New Pt→M (M = Ag, Tl) complexes based on anionic cyclometalated Pt(II) complexes

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Anionic cyclometalated complexes (NBu₄)[Pt(CNC)X] (X = Cl (**1**), CN (**2**), S-2py (pyridine-2-thiolate) (**3**); -CNC- = 2,6-di(phen-2-ide)-pyridine) have been used as precursors in the synthesis of heteropolynuclear Pt-Ag or Pt-Tl complexes containing donor-acceptor metal-metal bonds. Their reaction with AgClO₄ or [Ag(OCIO₃)(PPh₃)] produces complexes in which the nuclearity and structure seems to be determined by the ability of the ligand X to form bridges between the metals. Thus, the characteristic linear bridging of the cyano ligand leads to the formation of an octanuclear [{Pt(CNC)(μ-CN)}₄Ag₄] (**4**) or tetranuclear [{Pt(CNC)(μ-CN)}₂Ag(PPh₃)₂] (**6**) complexes, with CN bridges between different "Pt-Ag" units. However, the S-2py ligand can act as a bridge between Pt and Ag of the same "Pt-Ag" unit, giving rise to complex [{Pt(CNC)(S-2py)}₂Ag₂]·CH₂Cl₂ (**5**). On the other hand, the reaction of **1-3** with TlPF₆ yields the complexes [PtTl(CNC)Cl] (**7**), [PtTl(CNC)(CN)] (**8**), (NBu₄)[{Pt(CNC)(S-2py)}₂Tl] (**9**), while with [Tl(S-2py)] [PtTl(CNC)(S-2py)] (**10**) is obtained. The structures of all these Pt-Tl complexes show a great variation, with several geometric arrangements which sometimes co-exist in the same crystal structure: discrete Pt-Tl, Pt-Tl-Pt and Pt-Tl-Pt-Tl units, as well as infinite ...Pt-Tl-Pt-Tl... chains. This variability could be due to a lability of the Pt-Tl bonds and the ability of the thallium center to establish secondary interactions with donor atoms or aromatic π electron density from neighboring moieties.

Introduction

Interactions between closed (d¹⁰, d¹⁰ s²) or pseudo-closed (d⁸) shell metallic ions are a powerful tool in molecular and crystal engineering.¹⁻⁵ They have promoted the preparation of polynuclear metallic complexes that show very interesting structural features. Also, many of these complexes bear noteworthy photophysical properties, mostly related with their luminescent character.⁶⁻⁸ Moreover, their interest is growing lately as their presence is being recognised in polymetallic systems that play a crucial role in catalytic processes, such as C-C or C-X coupling reactions.⁹ In some of these processes, the formation of intermediate species with M-M' bonds which favour the interchange of the ligands bonded to the metal centres seems to be the key step of the catalytic cycle.¹⁰⁻²⁰

Many of these metallophilic interactions can be described as dative bonds in which an electron density rich basic metal centre donates its electron density to an acidic metal species with empty orbitals able to host it. Pt(II) (d⁸) in a square planar environment is the most frequent donor centre. Formally, it owns an electron pair located in its d_{z²} orbital, perpendicular to the complex main square plane, which can be donated to a suitable acidic centre. Among these latter, the most commonly reported is Ag(I)²¹⁻²⁴ and to a lesser extent Au(I),^{20, 24} Cu(I),^{10, 18, 25} Tl(I),²⁶⁻²⁹ Cd(II),^{30, 31} Hg(II),³² Pb(II)²⁷ and Zn(II).^{19, 33}

It has been found that the use of cyclometalated ligands in the Pt coordination sphere favors the formation of Pt→M dative bonds.^{6, 20-23, 32} Usually these ligands produce a lower steric hindrance that allows a better closeness of both metallic centres. Besides, the strong ligand field exerted by these

cyclometalated ligands causes an increase in the energy of the Pt d_{z²} orbital and promotes a stronger dative bond.

In the course of our previous work, we have reported the use of neutral Pt(II) complexes [Pt(CNC)(L)] (CNC = -CNC- = 2,6-di(phen-2-ide)-pyridine; L = PPh₃, SC₄H₈, CN^tBu) as starting materials in the synthesis of heteropolynuclear complexes containing Pt→M (M = Ag, Au, Tl)^{20, 24, 28, 34} dative bonds. These neutral precursors have proved to be very adequate for this purpose and they allowed preparing polymetallic complexes that show very interesting molecular architectures. Thus, the use of Tl(I) as the acidic metal led to the preparation of cyclic hexanuclear [PtTl(CNC)(CN^tBu)]₃³⁺ or tetranuclear [{Pt(CNC)}₃Tl]⁺ complexes,²⁸ while dinuclear [(CNC)(PPh₃)PtM(PPh₃)] or "sandwich" trinuclear [{(CNC)(PPh₃)Pt}₂M] complexes are obtained with Au(I) or Ag(I).^{20, 24} Besides, these latter complexes have the added interest that they show M-C interactions involving the CNC ligand which can be related with the potential participation of complexes with M-M' interactions in transmetalation processes.

In this paper we continue this study with the use of anionic [Pt(CNC)X]⁻ (X = Cl, CN, S-2py (pyridine-2-thiolate)) and their reactions toward Ag(I) or Tl(I) salts and complexes. It has been pointed out that anionic square planar Pt(II) complexes should be better precursors than their neutral analogues because the metal centre should have more electron density to be donated to the acidic metal acceptor. The X-ray structural determinations of the resulting complexes have shown some remarkable features.

Results

Preparation of the starting materials (NBu₄)[Pt(CNC)X] (X = Cl (**1**), CN (**2**), S-2py (**3**)).

The preparation of the starting materials (NBu₄)[Pt(CNC)X] used in the syntheses of the Pt–M complexes was achieved by reactions of [Pt(CNC)(dmsol)] with the corresponding NBu₄X. For X = Cl a new experimental method was developed (see experimental), while for X = CN and S-2py, literature methods, with some minor variations, were used.³⁵

The complexes **1–3** were identified and characterized by IR and ¹H NMR spectra. For **1**, its crystal structure was determined by X-ray diffraction. A view of the anion of complex **1** and a table with selected bond distances and angles appear in the Supporting Information (Figure S1 and Table S1). As expected, **1** shows a square planar environment for the Pt centre, with the CNC ligand also planar, and practically co-planar with the Pt square plane, and it is practically isostructural to the isoelectronic complex [Au(CNC)Cl]⁺.³⁶ Unlike to other similar Pd(II), Pt(II) or Au(III) square planar complexes,^{36–38} no intermolecular M–M or $\pi\cdots\pi$ contacts are found in **1**.

Reactions of (NBu₄)[Pt(CNC)X] (X = Cl (**1**), CN (**2**), S-2py (**3**)) with AgClO₄.

The reactions of the starting materials **1** and **2** with AgClO₄ in 1:1 molar ratio using CH₂Cl₂ (**1**) or acetone (**2**) as solvent, and in the absence of light, lead to the progressive precipitation of solids which were filtered off after 60 min of stirring. In the case of the S-2py (**3**) only a faint precipitate appears and in order to obtain a good yield the solution is evaporated to dryness after 30 min of stirring. The resulting solid is treated with ¹PrOH and the insoluble fraction is filtered off.

The scarce or zero solubility of these solids in acetone and in low or non-coordinating solvents such as CH₂Cl₂ or CHCl₃ limits their study by NMR or mass spectroscopy. Thus, deuterated dimethyl sulfoxide (dmsol-d₆) has to be used as the NMR solvent, but given its strong coordinative nature any possible Pt–M bond gets broken in solution and no further information can be obtained. In the case of the product obtained from **2**, it is not even soluble enough in dmsol-d₆ to record any NMR spectrum. At this point, the only information available for this solid came from their elemental analyses (see Experimental section) and its IR spectrum. The former agrees with the intended stoichiometry [PtAg(CNC)(CN)] while a remarkable feature for the latter is the displacement of the IR $\nu(\text{C}\equiv\text{N})$ band toward higher frequencies (2122 cm^{−1}) with respect to its starting material **2** (2092 cm^{−1}), a shift observed in bridged cyano complexes.

Nevertheless, suitable crystals for X-ray diffraction studies were obtained from slow diffusion of concentrated dimethylformamide (DMF) solutions of this solid into diethyl ether. The crystal structure reveals the existence of an

octanuclear cluster $[\{\text{Pt}(\text{CNC})(\mu\text{-CN})\}_4\text{Ag}_4]$ (**4**) (see Figure 1 and Table S2, Supporting Information).

One of the four "Pt(CNC)CN" fragments is disordered over two positions, each of the components giving rise to slightly different structural parameters with respect to the other fragments. Here, only one of the components of the disorder is used for descriptive purposes. A full insight of the complex can be obtained from the cif file available as Supporting Information.

The structure can be regarded as two "Pt(CNC)(CN)" fragments which sandwich two Ag centres. These "Pt₂Ag₂" units in turn are joined through the cyano ligands which bridge platinum and silver atoms of analogous units. In each "Pt₂Ag₂" unit the "Pt(CNC)(CN)" fragments are basically co-planar (dihedral angles: 4.5(2)° (Pt(1A)–Pt(1B)) γ 17.9(3)° (Pt(1C)–Pt(1D)). The two "Pt₂Ag₂" units are almost perpendicular one with respect to the other. Approximately, the core of complex **4** has a very distorted parallelepiped geometry in which the metallic centres occupy alternate vertex and the cyano ligands lie in the long edges (see Figure 1b).

Fig. 1. a) X-ray crystal structure of the complex $[\{\text{Pt}(\text{CNC})(\mu\text{-CN})\}_4\text{Ag}_4]$ (**4**). b) View of the core of the complex. For the sake of clarity, only one of the components of the disorder is represented.

Scheme 1. Proposed path for the formation of **5** and its evolution.

Each silver atom is bonded to two platinum centres with distances between 2.7740(11) and 3.0408(5) Å (see Table S2), in the range found for this kind of dative bonds.^{21–24} The Pt–Ag lines always lean toward the *ipso* carbon of the phenylene rings of the CNC ligands. As a consequence, the Ag–C_{ipso} distances are short, ranging from 2.466(14) and 2.577(5) Å (see Table S2), and indicating the existence of η^1 –Ag–C interactions. These interactions have been observed previously in other CNC complexes,^{20, 24, 39} or similar complexes containing other CN plane cyclometalated ligands such as benzoquinolate.^{21, 22} DFT calculations performed on these systems have showed that in these M⋯(Pt–C) interactions there is a substantial participation of the electron density contained along the Pt–C bond.²⁴

The structure confirms the bridging role of the cyano ligands which connect Pt and Ag centres from different “Pt₂Ag₂” units. The Pt–C–N–Ag sequence is relatively linear, with the larger deviation corresponding to the Ag–N–C angle, around 150° (see Table S2), as previously described in other “Pt–CN–Ag” or “Pt–CN–Cu” complexes.⁴⁰

Finally, the [{Pt(CNC)(μ-CN)}₄Ag₄] moieties in the crystal structure establish π ⋯ π interactions with the aromatic rings of the CNC ligands of neighbour complexes (C⋯C less than 3.5 Å), thus forming a supramolecular chain (see Figure S8, Supporting Information). This arrangement has been previously observed in other Pt(CNC) complexes.²⁸

In the case of the very insoluble material obtained from the reaction of (NBu₄)[Pt(CNC)(S-2py)] (**3**) with AgClO₄, their elemental analyses (see Experimental section) lead us to assign it a formula [PtAg(CNC)(S-2py)]. We also have detected a peak corresponding to the [{Pt(CNC)(S-2py)}₂Ag₂]+H⁺ species in its mass spectrum (see Experimental section). Besides, and despite its low solubility, a small amount of this solid could be dissolved in CH₂Cl₂ and the slow diffusion of this solution into *n*-hexane gave some few crystals suitable for X-ray diffraction studies. The crystal structure confirms again the 1:1 ratio between the metal centres, in this case being a tetranuclear complex of formula [{Pt(CNC)(S-2py)}₂Ag₂] (**5**) (see Figure 2 and Table S3, Supporting Information).

As in complex **4**, we find a “Pt₂Ag₂” unit in the structure of **5**. Thus, the two silver centres are located between the two “Pt(CNC)” units but in this case these are not coplanar (dihedral angle of 38.5°). The S-2py ligands are bridging the Pt and Ag atoms, but it is noteworthy that one of the mercaptopyridines has changed its coordination mode and is now N-bonded to Pt(1) and S-bonded to the two silver centres. Although the S-coordination of the S-2py ligand to the Pt centre is more often observed, its N-coordination has been reported once in the related compound [{Pt(C₆F₅)(S-

2py)(ppy)}₂Pb],³² which is prepared by reaction of [Pt(C₆F₅)(ppy)(dmsol)] with [Pb(S-2py)₂]. In any case, the structure of **5** reveals that the breakage of a Pt–S bond and concomitant formation of a Pt–N takes place. It is worth noting that when the crude solid from which crystals of **5** is obtained by recrystallization is dissolved in dmsol-d₆ with the aim to measure its ¹H NMR spectrum, signals corresponding to the complex [Pt(CNC)(dmsol)] are observed,²⁸ along three more signals which are attributed to some “Ag(S-2py)” complexes.⁴¹ Since S-2py is able to bridge Pt and Ag centres of the same “Pt₂Ag₂” unit, complex **5** could evolve through a path as the one represented in Scheme 1, finally giving [Pt(CNC)(dmsol)] and “Ag(S-2py)” as observed in its ¹H NMR spectra in dmsol. The crystal structure found in **5** would be a snapshot of this evolution.

The two silver centres show very different environments. Thus, Ag(1) is bonded to the two platinum atoms with Pt–Ag distances at the longer end for donor acceptor systems (3.0380(7) and 3.0360(7) Å) and no Ag(1)–C_{ipso} contacts are established (the Ag–C_{ipso} distances are above 3 Å). Besides, Ag(1) is bonded to a pyridinic nitrogen atom and the S atom of the “inverted” S-2py ligand. This S atom bridges the two silver centres, but with different Ag–S distances (Ag(1)–S(1) = 2.422(2), Ag(2)–S(1) = 2.601(2) Å). On the other hand, the Pt–Ag(2) distances are shorter (2.8659(7) and 2.8237(7) Å) and this silver centre contacts with two C_{ipso} atoms of the CNC ligands, with short Ag–C_{ipso} distances (Ag(2)–C(7) = 2.386(8) Å, Ag(2)–C(29) = 2.355(8) Å). Concomitantly, the Pt–Ag lines lean toward the phenylene rings of the CNC ligands in a greater extent for Ag(2).

Fig. 2 X-ray crystal structure of the complex [{Pt(CNC)(S-2py)}₂Ag₂] (**5**)

Chart 1. Atom numbering scheme used for the description of the NMR spectra.

The different bonding mode of the silver centres seems to indicate that given their acidic nature they seek electron density from the surroundings in a different way. The donation of the electron pair of the pyridinic nitrogen to Ag(1) and a closer Ag(1)-S(1) interaction seems to cause that this silver atom is not so avid for additional electron density, and thus the Pt-Ag(1) distances are longer and there is no need for additional Ag-C_{ipso} contacts. However, Ag(2) finds this additional electron density in stronger Pt-Ag interactions (leading to shorter Pt-Ag distances) and Ag-C_{ipso} contacts. The Ag(1)⋯Ag(2) separation is 2.891(1) Å, significantly shorter than for **4** (around 3.4 Å) which could indicate that some argentophilic interaction may exist.⁴²

Reactions of (NBu₄)[Pt(CNC)X] (X = Cl (**1**), CN (**2**), S-2py (**3**)) with [Ag(OCIO₃)(PPh₃)].

In order to prepare more Pt-Ag complexes, the reactions of the starting materials **1-3** with [Ag(OCIO₃)(PPh₃)] in 1:1 molar ratio were explored. Nevertheless, only in the case of the starting material **2** were the results successful, while in the other two cases, an interchange of ligands between the metal centres is observed.

Thus, the reaction of (NBu₄)[Pt(CNC)Cl] (**1**) with [Ag(OCIO₃)(PPh₃)] in acetone causes, after some minutes of stirring, the precipitation of AgCl. This solid is filtered off and after evaporation of the solvent, a yellow solid is obtained. This solid is identified (IR, NMR) as [Pt(CNC)(PPh₃)], previously prepared.²⁰

In the case of (NBu₄)[Pt(CNC)(S-2py)] (**3**), the reaction with [Ag(OCIO₃)(PPh₃)] in similar conditions yields a yellow solid which spectroscopic data, mainly NMR, indicate that it is a mixture of, again, [Pt(CNC)(PPh₃)] and a compound that causes the same mercaptopyridine signals than in the ¹H NMR spectrum of **5**, described above, which were attributed to unidentified “Ag(S-2py)” complexes.

Furthermore, the reaction of (NBu₄)[Pt(CNC)(CN)] (**2**) with [Ag(OCIO₃)(PPh₃)] in acetone at room temperature during 30 minutes in the absence of light causes the precipitation of a yellow brownish solid, which is filtered off and air dried. The IR spectrum of this solid lacks the signals corresponding to the NBu₄⁺ or ClO₄⁻ ions, confirming its neutral nature. Moreover, the ν(C≡N) band moves toward higher frequencies (2117 cm⁻¹) with respect to the starting material (2092 cm⁻¹) which is consistent with a bridging role for the cyano ligand.⁴³

Additionally, the elemental analysis for this solid is compatible with a formula [Pt(CNC)(CN)Ag(PPh₃)].

The ¹H NMR spectrum of this solid in CD₂Cl₂ (see Figure S13, Supporting Information) shows only four signals in the aromatic region which can be assigned to the CNC and PPh₃ ligands (see experimental section for the assignment of the signals). The pattern of the signals corresponding to the CNC ligand is significantly different from the one found in the starting material **2**. Particularly, the signal corresponding to H2 (see Chart 1a for the proton numbering Scheme) appears perceptibly deshielded (8.23 ppm) with respect to the starting material (7.88 ppm), which again is an indication of the existence of Pt→M bonds.^{20, 28, 39}

The ³¹P NMR spectrum in CD₂Cl₂ at room temperature only shows a broad signal. Successive spectra recorded while cooling down the sample show a progressive increasing of the resolution of this broad signal in such a way that at 193 K (see Figure 3) it appears as two doublets. This pattern is typical for the phosphorus atoms of a PPh₃ ligand bonded to a silver centre,^{22, 44} and caused by the coupling⁴⁴ of the ³¹P nucleus to the two isotopomers ¹⁰⁷Ag (abundance 51.8%) and ¹⁰⁹Ag (abundance 48.2 %) which have slightly different gyromagnetic constants, the Ag-P coupling constants being 638.7 Hz and 552.0 Hz. In addition, a remarkable feature of these doublets is that they show platinum satellites (²J_{P-Pt} = 100.5 Hz) that prove the existence of a Pt-Ag bond in solution.

The ¹⁹⁵Pt{¹H} NMR spectrum of the solid in CD₂Cl₂ is also consistent with the persistence of the Pt-Ag bond in solution. Thus, the spectrum at room temperature shows a broad singlet which resolves in a doublet of doublets at 193K (see Figure S14, Supporting Information). This signal is centred at -4012 ppm, which represent a downfield shift of 21 ppm with respect to the starting material **2**. Such displacement is in agreement with the existence of the intermetallic bond. The doublet of doublets is caused by a Pt-Ag coupling (¹J_{Pt-Ag} = 212.9 Hz) and a further Pt-P coupling (²J_{Pt-P(Ag)} = 108.6 Hz).

In the light of these results it is clear that the cyano starting material is able to stabilize a Pt-Ag complex in solution while the chloro or mercaptopyridine are not. Nevertheless, from the information given by the NMR it is not possible to determine the nuclearity of the complex in solution. The mass spectra (see Experimental) finds a peak corresponding to a dinuclear PtAg moiety, but equilibria in solution involving di and tetranuclear species may well be operating.

Figure 3. ³¹P NMR spectrum (CD₂Cl₂, 193K) of **6**.

Figure 4. X-ray crystal structure of the complex $[\text{Pt}(\text{CNC})(\mu\text{-CN})_2\{\text{Ag}(\text{PPh}_3)_2\}]$ (**6**).

A single crystal X-ray diffraction study could establish that on the solid we have a tetranuclear complex $[\text{Pt}(\text{CNC})(\mu\text{-CN})_2\{\text{Ag}(\text{PPh}_3)_2\}]$ (**6**) (see Figure 4 and Table S4, Supporting Information).

As can be seen in Figure 4, **6** is formed by two “(CNC)(CN)PtAg(PPh₃)” subunits which are linked by the two cyano ligands that bridge the Pt and Ag atoms of different subunits. The structure of a similar complex, $[\text{Pt}(\text{tolpy})(\text{CN})(\mu\text{-CN})_2\{\text{Ag}(\text{PPh}_3)_2\}]$ (Htolpy = 2-(4-tolyl)-pyridine), has recently been reported.⁴⁰

In **6**, the Pt-C-N-Ag sequence is fairly straight. The eight-member ring formed by the four metal atoms and the C and N of the cyano ligands does not depart dramatically from the planarity.

The best square plane environment of the platinum atoms are almost mutually perpendicular (dihedral angle 87.7(1)°). In each subunit there is a Pt-Ag bond with distances 2.9055(5) and 2.8652(5) Å, similar to the ones found in **4** (see above), slightly shorter than the ones found in the analogous $[\text{Pt}(\text{tolpy})(\text{CN})(\mu\text{-CN})_2\{\text{Ag}(\text{PPh}_3)_2\}]$ (2.9507(2) Å),⁴⁰ and in the range found for this kind of dative bonds.^{21–24} As in **4**, the Pt-Ag line is not perpendicular to the Pt square plane, but leans toward one of the phenylene rings of the CNC, resulting in short $\eta^1\text{-Ag-C}$ interactions. The coordination of the silver centre in **6** is completed by a PPh₃ ligand and a Ag-N bond established with the nitrogen atom of the CN ligand of the other subunit. Disregarding the Ag-C_{ipso} interaction, the coordination spheres of the silver centres are approximately trigonal. In fact, the structure of **6** can be derived from the previously described for **4**. The situation in the former is as in **4** each “Pt₂Ag₂” subunit is split in two “PtAg” halves by the phosphane ligand.

It is worth mentioning that the Ag-C_{ipso} interactions found in the crystal structures of **4**, **5** and **6** break the symmetry of the CNC ligand and thus, a static situation should cause an inequivalence of the signals of the CNC protons in the ¹H NMR spectra in solution. Unfortunately, only in the case of the **6**, solubility does allow a complete NMR study. Both at room temperature and at 193K the two halves of the CNC ligand are equivalent in the ¹H NMR spectra. Thus, either the Ag-C_{ipso} interaction is not present in solution, or an oscillating dynamic process involving the alternate formation and breaking of the

Ag-C_{ipso} interaction must be operating. This “metronome-like” process has been detected in the similar complexes $[(\text{CNC})(\text{PPh}_3)\text{PtAu}(\text{PPh}_3)]^+$ and $[(\text{CNC})(\text{PPh}_3)\text{Pt}_2\text{Au}]^+$,^{20, 24} for which the low temperature ¹H NMR spectrum shows the inequivalence of the two phenylene rings and thus a slowing of the oscillation. This difference in the energetic barrier of this process in these complexes with respect to **6** could be attributed to a stronger interaction in the gold complexes, where shorter Au-C_{ipso} distances (2.157(3)-2.225(3) Å) were found.

Reactions of (NBu₄)[Pt(CNC)X] (X = Cl (**1**), CN (**2**), S-2py (**3**)) with TIPF₆.

Different results are obtained in the reactions in acetone of equimolecular amounts of TIPF₆ with the starting materials (NBu₄)[Pt(CNC)X] depending on X. Thus, when X = Cl or CN, the precipitation of orange and yellow solids respectively is observed almost immediately. Identical solids (IR) are also obtained when the Pt/Cl ratio is 2:1. On the other hand, the same reactions with (NBu₄)[Pt(CNC)(S-2py)] as starting material do not produce the precipitation of a solid in the acetone solutions. After 35 minutes of stirring, the solution is evaporated to dryness, and the resulting solid treated with ¹PrOH, from which an insoluble dark brown solid can be filtered off. This solid, as its IR and NMR data indicate (see below) is also obtained regardless of the Pt/Cl ratio used (1:1 or 2:1).

Figure 5. a) Fragment of the infinite chain $[\text{PtI}(\text{CNC})\text{Cl}]_n$ found in the X-ray crystal structure of **7**. b) Supramolecular two-dimensional structure. The E and F $[\text{PtI}(\text{CNC})\text{Cl}]$ units (see Text) are represented in red. Cyan dotted lines represent $\eta\text{-arene-Tl}$ interactions shorter than 3.4 Å.

Due to the very scarce solubility of the solids obtained from the Cl and CN starting materials in acetone or CH₂Cl₂, no NMR studies can be performed in these or other non-coordinative usual solvents. Only in dmsO, a strong coordinative solvent, are these solids soluble enough to register their NMR spectra, and in these the absence of signals attributable to NBu₄⁺ (¹H NMR)

or PF_6^- (^{19}F NMR) is the most remarkable feature. The rest of signals in the proton spectrum correspond to the starting materials, and thus the existence of Pt-Tl bonds in these solutions cannot be established. For the solid obtained from the chloro starting material, despite it being little soluble in acetone, some very few small crystals were obtained from slow diffusion of saturated Me_2CO solutions of this solid into *n*-hexane. The quality of these crystals was far from ideal, being poor diffractors, but after some work in the resolution and refinement processes (see Experimental for crystallographic details) the crystal structure of $[\text{PtTI}(\text{CNC})\text{Cl}]$ (**7**) could be determined (see Figure 5 and Table S5, Supporting Information). Despite this structure is in agreement with a 1:1 Pt:Tl ratio, as expected, we cannot assure that it is representative of the composition of the bulk solid obtained from the reaction, since no elemental analysis coincident with this formula could be obtained from repeated preparations of the solid.

The structure confirms the existence of Pt-Tl bonds in the solid state. In the asymmetric part of the unit cell there are six “(CNC)ClPt-Tl” units which play different structural roles, giving rise to a two-dimensional framework. Four of these units (represented by the letters A-D) form a chain that, by repetition, becomes infinite (Figure 5a). The “ Pt_4Tl_4 ” asymmetric motif is 21.123(1) Å long.

The atom sequence $\cdots\text{Pt-Tl-Pt-Tl-Pt-Tl}\cdots$ is not linear. The Pt-Tl distances show a noticeable variability, with values between 2.8563(9) Å and 3.3644(9) Å. The Pt-Tl lines are not perpendicular to their Pt square planes, but the Tl atoms “lean” toward the chlorine atom of one of the neighbour “(CNC)ClPt” units, resulting relatively short Tl-Cl distances, of around 3.12 Å, which could be indicative of some Tl-Cl interaction. Tl(1C) is an exception to this feature since it is further than 3.5 Å from its closest chloro ligands and at the same time shows two of the shortest Pt-Tl distances (2.8882(9) Å, 2.9883(10) Å) and a less pronounced “leaning”. The variability of all these geometric parameters found in the four “(CNC)ClPt-Tl” units that form the Pt-Tl chain could be due to packing forces and the flexibility of the $\cdots\text{Pt-Tl-Pt-Tl-Pt-Tl}\cdots$ backbone. In this way, both the steric requirements of the crystal environment and the electronic requirements of the Tl(I) acidic centre, which receives electron density from the Pt centres and the Tl-Cl contacts can be fulfilled. It is worth mentioning that so far, only four other infinite one dimensional chains based solely in Pt-Tl bonds (no bridging ligands) have been reported: $(\text{NBu}_4)_n[\{\text{Pt}(\text{C}_6\text{F}_5)_4\}\text{TI}]_n$,⁴⁵ $[\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}\text{TI}(\text{Me}_2\text{CO})]_n$,²⁷ $(\text{NBu}_4)_n[\{\text{trans,trans,trans-PtTI}(\text{Pt}(\text{C}_6\text{F}_5)(\text{C}^{\wedge}\text{N})(\text{S}))_2(\text{C}\equiv\text{CFc})_2\}]_n$,⁴⁶ and $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\}\text{TI}(\text{S-2pyCF}_3)]_n$.²⁶

The other two “(CNC)ClPt-Tl” units present in the asymmetric part of the unit cell (denoted E and F) are not part of the chain. Their structural role is to bridge adjacent parallel chains through interactions established by Tl atoms (see Figure 5b). These interactions are of two types. Firstly, the two phenylene rings of the CNC ligands of the E and F units establish η -arene-Tl interactions with Tl centres of the neighbour chains, the shortest Tl-C distances being around 3.2 Å. Besides, the Tl atoms of the E and F units also show similar η -arene-Tl

interactions with the CNC ligands of the chain. The final result is a two dimensional distribution of parallel $\cdots\text{Pt-Tl-Pt-Tl-Pt-Tl}\cdots$ chains formed by the A-D units linked by the η -arene-Tl interactions of the E-F units.

In the case of the solid obtained from the cyano starting material **2**, their elemental analysis do correspond with the expected formulation $[\text{PtTI}(\text{CNC})(\text{CN})]$ (**8**) (see Experimental). Moreover, we were able to obtain crystals from this solid suitable for X-ray studies which reveal a structure in accordance with this formula. The structural determination confirms the existence of Pt-Tl bonds in this complex (see Figure 6 and Table S6, Supporting Information). Besides, the Pt-Tl units are connected through Tl-N interactions.

In the asymmetric unit of **8** there are two virtually identical $[\text{PtTI}(\text{CNC})(\text{CN})]$ moieties (see Figure 6a) with Pt-Tl distances 2.9241(3) and 2.9207(3) Å. These distances are in the short range found for this kind of intermetallic bond. For example, they are similar or slightly shorter to the ones reported in the “Pt(CNC)” complexes $[\{\text{Pt}(\text{CNC})(\text{tht})\}_3\text{TI}]^+$ (2.9088(5) Å) and $[\{\text{PtTI}(\text{CNC})(\text{CN}^t\text{Bu})\}_3]^{3+}$ (3.0143(3), 3.0488(3) and 3.0460(3) Å),²⁸ and slightly shorter than the ones found in other “(C $\wedge$ N)Pt-Tl”,^{47, 48} “(C $\wedge$ C)Pt-Tl”²⁹ or “(C $\wedge$ N)Pd-Tl” complexes.⁴⁹ The Pt-Tl lines are almost perpendicular to the best Pt square planes, such that the angles between the Pt $\cdots$ Tl vectors and perpendicular to the this plane are 8.5(1)° and 9.0(1)°.

Figure 6. a) Crystal structure of the two discrete $[\text{PtTI}(\text{CNC})(\text{CN})]$ units found in the X-ray crystal structure of **8**. b) Supramolecular arrangement showing the Tl-N interactions (dark blue) and the η -arene-Tl and π - π interactions (cyan).

Both $[\text{PtTI}(\text{CNC})(\text{CN})]$ moieties form supramolecular entities by means of Tl-N interactions (see Figure 6b). The Tl atoms are at contact distances from N atoms of the cyano ligands of neighbour complexes (Tl-N = 2.636(4)-2.683(5)). At the same

time, each N atom is contacting two different Tl centres. The cyano bridging mode $\mu_3\text{-kC:kN:kN}$ is not very common and has only previously been reported in the *cis*- and *trans*- $[\text{PtI}_2(\text{C}_6\text{F}_5)_2(\text{CN})_2]$ complexes, in which the Tl–N distances are slightly longer than in **8**.⁴⁷ As a result of these interactions, **8** shows a one-dimensional supramolecular framework as can be seen in Figure 6b. Other supramolecular structures have been found in similar Pt or Pd cyano complexes containing Pt(II)–Tl(I) or Pd(II)–Tl(I) bonds.^{48, 49} Moreover, the supramolecular arrangement of **8** can be described as a sort of “stair”, in such a way that all the steps are parallel, resulting in $\pi\cdots\pi$ interactions between the aromatic rings of CNC ligands (C–C distances 3.32–3.38 Å) and long η -arene–Tl (around 3.45 Å) interactions.

The dark brown solid obtained from the reaction of $(\text{NBu}_4)[\text{Pt}(\text{CNC})(\text{S-2py})]$ with TlPF_6 is soluble enough in common solvents as to be studied by NMR spectroscopy. The ^1H NMR spectrum of solutions of this solid in CD_2Cl_2 (see Figure S19, Supporting Information) shows the signals corresponding to the NBu_4^+ cation and a set of signals in the aromatic region caused by the CNC and S-2py ligands. However, these signals appear at different chemical shifts than in the starting material, and their integration with respect to the cation ones is consistent with the formula $(\text{NBu}_4)[\{\text{Pt}(\text{CNC})(\text{S-2py})\}_2\text{Tl}]$ (**9**) for this solid. The aromatic signals were assigned on the basis of a two-dimensional COSY (^1H – ^1H) experiment (see Figure S20, Supporting Information). Due to a relatively low solubility, the ^1H NMR spectra at lower temperatures are less defined, but basically they keep showing that there is one kind of S-2py and CNC ligands, that each maintain the equivalence of both halves.

It has been reported that in some complexes containing Pt–Tl bonds, there are equilibria in solution that involve the cleavage and formation of the intermetallic bond, such as the one represented below, that are faster than the NMR time of response.^{27, 28}

These equilibria are also observed in solutions of complex **9**, which supports the idea that there are Pt–Tl bonds in solution. Thus, the ^1H NMR spectrum of a solution of **9** to which a small amount of the starting material $(\text{NBu}_4)[\text{Pt}(\text{CNC})(\text{S-2py})]$ (**3**) has been added shows no signals of this starting material, but only one set of signals. These appear at slightly different ppm than the original signals of **9**, especially the ones corresponding to H3S-2py and H4S-2py (see Figure S21, Supporting Information). This observation is in agreement with the equilibrium above, and the addition of some amount of the starting material would cause a displacement of the equilibrium to the left.

It was possible to obtain crystals from solutions of **9** in CH_2Cl_2 , suitable for their study by X-ray diffraction. The determined structure confirms the trinuclear Pt_2Tl nature of complex **9** (see Figure 7 and Table S7, Supporting Information).

The trinuclear complex has a “sandwich” type structure in such a way that the Tl centre lies between two “Pt(CNC)(S-2py)” units. The thallium atom is bonded to the two platinum

centres with Pt–Tl distances of 2.8953(2) and 2.9184(2) Å. No $\text{Tl-C}_{ipso}(\text{CNC})$ interaction is present. The Pt–Tl distances are similar to other Pt–Tl–Pt sandwich complexes such as $(\text{NBu}_4)[\{\text{Pt}(\text{C}_6\text{F}_5)_2(\text{bzq})\}_2\text{Tl}]$ (range 2.8747(3)–2.9432(4) Å) and $(\text{NBu}_4)[\{\text{Pt}(\text{C}_6\text{F}_5)_2(\text{bzq})\}_2\text{Tl}(\text{THF})]$ (2.9352(6), 2.9705(6) Å) (bzq = 7,8-benzoquinolate).²⁷ The Pt–Tl–Pt line is rather straight (Pt(1)–Tl–Pt(2) angle 165.58(1)°) with the Pt–Tl vectors being almost perfectly perpendicular to the best Pt square planes (angles of the vectors and the perpendicular to this plane are only 3.8(1)° and 3.6(1)°). The S-2py ligands are acting as bridges between the metal centres, with the S atoms coordinated to Pt, and distances Tl–N somewhat long (2.671(4) Å and 2.710(4) Å), but in the range found in similar bonds.⁵⁰ Unlike to $[\{\text{Pt}(\text{CNC})(\text{S-2py})\}_2\text{Ag}_2]$ (**5**), no changes in the coordination mode of the S-2py ligand with respect to the starting material **3** are observed in **9**.

Finally, the $[\{\text{Pt}(\text{CNC})(\text{S-2py})\}_2\text{Tl}]^-$ anions establish $\pi\cdots\pi$ interactions with the aromatic rings of the CNC ligands of neighbour complexes ($\text{C}\cdots\text{C} \approx 3.4$ Å) forming a supramolecular chain (see Figure S22, Supporting Information).²⁸

Preparation of $[\text{PtTl}(\text{CNC})(\text{S-2py})]$ (**10**)

The different Pt/Tl ratio obtained in the products from the reactions of the starting materials $(\text{NBu}_4)[\text{Pt}(\text{CNC})\text{X}]$ with TlPF_6 is noteworthy. Thus, when $\text{X} = \text{Cl}$ or CN , 1:1 complexes **7** and **8** are obtained, while when $\text{X} = \text{S-2py}$, a 2:1 ratio is obtained in **9**. This may be related to the ability of the S-2py ligand to effectively bridge two metal centres which, at the same time, could be bonded through a strong, perpendicular Pt–Tl bond. This arrangement would be much more difficult for $\text{X} = \text{Cl}$ and virtually impossible for $\text{X} = \text{CN}$ for geometric reasons.

Figure 7. X-ray crystal structure of the complex anion of the structure $(\text{NBu}_4)[\{\text{Pt}(\text{CNC})(\text{S-2py})\}_2\text{Tl}]\cdot\text{CH}_2\text{Cl}_2$ (**9**).

However, we explored other starting materials in order to achieve the synthesis of a 1:1 Pt/Tl S-2py complex similar to **7** or **8**. Thus, we reacted $[\text{Pt}(\text{CNC})(\text{dmsO})]$ with $[\text{Tl}(\text{S-2py})]$. This thallium compound was prepared *in situ* by adding $\text{Tl}(\text{acac})$ to a pyridine-2-thiol solution (1:1 ratio) in CH_2Cl_2 . The resulting

solution is stirred for 35 min and then [Pt(CNC)(dmso)] (1:1) was added, allowing the mixture further stirring for 10 min. The solution was concentrated to ca. 2 mL and the addition of n-hexane caused the precipitation of a brown solid that was filtered off. Spectroscopical and analytical data for this solid are consistent with a formula [PtTI(CNC)(S-2py)] (**10**).

The most remarkable feature of the ^1H NMR spectrum of a solution of **10** in CD_2Cl_2 at room temperature (see Figure S24, Supporting Information) is the downfield displacement of the H2 signal of the CNC ligand (see Chart 1 for the NMR atom numbering scheme) 0.45 ppm, with respect to the analogous signal in the starting material. Remarkably, the ^1H NMR spectrum in $\text{dmso}-d_6$ is also different from the ones obtained for [Pt(CNC)(dmso)] or the mononuclear [Pt(CNC)(S-2py)] (see Figure S25, Supporting Information) which indicates that, if formed, the Pt–TI bond would survive to some extent in donor solvents such as dmso.

The existence of equilibria in solutions of **10**, analogous to the ones proposed above for **9**, has also been investigated. Also in this case, the addition of small amounts of $(\text{NBu}_4)[\text{Pt}(\text{CNC})(\text{S}-2\text{py})]$ (**3**) to solutions of **10** in CD_2Cl_2 does not cause the appearance of signals for the former in their ^1H NMR spectra, but the resultant signals appear at values of chemical shift intermediate between the two. This is consistent with the presence of such equilibria, faster than the NMR time of response.

By recrystallizing the solid **10** (see Experimental section) it was possible to obtain crystals that were studied by X-ray diffraction. The structure determined confirms the presence of Pt–TI bonds (see Figure 8 and Table S8, Supporting Information).

Three “PtTI” units with different structural roles lie in the asymmetric part of the unit cell. Thus, Pt(1), Pt(2), TI(1) and TI(2) form a discrete tetranuclear unit (see Figure 8b). TI(2) is simultaneously bonded to the two Pt atoms with Pt–TI distances of 2.9991(9) and 2.8222(9) Å, while TI(1) is only bonded to Pt(1) with a distance 2.8324(9) Å. The TI(1)–Pt(1)–TI(2) and Pt(2)–TI(2)–Pt(1) are 158.64(3)° and 155.90(3)° respectively. Besides, the S-2py ligands act as bridges between the Pt and TI, always with the S atom coordinated to Pt and the N atom to TI.

On the other hand, Pt(3) and TI(3) are forming an infinite –Pt–TI–Pt–TI– linear chain (see Figure 8c). The Pt(3)–TI(3) distances are 2.9183(9) and 2.8839(9) Å. The angles involving the metals are TI(3)–Pt(3)–TI(3) 161.48(3)° and Pt(3)–TI(3)–Pt(3) 144.30(3)°. Again, the pyridine-2-thiolate is bridging both metallic centres.

The tetranuclear subunit interacts with the chain through intermolecular TI...S contacts (in red in Figure 8a), with TI–S distances of around 3.25 Å. There are longer TI...S contacts (ca. 3.81 Å) between different tetranuclear subunits (in cyan in Figure 8a).

Figure 8. a) X-ray crystal structure of [PtTI(CNC)(S-2py)] (**10**). b) View of the tetranuclear subunit. c) View of the infinite chain.

Discussion

Pt–Ag complexes. The common motif found in the structures of **4** and **5** is the tetranuclear “Pt₂Ag₂” core. Very few structures with this disposition of the metal centres have been reported so far: $\text{trans}-[\{\text{PtAg}(\text{C}_6\text{F}_5)_2\text{Cl}_2\}_2]^{2-}$,⁵¹ $[\{(\text{C}_8\text{H}_6\text{N}_2\text{Cl}_4)\text{Me}_2\text{PtAg}(\text{SO}_3\text{CF}_3)\}_2]^{2-}$,²⁵ $[\{\text{PtAg}(\text{bzq})\text{Me}(\text{PPh}_2\text{C}_6\text{H}_5\text{N})\}_2]^{2+}$,⁵² $[\{(\text{C}_6\text{F}_5)_2(\text{acac})\text{PtAg}(\text{CH}_2\text{Cl}_2)\}_2]^{2-}$,⁵³ and $[\{\text{PtAg}(\text{bipy})(\text{C}_6\text{H}_4\text{S}_2)\}_2]^{2+}$.⁵⁴ Some of these complexes show some asymmetry in the “Pt₂Ag₂” core with a pair of Pt–Ag distances significantly longer than the other two and in all cases the silver centres are also bonded to other atoms, either from a ligand of the coordination sphere of the Pt atom, thus acting as a bridge, or from an “external” ligand, frequently a solvent molecule of an anion (or both).

It is noteworthy that the reactions of the neutral analogous products [Pt(CNC)L] (L = dmso, PPh₃, SC₄H₈) with AgClO₄ yield

the trinuclear sandwich complexes $[\{\text{Pt}(\text{CNC})\text{L}\}_2\text{Ag}]^+$, even when the reaction is attempted in an equimolar Pt:Ag ratio.²⁴ The reason for the anionic starting materials giving crystal structures with “ Pt_2Ag_2 ” cores, while the neutral produce “ Pt_2Ag ” ones could be the increase of the electron density on the Pt fragment in the former because of its anionic nature. Thus, the higher basicity of the platinum enables it to “trap” two acidic Ag centres between the planar Pt fragments.

Regarding the differences in the insolubility of the solids **4** and **5**, they may be related to the different abilities of the Cl, CN or S-2py ligands to bridge the Pt and Ag centres, which in turn affects to the overall nuclearity of the resulting complexes. The ability of the cyano ligand to act as a linear $\mu_2\text{-}\kappa\text{C}:\kappa\text{N}$ bridge leads to the formation of the octanuclear complex as found in the structure **4** by coupling two “ Pt_2Ag_2 ” units. In contrast, the S-2py ligand can act as a bridge between Pt and Ag of the same “ Pt_2Ag_2 ” unit, giving rise to complex found in **5** that is “only” tetranuclear.

When the silver starting material has a triphenylphosphane attached the reactions with **1** and **3** take place with an interchange of ligands, and rendering $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ and AgCl for **1** and the tentative “ $\text{Ag}(\text{S-2py})$ ” complexes for **3**. Scheme 2 proposes two possible routes through which this ligand interchange could take place in solution. However, the reaction with the cyano starting material **2** eventually yields crystals (**6**) in which a stable Pt-Ag product, namely $[\{\text{Pt}(\text{CNC})(\mu\text{-CN})\}_2\{\text{Ag}(\text{PPh}_3)\}_2]$ is present. This is likely due to the impossibility of the CN ligand to establish interaction with the same Ag centre bonded to the Pt to which it is coordinated due to its linear nature. Since the interchange of ligands cannot progress in this case, the stable tetranuclear complex found in **6** can be isolated.

The presence of Pt-M^{10-12} or $\text{Pd-M}^{13, 14}$ ($\text{M} = \text{Ag}, \text{Au}, \text{Cu}$) species has been postulated or detected in transmetalation and ligand interchange processes of great interest in cooperative catalysis.⁵⁵ A similar CNC complex containing Pt-M bonds ($\text{M} = \text{Ag}, \text{Au}$) has been proposed as snapshots of such

Pt-Tl complexes. The systematization of the structures determined from recrystallization of the solids obtained in the reaction of the Pt starting materials with Tl(I) salts is more complicated. $\text{Pt(II)} \rightarrow \text{Tl(I)}$ heteropolynuclear clusters have been reported to present a wide array of structures: di (PtTl),^{26, 48, 56-59} tri (PtTl_2 ,⁶⁰⁻⁶³ Pt_2Tl ^{27, 29, 45, 64-67}), tetra (“paired” (PtTl)₂,^{47, 48, 68-71} trigonal Pt_3Tl ^{28, 34}), hexanuclear clusters (Pt_2Tl_4 ,⁴⁶ Pt_3Tl_3 ²⁸), or infinite chains or networks.^{26, 27, 45, 47, 66, 71-73} In the case of **7** and **10** even two different structural arrangements are present in the same crystal structure. Thus, for **7**, a linear infinite chain solely supported by Pt-Tl bonds coexists with discrete “ PtTl ” units. Similarly, in **10** a similar linear chain shares the same crystal with discrete tetranuclear linear “ Pt_2Tl_2 ” moieties. In both structures, as well as in **8**, there are secondary interactions, in which the Tl centres participate, that join the different structural motifs giving rise to elaborate supramolecular patterns.

The only discrete Pt-Tl complex whose structure has been determined is the trinuclear $(\text{NBu}_4)[\{\text{Pt}(\text{CNC})(\text{S-2py})\}_2\text{Tl}]$ present in **9**, even when the Pt/Tl ratio used for the starting materials is 1:1. It is noteworthy that the expected S-2py 1:1 complex in **10** is only obtained through a different path that involves the previous formation in situ of $[\text{Tl}(\text{S-2py})]$, and that involves the breaking of a Tl-S bond and the formation of a Pt-S one. Similar results have been reported in the reactions of $[\text{Tl}(\text{S-2py})]$ with $[\text{Pt}(\text{C}_6\text{F}_5)(\text{C}^*\text{N})(\text{S})]$ [$\text{C}^*\text{N} = \text{ppy}, \text{bzq}; \text{S} = \text{dmsO}, \text{Me}_2\text{CO}$],²⁶ which give discrete $[(\text{C}_6\text{F}_5)(\text{C}^*\text{N})(\text{S-2py})\text{PtTl}]$, with a bridging S-2py ligand S- bonded to Pt and N- bonded to Tl. However, the use of the related $[\text{Tl}(\text{S-2py-}\text{CF}_3)]$ starting material give 1:1 Pt-Tl chains in which either the S atoms are bridging both metal atoms or the S-2py- CF_3 ligand is not acting as a bridge at all.²⁶

From all these observations, it seems that the geometry adopted by Pt-Tl complexes can be very varied. Factors such as the possibility of the ligands to act as a bridge, the existence of secondary interactions or even the packing forces in the crystal environment play a very important and unpredictable

Scheme 2 Possible routes of ligand interchange between $[\text{Pt}(\text{CNC})\text{X}]^-$ and $[\text{Ag}(\text{PPh}_3)]^+$ in solution transmetalation mechanisms.^{20, 24}

role in the final structure. This may be related with the

dynamic behaviour of the Pt–Tl complexes in solution, for which, as mentioned above, equilibria involving cleavage and re-formation of the intermetallic bonds are detected.

In any case, a remarkable difference between the Pt–Ag and the Pt–Tl complexes, not only described here, but also in the literature, is that the former exhibit interactions of the silver centre with the ipso carbon atoms of the CNC (or other cyclometalated planar ligands such as bzq or phpy),^{21–24, 39, 44, 52, 74, 75} while the Tl complexes never show something similar.^{26–28}

Conclusions

The anionic complexes (NBu₄)[Pt(CNC)X], **1–3**, can be used successfully to prepare heteropolynuclear complexes with Pt→Ag or Pt→Tl dative bonds. However, their negative charge does not appear to dramatically affect the stability of the complexes formed or the strength of the intermetallic interactions. Similar Pt–Ag or Pt–Tl bond distances are found in structures of complexes in which the platinum centre is part of a neutral precursor. A more important factor seems to be the nature of the ligand attached to the “Pt(CNC)” fragment. Thus, the geometry of this ligand, and the disposition of its potentially donor atoms is the key feature for the adopted crystal structure. In the case of CN, its linear bridging feature causes higher nuclearity complexes since it is only able to connect atoms of different “Pt–M” units. On the other hand, the pyridine-2-thiolate ligand, with two different potential donor atoms and an intrinsic greater flexibility, can bridge metal atoms of the same “Pt–M” resulting in lower nuclearities.

In the case of the Tl complexes, the structural complexity increases. Even in the same crystal, similar “Pt–Tl” units can adopt different structural roles. This might be due to the apparent lability of the Pt→Tl bonds, as it is pointed out in the equilibria detected in solution, and the ability of the thallium center to establish secondary interactions with donor atoms or aromatic π electron density from neighboring moieties. The sum of all these relatively weak interactions, along with other packing forces present in the crystal, could be the reason for which a particular structural arrangement is adopted.

Experimental

General considerations.

A modification of the method reported in the literature²⁸ was used to prepare the starting material [Pt(CNC)(dmsO)] (–CNC– = 2,6-di(phen-2-ide)-pyridine) (see below). (NBu₄)[Pt(CNC)(S-2py)] (**3**) was also prepared following the method reported in the literature.³⁵ Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS analyser. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (ATR in the range 250–4000 cm^{–1}). Mass spectrometry was performed with the Microflex matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) Bruker, an Autoflex III MALDI-TOF Bruker or Esquire 3000 + Bruker instruments. ¹H, ¹³C, ³¹P and ¹⁹⁵Pt {¹H} NMR spectra were recorded on a Bruker AV-400, AV-300 or ARX-300 spectrometer using the standard references: SiMe₄

for ¹H, CFCl₃ for ¹³C, 85% H₃PO₄ for ³¹P and Na₂PtCl₆ in D₂O for the ¹⁹⁵Pt.

Safety note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with great caution.

Preparation of (NBu₄)[Pt(CNC)Cl] (**1**).

To a solution of [Pt(CNC)(dmsO)] (0.100 g, 0.199 mmol) in MeOH (25 mL) at room temperature, NBu₄Cl (0.066 g, 0.239 mmol) was added. After 4 days of stirring the reaction mixture under an Ar atmosphere, the solution was evaporated to dryness. The resulting solid was stirred with 15 mL of MeOH for 5 minutes and the mixture was again evaporated. Diethyl ether (10 mL) was added on the orange solid precipitate which appeared, and the resulting suspension was filtered off, washed three times with diethyl ether (5 mL) and air dried (0.117 g, 84 %).

Anal. Found: C, 56.09; H, 6.56; N, 4.15. Calcd for C₃₃H₄₇ClN₂Pt: C, 56.44.; H, 6.75; N, 3.99. IR ($\nu_{\max}$ /cm^{–1}): 1593 (m, NC), 1575 (w, NC), 1556 (w, NC), 1538 (w, NC), 886 (m, NBu₄⁺), 319 (s, Pt-Cl). ¹H NMR (400.132 MHz, CD₂Cl₂, 298 K. See Chart 1 for the H numbering scheme): δ = 7.83 (2H, dd, ³J_{H2-H3} = 7.3 Hz, ⁴J_{H2-H4} = 1.0 Hz, ³J_{H2-Pt} = 23.7 Hz, H2), 7.50 (1H, t, ³J_{H7-H6} = 7.9 Hz, H7), 7.37 (2H, dd, ³J_{H5-H4} = 7.5 Hz, ⁴J_{H5-H3} = 1.0 Hz, H5), 7.23 (2H, td, ³J_{H3-H4} = ³J_{H3-H2} = 7.3 Hz, ⁴J_{H3-H5} = 1.0 Hz, H3), 7.17 (2H, d, ³J_{H6-H7} = 7.9 Hz, H6), 6.99 (2H, td, ³J_{H4-H3} = ³J_{H4-H5} = 7.5 Hz, ⁴J_{H4-H2} = 1.0 Hz, H4), 3.03 (2H, t, ³J_{H α -H β} = 7.5 Hz, H α (CH₂-NBu₄⁺)), 1.35 (2H, q, ³J_{H β -H γ} = ³J_{H β -H α} = 7.5 Hz, H β (CH₂-NBu₄⁺)), 1.17 (2H, sext, ³J_{H γ -H δ} = ³J_{H γ -H β} = 7.5 Hz, H γ (CH₂-NBu₄⁺)), 0.83 (3H, t, ³J_{H δ -H γ} = 7.5 Hz, H δ (CH₃-NBu₄⁺)). ¹H NMR (400.132 MHz, dmsO-d₆, 298 K): δ = 7.84 (1H, t, ³J_{H7-H6} = 7.8 Hz, H7), 7.77 (2H, d, ³J_{H2-H3} = 7.2 Hz, H2), 7.65 (2H, d, ³J_{H6-H7} = 7.8 Hz, H6, overlapped with H5), 7.64 (2H, d, ³J_{H5-H4} = 7.3 Hz, H5, overlapped with H6), 7.19 (2H, t, ³J_{H3-H4} = ³J_{H3-H5} = 7.2 Hz, H3), 7.07 (2H, t, ³J_{H4-H3} = ³J_{H4-H5} = 7.2 Hz, H4), 3.15 (2H, t, ³J_{H α -H β} = 7.3 Hz, H α (CH₂-NBu₄⁺)), 1.55 (2H, m, H β (CH₂-NBu₄⁺)), 1.29 (2H, sx, ³J_{H γ -H β} = ³J_{H γ -H δ} = 7.3 Hz, H γ (CH₂-NBu₄⁺)), 0.92 (3H, t, ³J_{H δ -H γ} = 7.3 Hz, H δ (CH₃-NBu₄⁺)). ¹³C{¹H} NMR (100.624 MHz, CD₂Cl₂, 298 K): δ = 174.9 (s, C1), 168.5 (s, C8), 149.3 (s, C9), 137.6 (s, C7), 135.5 (s, C2), 130.5 (s, C3), 123.2 (s, C5), 122.5 (s, C4), 113.8 (s, C6). ¹⁹⁵Pt{¹H} NMR (85.679 MHz, CD₂Cl₂): δ = –3506 (br. s, 298 K), –3545 (s, 193 K). ¹⁹⁵Pt{¹H} NMR (64.324 MHz, dmsO-d₆): δ = –3937 (s). Mass spectra MALDI- DIT: m/z = 460 [Pt(CNC)(Cl)]⁺.

Preparation of (NBu₄)[Pt(CNC)(CN)] (**2**).

This complex was prepared by a modified procedure.³⁵ To a solution of [Pt(CNC)(dmsO)] (0.100 g, 0.199 mmol) in CH₂Cl₂ (20 mL) at room temperature, NBu₄CN (0.063 g, 0.219 mmol) was added. After 30 minutes of stirring the reaction mixture, equal volume of water was then added and the mixture was vigorously stirred for 4 min. More water was added (20 mL) and the upper (aqueous) layer was decanted. The methylene chloride solution was dried with MgSO₄, filtered, and the filtrate was diluted with hexane (20 mL). The yellowish orange solid formed was filtered and air dried (0.106 g, 77 %).

Anal. Found: C, 58.72; H, 6.84; N, 6.12. Calcd for C₃₄H₄₇N₃Pt: C, 58.94; H, 6.84; N, 6.06. IR ($\nu_{\max}$ /cm^{–1}): 2092 (m, C $\equiv$ N), 1596 (m,

NC), 1575 (w, NC), 1560 (w, NC), 1541 (w, NC), 880 (m, NBu_4^+). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.679 MHz, CD_2Cl_2): $\delta = -4008$ (s, 298 K), -4033 (s, 193 K). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (64.324 MHz, $\text{dmsO}-d_6$): $\delta = -4008$ (s, 298 K). Mass spectra MALDI- DIT: $m/z = 450$ $[\text{Pt}(\text{CNC})(\text{CN})]^-$.

Preparation of $[\{\text{Pt}(\text{CNC})(\mu\text{-CN})\}_4\text{Ag}_4]$ (4).

To a solution of $(\text{NBu}_4)[\text{Pt}(\text{CNC})(\text{CN})]$ (0.050 g, 0.072 mmol) in acetone (20 mL) at room temperature and protected from light, AgClO_4 (0.015 g, 0.072 mmol) was added. After 1 hour of stirring, the wine red solid formed was filtered, washed with n-hexane (5 mL) and air dried (0.037 g, 91%).

Anal. Found: C, 38.38; H, 2.43; N, 5.02. Calcd for $\text{C}_{72}\text{H}_{44}\text{Ag}_4\text{N}_8\text{Pt}_4$: C, 38.73; H, 1.99; N, 5.02. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2122 (m, $\text{C}\equiv\text{N}$), 1601 (m, NC), 1576 (w, NC), 1561 (w, NC), 1545 (w, NC).

Preparation of $[\{\text{Pt}(\text{CNC})(\text{S-2py})\}_2\text{Ag}_2]$ (5).

To a solution of $(\text{NBu}_4)[\text{Pt}(\text{CNC})(\text{S-2py})]$ (0.080 g, 0.10 mmol) in acetone (20 mL) at room temperature and protected from light, AgClO_4 (0.021 g, 0.10 mmol) was added. After 30 minutes of stirring, the reaction mixture was evaporated to dryness. The orange solid formed was extracted with iPrOH (10 mL), filtered, washed with n-hexane (5 mL) and air dried (0.030 g, 45%).

Anal. Found: C, 41.07; H, 2.85; N, 4.25; S, 4.85. Calcd for $\text{C}_{44}\text{H}_{30}\text{Ag}_2\text{N}_4\text{Pt}_2\text{S}_2$: C, 41.13; H, 2.35; N, 4.36; S, 4.99. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 1595 (m, NC), 1576 (m, NC), 1558 (w, NC), 1540 (w, NC).

Mass spectra ESI+: $m/z = 1285$ $[\{\{\text{Pt}(\text{CNC})(\text{S-2py})\}_2\text{Ag}_2\text{H}\}]^+$.

Preparation of $[\{\text{Pt}(\text{CNC})(\mu\text{-CN})\}_2\{\text{Ag}(\text{PPh}_3)\}_2]$ (6).

To a solution of $(\text{NBu}_4)[\text{Pt}(\text{CNC})(\text{CN})]$ (0.059 g, 0.085 mmol) in acetone (20 mL) at room temperature and protected from light, $[\text{Ag}(\text{ClO}_3)(\text{PPh}_3)]$ (0.040 g, 0.085 mmol) was added. After 30 minutes of stirring, the orange-brown solid formed was filtered, washed with n-hexane (5 mL) and air dried (0.061 g, 87%).

Anal. Found: C, 52.55; H, 3.14; N, 3.03. Calcd. for $\text{C}_{72}\text{H}_{50}\text{Ag}_2\text{N}_4\text{P}_2\text{Pt}_2$: C, 52.76; H, 3.07; N, 3.42. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2117 (m, $\text{C}\equiv\text{N}$), 1596 (m, NC), 1575 (w, NC), 1560 (w, NC), 1542 (w, NC), 516 (m, PPh_3), 502 (m, PPh_3). ^1H NMR (400.132 MHz, CD_2Cl_2 , 298 K): $\delta = 8.23$ (2H, dd, $^3J_{\text{H2-H3}} = 7.5$ Hz, $^4J_{\text{H2-H4}} = 1.2$ Hz, $^3J_{\text{H2-Pt}} = 32.9$ Hz, H2), 7.34 (7H, m, H3, H4 and PPh_3), 7.18 (15H, m, H5, H7 and PPh_3), 6.85 (2H, d, $^3J_{\text{H6-H7}} = 8.0$ Hz, H6). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.624 MHz, CD_2Cl_2 , 298 K): 167.2 (s, C8), 162.8 (s, C1), 151.8 (s, C9), 140.0 (s, C2), 139.8 (s, C7), 134.1 (d, $^2J_{\text{C-P}} = 16.8$ Hz, C- PPh_3), 132.1 (s, C- PPh_3), 131.8 (s, CN), 131.5 (s, C- PPh_3), 130.5 (s, C3), 129.1 (d, $^3J_{\text{C-P}} = 10.0$ Hz, C- PPh_3), 125.1 (s, C4), 124.6 (s, C5), 115.1 (s, C6). ^{31}P NMR (161.992 MHz, CD_2Cl_2 , 193 K): $\delta = 4.26$ (dd, $^1J_{\text{P-Ag}} = 638.7$ Hz, $^1J_{\text{P-Ag}} = 552.0$ Hz, $^2J_{\text{P(Ag)-Pt}} = 100.5$ Hz). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (64.324 MHz, CD_2Cl_2): $\delta = -3971$ (s, 298 K), -4012 (ddd, $^1J_{\text{Pt-Ag}} = 212.9$ Hz, $^2J_{\text{Pt-P(Ag)}} = 108.6$ Hz, 193 K). Mass spectra MALDI+ DIT: $m/z = 558$ $[\{\text{Pt}(\text{CNC})(\text{CN})\}\text{Ag}]$, 369 $[\text{Ag}(\text{PPh}_3)]^+$.

Preparation of $[\text{PtTI}(\text{CNC})\text{Cl}]$ (7).

To a solution of $(\text{NBu}_4)[\text{Pt}(\text{CNC})\text{Cl}]$ (0.050 g, 0.072 mmol) in acetone (20 mL) at room temperature, TIPF_6 (0.025 g, 0.072 mmol) was added. After 45 minutes of stirring, the orange solid formed was filtered, washed with n-hexane (5 mL) and air dried (0.022 g, 46%).

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 1595 (m, NC), 1571 (w, NC), 1557 (w, NC), 1538 (w, NC), 319 (m, Pt-Cl).

Preparation of $[\text{PtTI}(\text{CNC})(\text{CN})]$ (8).

To a solution of $(\text{NBu}_4)[\text{Pt}(\text{CNC})(\text{CN})]$ (0.050 g, 0.072 mmol) in acetone (20 mL) at room temperature, TIPF_6 (0.025 g, 0.071 mmol) was added. After 30 minutes of stirring, the yellow solid formed was filtered, washed with n-hexane (5 mL) and air dried (0.026 g, 54%).

Anal. Found: C, 33.01; H, 1.41; N, 4.21. Calcd for $\text{C}_{18}\text{H}_{11}\text{N}_2\text{PtTI}$: C, 33.02; H, 1.69; N, 4.28. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2075 (s, $\text{C}\equiv\text{N}$), 1595 (m, NC), 1575 (w, NC), 1559 (w, NC), 1542 (w, NC).

Preparation of $(\text{NBu}_4)[\{\text{Pt}(\text{CNC})(\text{S-2py})\}_2\text{TI}]$ (9).

To a solution of $(\text{NBu}_4)[\text{Pt}(\text{CNC})(\text{S-2py})]$ (0.100 g, 0.120 mmol) in acetone (25 mL) at room temperature, TIPF_6 (0.024 g, 0.060 mmol) was added. After 35 minutes of stirring, the reaction mixture was evaporated to dryness. The brown solid formed was extracted with iPrOH (10 mL), filtered, washed with n-hexane (5 mL) and air dried (0.081 g, 83%).

Anal. Found: C, 47.25; H, 5.04; N, 4.69; S, 4.18. Calcd for $\text{C}_{60}\text{H}_{66}\text{N}_5\text{Pt}_2\text{S}_2\text{TI}$: C, 47.54; H, 4.39; N, 4.62; S, 4.23.

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 1593 (w, NC), 1575 (m, NC), 1557 (w, NC), 1538 (w, NC), 880 (w, NBu_4^+). ^1H NMR (400.132 MHz, CD_2Cl_2 , 298 K): $\delta = 7.93$ (2H, dd, $^3J_{\text{H2S-2py-H3S-2py}} = 6.0$ Hz, $^4J_{\text{H2S-2py-H4S-2py}} = 2.0$ Hz, H2S-2py), 7.70 (2H, d, $^3J_{\text{H5S-2py-H4S-2py}} = 8.0$ Hz, H5S-2py), 7.63 (2H, t, $^3J_{\text{H7-H6}} = 8.0$ Hz, H7), 7.47 (4H, m, H4), 7.35 (8H, m, H2 and H6), 7.24 (2H, td, $^3J_{\text{H4S-2py-H5S-2py}} = ^3J_{\text{H4S-2py-H3S-2py}} = 8.0$ Hz, $^4J_{\text{H4S-2py-H2S-2py}} = 2.0$ Hz, H4S-2py), 7.02 (8H, m, H3 and H5), 6.80 (2H, t, $^3J_{\text{H3S-2py-H2S-2py}} = ^3J_{\text{H3S-2py-H4S-2py}} = 6.0$ Hz, H3S-2py), 3.03 (2H, t, $^3J_{\text{H}\alpha\text{-H}\beta} = 7.3$ Hz, $\text{H}\alpha$ ($\text{CH}_2\text{-NBu}_4^+$)), 1.43 (2H, m, $\text{H}\beta$ ($\text{CH}_2\text{-NBu}_4^+$)), 1.25 (2H, sext, $^3J_{\text{H}\gamma\text{-H}\delta} = ^3J_{\text{H}\gamma\text{-H}\delta} = 7.3$ Hz, $\text{H}\gamma$ ($\text{CH}_2\text{-NBu}_4^+$)), 0.89 (3H, t, $^3J_{\text{H}\delta\text{-H}\gamma} = 7.3$ Hz, $\text{H}\delta$ ($\text{CH}_3\text{-NBu}_4^+$)).

Preparation of $[\text{PtTI}(\text{CNC})(\text{S-2py})]$ (10).

To a solution of $\text{TI}(\text{acac})$ (0.050 g, 0.016 mmol) in CH_2Cl_2 (20 mL) at room temperature, pyridine-2-thiol (0.018 g, 0.016 mmol) was added. After 35 minutes of stirring, $[\text{Pt}(\text{CNC})(\text{dmsO})]$ (0.083 g, 0.016 mmol) was added to the reaction mixture. The resulting solution was stirred during 10 minutes, concentrated to 2-3 mL and n-hexane (10 mL) was added. The brown solid formed was filtered and air dried (0.070 g, 57%).

Anal. Found: C, 35.23; H, 2.37; N, 3.61; S, 4.85. Calcd for $\text{C}_{22}\text{H}_{15}\text{N}_2\text{PtSTI}$: C, 35.76; H, 2.05; N, 3.79; S, 4.34.

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 1594 (w, NC), 1575 (m, NC), 1558 (w, NC), 1540 (w, NC). ^1H NMR (400.132 MHz, CD_2Cl_2 , 298 K): $\delta = 8.13$ (1H, d, $^3J_{\text{H2S-2py-H3S-2py}} = 6.0$ Hz, H2S-2py), 7.83 (1H, d, $^3J_{\text{H5S-2py-H4S-2py}} = 8.2$ Hz, H5S-2py), 7.71 (1H, t, $^3J_{\text{H7-H6}} = 8.0$ Hz, H7), 7.55 (2H, m,

H4), 7.46 (3H, m, H4S-2py and H6), 7.32 (2H, m, H2), 7.10 (5H, m, H3S-2py, H3 and H5).

Mass spectra MALDI+ DIT: $m/z = 739$ $[[\{\text{Pt}(\text{CNC})(\text{S-2py})\}\text{TI}]+\text{H}]^+$, 535 $[[\{\text{Pt}(\text{CNC})(\text{S-2py})\}+\text{H}]^+$.

X-ray structure determinations.

Crystal data and other details of the structure analyses are presented in Tables S9 and S10 (Supporting Information). Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a concentrated solution of the complex in 3 mL of CH_2Cl_2 (**1**, **5**, **6**, **9**, **10**), dimethylformamide (**4**, **8**) or Me_2CO . (**7**). Crystals were mounted at the end of quartz fibres. The radiation used in all cases was graphite monochromated Mo K_α ($\lambda = 0.71073$ Å). X-ray intensity data were collected on an Oxford Diffraction Xcalibur diffractometer. The diffraction frames were integrated and corrected from absorption by using the CrysAlis RED program.⁷⁶ The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 with different versions of the SHELXL program⁷⁷ (see cif in the Supporting Information). All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their attached parent atoms (1.5 times for the methyl hydrogen atoms). For **4**, **7** and **10** only small crystals of mediocre quality could be obtained. For the structure of **4**, one of the "Pt(CNC)CN" fragments is disordered over two orientations which were refined with partial occupancy 0.531/0.469. Also, three dimethylformamide molecules, used as crystallization solvent, were present and disordered. Restraints on some geometrical and thermal parameters of some of the disordered atoms were used. For the structure of **7**, an acetone solvent molecule and a water molecule share the same site and they were refined with partial occupancy 0.15 (water)/0.70 (acetone). No hydrogens were added for this low occupancy water molecule and the oxygen was refined isotropically. Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Tables S9 and S10 (Supporting Information). CCDC 1858213-1858220 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

Conflicts of interest

There are no conflicts to declare.

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