Inorganic Chemistry
Communication
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Synthesis and Characterization of a “Pt_3Tl” Cluster Containing an Unprecedented Trigonal Environment for Thallium(I)

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Ⓢ *Supporting Information*

ABSTRACT: The tetranuclear $[\{Pt(CNC)(tht)\}_3Tl](PF_6)$ (tht = tetrahydrothiophene; SC_4H_8; CNC = *C,N,C*-2,6-$NC_5H_3(C_6H_4\text{-}2)_2$; **2**) cluster has been prepared by the reaction of [Pt(CNC)(tht)] (**1**) and $TlPF_6$ (molar ratio 3:1) and structurally characterized. The Tl^I atom is bonded to three Pt^{II} centers bearing a perfect trigonal coordination. The $Pt^{II}-Tl^I$ bonds are unsupported by any bridging ligand and are the shortest of this kind reported so far [2.9086(5) Å]. These intermetallic bonds persist in a CD_2Cl_2 solution, as shown by the $^{195}Pt\{^1H\}$ NMR spectrum of **2** at 193 K, in which a Pt−Tl coupling of 8.9 kHz is observed.

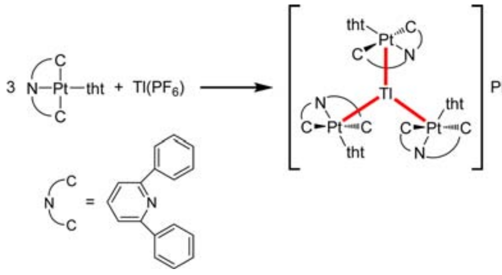
Heterometallic compounds featuring metallophilic interactions are interesting chemical species that are currently undergoing a tremendous upsurge.[1] Those interactions mainly involve metal−metal dative bonds between Lewis-acidic (acceptor) and Lewis-basic (donor) metal fragments,[1] and they have been used as a tool in the field of crystal or molecular engineering, linking different subassemblies and resulting in a wide array of structural types.[1,2] In many cases, complexes containing these metal−metal bonds have been shown to exhibit photophysical and photochemical properties, such as luminescence, attributable to the existence of metallophilic interactions.[1,2]

Tl centers in either of its common oxidation states, Tl^I [3,4] and Tl^{III},[3d,5] are fairly represented acceptors in this sort of heteropolynuclear cluster. The latter ion has a d^{10} electron configuration whereas $Tl^I(d^{10}s^2)$ is a typical case of “inert pair” species.[3b,4k] The nature of the heterometallic compound $[NBu_4]_2[Tl\{Pt(C_6F_5)_4\}_2]$, formally containing Tl^{II}, is certainly more complex because the unpaired electron is almost uniformly delocalized along the Pt−Tl−Pt axis.[6]

Among their donor counteparts, $Pt^{II}(d^8)$ is one of the most usual, and several structural configurations have been reported: discrete dinuclear PtTl,[4b−f] trinuclear $PtTl_2$[4a,g−i] or Pt_2Tl “sandwiches”,[4k−n] tetranuclear “paired” $(PtTl)_2$,[4b,o−s] or infinite networks.[4k,n,p,st] Often, the Pt−Tl bonds are supported by bridging ligands between the two metallic centers, and/or the Tl atoms bear additional ligands.

In the course of our current research, we have developed synthetic methods for the preparation of complexes containing Pt−M bonds with the use of strong ligand-field cyclometalated C^N ligands, such as 7,8-benzoquinolinate (bzq).[2a,d,7] This strong ligand field causes the d_{z^2} platinum orbital to raise its energy and favors the formation of stronger Pt→M dative bonds.[8] In this Communication, we report the use of a platinum precursor containing the tridentate cyclometalated *C,N,C*-2,6-$NC_5H_3(C_6H_4\text{-}2)_2$ (CNC; see Scheme 1) ligand in the preparation of an unprecedented Pt_3Tl cluster with three unsupported Pt^{II}→Tl^I bonds in which the Tl center exhibits a symmetric trigonal-planar environment.

Scheme 1



Complex [Pt(CNC)(tht)] (tht = tetrahydrothiophene; SC_4H_8, **1**) has been prepared by replacing the dimethyl sulfoxide (dmso) ligand in [Pt(CNC)(dmso)][9] with tht. The crystal structure of **1** has been determined by X-ray diffraction (see Figure S1, Supporting Information) and shows, as expected, square-planar coordination for the platinum, with structural parameters very similar to those reported for platinum complexes containing this[9] or similar tridentate CNC ligands.[10] No intermolecular $\pi\cdots\pi$ interactions between the aromatic rings of the CNC plane ligands are present in **1**; interactions are found in the analogous [Pt(2,6-diphenylisonicotinate)(tht)],[10] as well as in other square-planar platinum(II) complexes containing planar cyclometalated ligands such as 2,6-diphenylisonicotinate[2b,10] or bzq.[2a,7,11]

The reaction of 3 equiv of **1** with 1 equiv of $TlPF_6$ in dichloromethane results, after workup of the solution, in a red solid, the spectroscopic and analytical data of which correspond to the formula $[\{Pt(CNC)(tht)\}_3Tl](PF_6)$ (**2**; Scheme 1). Regardless of the Pt/Tl ratios used, no compounds with different stoichiometries are detected and always **2** and the corresponding unreacted reactives are obtained.

Suitable crystals for X-ray studies of **2** were obtained, and the crystal structure of its cation is represented in Figure 1. As can be

Received: January 22, 2013
Published: April 15, 2013

dx.doi.org/10.1021/ic400167w | *Inorg. Chem.* 2013, 52, 5627−5629

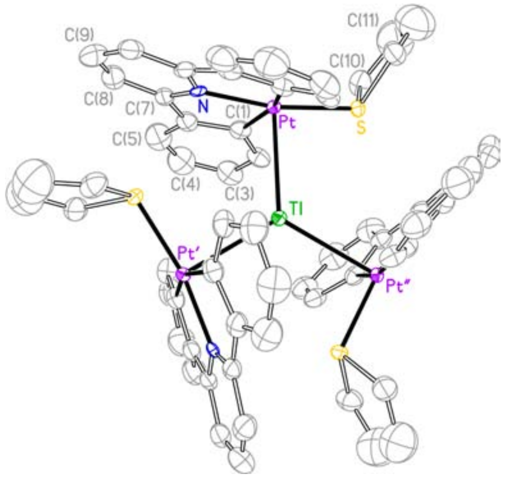


Figure 1. Molecular structure of the cation of complex **2**.

seen, **2** is a tetranuclear Pt_3Tl cluster in which the Tl^I center lies in a 3-fold axis and, thus, the three Pt atoms form a perfect equilateral triangle, in the center of which lies the Tl atom, with all of the Pt−Tl−Pt angles being exactly 120°. Because of the molecular symmetry, the three Pt−Tl distances are the same, 2.9088(5) Å. To the best of our knowledge, this value is the shortest reported so far for a $Pt^{II}-Tl^{I}$ bond unassisted by any bridging ligand or by pairing $(PtTl)_2$ metallocycle systems. The trigonal environment of the Tl center seems to indicate the steric inactivity of its lone $6s^2$ electron pair. Some complexes M_3Tl^{III} with a symmetrical trigonal environment for the Tl^{III} center are known. These involve carbonyl complexes of low-valent metals with the general formula $[\{M(CO)_x(\eta\text{-}C_5H_5)\}_3(\mu_3\text{-}Tl)]$ ($x = 3$, M = Cr, Mo;[5a] $x = 2$, M = Ru,[3d] Fe[5b]) or $[\{M(CO)_4\}_3(\mu_3\text{-}Tl)]^{n-}$ ($n = 0$; M = Cr;[5b] $n = 3$, M = Fe[5b]). Nevertheless, **2** is the first thallium(I) complex in which this striking trigonal environment is found.

Each Pt atom lies in the center of a square plane, which is perpendicular to the corresponding Pt−Tl line, the disposition of which is usually found in complexes showing Pt→M dative bonds, and which maximizes the overlapping of the full $5d_{z^2}$ Pt^{II} orbital and the empty orbitals of the acidic metal center.[4b,f,l] It is more likely that the disposition adopted by the three bulky "Pt(CNC)(tht)" is optimal (and perhaps the only one possible) to accommodate them around the Tl atom. The tht rings are bent away from the interior of the Pt_3Tl core, thus minimizing repulsion with the CNC ligand of the adjacent unit. Moreover, the plane of the CNC ligands is distorted in such a way that their pyridine rings, the closest to the tht ligand of the adjacent unit, are moved back from the best platinum square plane, while the two phenylene rings, which have less steric hindrance, move slightly inside the center of the core. It is noteworthy that, despite the apparent steric hindrance, the Pt−Tl distances are short for these kinds of complexes.

Each of the phenylene rings of the CNC ligands establishes $\pi\cdots\pi$ interactions with another ring of a neighboring cation, and as a result, each $[\{Pt(CNC)(tht)\}_3Tl]^+$ complex is surrounded by six congeners (see Figure S2, Supporting Information), with the interplanar distances being about 3.3 Å. As mentioned previously, these $\pi\cdots\pi$ interactions have been found for complexes containing planar cyclometalated ligands[2,7,10,11]

As far as we know, there are only three other reports of clusters in which three donor metal atoms are simultaneously bonded to a Tl^I center. One is $[\{Pt(1,2\text{-propyldiamine})(NHCO^tBu)_2\}_4Tl_4][Pt(CN)_4]_2$[4] in which infinite Pt−Tl chains are linked via half of the Tl atoms, resulting in a 3D network. Nevertheless, in this case, the environment of the Tl atom connected to three Pt atoms is not symmetric, with longer Pt−Tl bond distances (range 2.986−3.250 Å) and $NHCO^tBu$ ligands bridging Pt and Tl. The other two present a family of six gold(I) complexes,[3b,c] which are basically prepared by the incorporation of $[AuR_2]^-$ to $[AuTlR_2]_n$ (R = C_6Cl_5, 3,5-$C_6Cl_2F_3$, 2-C_6F_4Br, and 2-C_6F_4I) chains and the formation of a third Au−Tl bond. The Au−Tl distances range from 2.935 to 3.466 Å, and the environments of the Tl atoms are planar, but not symmetrical, being better described as distorted T-shaped.

The ^1H NMR spectra of **1** and **2** in CD_2Cl_2 show the corresponding signals for the CNC and tht ligands (see the experimental details). On the NMR time scale, both halves of these ligands are equivalent, and thus six and two signals are observed for CNC and tht, respectively. The most significant shift of the signals observed in the spectrum of **2** with respect to **1** is the corresponding *o*-phenyl proton (H^2) of the CNC ligand, which moves upfield 0.66 ppm.

The presence of $Pt^{II}\rightarrow Tl^{I}$ dative bonds in solution is supported by $^{195}Pt\{^1H\}$ NMR spectroscopy. In a CD_2Cl_2 solution at room temperature, compound **1** shows a structured ^{195}Pt resonance at −3914 ppm, due to the quadrupolar nature of ^{14}N of the CNC ligand, whereas **2** does not show any signal at either room temperature or 193 K. It appears that compound **2** dissociates in solution to give an equilibrium mixture of different platinum/thallium species, which are mutually converted on the ^{195}Pt NMR time scale. However, upon the addition of excess $TlPF_6$, a ^{195}Pt NMR signal at −3157 ppm is observed. This downfield shift (ca. 760 ppm) is consistent with the formation of Pt→M dative bonds in solution and is caused by a decrease of the electron density around the Pt center upon coordination to M^+.[2,12] Exactly the same dissociation process at the ^{195}Pt NMR time scale was formerly observed in solutions of compounds with Pt→Cd[12c] and Pt→Ag[12a,d] dative bonds.

Variable-temperature $^{195}Pt\{^1H\}$ NMR experiments were performed on a CD_2Cl_2 solution of **2** with $TlPF_6$ in excess (see Figure 2a). At 193 K, it shows a doublet at −3100 ppm due to Pt−Tl coupling (J_{Pt-Tl} = 8.9 kHz), which collapses to a broad signal at 243 K. This coupling constant value is similar to that observed in reported compounds with $Pt^{II}\rightarrow Tl^{I}$ dative bonds.[4c,d,13] The $J(^{195}Pt-^{203}Tl)$ and $J(^{195}Pt-^{205}Tl)$ coupling constants cannot be measured because of the broadness of the signals. At 193 K, the ^{195}Pt NMR spectrum of **1** barely changes; it

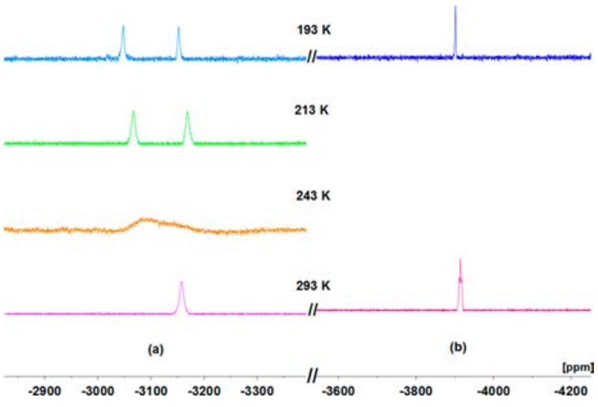


Figure 2. $^{195}Pt\{^1H\}$ NMR spectra of compounds: **2** + $TlPF_6$ exc. (a) and **1** (b) in CD_2Cl_2 at variable temperature.

displays a singlet at −3901 ppm (see Figure 2b). Both ^{195}Pt resonances appear downfield-shifted with respect to those at room temperature and the difference between them has increased up to 801 ppm. The solid-state ^{195}Pt NMR spectra of **1** and **2** have also been recorded and are in agreement with the solution spectra at low temperature and with an excess of $TlPF_6$ described here (see Figures S3−S5, Supporting Information).

Thus, from the solution ^{195}Pt NMR spectra, it seems that when an excess of $TlPF_6$ is added and at low temperature, the equilibrium is displaced completely toward the Pt_3Tl tetranuclear complex, which is the only platinum/thallium species present in solution in these conditions and matches with the X-ray structure. Therefore, the excess of thallium in the media just prevents the dissociation process. The remarkable downfield shifts (>750 ppm) in relation to its precursor (**1**) and the extraordinarily large value of the $Pt^{II}-Tl^{I}$ coupling constant (8.9 kHz) are indicative of a fairly strong $Pt\rightarrow Tl$ dative bond.

It is worth noting that the sample with excess of $TlPF_6$ showed ^{1}H NMR spectra at 293 and 193 K almost identical with that of compound **2**, supporting the idea that there is only one platinum/thallium species in solution in these conditions.

Preliminary studies on solid samples of **1** and **2** have shown that they exhibit luminescent properties, which are currently being investigated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details on the experimental procedures and equipment used, NMR data for complexes **1** and **2**, drawing of the molecular structure of complex **1**, drawing of the supramolecular arrangement of the cations of complex **2** showing the intermolecular $\pi\cdots\pi$ interactions, selected bond distances and angles for complexes **1** and **2**, CIF files for the structures of complexes **1** and **2**, and solid-state ^{195}Pt NMR spectra of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Spanish MICINN (DGPTC/FEDER; Projects CTQ2008-06669-C02-01/BQU and CTQ2012-35251).

■ REFERENCES

(1) (a) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597−636. (b) Moret, M.-E. *Top. Organomet. Chem.* **2011**, *35*, 157−184. (c) Bauer, J.; Braunschweig, H.; Dewhurst, R. D. *Chem. Rev.* **2012**, *112*, 4329−4346.

(2) (a) Forniés, J.; Ibáñez, S.; Lalinde, E.; Martín, A.; Moreno, M. T.; Tsipis, A. C. *Dalton Trans.* **2012**, *41*, 3439−3451. (b) Fuertes, S.; Woodall, C. H.; Raithby, P. R.; Sicilia, V. *Organometallics* **2012**, *31*, 4228−4240 and references cited therein. (c) Díez, A.; Lalinde, E.; Moreno, M. T. *Coord. Chem. Rev.* **2011**, *255*, 2426−2447. (d) Martín, A.; Belío, U.; Fuertes, S.; Sicilia, V. *Eur. J. Inorg. Chem.* **2013**, 2231−2247.

(3) (a) Fernández, E.; Garau, A.; Laguna, A.; Lasanta, T.; Lippolis, V.; López de Luzuriaga, J. M.; Montiel, M.; Olmos, M. E. *Organometallics* **2010**, *29*, 2951−2959. (b) Fernández, E. J.; Laguna, A.; López de Luzuriaga, J. M.; Montiel, M.; Olmos, M. E.; Pérez, J. *Organometallics* **2005**, *24*, 1631−1637. (c) Fernández, E. J.; Laguna, A.; Lasanta, T.; López de Luzuriaga, J. M.; Montiel, M.; Olmos, M. E. *Organometallics* **2008**, *27*, 2971−2979. (d) Bytheway, I.; Griffith, C. S.; Koutsantonis, G. A.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2007**, 3240−3246. (e) Casado, M. A.; Pérez-Torrente, J. J.; López, J. A.; Ciriano, M. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **1999**, *38*, 2482−2488. (f) Halcovitch, N. R.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Can. J. Chem.* **2009**, *87*, 139−145. (g) Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reddy, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 4123. (h) Balch, A. L.; Neve, F.; Olmstead, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 2995−3001. (i) Lanci, M. P.; Remy, M. S.; Kaminsky, W.; Mayer, J. M.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 15618−15620. (j) Balch, A. L.; Davis, B. J.; Fung, E. Y.; Olmstead, M. M. *Inorg. Chim. Acta* **1993**, *212*, 149−156.

(4) (a) Nagle, J. K.; Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 319−321. (b) Forniés, J.; Fuertes, S.; Martín, A.; Sicilia, V.; Gil, B.; Lalinde, E. *Dalton Trans.* **2009**, 2224−2234. (c) Usón, R.; Forniés, J.; Tomás, M.; Garde, R.; Merino, R. *Inorg. Chem.* **1997**, *36*, 1383−1387. (d) Balch, A. L.; Rowley, S. P. *J. Am. Chem. Soc.* **1990**, *112*, 6139−6140. (e) Oberbeckmann-Winter, N.; Braunstein, P.; Welter, R. *Organometallics* **2004**, *23*, 6311−6318. (f) Forniés, J.; Fortuño, C.; Ibáñez, S.; Martín, A. *Inorg. Chem.* **2008**, *47*, 5978−5987. (g) Charmant, J. P. H.; Forniés, J.; Gómez, J.; Lalinde, E.; Merino, R. I.; Moreno, M. T.; Orpen, A. G. *Organometallics* **2003**, *22*, 652−656. (h) Liu, F.; Chen, W.; Wang, D. *Chin. J. Struct. Chem.* **2006**, *25*, 677. (i) Berenguer, J. R.; Fernández, J.; Lalinde, E.; Sánchez, S. *Chem. Commun.* **2012**, *48*, 6384−6386. (j) Song, H. B.; Zhang, Z.-Z.; Hui, Z.; Che, C.-M.; Mak, T. C. W. *Inorg. Chem.* **2002**, *41*, 3146−3154. (k) Falvello, L. R.; Forniés, J.; Garde, R.; García, A.; Lalinde, E.; Moreno, M. T.; Steiner, A.; Tomás, M.; Usón, I. *Inorg. Chem.* **2006**, *45*, 2543−2552. (l) Renn, O.; Lippert, B.; Mutikainen, I. *Inorg. Chim. Acta* **1993**, *208*, 219−223. (m) Chen, W.; Liu, F.; Xu, D. X.; Matsumoto, K.; Kishi, S.; Kato, M. *Inorg. Chem.* **2006**, *45*, 5552−5560. (n) Stork, J. R.; Olmstead, M. M.; Fettinger, J. C.; Balch, A. L. *Inorg. Chem.* **2006**, *45*, 849−857. (o) Forniés, J.; García, A.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2008**, *9*, 3651−3660. (p) Stork, J. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 6512−6513. (q) Díez, A.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Sánchez, S. *Dalton Trans.* **2007**, 3653−3660. (r) Díez, A.; Fernández, J.; Lalinde, E.; Moreno, M. T.; Sánchez, S. *Inorg. Chem.* **2010**, *49*, 11606−11618. (s) Berenguer, J. R.; Forniés, J.; Gil, B.; Lalinde, E. *Chem.—Eur. J.* **2006**, *12*, 785−795. (t) Wu, G.; Wang, D. *J. Cluster Sci.* **2007**, *18*, 406−413.

(5) (a) Clarkson, L. M.; Clegg, W.; Hockless, D. C. R.; Norman, N. C.; Marder, T. B. *J. Chem. Soc., Dalton Trans.* **1991**, 2229−2239. (b) van Hal, J. W.; Alemany, L. B.; Whitmire, K. H. *Inorg. Chem.* **1997**, *36*, 3152−3159.

(6) Usón, R.; Forniés, J.; Tomás, M.; Garde, R. *J. Am. Chem. Soc.* **1995**, *117*, 1837−1838.

(7) Forniés, J.; Sicilia, V.; Casas, J. M.; Martín, A.; López, J. A.; Larraz, C.; Borja, P.; Ovejero, C. *Dalton Trans.* **2011**, *40*, 2898−2912.

(8) Aullón, G.; Álvarez, S. *Inorg. Chem.* **1996**, 3137−3144.

(9) Cave, G. W. V.; Alcock, N. W.; Rourke, J. P. *Organometallics* **1999**, *18*, 1801−1803.

(10) Fuertes, S.; Brayshaw, S. K.; Raithby, P. R.; Schiffers, S.; Warren, M. R. *Organometallics* **2012**, *31*, 105−119.

(11) Berenguer, J. R.; Lalinde, E.; Moreno, M. T.; Sánchez, S.; Torroba, J. *Inorg. Chem.* **2012**, *51*, 11665−11679.

(12) (a) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **2001**, *123*, 743−744. (b) Berenguer, J. R.; Fernández, J.; Gil, B.; Lalinde, E.; Sánchez, S. *Inorg. Chem.* **2010**, *49*, 4232−4244. (c) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **1999**, *121*, 7405−7406. (d) Janzen, D. E.; Mehne, L. F.; Van Derveer, D. G.; Grant, G. J. *Inorg. Chem.* **2005**, *44*, 8182−8184.

(13) Maliarik, M.; Nagle, J. K.; Ilyukhin, A.; Murashova, E.; Mink, J.; Skripkin, M.; Glaser, J.; Kovacs, M.; Horváth, A. *Inorg. Chem.* **2007**, *46*, 4642−4653.