD$_3$)$_2$CO, r.t.), the

11
stable, isolated in pure form

12
unstable, not isolated in pure form
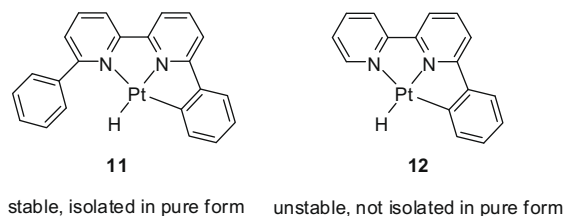
hydride signal is observed at δ –10.67, flanked by satellites, in the 1:4:1 integral ratio expected for a mononuclear platinum hydride (^{195}Pt, natural abundance ca. 33%). The resonance is shielded compared to that of complex **12**, δ –9.72, likely due to the shielding cone of the phenyl ring in close proximity. The value of the ^{195}Pt–H coupling constant, 1504 Hz, is large but in line with those previously reported for the few platinum(II) N,N,C cyclometallated hydrides with a trans Pt-N arrangement [23]. Our recent experience in this field suggests that these rare cyclometalated platinum(II) hydrides need some kind of additional help to gain stability. Help may be provided by an ancillary ligand, as in $[Pt(N,C)(PPh_3)H]$ (N,C = N^C(3) cyclometalated 6-R-2,2'-bipyridine, R = t-butyl, Ph) [24], by a Pt–Pt contribution [24], or by intramolecular weak interactions [23]. We have recently reported that in the case of $[Pt(N,N,C)H]$ species derived from 6-benzyl-2,2'-bipyridines, the cyclometalated ring adopts a boat conformation with a "pre-agostic" interaction between the metal and a hydrogen of the substituent on the benzylic carbon atom. The nature of the substituent here has a clear cut effect on the stability of the hydrido complex [23].


un stable

very stable
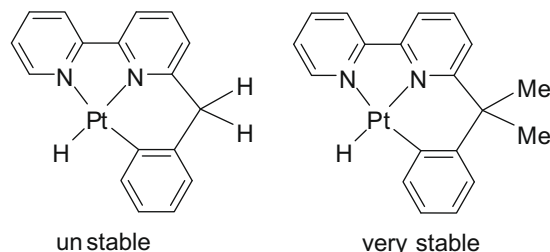
The different stability of the **L** and **L'** hydrides **11** and **12** is clearly related to the second phenyl ring in **11**, which is likely to prevent any easy reaction path eventually leading to decomposition of the molecule. It is also worth noting that in the case of **L**, in contrast to **L'**, no dinuclear hydride $[(N,N,C)Pt(\mu-H)Pt(N,N,C)]^+$ is observed.

Attempts to obtain palladium(II) hydrido species analogous to **11** failed: addition of NaBH$_4$ to a solution of complex **2** in THF resulted in fast reduction to palladium black, even under mild conditions.

As already noted, the outcome of the reaction of substituted 2,2'-bipyridine with platinum(II) results either in N,N,C or in N',C(3) cyclometallation ("rollover"), mainly depending on the nature of the platinum precursor. In the case of the disubstituted 6,6'-Ph$_2$-2,2'-bipy, cyclometallation can even imply multiple C–H activation to give compound **G**, $[Pt(L-2H)(DMSO)]$, shown in Chart 2, which is rather unusual having two carbon ligands in mutual trans position.

The N,N,C coordination behaviour shown in complex **1** and the C,N,C coordination observed in compound **G** can be connected through the reaction of **G** with HCl:
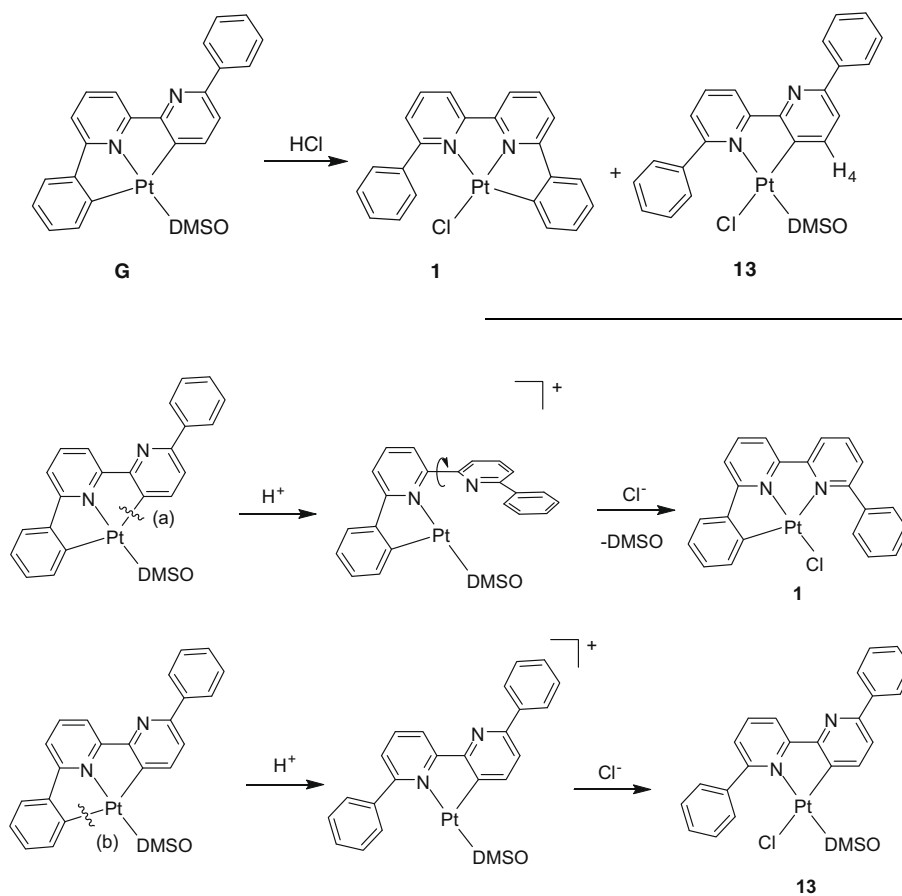
Scheme 1.

The reaction, carried out in damp acetone, eventually results in the cleavage of the platinum–carbon bonds. Two species are formed which can be separated taking advantage of their different solubility. The less soluble one was easily identified as complex **1**, the other one as the "rollover" cyclometallate **13**. The ^{1}H NMR spectrum of **13** is consistent with a N',C(3) coordination, showing a singlet with satellites at δ 3.46 (6 H, J_{Pt-H} = 22.8 Hz), in line with a DMSO *trans* to a nitrogen ligand [25], and a doublet at δ 8.60, J_{Pt-H} = 36 Hz, that can be ascribed to the H$_4$ proton.

Compounds **1** and **13** may likely be derived, as shown below, from the attack to one or the other Pt–C(sp^2) bonds that leaves vacant a coordination site (Scheme 1). In the first case, (a) the breaking of the Pt–C(3) bond is followed by rotation of the pyridine ring and coordination of the free nitrogen atom. In the second case, (b) the Pt–C bond breaking is followed by chloride coordination.

The reactions depicted in Scheme 1 entails an attack to C(sp^2) atom: actually, in the absence of experimental evidence, attack of the proton to platinum atom to give a Pt(IV) hydride cannot be ruled out.

Complex **13** is the first "rollover" derivative up to now reported with a substituent of the bipyridine in proximity of the coordinated nitrogen.

3. Conclusions

In this work we have described the synthesis of the new cyclometallates [Pt(L–H)Cl], **1**, and [Pd(L–H)Cl], **2**, (L = 6,6′-diphenyl-2,2′-bipyridine) and compared their structure and reactivity with that of the corresponding cyclometallates of 6-phenyl-2,2′-bipyridine, L′. The X-ray analysis of compound **2** provides evidence for

a terdentate N^N^C behaviour of the ligand and underlines the effects in the solid state of the additional, not metallated, phenyl ring. Despite the differences observed in the solid state, replacement of chloride in compounds **1** and **2** by neutral ligands, *e.g.*, CO and PPh$_3$, carried out by means of silver salts, results in the same type of cationic species described also for [Pt(L′–H)Cl]. At variance, reaction of [Pt(L–H)Cl], **1**, with Na[BH$_4$] is remarkable as it allowed us to isolate a terminal hydride [Pt(L–H)H], **11**: the corresponding [Pt(L′–H)H], **12**, has been reported to be unstable in the solid state and it was only identified in solution in a mixture of mono- and dinuclear hydrides. The N^N^C cyclometallated platinum(II) hydrides are very rare: complex **11** is the first isolated species with a [5,5] fused ring. The stability of the few previously reported examples with a [5,6] fused ring was shown to be enhanced by weak interactions of the metal with C–H bonds on the substituents of the 2,2′-bipyridine: the stability of compound **11** is clearly related to the additional, pendant phenyl ring. The isolation of complex **11** in reasonable yields will enable investigations on the reactivity of the Pt–H bonds in these rare species, up to now hampered by difficulties in their synthesis and isolation in pure form.

4. Experimental

All the solvents were purified and dried according to standard procedures [26]. The ligand 6,6′-diphenyl-2,2′-bipyridine (L) and [Pt(Me)$_2$(DMSO)$_2$] were synthesized according to Refs. [18,27], respectively. Elemental analyses were performed with a Perkin–Elmer elemental analyser 240B by Mr. Antonello Canu (Dipartimento di Chimica, Università degli studi di Sassari, Italy). Infrared spectra

were recorded with a FT-IR Jasco 480P using nujol mulls. ^{1}H and ^{31}P NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 300.0 and 121.4 MHz, respectively. Chemical shifts are given in ppm relative to internal TMS (^{1}H) and external 85% H_3PO_4 (^{31}P), J values are given in Hz. The H–H 2D COSY spectrum was performed by means of a standard pulse sequence. Conductivities were measured with a Philips PW 9505 conductimeter.

4.1. Preparations

4.1.1. Synthesis of [Pt(L–H)Cl] (**1**)

To a solution of $K_2[PtCl_4]$ (306.5 mg, 0.74 mmol) in H_2O (10 mL) were added, under vigorous stirring, 250 mg of L (0.81 mmol) and 3.7 mL of 2 N HCl. The mixture was heated to reflux for 5 days, then it was cooled and the precipitate formed was filtered off and washed with water, ethanol and diethyl ether. The crude product was recrystallised from dichloromethane/diethyl ether to give the analytical sample as an orange solid. Yield: 50%. Mp: >260 °C. Anal. Calc. for $C_{22}H_{15}ClN_2Pt$: C, 49.12; H, 2.81; N, 5.21. Found: C, 49.37; H, 2.94; N, 4.93%. ^{1}H NMR (CDCl$_3$): δ 7.07 (td, 1H, J_{H-H} = 6.6 Hz, J_{H-H} = 0.9 Hz, H$_{5''}$); 7.13 (td, 1H, J_{H-H} = 7.9 Hz, J_{H-H} = 1.3 Hz, H$_{4''}$); 7.33 (dd, 1H, H$_{6''}$); 7.50 (dd partially overlapping, 1H, H$_5$), 7.53 (m, 3H, Hm + Hp PPh$_3$); 7.65 (dd, 1H, J_{H-H} = 7.0 Hz, H$_3$); 7.70 (m, 2H, Ho PPh$_3$); 7.72 (partially overlapping, 1H, H$_{5'}$); 7.77 (dd, 1H, H$_{3''}$); 7.86 (t, 1H, J_{H-H} = 8.1 Hz, H$_4$); 7.95 (dd, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.3 Hz, H$_{3'}$); 8.05 (t, 1H, J_{H-H} = 7.7 Hz, H$_{4'}$). Assignments are based on a 2D COSY spectrum.

4.1.2. Synthesis of [Pd(L–H)Cl] (**2**)

Complex **2** was obtained following the same procedure of complex **1**, using Na$_2$[PdCl$_4$] instead of K$_2$[PtCl$_4$]. Yield: 46%. Mp: >260 °C. Anal. Calc. for $C_{22}H_{15}ClN_2Pd$: C, 58.82; H, 3.37; N, 6.24. Found: C, 58.46; H, 3.19; N, 6.07%. ^{1}H NMR (CDCl$_3$): δ 7.04–7.09 (m, 2H, H$_{meta}$); 7.33 (m, 1H, H$_{6''}$); 7.52–7.58 (m, 4H, aromatics); 7.61 (m, 1H, H$_{3''}$); 7.70–7.78 (m, 3H, aromatics); 7.82–7.90 (m, 2H, aromatics); 7.95–8.00 (m, 2H, H$_4$, H$_3$ or H$_{4'}$, H$_{3'}$).

Compounds [Pt(L'–H)Cl] and [Pd(L'–H)Cl] can be obtained in a similar way from L' instead of L.

4.1.3. Synthesis of [Pt(L–H)(CO)][BF$_4$] (**6**)

AgBF$_4$ (21.4 mg, 0.11 mmol) was added under vigorous stirring to an acetone solution of 1 (20 mL, 60 mg, 0.11 mmol). The precipitate formed (AgCl) was filtered off and CO was bubbled into the solution at room temperature for 12 h. Then the solution was concentrated to a small volume and treated with n-hexane. The precipitate formed was filtered off and washed with n-hexane to give the analytical sample. Yield: 60%. Mp: 120 °C. Anal. Calc. for $C_{23}H_{15}BF_4N_2OPt$: C, 44.75; H, 2.45; N, 4.54. Found: C, 44.47; H, 2.41; N, 4.52%. ^{1}H NMR (CDCl$_3$): δ 7.09–7.19 (m, 2H, aromatics); 7.50–7.65 (m, 7H, aromatics); 7.78 (d, 1H, J_{H-H} = 8.0 Hz, aromatics); 7.86 (d, 1H, J_{H-H} = 7.8 Hz, aromatics); 8.27 (t, 1H, J_{H-H} = 8.0 Hz, H$_4$ or H$_{4'}$); 8.42–8.51 (m, 2H, H$_5$ or H$_{5'}$, H$_4$, or H$_{4'}$); 8.76 (d, 1H, J_{H-H} = 7.1 Hz, H$_5$ or H$_{5'}$). IR (Nujol, υ_{max}/cm^{-1}): 2108s (CO), 1066s, broad (BF$_4^-$).

4.1.4. Synthesis of [Pt(L–H)(PPh$_3$)][BF$_4$] (**7**)

AgBF$_4$ (42.8 mg, 0.22 mmol) was added under vigorous stirring to an acetone solution of 1 (20 mL, 120 mg, 0.11 mmol). The precipitate formed (AgCl) was filtered off and solid PPh$_3$ (1:1 molar ratio) was added to the filtered solution. The solution was stirred at room temperature for 3 h, then it was concentrated to a small volume and treated with n-hexane. The precipitate formed was filtered off and washed with n-hexane to give the analytical sample. Yield: 90%. Mp: 189 °C. Anal. Calc. for $C_{40}H_{30}BF_4N_2PPt \cdot 3H_2O$: C, 53.05; H, 4.01; N, 3.09. Found: C, 52.96; H, 3.97; N, 3.44%. ^{1}H NMR (CDCl$_3$): δ 6.39 (dd, 1H, J_{H-H} = 7.1 Hz);

6.62 (td, 1H, J_{H-H} = 8.1 Hz); 6.98–7.62 (m, 23H, aromatics); 7.86 (dd, 1H J_{H-H} = 8.1 Hz); 8.32 (m, 2H); 8.55 (dd, 1H, J_{H-H} = 8.4 Hz); 8.75 (dd, 1H, J_{H-H} = 8.1 Hz). ^{31}P NMR (CDCl$_3$): δ 20.05 ppm, $^1J_{Pt-P}$ = 4262 Hz. IR (Nujol, υ_{max}/cm^{-1}): 1060 s, broad (BF$_4^-$).

4.1.5. Synthesis of [Pd(L–H)(CO)][BF$_4$] (**8**)

AgBF$_4$ (38.9 mg, 0.20 mmol) was added under vigorous stirring to an acetone solution of 2 (60 mL, 0.20 mmol). The precipitate formed (AgCl) was filtered off and CO was bubbled into the solution at room temperature for 2 h. Then the solution was concentrated to dryness to give a crude product. Crystallisation of compound **8** from the crude of from the reaction solution produced partial decomposition. Yield: 60%. ^{1}H NMR (CDCl$_3$): δ 7.02 (dd, 1H, J_{H-H} = 7.9 Hz); 7.12 (dt, 1H, J_{H-H} = 7.5 Hz, J_{H-H} = 1.5 Hz); 7.28 (m, 1H, partially overlapping with the solvent); 7.54–7.68 (m, 7H), 7.77 (dd, 1H, J_{H-H} = 7.0 Hz, J_{H-H} = 1.6 Hz); 8.30 (t, 1H, J_{H-H} = 8.0 Hz); 8.39 (t, 1H, J_{H-H} = 8.0 Hz); 8.46 (d, 1H, J_{H-H} = 8.1 Hz); 8.71 (dd, 1H, J_{H-H} = 8.2 Hz). IR (CHCl$_3$, υ_{max}/cm^{-1}): 2130s; (Nujol, υ_{max}/cm^{-1}): 2135s, 1060s, broad (BF$_4^-$).

4.1.6. Synthesis of [Pd(L–H)(PPh$_3$)][BF$_4$] (**9**)

AgBF$_4$ (38.9 mg, 0.20 mmol) was added under vigorous stirring to an acetone solution of 2 (60 mL, 0.20 mmol). The precipitate formed (AgCl) was filtered off and solid PPh$_3$ (1:1 molar ratio) was added to the filtered solution. The solution was stirred at room temperature for 1 h, then it was concentrated to a small volume and treated with diethyl ether. The precipitate formed was filtered off and washed with diethyl ether to give the analytical sample. Yield: 88%. Mp: 235–240 °C (dec). Anal. Calc. for $C_{40}H_{30}BF_4N_2PPd$: C, 62.98; H, 3.96; N, 3.67. Found: C, 62.84; H, 3.91; N, 3.55. ^{1}H NMR (CDCl$_3$): δ 6.39 (d, 1H, J_{H-H} = 7.8 Hz); 6.67 (dt, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.7 Hz); 7.09–7.32 (m, 18H); 7.41–7.48 (m, 4H), 7.63 (dd, 1H, J_{H-H} = 7.8 Hz, J_{H-H} = 1.6 Hz); 7.89 (d, 1H, J_{H-H} = 8.0 Hz); 8.26 (t, 1H, J_{H-H} = 7.9 Hz); 8.32 (t, 1H, J_{H-H} = 7.9 Hz); 8.49 (d, 1H, J_{H-H} = 7.8 Hz); 8.65 (d, 1H, J_{H-H} = 7.8 Hz). ^{31}P NMR (CDCl$_3$): δ 33.25 ppm. IR (Nujol, υ_{max}/cm^{-1}): 1090s, 1060s, broad (BF$_4^-$).

4.1.7. Synthesis of [Pd(L'–H)(CO)][BF$_4$] (**10**)

AgBF$_4$ (39.0 mg, 0.20 mmol) was added under vigorous stirring to an acetone solution of [Pd(L'–H)Cl] (60 mL, 0.20 mmol). The precipitate formed (AgCl) was filtered off and CO was bubbled into the solution at room temperature for 2 h. The precipitate formed was filtered off and washed with CH$_2$Cl$_2$ to give the analytical sample as a yellow solid. Yield 92%. Mp: 200 °C. Anal. Calc. for $C_{17}H_{11}N_2BF_4OPd$: C, 45.12; H, 2.45; N, 6.19. Found: C, 44.56; H, 2.27; N, 5.84. IR (Nujol, υ_{max}/cm^{-1}): 2130s (CO), 1060 s, broad (BF$_4^-$).

4.1.8. Synthesis of [Pt(L–H)H] (**11**)

To a solution of 1 (135 mg, 0.25 mmol) in anhydrous THF (90 mL) was added, under argon, NaBH$_4$ (29.1 mg, 0.77 mmol). The mixture was stirred at room temperature for 3 h, then it was filtered and the resulting solution was concentrated to a small volume. Addition of n-pentane produced a precipitate that was filtered off and washed with n-pentane to give the analytical sample as a red solid. Yield: 73 mg, 58%. Mp: 176 °C. Anal. Calc. for $C_{22}H_{16}N_2Pt$: C, 52.48; H, 3.20; N, 5.56. Found: C, 52.26; H, 2.99; N, 5.25. ^{1}H NMR (CD$_3$)$_2$CO: δ −10.67 (s, broad, 1H, J_{Pt-H} = 1504 Hz, Pt–H); 6.94–6.88 (m, 2H, aromatics); 7.53–7.41 (m, 5H, aromatics); 7.96–7.79 (m, 4H, aromatics); 8.17–8.04 (m, 2H, aromatics); 8.38–8.31 (m, 2H, aromatics). IR (Nujol, υ_{max}/cm^{-1}): 2114.

4.1.9. Reaction of [Pt(L–2H)(DMSO)], compound **G**, with HCl

To a solution of [Pt(L–2H)(DMSO)] (85 mg, 0.14 mmol) in acetone (40 mL) were added 1.4 mL of 0.1 N HCl and a few drops of DMSO. The mixture was stirred at room temperature for 3 h, then

evaporated to dryness. The solid obtained was dissolved in dichloromethane. The solution was filtered over a Phase Separator (PS) filter, concentrated to small volume and treated with diethyl ether. The precipitated formed was filtered and washed with diethyl ether to give complex 1 as an orange solid (Yield 33%). The filtered solution was evaporated to dryness. The solid obtained was crystallised from dichloromethane and *n*-pentane, to give complex **13** as a yellow solid. Yield: 53.5 mg, 62%. Mp: dec at 130 °C. Anal. Calc. for $C_{24}H_{22}N_2OPtS$: C, 46.79; H, 3.44; N, 4.55. Found: C, 46.58; H, 3.57; N, 4.36%. ^1H NMR (CDCl$_3$): δ 3.46 (s, 6H, $J_{Pt–H}$ = 22.8 Hz, Me(DMSO)); 7.40–7.62 (m, 8H, aromatics); 7.92 (d, 2H, $J_{H–H}$ = 6.3 Hz, H$_{o''}$ or H$_{o'''}$); 8.04 (t, 1H, $J_{H–H}$ = 7.8 Hz, H$_{4'}$); 8.11 (dd, 2H, $J_{H–H}$ = 6.8 Hz, H$_{o'''}$ or H$_{o''}$); 8.48 (dd, 1H, $J_{H–H}$ = 7.8 Hz, H$_{3'}$); 8.60 (d, 1H, $J_{H–H}$ = 8.3 Hz, $J_{Pt–H}$ = 36 Hz, H$_4$).

4.2. X-ray data collection and structure determination

Crystal data are summarized in Table 2. The diffraction experiment was carried out on a Bruker APEX II CCD area-detector diffractometer at 296 K, using Mo Kα radiation (λ = 0.71073) with a graphite crystal monochromator in the incident beam. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT [28], and an empirical absorption correction was applied (SADABS) [29] to the collected reflections. The calculations were performed using the Personal Structure Determination Package [30] and the physical constants tabulated therein [31]. The structure was solved by direct methods (SHELXS) [32] and refined by full-matrix least squares using all reflections and minimizing the function $\sum w(F_o^2 - kF_c^2)^2$ (refinement on F^2). All the non-hydrogen atoms were refined with anisotropic thermal factors. All the hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter U being 1.10 times that of the atom to which they are attached, and not refined. In the final Fourier map the maximum and minimum residuals were +1.65(49) e Å^{-3} at 1.12 Å from Pd, and $-1.44(49)$ e Å^{-3}.

Supplementary data

CCDC 730185 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table 2
Crystallographic data.

Compound	**2**
Formula	$C_{22}H_{15}ClN_2Pd$
M	449.23
Colour	Yellow
Crystal system	Triclinic
Space group	$P\overline{=}1$
a/Å	15.189(1)
b/Å	15.655(1)
c/Å	17.136(1)
α/°	63.3501
β/°	75.9901
γ/°	86.3901
U/Å^3	3519.1(5)
Z	8
$F(0\,0\,0)$	1792
D_c/g cm^{-3}	1.696
T/K	296
Crystal dimensions (mm)	$0.04 \times 0.10 \times 0.15$
μ (Mo Kα)/cm^{-1}	12.00
Minimum and maximum transmissions	
Factors	0.703–1.000
Scan mode	ω
Frame width/°	0.40
Time per frame/s	25
No. of frames	2700
Detector-sample distance/cm	6.00
θ-Range	3–26
Reciprocal space explored	Full sphere
No. of reflections (total; independent)	58,172, 15,673
R_{int}	0.0819
Final R_2 and R_{2w} indices[a] (F^2, all reflections)	0.092, 0.080
Conventional R_1 index [$I > 2\sigma(I)$]	0.051
Reflections with $I > 2\sigma(I)$	7242
No. of variables	937
Goodness-of-fit[b]	0.963

[a] $R_2 = [\sum(|F_o^2 - kF_c^2| / \sum F_o^2]$, $R_{2w} = [\sum w(F_o^2 - kF_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.
[b] $[\sum w(F_o^2 - kF_c^2)^2 / (N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$. $\sigma(F_o^2) = [\sigma^2(F_o) + (0.02F_o^2)^2]^{1/2}$, N_o is the number of observations and N_v the number of variables.

References

[1] (a) I. Omae, Chem. Rev. 79 (1979) 287;
(b) E.C. Constable, Polyhedron 9/10 (1984) 1037;
[c] A.D. Ryabov, Chem. Rev. 90 (1990) 403;
[d] G.R. Newkome, W.E. Puckett, V.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451;
[e] I. Omae, Organometallic Intramolecular-Coordination Compounds, Elsevier Science Publishers, Amsterdam, New York, 1986;
[f] V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, Russ. Chem. Rev. 57-3 (1988) 250;
[g] I. Omae, Coord. Chem. Rev. 248 (2004) 995.
[2] [a] See, for example: M. Albrecht, R.A. Gossage, A.L. Speck, G. van Koten, J. Am. Chem. Soc. 121 (1999) 11898;
[b] J.T. Singleton, Tetrahedron 59 (2003) 1837;
[c] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527.
[3] [a] See, for example: L.N. Lewis, J. Am. Chem. Soc. 108 (1986) 743;
[b] J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917;
[c] J.S. Fossey, C.J. Richards, Organometallics 23 (2004) 367;
[d] I.P. Beletskaya, A.V. Cheprakov, J. Organomet. Chem. 689 (2004) 4055.
[4] [a] See, for example: D.P. Lydon, J.P. Rourke, Chem. Commun. (1997) 1741;
[b] P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215.
[5] [a] See, for example: G. Marcon, S. Carotti, M. Coronnello, L. Messori, E. Mini, P. Orioli, T. Mazzei, M.A. Cinellu, G. Minghetti, J. Med. Chem. 45 (2002) 1672;
[b] L. Messori, G. Marcon, M.A. Cinellu, M. Coronnello, E. Mini, C. Gabbiani, P. Orioli, Bioorg. Med. Chem. 12 (2004) 6039;
[c] C. Navarro-Ranninger, I. López-Solera, V.M. González, J.M. Perez, A. Alvarez-Valdés, A. Martin, P.R. Raithby, J.R. Masaguer, C. Alonso, Inorg. Chem. 35 (1996) 5181;
[d] J.D. Higgins, L. Neely, S. Fricker, J. Inorg. Biochem. 49 (1993) 149;
[e] A.G. Quiroga, J.M. Perez, E.I. Montero, D.X. West, C. Alonso, C. Navarro-Ranninger, J. Inorg. Biochem. 75 (1999) 293;;
[f] E.G. Rodrigues, L.S. Silva, D.M. Fausto, M.S. Hayashi, S. Dreher, E.L. Santos, J.B. Pesquero, L.R. Travassos, A.C.F. Caires, Int. J. Cancer 107 (2003) 498.
[6] [a] See, for example: A.F.M.J. van der Ploeg, G. van Koten, H.C. Stam, Inorg. Chem. 21 (1982) 2878;
[b] M. Albrecht, R.A. Gossage, M. Lutz, A.L. Spek, G. van Koten, Chem. Eur. J. 6 (2000) 1431;
[c] M. Albrecht, M. Schlupp, J. Batgon, G. van Koten, Chem. Commun. (2001) 1874;
[d] M. Albrecht, R.A. Gossage, U. Frey, A.W. Ehlers, E.J. Baerends, A.E. Merbach, G. van Koten, Inorg. Chem. 40 (2001) 850;
[e] K.-H. Wong, M.C.-W. Chan, C.-M. Che, Chem. Eur. J. 5 (1999) 2845;
[f] P.K.M. Siu, S.-W. Lai, W. Lu, N. Zhu, C.-M. Che, Eur. J. Inorg. Chem. (2003) 2749;
[g] Q.-Z. Yang, L.-Z. Wu, H. Zhang, B. Chen, Z.-X. Wu, L.-P. Zhang, C.-H. Tung, Inorg. Chem. 43 (2004) 5195.
[7] [a] See, for example: M. Albrecht, M. Lutz, A.L. Spek, G. van Koten, Nature 40 (2000) 970;
[b] P. Steenwinkel, D.M. Grove, N. Veldman, A.L. Spek, G. van Koten, Organometallics 17 (1998) 5647;
[c] M. Albrecht, G. van Koten, Angew. Chem., Int. Ed. (2001) 3750.
[8] [a] See, for example: J.W. Slater, D.P. Lydon, J.P. Rourke, J. Organomet. Chem. 645 (2002) 246;
[b] D.P. Lydon, J.P. Rourke, Chem. Commun. (1997) 1741;
[c] J. Buey, L. Diez, P. Espinet, H. -S. Kitzerow, J.A. Miguel, Appl. Phys. B 66 (1998) 355;

[d] J. Buey, L. Diez, P. Espinet, H.-S. Kitzerow, J.A. Miguel, Chem. Mater. 8 (1996) 2375.

[9] [a] S.W. Lai, T.C. Cheung, M.C.W. Chan, K.K. Cheung, S.M. Peng, C.M. Che, Inorg. Chem. 39 (2000) 255;
[b] S.W. Lai, C.W. Chan, K.K. Cheung, C.M. Che, Organometallics 18 (1999) 3327;
[c] Y.Y. Lin, S.C. Chan, M.C.W. Chan, Y.J. Hou, N. Zhu, C.M. Che, Y. Liu, Y. Wang, Chem. Eur. J. 9 (2003) 1263;
[d] W. Lu, B.X. Mi, M.C.W. Chan, Z. Hui, C.M. Che, N. Zhu, S.T. Lee, J. Am. Chem. Soc. 126 (2004) 4958;
[e] J.A.G. Williams, A. Beeby, E.S. Davies, J.A. Weinstein, C. Wilson, Inorg. Chem. 42 (2003) 8609;
[f] H. Jude, J.A.K. Bauer, W.B. Connick, Inorg. Chem. 44 (2005) 1211.

[10] [a] See, for example: G. Minghetti, M.A. Cinellu, G. Chelucci, S. Gladiali, F. Demartin, M. Manassero, J. Organomet. Chem. 307 (1986) 107;
[b] G. Minghetti, M.A. Cinellu, S. Stoccoro, A. Zucca, M. Manassero, J. Chem. Soc., Dalton Trans. (1995) 777;
[c] F. Neve, A. Crespini, S. Campagna, Inorg. Chem. 36 (1997) 6150;
[d] M.-C. Tse, K.-K. Cheung, M.C.W. Chan, C.-M. Che, Chem. Commun. (1998) 2295;
[e] K.-H. Wong, M.C. Chang, C.-M. Che, Chem. Eur. J. 5 (1999) 2845;
[f] S.-W. Lai, M. C.-W. Chan, K.-K. Cheung, C.-M. Che, Organometallics 18 (1999) 3327;
[g] J.H.K. Yip, Suwarno, J.J. Vittal, Inorg. Chem. 39 (2000) 3537;
[h] G. Sanna, G. Minghetti, A. Zucca, M.I. Pilo, R. Seeber, F. Laschi, Inorg. Chim. Acta 305 (2000) 189;
[i] W. Lu, N. Zhu, C.-M. Che, Chem. Commun. (2002) 900;
[j] W. Lu, B.-X. Mi, M.C.W. Chan, Z. Hui, N. Zhu, S.-T. Lee, C.-M. Che, Chem. Commun. (2002) 206;
[k] S.-W. Lai, H.-W. Lam, W. Lu, K.-K. Cheung, C.-M. Che, Organometallics 21 (2002) 226;
[l] A. Capapé, M. Crespo, J. Granell, M. Font-Bardía, X. Solans, J. Organomet. Chem. 690 (2005) 4309;
[m] M. Crespo, M. Font-Bardía, X. Solans, J. Organomet. Chem. 691 (2006) 444.

[11] [a] D.M. Grove, G. van Koten, J.N. Louwen, J.G. Noltes, A.L. Spek, H.J.C. Ubbels, J. Am. Chem. Soc. 104 (1982) 6609;
[b] J. Terheijden, G. van Koten, F. Muller, D.M. Grove, K. Vrieze, E. Nielsen, C.H. Stam, J. Organomet. Chem. 315 (1986) 401;
[c] M.A. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750;
[d] S. Back, M. Albrecht, A.L. Spek, G. Rheinwald, H. Lang, G. van Koten, Organometallics 20 (2001) 1024;
[e] G. Rodriguez, : Albrecht, J. Schoenmaker, A. Ford, M. Lutz, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 124 (2002) 5127;
[f] D.J. Cardenas, A.M. Echavarren, M.C. Ramirez de Arellano, Organometallics 18 (1999) 3337.

[12] [a] C. Cornioley-Deuschel, T. Ward, A. von Zelewsky, Helv. Chim. Acta 71 (1988) 130;
[b] G.W.V. Cave, N.W. Alcock, J.P. Rourke, Organometallics 18 (1999) 1801;
[c] G.W.V. Cave, F.P. Fanizzi, R.J. Deeth, W. Eddington, J.P. Rourke, Organometallics 19 (2000) 1355;
[d] W. Lu, M.C.W. Chan, K.-K. Cheung, C.-M. Che, Organometallics 20 (2001) 2477;
[e] C.P. Newman, G.W.V. Cave, M. Wong, W. Errington, N.W. Alcock, J.P. Rourke, J. Chem. Soc., Dalton Trans. (2001) 2678;
[f] V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong, X.-X. Lu, K.-K. Cheung, N. Zhu, Chem. Eur. J. 8 (2002) 4066.

[13] (a) e.g. C.M. Che, J. Am. Chem. Soc. 126 (2004) 7639;
[b] K.H. Wong, K.K. Cheung, M.C.W. Chan, C.M. Che, Organometallics 17 (1998) 3505;
[c] W. Lu, M.C.W. Chan, K.K. Cheung, C.M. Che, Organometallics 20 (2001) 2477;
[d] A.S. Ionkin, W.J. Marshall, Y. Wang, Organometallics 24 (2005) 619.

[14] [a] e.g. E. Constable, R.P.G. Henney, T.A. Leese, D.A. Tocher, J. Chem. Soc. Chem. Commun. (1990) 513;
[b] S. -W. Lai, M. C. -W. Chan, T. -C. Cheung, S. -M. Peng, C. -M. Che, Inorg. Chem. 38 (1999) 4046;
[c] C. -K. Koo, Y. -M. Ho, C. -F. Chow, M. H. -W. Lam, T. -C. Lau, W. -Y. Wong, Inorg. Chem. 46 (2007) 3603.

[15] [a] D.J. Cárdenas, A.M. Echavarren, M.C.R. Arellano, Organometallics. 18 (1999) 3337;
[b] W. Sotoyama, T. Satoh, N. Sawatari, H. Inoue, Appl. Phys. Lett. 86 (2005) 153505;
[c] S.J. Farley, D.L. Rochester, A.L. Thompson, J.A.K. Howard, J.A.G. Williams, Inorg. Chem. 44 (2005) 9690;
[d] M. Cocchi, D. Virgili, V. Fattori, D.L. Rochester, J.A.G. Williams, Adv. Funct. Mater. 17 (2007) 285.

[16] [a] V. W. -W. Yam, R. P. -L. Tang, K. M. -C. Wong, X. -X. Lu, K. -K. Cheung, N. Zhu, Chem. Eur. J. 8 (2002) 4066;
[b] S.C.F. Kui, S. S. -Y. Chui, C. -M. Che, N. Zhu, J. Am. Chem. Soc. 128 (2006) 8297.

[17] A. Zucca, A. Doppiu, M.A. Cinellu, S. Stoccoro, G. Minghetti, M. Manassero, Organometallics 21 (2002) 783.

[18] A. Zucca, G.L. Petretto, S. Stoccoro, M.A. Cinellu, G. Minghetti, M. Manassero, C. Manassero, L. Male, A. Albinati, Organometallics 25 (2006) 2253.

[19] F. Neve, A. Crispini, C. Di Pietro, S. Campagna, Organometallics 21 (2002) 3511.

[20] C. Wing Chan, T. Fong Lai, C. Ming Che, S. Ming Pen, J. Am. Chem. Soc. 115 (1993) 11245.

[21] [a] A. Zucca, S. Stoccoro, M.A. Cinellu, G. Minghetti, M. Manassero, M. Sansoni, Eur. J. Inorg. Chem. (2002) 3336;
[b] M.A. Cinellu, A. Zucca, S. Stoccoro, G. Minghetti, M. Manassero, M. Sansoni, J. Chem. Soc., Dalton Trans. (1996) 4217.

[22] F.A Cotton, G. Wilkinson, C.A Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th ed., John Wiley & Sons Inc., New York, 1999.

[23] A. Zucca, S. Stoccoro, M.A. Cinellu, G.L. Petretto, G. Minghetti, Organometallics 26 (2007) 5621.

[24] G. Minghetti, S. Stoccoro, M.A. Cinellu, G.L. Petretto, A. Zucca, Organometallics 27 (2008) 3415.

[25] [a] G. Minghetti, S. Stoccoro, M.A. Cinellu, B. Soro, A. Zucca, Organometallics 22 (2003) 4770;
[b] A. Zucca, G.L. Petretto, S. Stoccoro, M.A. Cinellu, M. Manassero, C. Manassero, G. Minghetti, Organometallics 28-7 (2009) 2150.

[26] Vogel's Textbook of Practical Organic Chemistry, 5th ed., Longman Scientific and Technical Ed., Harlow, 1989.

[27] [a] C. Eaborn, K. Kundu, A. Pidcock, J. Chem. Soc., Dalton Trans. (1981) 933;
[b] R. Romeo, L. Monsù Scolaro, Inorg. Synth. 32 (1998) 153.

[28] SAINT Reference Manual, Siemens Energy and Automation, Madison, W1, 1994–1996.

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

[30] B.A. Frenz, Comput. Phys. 2 (1988) 42.

[31] Crystallographic Computing 5, Oxford University Press: Oxford, UK, 1991, p. 126 (Chapter 11).

[32] G.M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Gottingen, Germany, 1985.