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# Dinuclear platinum(II) complexes with bridging twofold deprotonated 2,2′:6′,2″-terpyridine. New molecules with a 3,5-diplatinated-pyridyl inner core: $[Pt_2(terpy\text{-}2H)(Me)_2(L)_2]$, $[Pt_2(terpy\text{-}2H)(X)_2(L)_2]$ and $[Pt_2(terpy\text{-}2H)(H)_2(L)_2]$ (L = neutral ligand; X = halide) – Crystal and molecular structure of $[Pt_2(terpy\text{-}2H)(Cl)_2(PPh_3)_2]$

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**Abstract**

A series of dinuclear platinum complexes where the metal ions are linked by a twofold deprotonated 2,2′:6′,2″-terpyridine (terpy) has been synthesized. Reaction of *cis*-$[Pt(Me)_2(DMSO)_2]$ with terpy in toluene at 90 °C (molar ratio Pt:terpy 2:1) results in activation of the C(3)- and C(5)–H bonds of the inner pyridinic ring to give the cyclometalated dinuclear derivative $[Pt_2(terpy\text{-}2H)(Me)_2(DMSO)_2]$ (**1a**), (*trans* Me–Pt–N). From complex **1a**, substitution of DMSO with neutral two-electron donors, L, allows isolation of a number of new species $[Pt_2(terpy\text{-}2H)(Me)_2(L)_2]$ with the same N,C^C,N bridging ligand. The "$Pt_2(terpy\text{-}2H)$" fragment is very robust: it is not affected by alkylating reagents such as MeI or acids such as $HPF_6$ or even HCl. Nevertheless the latter acid cleaves the Pt–Me bond affording another series of complexes having a chloride in place of a methyl, $[Pt_2(terpy\text{-}2H)(Cl)_2(L)_2]$, (*trans*-Cl–Pt–C). The structure of complex **7**, $[Pt_2(terpy\text{-}2H)(Cl)_2(PPh_3)_2]$, has been solved by X-ray analysis: the platinum atoms are in a tetrahedrally distorted square planar coordination. The inner framework of the molecule is not flat: the dihedral angle between the best planes of the metal ions is 37.2(1)°. The coordinated chlorides can be abstracted to give cationic solvento derivatives or exchanged with other anions such as iodides. Exchange with $[BH_4]^-$ allows to obtain the corresponding hydrides, examples of very rare C,N cyclometalated platinum(II) hydrides. Finally a two step approach allows the synthesis of unsymmetric derivatives, $[Pt_2(terpy\text{-}2H)(Cl)_2(L)(L')]$, with different ligands around each platinum atom. The surprising deprotonation of terpy, typically a neutral ligand, points to the potential of the "$Pt(Me)_2$" fragment in the intramolecular C–H bond activation.


*Keywords:* Platinum; Cyclometallated compounds; Nitrogen ligands; Crystal structure

## 1. Introduction

The potentially terdentate ligand 2,2′:6′,2″-terpyridine (terpy) was firstly isolated by Morgan and Burstall nearly 70 years ago [1]. Since the beginning this ligand has been widely studied due to the outstanding properties of its metal-bound derivatives [2]. In recent years terpyridine transition metal complexes have attracted great interest due to their photophysical and photochemical as well as biological properties [3]. At present, one of the most promising fields is the application in supramolecular chemistry

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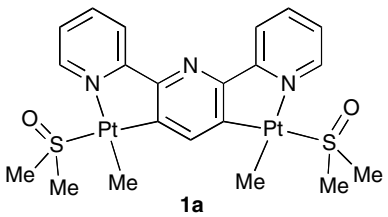
(molecular wires [4], devices for the harvesting of light energy [5]). In particular platinum(II) complexes are well-suited to interact with proteins [6], to intercalate with DNA [7], to oligomerize both in solution and in the solid state [8].

Mostly 2,2′:6′,2″-terpyridine acts as an *N*,*N*′,*N*″ endo-terdentate ligand, classical examples being [Pt(terpy)Cl] [8a,9] and $[Ru(terpy)_2]^{2+}$ [10,11]. Cyclometalation had been observed only when a terminal nitrogen was protected through quaternization [12]. Only recently have a few examples of cyclometalated derivatives been reported when it was found that the reaction of terpy with electron-rich platinum complexes, $[Pt(Me)_2(L)_2]$, yields dinuclear cyclometalated derivatives, $[Pt_2(terpy\text{-}2H)(Me)_2(L)_2]$ in which terpy acts as a twofold deprotonated N,C^C,N ligand [13]. This unexpected cyclometalation, which implies activation of two C–H bonds of the inner pyridine ring, can be envizaged as a particular case of the ''rollover'' N^C' metalation previously observed for 6-substituted 2,2′-bipyridines [14]. In some cases, e.g. with 6-phenyl-2,2′-bipyridine, the ''rollover'' metalation produces multi-metalated dinuclear compounds [15]. In this case, with terpy, it is notable that molecules are formed which have a diplatinated-3,5-pyridyl inner core, a motif that, at the best of our knowledge, is unprecedented.

Owing to the novelty of these cyclometalated derivatives we deemed worth to extend the series of the dinuclear $[Pt_2(terpy\text{-}2H)(Me)_2(L)_2]$ species by substitution of the neutral ligand L, and to study some aspects of their reactivity, in particular as for the platinum–carbon bonds.

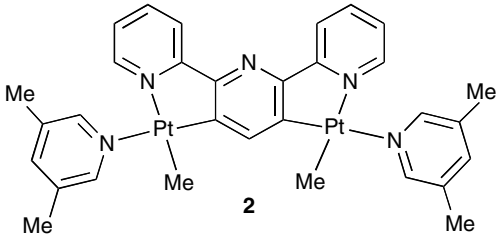
## 2. Results and discussion

As previously reported the reaction of *cis*-$[Pt(Me)_2(DMSO)_2]$ with terpy (molar ratio Pt/terpy 2:1, toluene, 90 °C) yields the unusual dinuclear cyclometalated species $[Pt_2(terpy\text{-}2H)(Me)_2(DMSO)_2]$ (**1a**), where a twofold deprotonated 2,2′:6′,2″-terpyridine (terpy) links two platinum atoms [13]. As far as we know this was the first example of a cyclometalated terpy. From compound **1a** other complexes were obtained by substitution of DMSO with neutral ligands (e.g. MeCN **1b**, CO **1c**, $PPh_3$ **1d**, $PCy_3$ **1e**)




**1a**

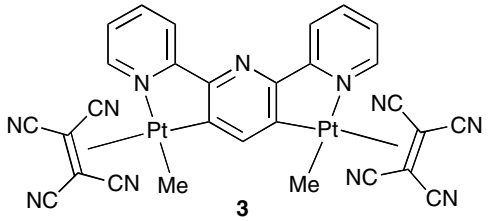
Here we show that displacement from compound **1a** of both the coordinated DMSO can also be achieved with heterocyclic nitrogen ligands such as 3,5-lutidine, or even with some alkenes. The reactions, however, are more difficult. With lutidine complete substitution requires a large excess of ligand, heating and a long reaction time: working at 50 °C, complex **2**, $[Pt_2(terpy\text{-}2H)(Me)_2(3,5\text{-lutidine})_2]$, can be obtained in fairly good yields.




**2**

At variance with **1b** and **1c** which are almost insoluble in most solvents, complex **2** is soluble, likely due to non-coplanarity of the coordinated lutidine. In the $^1H$ NMR spectrum the two metal-bonded methyl groups appear as one singlet with satellites ($\delta$ 0.94, 6H, $^2J(Pt\text{–}H) = 86.4$ Hz): the $^{195}Pt$–H coupling constant is in agreement with a methyl group *trans* to a nitrogen atom, as in **1a**. The four methyl groups of the lutidine appear as one singlet at $\delta$ 2.43 (12H); in the aromatic region, in addition to the lutidine *ortho*- and *para*-protons, five resonances in a 2:2:2:2:1 integral ratio account for the terpyridine protons. On the whole the spectrum is indicative of a symmetric species. The FAB mass spectrum (positive ions), shows the molecular ion at *m*/*z* 865.

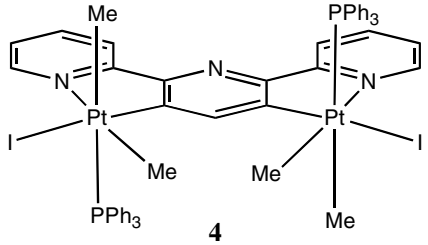
Reactions with alkenes were undertaken with the aim to compare the behaviour of the metallorganic fragment ''$Pt_2(terpy\text{-}2H)(Me)_2$'' towards a σ-donor/π-acceptor ligand such as CO, with that towards π-donor/π-acceptor molecules. The reactivity of complex **1a** towards olefines is not straightforward. The nature of the substituents on the olefinic ligand is crucial: in the case of $CH_2{=}CH_2$ and $CH_2{=}CH\text{–}CN$ no reaction occurs whereas with the strongly π acceptor $(NC)_2C{=}C(CN)_2$ (TCNE) displacement of the DMSO ligands occurs and a new complex, **3**, can be isolated. Unfortunately, complex **3** is poorly soluble in common organic solvents, thus its formulation as $[Pt_2(terpy\text{-}2H)(Me)_2(TCNE)_2]$ mainly rests on analytical values and IR spectra, $\nu(C{\equiv}N)$ 2218, 2135 $cm^{-1}$.




**3**

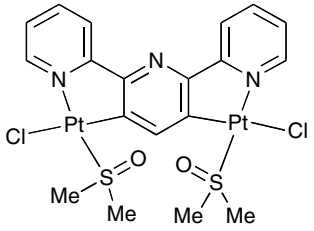
In the cyclometalated complexes **1a**–**3** the nitrogen atom of the central pyridine ring is not involved in coordination and we were eager to investigate how its donor capability was affected by metalation. Firstly we studied the reactivity of **1a** with acids having non-coordinating anion such as $HPF_6$(aq), or $HPF_6 \cdot$ 18-crown-6 ether. In no case, under various conditions, protonation of the nitrogen atom was observed. Furthermore, in some cases decomposition to

metal occurs. Attempts to alkylate the nitrogen atom in **1a** likewise failed: however with methyl iodide an oxidative addition occurs to give a number of species, possibly isomers, not easily separable. At variance, in the reaction of the phosphino complex $[Pt_2(terpy\text{-}2H)(Me)_2(PPh_3)_2]$ (**1d**), only one species, **4**, is formed as indicated by the $^{31}P\{^1H\}$ NMR spectrum which shows one singlet with satellites: the $^{195}Pt$–P coupling constant ($^1J_{Pt-P} = 985.0$ Hz) supports a Pt(IV) complex [16]. The $^1H$ NMR spectrum shows the presence of two different Pt–Me groups ($\delta$ 1.18, d, 6H, $^2J_{Pt-H} = 60.3$ Hz, $^3J_{P-H} = 7.3$ Hz; $\delta$ 1.78, d, 6H, $^2J_{Pt-H} = 70.6$ Hz, $^3J_{P-H} = 7.6$ Hz), one H4′ proton (s, 1H, $^3J_{Pt-H} = 48.8$ Hz) and one signal for the H6″ at $\delta$ 9.34. Overall the NMR spectra give evidence for a symmetric species but do not allow to distinguish between molecules with the axial methyls on the same or the opposite side of the $Pt_2$(terpy-2H) plane. According to the literature data [17] $^1H$ NMR parameters, in particular the $^2J_{Pt-H}$ and $^3J_{P-H}$ relevant to the Me resonances, support an arrangement around each platinum atom with a methyl *trans* to N, $^2J_{Pt-H} = 70.6$ Hz, and the other one, $^2J_{Pt-H} = 60.3$ Hz, *trans* to $PPh_3$, not to the iodine atom. This implies that an isomerization process takes place, as previously reported in the oxidative addition of MeI to analogous substrates [17c,17e]. If steric effects are also taken into account the most probable isomer for **4** is:



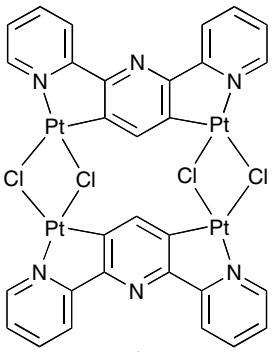

**4**

Having ascertained the scarce reactivity of the uncoordinated nitrogen atom, in particular towards protonation or alkylation, we studied the reaction of complex **1a** with HCl. When the reaction was carried out in acetone with a 1:1 Pt:HCl molar ratio two species were isolated in the solid state, complexes **5** and **6**, soluble and insoluble respectively, in the reaction medium. Complex **5** analyses for $[Pt_2(terpy\text{-}2H)(Cl)_2(DMSO)_2]$: the $^1H$ NMR spectrum, compared to that of **1a**, clearly shows the absence of methyl groups bound to platinum. The singlet due to the H4′ proton at $\delta$ 9.01, $^3J_{Pt-H} = 44.7$ Hz (vs. $\delta$ 8.38, $^3J_{Pt-H} = 53.7$ Hz in **1a**) is flanked by satellites in an approximate 1:2.2:1 integral ratio characteristic of a coupling with two chemically equivalent platinum atoms. The signal at $\delta$ 3.62, relevant to the DMSO protons, shows a $^3J_{Pt-H}$ indicative of a ligand *trans* to a nitrogen rather than to a carbon atom ($^3J_{Pt-H} = 24.4$ Hz vs. $^3J_{Pt-H} = 18.1$ Hz in **1a**). In agreement, in the IR spectrum the value of the Pt–Cl stretch ($\nu_{max} = 267\ cm^{-1}$) [18] is consistent with **5** being the isomer with Cl *trans* to the carbon atom. Isomerization on going from **1a** to **5** is justified taking into account the lower *trans* influence of Cl compared to DMSO.




**5**

Complex **6** can be hardly characterized in solution due to its scarce solubility in common organic solvents: a $^1H$ NMR spectrum can be obtained only in deuterated DMSO. Under these conditions the spectrum of **6** is almost superimposable to that of complex **5** in the same solvent. Likely, **6** is a dimer with bridging chlorides derived from **5** by dissociation of DMSO; in DMSO the bridge is split to give again complex **5**. In agreement compound **5** can be obtained as the only product when the reaction of **1a** with HCl is carried out in the presence of a small amount of DMSO.



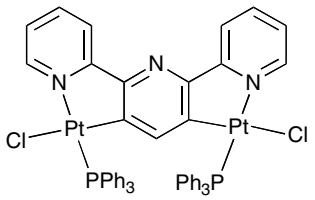

**6**

The result of the reaction of compound **1a** with HCl, which entails the cleavage of the methyl–platinum bond without affecting the dinuclear "$Pt_2$(terpy-2H)" fragment suggests that a new series of complexes having a chlorine in place of an alkyl may be synthesized.

### *2.1. Synthesis of $[Pt_2(terpy\text{-}2H)(Cl)_2(L)_2]$ (L = neutral ligand)*

In complex **5**, at variance with complex **1a**, the DMSO ligands are *trans* to a nitrogen atom. It should therefore be expected that substitution reactions in **5** may be more difficult than in **1a**. Nevertheless, reaction of complex **5** with $PPh_3$ in mild conditions affords complete substitution of the coordinated DMSOs to give $[Pt_2(terpy\text{-}2H)(Cl)_2(PPh_3)_2]$ (**7**). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet with satellites at $\delta$ 18.15 : the high value of $^1J_{Pt-P}$, 4327 Hz, is consistent with a phosphorus *trans* to a nitrogen

atom. In the $^1$H NMR spectrum the resonance of the H4′ proton, a singlet at $\delta$ 6.72, is markedly shifted upfield with respect to complex **5** ($\delta$ 9.01) owing to the $PPh_3$ ligands in adjacent positions. The overall spectrum, also in this case is indicative of a symmetric molecule so that **7** can be described as follows:




**7**

Complex **7** can also be obtained by reaction of **6** with $PPh_3$ under the same experimental conditions. The structure of complex **7** has been solved by X-ray diffraction. An ORTEP view of the complex molecule **7** is shown in Fig. 1.

Principal bond parameters are listed in Table 1. Disregarding the phosphinic phenyl rings, the molecule possesses an idealized $C_2$ symmetry, with the twofold axis passing through atoms N2 and C8. A projection of the inner core of the molecule down the idealized twofold axis is shown in Fig. 2.

As can be seen, the inner framework of the molecule is not flat, probably because of the need to relieve non-bonding repulsions between the two bulky $PPh_3$ ligands. Each of the two Pt atoms displays a tetrahedrally distorted square-planar coordination. Maximum deviations from the least-squares plane of Pt1 are +0.148(4) and −0.174(3) Å for C7 and N1, respectively. The corresponding values for Pt2 are 0.168(3) and −0.152(4) Å for N3 and C9, respectively. The dihedral angle between the best planes of the metal atoms is 37.2(1)°. All the observed Pt–ligand bond lengths are as expected if the *trans*-influence of C ($sp^2$) and P atoms are considered. Thus, the Pt–N and Pt–C distances found here can be compared with those found in $[Pt_2(terpy\text{-}2H)(Me)_2(CO)_2]$ (**1c**): here we find Pt1–N1 = 2.101(3) and Pt2–N3 2.100(3) Å, in **1c** Pt1–N1 = 2.137(5) and Pt2–N3 2.124(5) Å. The slight shortening observed here is due to the *trans*-influence of P being lower than that of C($sp^3$). The present bond lengths of Pt1–C7 and Pt2–C9 are 2.007(3) and 2.013(4) Å, respectively; in **1c** Pt1–C7 = 2.050(6) and Pt2–C9 2.051(5) Å. Also in this case the shortening in the present molecule is due to the lower *trans*-influence of Cl with respect to that of CO. The present Pt1–P1 and Pt2–P2 bond lengths, 2.230(1) and

Table 1
Selected distances (Å) and angles (°) in **7** with estimated standard deviations (esd's) on the last figure in parentheses

| | | | |
|---|---|---|---|
| Pt(1)–Cl(1) | 2.379(1) | Pt(1)–P(1) | 2.230(1) |
| Pt(1)–N(1) | 2.101(3) | Pt(1)–C(7) | 2.007(3) |
| Pt(2)–Cl(2) | 2.386(1) | Pt(2)–P(2) | 2.237(1) |
| Pt(2)–N(3) | 2.100(3) | Pt(2)–C(9) | 2.013(4) |
| N(2)–C(6) | 1.339(5) | N(2)–C(10) | 1.346(5) |
| C(6)–C(7) | 1.400(5) | C(7)–C(8) | 1.409(5) |
| C(8)–C(9) | 1.413(5) | C(9)–C(10) | 1.398(6) |
| Cl(1)–Pt(1)–P(1) | 92.9(1) | Cl(1)–Pt(1)–N(1) | 90.5(1) |
| Cl(1)–Pt(1)–C(7) | 170.0(1) | P(1)–Pt(1)–N(1) | 168.3(1) |
| P(1)–Pt(1)–C(7) | 96.6(1) | N(1)–Pt(1)–C(7) | 81.0(1) |
| Cl(2)–Pt(2)–P(2) | 89.7(1) | Cl(2)–Pt(2)–N(3) | 89.6(1) |
| Cl(2)–Pt(2)–C(9) | 168.2(1) | P(2)–Pt(2)–N(3) | 170.8(1) |
| P(2)–Pt(2)–C(9) | 100.7(1) | N(3)–Pt(2)–C(9) | 81.0(1) |

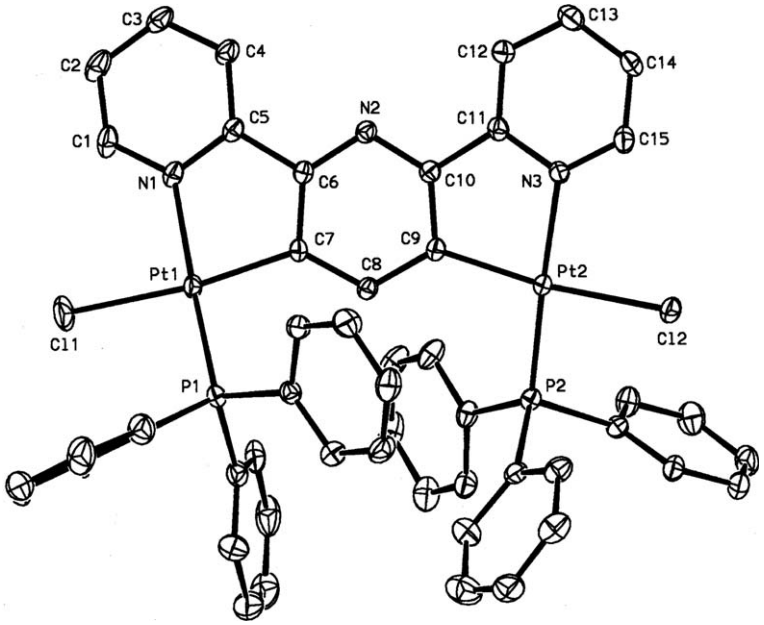



Fig. 1. ORTEP view of compound **7**. Ellipsoids are drawn at the 30% probability level.

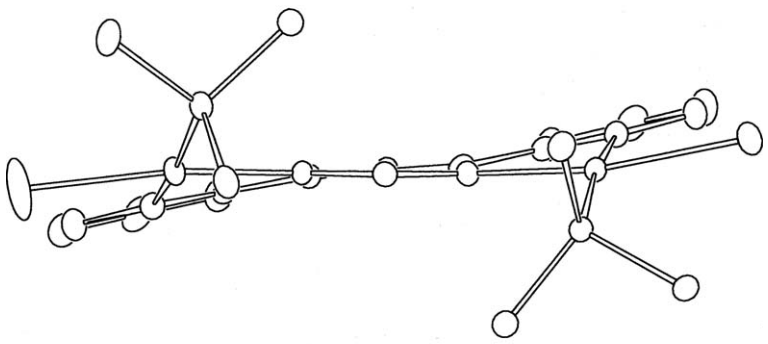
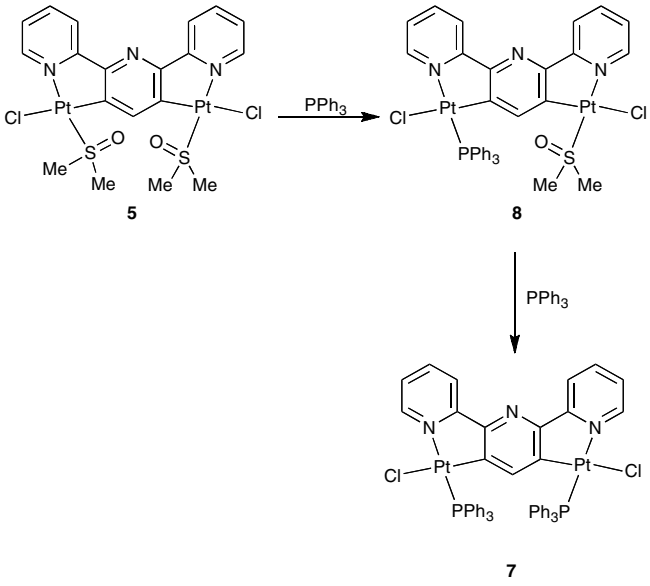


Fig. 2. A projection of **7** down the idealized twofold axis C8–N2. Only the first atoms of the phosphinic phenyl rings have been shown, for clarity.

2.237(1) Å, respectively, are very similar to those found in $[Pt_2(L)Cl(PPh_3)_2]$, compound **17** [15b] ($H_3L$ = 6-phenyl-2,2′-bipyridine), Pt1–P1 2.225(1) and Pt2–P2 2.231(1) Å (in **17** the Pt–P bonds are also *trans*- to pyridinic nitrogen atoms). The present Pt1–Cl1 and Pt2–Cl2 distances 2.379(1) and 2.386(1) Å, respectively, are very long because of the *trans*-influence of C($sp^2$). They can be compared to the Pt–Cl bond length, 2.395(2) Å, found in **18**, $[PtCl(L)(SMe_2)]$ (HL = 6-phenyl-2,2′-bipyridine) [14a], where the Pt–Cl bond is also *trans*- to a C($sp^2$) atom. As previously found in **1c**, the strain imposed on terpyridine by its bridging behaviour is apparent in the intra-ring angles of the N2 ring, which range 114.8(3)–126.3(3)°. Bond lengths within this ring (see Table 1) indicate no loss of aromaticity, and each of the three pyridinic rings is planar. However, as can be seen in Fig. 2, the three rings are not coplanar, the dihedral angles between their best planes being: N1 ring–N2 ring 10.5(4)°, N2 ring–N3 ring 11.9(5)°, and N1 ring–N3 ring 3.5(7)°.

In the crystal packing of **7** there are couples of molecules related by an inversion centre and kept together by graphitic interactions, as shown in Fig. 3. The distance between the planes of overlapping rings is about 3.40 Å. The couples of molecules that generate the packing are kept together by normal van der Waals contacts.

To check whether a selective substitution of the DMSO ligands in **5** can be attained, the reaction with $PPh_3$ was carried out also with a 1:1 molar ratio. A monosubstituted complex, $[Pt_2(terpy\text{-}2H)(Cl)_2(DMSO)(PPh_3)]$ (**8**), was isolated as the only product. The characterization of compound **8** mainly rests on analytical and NMR data. In particular, in the $^1H$ NMR spectrum, both the resonances of the coordinated DMSO and $PPh_3$ ligands are observed. In the aromatic region the symmetry displayed by the species previously described is missing as shown e.g. by the H6 and H6″ protons which are no more equivalent (H6″: $\delta$ 9.44, d, $^3J_{Pt-H}$ = 32 Hz; H6: $\delta$ 9.85, dd, $^3J_{Pt-H}$ = 28 Hz, $^4J_{P-H}$ = 4.5 Hz). Compound **8** can further react with $PPh_3$ to afford compound **7**.




**5** **8** **7**

The reaction proceeds in two steps indicating that substitutions do not occur simultaneously on both the metallic centres; the second $PPh_3$ coordinates only after replacement of one DMSO, suggesting an electronic interaction between the metallic centres which are linked trough the deprotonated terpy.

At variance with $PPh_3$, the reaction of **5** with the more bulky and basic $PCy_3$ at room temperature affords mixtures of a mono- and a di-substituted product. The disubstituted complex **9** can be obtained as the only product from complex **5** or **6** working in dichloromethane at reflux. In the $^{31}P\{^1H\}$ NMR spectrum the single resonance observed at $\delta$ 18.64 ($^1J_{Pt-P}$ = 4024 Hz) gives evidence for a symmetric species having a *trans* P–Pt–N arrangement.

In complex **5** both the DMSO molecules can also be replaced by 3,5-lutidine: in this case excess of ligand and heating are required to obtain complex **10**, $[Pt_2(terpy\text{-}2H)(Cl)_2(3,5\text{-lutidine})_2]$. In the $^1H$ NMR spectrum remarkable is the shift of the H4′ signal ($\delta$ 5.80 with satellites 1:2.2:1,

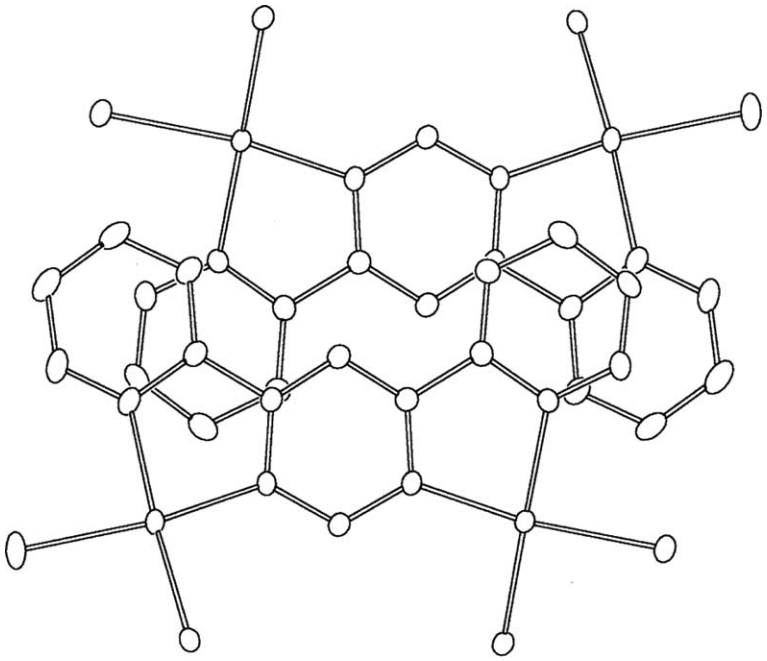
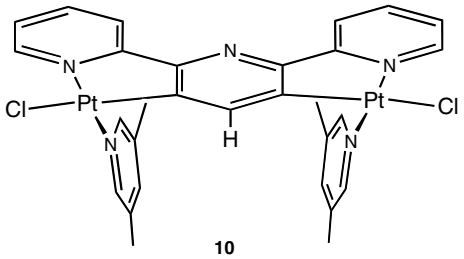


Fig. 3. A couple of molecules showing graphitic interactions in the crystal packing of **7** (see text). Phenyl rings have been omitted.

$^3J_{Pt-H} = 43.5$ Hz) strongly shielded with respect to **5** ($\delta$ 9.01), as expected for a proton lying in the shielding cone of the aromatic rings of the lutidine.

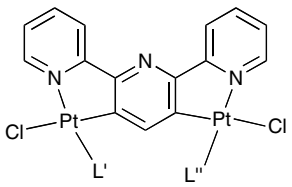


**10**

The reaction of complexes **5** and **7** with CO gives compounds **11**, $[Pt_2(terpy\text{-}2H)(Cl)_2(DMSO)(CO)]$ and **12**, $[Pt_2(terpy\text{-}2H)(Cl)_2(PPh_3)(CO)]$, respectively. The IR spectra of the isolated products show a strong band at 2093 $cm^{-1}$ assignable to the stretching vibration of a terminal carbonyl. The $^1H$ NMR spectrum of complex **11** gives evidence for a coordinated DMSO ($\delta$ 3.68, $^3J_{Pt-H} = 22.5$ Hz) suggesting that partial substitution occurred. In agreement, complex **11** is not symmetric, as shown by two resonances for the H6 and H6″ protons ($\delta$ 9.44 and $\delta$ 9.59): furthermore two different couplings of H4′ with $^{195}Pt$ ($\delta$ 8.78, $^3J_{Pt-H} = 43$ Hz, $^3J_{Pt'-H} = 67$ Hz) indicate that the two platinum atoms are not equivalent. Finally, the FAB (positive ions) mass spectrum shows the molecular ion of compound **11** at *m*/*z* 796. The reaction of **7** proceeds under mild conditions (r.t., 1 atm) to give **12** in high yields (>90%). The substitution by CO of only one of the neutral ligands in complexes **5** and **7** may be due to the scarce solubility of compounds **11** and **12**: after the first substitution, coordination of the second CO might be hampered by their precipitation in the reaction medium.

The new complexes **7**–**12**, obtained in one or two steps from compound **5** by substitution of DMSO with neutral ligands, are collected in Scheme 1. All of them show an extraordinary thermal stability.

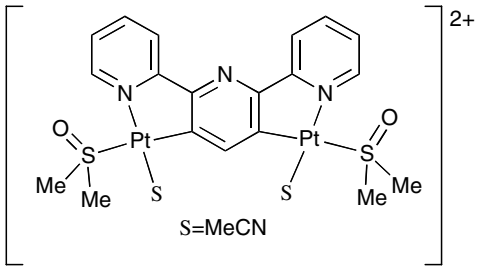
Although in **5** and **7**–**12** the chloride is coordinated *trans* to a $C(sp^2)$ atom, a high *trans*-influence and *trans*-effect donor, the Pt–Cl bond is not cleaved by neutral nucleophiles (e.g. DMSO, CO, $PPh_3$ in the case of **5** or CO in the case of **7**) even in the presence of $Na[BF_4]$ (acetone solution). The substitution of the chloride in **5** with neutral ligands was also attempted in dichloromethane in the



| Compound | L' | L'' |
|---|---|---|
| **5** | DMSO | DMSO |
| **7** | $PPh_3$ | $PPh_3$ |
| **8** | DMSO | $PPh_3$ |
| **9** | $PCy_3$ | $PCy_3$ |
| **10** | 3,5-lut | 3,5-lut |
| **11** | DMSO | CO |
| **12** | CO | $PPh_3$ |

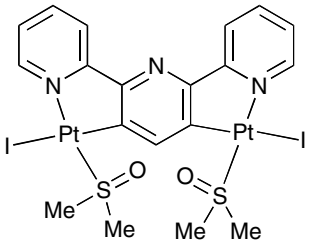
Scheme 1.

presence of the Brookhart's salt, $Na\{B[C_6H_3(CF_3)_2]_4\}$ [19], to take advantage of the insolubility of NaCl. In absence of a coordinating solvent decomposition occurs, whereas when a small amount of acetonitrile is added, the ionic complex **13**, $[Pt_2(terpy\text{-}2H)(DMSO)_2(MeCN)_2]\{B[C_6H_3(CF_3)_2]_4\}_2$, is isolated. Complex **13** is extremely soluble in common organic solvents, making its purification a difficult task. The $^1H$ NMR shows signals at $\delta$ 3.57 (12H) and 2.25 (6H) due to coordinated DMSO and acetonitrile, respectively. The $^{195}Pt$–H coupling suggests a DMSO coordinated *trans* to a carbon atom ($^3J_{Pt-H} = 19.3$ Hz). A single signal for the H6, H6″ protons ($\delta$ 9.58), is consistent with a symmetric formulation



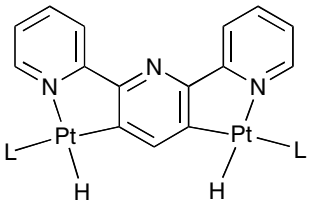

**13**

Substitution of the chloride with a coordinating anion is easier, as shown by the reaction of **5** with lithium iodide to give $[Pt_2(terpy\text{-}2H)(I)_2(DMSO)_2]$ (**14**). In the IR spectrum substitution of $I^-$ for $Cl^-$ is indicated by the disappearance of the absorption at 267 $cm^{-1}$ assigned in **5** to $\nu$(Pt–Cl). In the $^1H$ NMR the single signal of the H6 ed H6″ protons is strongly deshielded, $\delta$ 10.22, as previously observed when an iodide is in close proximity of a pyridinic ring [20].




**14**

In complexes **5** and **7**, the chloride, coordinated *trans* to the carbon atom, can also be substituted by hydride transfer from $Na[BH_4]$, to give **15**, $[Pt_2(terpy\text{-}2H)(H)_2(DMSO)_2]$ and **16,** $[Pt_2(terpy\text{-}2H)(H)_2(PPh_3)_2]$, respectively.




L= DMSO, **15**; $PPh_3$, **16**

Complex **15** is unstable in the solid state and its characterization mainly rests on the $^1H$ NMR spectra: a signal in the hydridic region, $\delta$ −15.54, with satellites (1:4:1), gives evidence for a terminal Pt–H bond. The high value of the platinum–hydrogen coupling constant, $^1J_{Pt-H} = 1567$ Hz, is in line with that previously reported for a N,N,C-cyclometallated species, 1606 Hz [21], where the hydride is *trans* to an $sp^2$ nitrogen atom: this implies that substitution of $H^-$ for $Cl^-$ occurs with isomerization, as expected taking account of the high *trans*-influence of both a carbon and a hydride donor (*trans*-phobia) [22]. At variance, complex **16**, $[Pt_2(terpy\text{-}2H)(H)_2(PPh_3)_2]$, is stable in the solid state: the analytical data fit the indicated formulation. The $^1H$ NMR spectrum shows a doublet at $\delta$ −15.53, $^2J_{P-H} =$ 24 Hz, with satellites due to coupling to $^{195}Pt$ ($^1J_{Pt-H} =$ 1444.5 Hz); in the $^{31}P$ $\{^1H\}$ NMR spectrum a resonance, observed at $\delta$ 32.89, is coupled to $^{195}Pt$ with $^1J_{Pt-P} =$ 2072.0 Hz, a value consistent with a phosphorus *trans* to a high *trans*-influence donor.

Complexes **15** and **16** are rare examples of cyclometalated N,C platinum(II) hydrides: as far as we know the only species isolated is [Pt(L–H)H] (L = 6-(1-methylbenzyl)-2,2′-bipyridine) where L–H is the tridentate N,N,C ligand coordinated via the two bipyridine nitrogens and an ortho carbon of the phenyl of the chiral methylbenzyl group [21]. Quite recently evidence for a similar [Pt(N,N,C)H] species has been detected in solution [23]. The reactivity of the Pt–H bond in platinum(II) derivatives with nitrogen ligands is therefore completely unknown. It is worth to remind that, in contrast, Pt(IV) hydride complexes with nitrogen ligands have been widely investigated in the frame of the studies on the intermolecular hydrocarbon C–H activation [24].

## 3. Conclusions

We have described the synthesis of a number of platinum(II) complexes where two metal atoms are linked by a twofold deprotonated 2,2′:6′,2″terpyridine (terpy). Their synthesis, which entails the activation of two C–H bonds, is promoted by the electron-rich fragment "$Pt(Me)_2$". The electron- delocalized motif which bridges the platinum atoms, (terpy-2H), is robust so that from the parent compound **1a**, $[Pt_2(terpy\text{-}2H)(Me)_2(DMSO)_2]$, an extensive series of methyl derivatives, **1b**–**1e** and **2**–**4**, was easily obtained by substitution of DMSO with neutral ligands. Likewise, the bridging ligand is not affected by strong acids such as $HPF_6$, and is not cleaved even by HCl: reaction of the latter with the methyl derivatives affords a new series of complexes, **5**–**10**, having a chloride in place of a methyl group. The structure of one of them, $[Pt_2(terpy\text{-}2H)(Cl)_2(PPh_3)_2]$ (**7**), solved by X-ray diffraction analysis gives evidence for a *trans* Cl–Pt–C arrangement and shows that, at least in this case, the inner framework of the molecule is not flat. Furthermore other species can be obtained by halide exchange, e.g. $I^-$ for $Cl^-$, or by chloride abstraction to give cationic solvento species. Exchange of the chloride

with $H^-$ provides C,N cyclometalated platinum(II) hydrides that are extremely rare. A two step approach allows the synthesis of unsymmetric derivatives having different ligands around each platinum atom. Most of the derivatives here described display a high thermal stability.

In conclusion we have shown that the reaction of the fragment "$Pt(Me)_2$" with terpy leads, through an unexpected behaviour of the ligand, to a variety of new species. This once again calls the attention to the potential of the diorgano platinum(II) derivatives in the intramolecular C–H activation, as recently reported by us also in the case of the 6-substituted 2,2′-bipyridines. It is also worth noting that the reactivity of these fragments is of paramount importance in the intermolecular C–H activation.

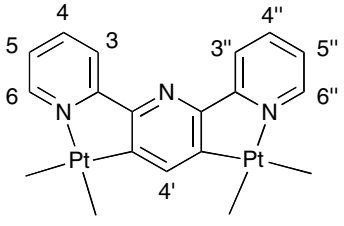
## 4. Experimental

### 4.1. Materials

All the solvents were purified and dried before use according to standard methods [25]. The reactions were performed in air unless otherwise indicated. $[Pt_2(terpy\text{-}2H)(Me)_2(DMSO)_2]$ (**1a**) and $[Pt_2(terpy\text{-}2H)(Me)_2(PPh_3)_2]$ (**1d**) have been synthesized according to the literature procedures [13].

### 4.2. Measurements

Elemental analyses were performed with a Perkin–Elmer elemental analyser 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari, Italy). Infrared spectra were recorded with FT-IR Jasco 480P or Perkin–Elmer 983 spectrophotometers using Nujol mulls. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature (20 °C) 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 ($^1H$) and external 85% $H_3PO_4$ ($^{31}P$); coupling constants are given in Hz. The mass spectrometric measurements were performed on a VG 7070EQ instrument, equipped with a PDP 11-250J data system and operating under positive ion fast bombardment (FAB) conditions with 3-nitrobenzyl alcohol as supporting matrix.




numbering Scheme

### 4.3. Syntheses

#### 4.3.1. $[Pt_2(terpy\text{-}2H)(Me)_2(3,5\text{-}Me_2\text{-}pyridine)_2]$ (**2**)

To a solution of **1a** (90.0 mg, 0.112 mmol) in acetone (40 ml) were added 50 μl of 3,5-$Me_2$-pyridine (0.25 mmol). The reaction was stirred at 50 °C for two days and the resulting solution was evaporated to dryness, crystallized from dichloromethane/hexane and dried in vacuo to give the analytical sample (58.2 mg, 60%) as a yellow solid. M.p. 200 °C (dec), (Calc. for $C_{31}H_{33}N_5Pt_2$: C, 43.01; H, 3.84; N, 8.09. Found: C, 42.84; H, 3.99; N, 7.82%.) $\nu_{max}$(Nujol)/cm$^{-1}$ 1595m, 1555m, 1509m, 1145m, 1114m, 1071m; $\delta_H$ (300 MHz; acetone-$D_6$; $Me_4Si$) 0.94 (6H, s, $CH_3$–Pt, $^2J_{Pt-H}$ 86.4); 2.43 (12H, s, $CH_3$ (3,5-$Me_2$-pyridine); 7.18 (2H, td, H5, H5″); 7.69 (2H, s, $H_4$(3,5-$Me_2$-pyridine)); 7.80 (2H, dd, H3, H3″); 7.96 (2H, td, H4, H4″); 8.32 (2H, d, H6, H6″); 8.51–8.53 (5H, m, H4′, $H_2$ (3,5-$Me_2$-pyridine)); *m/z* (FAB) 865 ($M^+$), 850 ($M-CH_3^+$), 744 ($M-CH_3$–$C_7H_9N)^+$), 728 ($M-2CH_3$–$C_7H_9N^+$), 652 ($M-2(C_7H_9N)^+$), 636 ($M-CH_3$–$2(C_7H_9N)^+$), 621 ($M-2CH_3$–$2(C_7H_9N)^+$), 442 ($M-CH_3$–$2(C_7H_9N)$–Pt+$H^+$), 427 ($M-2CH_3$–$2(C_7H_9N)$–Pt+$H^+$).

#### 4.3.2. $[Pt_2(terpy\text{-}2H)(Me)_2(TCNE)_2]$ (**3**)

To a solution of **1a** (50.0 mg, 0.062 mmol) in 40 ml of dichloromethane were added 15.8 mg of tetracyanoethylene, TCNE, (0.123 mmol). The reaction was stirred at room temperature for two days. The precipitate formed was filtered off, washed with diethyl ether (5 × 20 ml) and dried in vacuo to give the analytical sample (55.1 mg, 98%). M.p. > 270 °C, (Calc. for $C_{29}H_{15}N_{11}Pt_2$: C, 38.37; H, 1.67; N, 16.97. Found: C, 38.21; H, 1.75; N, 16.66%.). $\nu_{max}$(Nujol)/cm$^{-1}$ 2218s, 2135s, 1610s, 1564s, 1265m, 1039m.

#### 4.3.3. $[Pt_2(terpy\text{-}2H)(Me)_4I_2(PPh_3)_2]$ (**4**)

To a solution of **1d** (85.0 mg, 0.072 mmol) in 50 ml of acetone were added 0.5 ml of MeI (d = 2.28 g/ml; 8.03 mmol). The mixture was stirred for 2 h at 30 °C, then concentrated and treated with diethyl ether. The yellow precipitate formed was filtered, washed with diethyl ether and dried in vacuo to give the analytical sample (69.4 mg, 66%) as a yellow solid. M.p. 170–172 °C (Calc. for $C_{55}H_{51}N_3I_2P_2Pt_2$: C, 45.25; H, 3.52; N, 2.88. Found: C, 45.09; H, 3.64; N, 2.79%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 1605(m), 1564(m), 1520(m), 1090(s), 1034(m), 745(s), 695(s); $\delta_H$ (300 MHz; $CDCl_3Me_4Si$) 1.18 (6H, d, $CH_3$–Pt, $^2J_{Pt-H}$ 60.3, $^3J_{P-H}$ 7.3); 1.78 (6H, d, $CH_3$–Pt, $^2J_{Pt-H}$ 70.6, $^3J_{P-H}$ 7.6); 7.04–7.45 (30H, m, aromatics); 7.53 (1H, s, H4′, $^3J_{Pt-H}$48.8); 7.68–7.83 (4H, m, aromatics); 8.20 (2H, d, aromatics, $J_{H-H}$ 8.0); 9.34 (2H, d, H6, H6″, $^3J_{Pt-H}$ 10.7, $J_{H-H}$ ca. 5.4). $\delta_P$ (121.4 MHz, $CDCl_3$, $H_3PO_4$) $\delta = -11.58$ (s, $^1J_{Pt-P}$ 985.0).

#### 4.3.4. $[Pt_2(terpy\text{-}2H)(Cl)_2(DMSO)_2]$ (**5**)

To a solution of **1a** (90.0 mg, 0.112 mmol) in acetone (50 ml) were added 1.5 mL of DMSO and 2.26 ml of aqueous 0.1 M HCl (0.226 mmol). After the addition of HCl the solution colour changed to yellow. The mixture was stirred for 3 h at room temperature, then concentrated to small volume. The precipitate formed was filtered, washed with $H_2O$, EtOH and $Et_2O$, and dried in vacuo to give

the analytical sample (80.8 mg, 85%) as an orange-yellow solid. M.p. > 270° (Calc. for: $C_{19}H_{21}N_3Cl_2O_2Pt_2S_2$: C, 26.89; H, 2.49; N, 4.95. Found: C, 27.09; H, 2.58; N, 5.00%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 1609(m), 1564(m), 1518(m), 1138(m), 267(m). $\delta_H$ (300 MHz; acetone-$D_6$; $Me_4Si$) 3.62 (12H, s, $CH_3$ (DMSO) $^3J_{Pt-H}$ 24.4); 7.62 (2H, ddd, H5, H5″, $J_{H-H}$ 7.5, 5.7, 1.5); 8.21(2H, td, H4, H4″, $J_{H-H}$7.5, 1.5); 8.39 (2H, d, H3, H3″, $J_{H-H}$ 7.5); 9.01 (1H, s, H4′, $^3J_{Pt-H}$ 44.7); 9.60 (2H, dd, H6, H6″, $^3J_{Pt-H}$ 35, $J_{H-H}$ 5.1); *m/z* (FAB) 814 (M−Cl + H$^+$), 770 (M−DMSO$^+$), 734 (M−Cl–DMSO$^+$), 691 (M−2DMSO$^+$), 656 (M−Cl–2DMSO$^+$), 620 (M−2Cl–2DMSO–H$^+$), 426 (M−2Cl–2DMSO–Pt$^+$).

### 4.3.5. Reaction between $[Pt_2(terpy\text{-}2H)(Me)_2(DMSO)_2]$ and HCl

To a solution of **1a** (75 mg, 0.088 mmol) in 150 ml of acetone were added 1.8 ml of 0.1 M HCl (0.18 mmol). The colour of the solution changed to yellow and an orange precipitate formed. The mixture was stirred for 3 h at room temperature. The precipitate formed was filtered and washed with acetone (3 × 30 ml) to give complex **6** (25.6 mg, yield 42%) as a dark-orange solid. The filtered solution was concentrated: the precipitate formed was filtered, washed with $H_2O$, EtOH and $Et_2O$, and dried in vacuo to give complex **5** (35.8 mg, 48%) as an orange-yellow solid.

Complex **6**: m.p. > 270 °C. (Calc. for $C_{30}H_{18}N_6Cl_4Pt_4$: C, 26.02; H, 1.31; N, 6.07. Found: C, 26.28; H, 1.24; N, 5.89%); $\nu_{max}$(Nujol)/cm$^{-1}$ 1609m, 1565m, 1520m, 1290m, 327w, 250w, 243w; $\delta_H$ (300 MHz; DMSO; $Me_4Si$) 7.66 (2H, t, H5, H5″); 8.22 (2H, t, H4, H4″); 8.33 (2H, d, H3, H3″); 8.83 (1H, s, H4′, $^3J_{Pt-H}$, 37.2); 9.47 (2H, d, H6, H6″).

### 4.3.6. $[Pt_2(terpy\text{-}2H)(Cl)_2(PPh_3)_2]$ (7)

*Method A*. To a suspension of **5** (40.0 mg, 0.047 mmol) in 15 ml of dichloromethane were added 24.7 mg of $PPh_3$ (0.094 mmol). The yellow solution formed was stirred for 1 h, then concentrated to small volume and treated with hexane. The precipitate formed was filtered, washed with hexane and dried in vacuo to give the analytical sample (52.0 mg, 91%) as a yellow solid.

*Method B*. To a suspension of **6** (76.0 mg, 0.055 mmol) in dichloromethane (20 ml) were added 57.6 mg of $PPh_3$ (0.220 mmol). The yellow solution formed was stirred at room temperature for 2 h, then concentrated to small volume. The precipitate formed after addition of hexane (40 ml) was filtered, washed with hexane (3 × 30 ml) and dried in vacuo to give the analytical sample (51.5 mg, 77%) as a yellow solid. M.p. > 270 °C (Calc. for $C_{51}H_{39}N_3Cl_2P_2Pt_2$: C, 50.34; H, 3.23; N, 3.45. Found: C, 50.09; H, 3.36; N, 3.77%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 1607m, 1565m, 1510m, 1282w, 1187w, 1156w, 1099s, 757s, 695s; $\delta_H$ (300 MHz; $CDCl_3$ $Me_4Si$) 6.72 (1H, t, H4′, $^3J_{Pt-H}$ 50.1, $^4J_{P-H}$ 2.7); 7.73–7.87 (32H, m, aromatics ($PPh_3$), H5, H5″); 7.95 (2H, dt, H4, H4″); 8.34 (2H, d, H3, H3″); 9.65 (2H, m, H6, H6″, $^3J_{Pt-H}$ 23.4, $^4J_{P-H}$ 4.2). $\delta_P$ (121.4 MHz, $CDCl_3$ $H_3PO_4$) $\delta = 18.15$ (s, $^1J_{Pt-P}$, 4327); *m/z* (FAB) 1215 (M)$^+$, 1181(M−Cl)$^+$, 1145 (M−2Cl)$^+$, 918 (M−Cl–$PPh_3$)$^+$, 883 (M − 2*Cl*–$PPh_3^+$), 689 (M−2Cl–$PPh_3$–Pt+H$^+$), 621 (M − 2Cl–2$PPh_3^+$), 427 (M−2Cl–2$PPh_3$–Pt$^+$).

### 4.3.7. $[Pt_2(terpy\text{-}2H)(Cl)_2(PPh_3)(DMSO)]$ (8)

To a suspension of **5** (43.0 mg, 0,051 mmol) in dichloromethane (10 ml) were added 13.3 mg of $PPh_3$ (0.051 mmol). The resulting solution was stirred for 1 h at room temperature, then concentrated to small volume. The yellow precipitate formed after addition of hexane (30 ml) was filtered off, washed with hexane and dried in vacuo to give the analytical sample (43.2 mg, 78%) as a yellow solid. M.p. > 270 °C (Calc. for $C_{35}H_{30}N_3Cl_2OPSPt_2$ $3H_2O$: C, 38.68; H, 3.34; N, 3.87. Found: C, 38.62; H, 2.83; N, 3.99%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 1600m, 1565m, 1510m, 1142m, 1095s; $\delta_H$ (300 MHz; $CDCl_3$ $Me_4Si$) 3.06 (6H, s, $CH_3$(DMSO), $^3J_{Pt-H}$ 21.5); 7.31–7.98 (20H, m, aromatics); 8.26, (1H, d, H3″, $J_{H-H}$ 8.0); 8.34 (1H, d, H3, $J_{H-H}$8.0); 9.44 (1H, d, H6″, $^3J_{Pt-H}$ 32, $J_{H-H}$5.8); 9.85 (1H, dd, H6, $^3J_{Pt-H}$ 28, $^4J_{P-H}$ ca. 4.5). $\delta_P$ (121.4 MHz, $CDCl_3$, $H_3PO_4$) 23.70 (s, $^1J_{Pt-P}$ 4307).

### 4.3.8. $[Pt_2(terpy\text{-}2H)(Cl)_2(PCy_3)_2]$ (9)

To a suspension of **5** (50.0 mg, 0,059 mmol) in dichloromethane (10 ml), under argon atmosphere, were added 45.0 mg of $PCy_3$ (0.160 mmol). The yellow solution formed was stirred for 7 h at reflux temperature, then evaporated to dryness and crystallized from dichloromethane/diethyl ether to give the analytical sample (47.3 mg, 64%) as a yellow solid. M.p. > 270 °C; (Calc. for $C_{51}H_{75}N_3Cl_2P_2Pt_2$: C, 48.88; H, 6.03; N, 3.35. Found: C, 48.55; H, 5.96; N, 3.00%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 1605m, 1562m, 1506 m, 1005s; $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$) 1.1–2.1 (66H, m); 7.31 (2H, m, H5, H5″); 7.74 (1H, s, H4′, $^3J_{Pt-H}$ ca. 22); 7.88 (2H, dt, H4, H4″, $J_{H-H}$7.6, 1.5); 8.14 (2H, d, H3, $H_{3''}$, $J_{H-H}$7.6); 9.59 (2H, m, $H_6$, H6″, $^3J_{Pt-H}$ 40.0, $^4J_{P-H}$ 4.2). $\delta_P$ (300 MHz; $CDCl_3$; $H_3PO_4$) 18.64 (s, $^1J_{Pt-P}$ 4024).

Complex **9** can also be obtained by reaction of **6** with $PCy_3$ in dichloromethane at reflux temperature for 7 h (yield 50%).

### 4.3.9. $[Pt_2(terpy\text{-}2H)(Cl)_2(3,5\text{-}Me_2\text{-}pyridine)_2]$ (10)

To a solution of **5** (90 mg, 0.106 mmol) in acetone (40 ml) were added 50 μL of 3,5-$Me_2$-pyridine (0.248 mmol). The solution was stirred at 50 °C for 2 days, then evaporated to dryness. The solid obtained was crystallized from dichloromethane/hexane and dried in vacuo to give the analytical sample (79.3 mg, 81%) as a yellow solid. M.p. > 270 °C. (Calc. for $C_{29}H_{27}N_5Cl_2Pt_2 \cdot H_2O$: C, 37.67; H, 3.16; N, 7.57. Found: C, 37.34; H, 3.30; N, 7.43%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 1600m, 1559m, 1510m, 1255m, 1140m, 1110m, 1070m. $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$) 2.23 (12H, s, $CH_3$ (3,5-$Me_2$-pyridine)); 5.80 (1H, s, H4, $^3J_{Pt-H}$ 43.5); 7.23–7.29 (4H, m, H5, H5″, H4 (3,5-$Me_2$-pyridine)); 7.88 (td, 2H, H4, H4″, $J_{H-H}$ 7.8, 1.0); 8.15 (2H, d, H3, H3″, $J_{H-H}$ 7.8); 8.46 (4H, s, H2, H6 (3,5-$Me_2$-pyridine), $^3J_{Pt-H}$ 44.4); 9.58 (2H, d, H6, H6″, $^3J_{Pt-H}$ 28.3, $J_{H-H}$ 6.0);

*m/z* (FAB) 905 ($M^+$), 871 ($M-Cl^+$), 799 ($M-C_7H_9N^+$), 763 ($M-Cl-C_7H_9N^+$), 728 ($M-2Cl-C_7H_9N^+$), 656 ($M-Cl-2(C_7H_9N)^+$), 621 ($M-2Cl-2(C_7H_9N)^+$), 463 ($M-Cl-2(C_7H_9N)-Pt^+$), 427 ($M-2Cl-2(C_7H_9N)-Pt^+$).

#### 4.3.10. [$Pt_2$(terpy-2H)(Cl)$_2$(DMSO)(CO)] (**11**)

CO at atmospheric pressure was bubbled into a solution of **5** (50.0 mg, 0.059 mmol) in 50 ml of dichloromethane. The solution was stirred for 1 h during which a red suspension was formed. The mixture was concentrated to small volume and treated with diethyl ether. The red-orange precipitate formed was filtered, washed with diethyl ether and dried in vacuo to give the analytical sample (33.0 mg, 70%) as an orange solid. M.p. > 270° (Calc. for $C_{18}H_{15}N_3Cl_2O_2Pt_2S$: C, 27.08; H, 1.89; N, 5.26. Found: C, 27.24; H, 1.47; N, 5.36%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 2093 s, 1613m, 1565m, 1537m, 1269m, 798m, 767m, 731m. $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$) 3.68 (6H, s, $CH_3$(DMSO), $^3J_{Pt-H}$ 22.5); 7.44 (2H, m, H5, H5″); 8.00 (2H, m, H4, H4″); 8.22 (2H, m, H3, H3″); 8.78 (1H, s, H4′, $^3J_{Pt-H}$43, $^3J_{Pt-H}$ 67); 9.44 (1H, d, H6, $^3J_{Pt-H}$ 24); 9.59 (1H, d, H6″, $^3J_{Pt-H}$ 32.4); *m/z* (FAB) 796 ($M^+$), 763 ($M-Cl^+$), 684 ($M-Cl-DMSO^+$), 656 ($M-Cl-DMSO-CO^+$), 621 ($M-2Cl-DMSO-CO^+$), 426 ($M-2Cl-DMSO-CO-Pt^+$).

#### 4.3.11. [$Pt_2$(terpy-2H)(Cl)$_2$($PPh_3$)(CO)] (**12**)

CO at atmospheric pressure was bubbled under stirring for 3 h into a solution of **7** (40.0 mg, 0,033 mmol) in 30 ml of acetone. The orange yellow precipitate formed was filtered, washed with diethyl ether and dried in vacuo to give the analytical sample (29.5 mg, 91%) as an orange yellow solid. M.p. > 270 °C. (Calc. for $C_{34}H_{24}N_3Cl_2OPPt_2$: C, 41.56; H, 2.46; N, 4.28. Found: C, 41.48; H, 2.01; N, 4.21%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 2093s, 1607m, 1560m, 1095m. $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$) 7.09 (1H, d, H4′, $^3J_{Pt-H}$ 63, $^4J_{P-H}$ 2.9); 7.77–7.84 (17H, m, aromatics ($PPh_3$), H5, H5″); 7.99 (2H, m, $H_4$, $H_{4''}$); 8.26 (d, 1H, H3″); 8.31 (1H, m, H3); 9.30 (1H, d, H6″, $^3J_{Pt-H}$ 25.2); 9.85 (1H, t, H6, $^3J_{Pt-H}$ 33.6 , $^4J_{P-H}$ 4.4). $\delta_P$ (121.4 MHz; $CDCl_3$; $H_3PO_4$) 22.86 (s, $^1J_{Pt-P}$ 4266).

#### 4.3.12. [$Pt_2$(terpy-2H)$(CH_3CN)_2(DMSO)_2$][$BAr'_4$]$_2$ (**13**)

To a solution of **5** (61.5 mg, 0.072 mmol) in dichloromethane (30 ml) were added 128.4 mg of Na[$BAr'_4$] (0.145 mmol). The mixture was stirred for 5 h at room temperature under argon, then filtered to remove the NaCl formed and concentrated to dryness. The crude obtained was washed with pentane and dried in vacuo to give the analytical sample (103 mg, ca. 60%) as a yellow solid. M.p. 95–97 °C; $\nu_{max}$(Nujol)/cm$^{-1}$ 1610m, 1563m, 1509m, 1140br. $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$) 2.25 (6H, s, $CH_3CN$); 3.57 (12H, s, $CH_3$ (DMSO), $^3J_{Pt-H}$ 19.3); 7.17 (2H, m, H5, H5″ or H4, H4″); 7.39 (2H, m, H4, H4″ or H5, H5″); 7.54 (8H, s, H*p*); 7.70 (16H, s, H*o*); 8.26 (2H, dd, H3, H3″); 8.51 (1H, s, H4′, $^3J_{Pt-H}$ 43.2); 9.58 (d, 2H, H6, H6″, $^3J_{Pt-H}$ 33.6). $\Lambda_M$ ($3\times10^{-4}$ M, acetone) = 120 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

#### 4.3.13. [$Pt_2$(terpy-2H)(I)$_2$(DMSO)$_2$] (**14**)

To a suspension of **5** (65.0 mg, 0.077 mmol) in acetone (30 ml) were added 40.3 mg (0.30 mmol) of LiI. The yellow solution formed was stirred for 4 days, then evaporated to dryness and crystallized from dichloromethane/diethyl ether to give the analytical sample (34.0 mg, 40%) as a yellow solid. M.p. > 270 °C. (Calc. for $C_{19}H_{21}N_3I_2O_2S_2Pt_2{\cdot}E_2O$ (NMR criterion): C, 24.99; H, 2.83; N, 3.80. Found: C, 25.27; H, 3.11; N, 3.46%.); $\nu_{max}$(Nujol)/cm$^{-1}$ 1610m, 1563m, 1510m, 1135m. $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$) 3.92 (12H, s, $CH_3$ (DMSO), $^3J_{Pt-H}$ 22.9); 7.30 (2H, m, H5, H5″); 7.94 (2H, t, H4, H4″); 8.29 (2H, d, H3, H3″); 9.11 (1H, s, H4″, $^3J_{Pt-H}$ 45); 10.22 (2H, d, H6, H6″, $^3J_{Pt-H}$ 36).

#### 4.3.14. [$Pt_2$(terpy-2H)(H)$_2$(DMSO)$_2$] (**15**)

To a suspension of **5** (50.0 mg, 0.059 mmol) in THF (30 ml) were added 14.0 mg (0.373 mmol) of Na[$BH_4$] dissolved in 10 ml of THF. A red precipitate immediately formed. The suspension was stirred for 4 h, then it was filtered and the precipitate was washed with dichloromethane and diethyl ether to give 32.2 mg of a brown solid. $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$) −15.54 (2H, s, $^1J_{Pt-H}$ 1567).

#### 4.3.15. [$Pt_2$(terpy-2H)(H)$_2$($PPh_3$)$_2$] (**16**)

To a solution of [$Pt_2Cl_2(PPh_3)_2$(terpy-2H)] (85.0 mg 0.070 mmol) in THF (30 ml) were added 11.0 mg (0.29 mmol) of Na[$BH_4$] dissolved in 10 ml of THF. The colour turned to red and a yellow precipitate was formed. The mixture was stirred for 4 h, then cooled with an ice bath and evaporated to small volume. The precipitate formed by treatment with hexane was filtered, washed with hexane and recrystallized from $CHCl_3/Et_2O$ to give the analytical sample (62.1 mg, 70%), m.p. 105 °C (dec). (Calc. for $C_{51}H_{41}N_3P_2Pt_2\cdot CHCl_3$: C, 49.28; H, 3.34; N, 3.32. Found: C, 49.15; H, 2.97; N, 3.26%.). $\nu_{max}$(Nujol)/cm$^{-1}$ 2209w, 1604m, 1564m, 1511m, 1095s. $\delta_H$ (300 MHz; $CDCl_3$; $Me_4Si$) −15.53 (2H, d, *H*–Pt, $^1J_{Pt-H}$ 1444.5, $^2J_{P-H}$ 24.1); 6.68 (2H, m, H5, H5″); 7.35–7.48 (20H, m, aromatics), 7.56–7.76 (14H, m, aromatics); 8.37 (d, 2H, $J_{H-H}$ 7.7, aromatics); 9.14 (1H, t, H4′, $^3J_{Pt-H}$ 64.5, $^4J_{P-H}$ 6.2, $J_{H-H}$ 6.2). $\delta_P$ (121.4 MHz; $CDCl_3$; $H_3PO_4$) 32.89 (s, $^1J_{Pt-P}$ 2072).

#### 4.3.16. X-ray data collection and structure determination

Crystal data are summarized in Table 2. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 223 K, using Mo Kα radiation ($\lambda = 0.71073$) 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 [26], and an empirical absorption correction was applied (SADABS) [27] to the collected reflections. The calculations were performed using the Personal Structure Determination Package [28] and the physical constants tabulated therein [29]. The structure was solved by direct methods (SHELXS) [30]

Table 2
Crystallographic data

| | |
|---|---|
| Compound | **7** |
| Formula | $C_{51}H_{39}Cl_2N_3P_2Pt_2$ |
| $M$ | 1216.93 |
| Colour | Yellow |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ (Å) | 10.461(1) |
| $b$ (Å) | 13.656(1) |
| $c$ (Å) | 15.700(2) |
| $\alpha$ (°) | 90.11 (1) |
| $\beta$ (°) | 96.09 (1) |
| $\gamma$ (°) | 97.01 (1) |
| $U$ (Å$^3$) | 2213.3(4) |
| $Z$ | 2 |
| $F(000)$ | 1172 |
| $D_c$ (g cm$^{-3}$) | 1.826 |
| $T$ (K) | 223 |
| Crystal dimensions (mm) | $0.07 \times 0.17 \times 0.19$ |
| $\mu$ (Mo K$\alpha$) (cm$^{-1}$) | 66.11 |
| Minimum and maximum transmission factors | 0.684–1.000 |
| Scan mode | $\omega$ |
| Frame width (°) | 0.30 |
| Time per frame (s) | 20 |
| Number of frames | 2450 |
| Detector–sample distance (cm) | 4.00 |
| $\theta$-Range | 3–26 |
| Reciprocal space explored | Full sphere |
| Number of reflections (total; independent) | 36 179; 13 206 |
| $R_{int}$ | 0.0512 |
| Final $R_2$ and $R_{2w}$ indices[a]($F^2$, all reflections) | 0.055, 0.067 |
| Conventional $R_1$ index [$I > 2\sigma(I)$] | 0.030 |
| Reflections with $I > 2\sigma(I)$ | 8505 |
| Number of variables | 541 |
| Goodness-of-fit[b] | 0.984 |

[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 $w = 4F_o^2/\sum(F_o^2)^2$, $\sum(F_o^2) = [\sum^2(F_o^2) + (pF_o^2)^2]^{1/2}$, $N_o$ is the number of observations, $N_v$ the number of variables, and $p$, the ignorance factor, =0.02.

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. The hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter $B$ 1.10 times that of the carbon atom to which they are attached, and not refined. In the final Fourier map the maximum residual was 1.69(54) e Å$^{-3}$ at 0.73 Å from Pt(2). CCDC No. 604223 contains the supplementary crystallographic data for this paper.

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