

Palladastannatrane – a $\text{Pd}^{\text{II}} \rightarrow \text{Sn}^{\text{IV}}$ Dative Bond

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The reaction of *N*-methyl-2-mercaptoimidazole (methimazole, Hmt) with $\text{NaN}(\text{SiMe}_3)_2$, $[\text{PdCl}_2(\text{L})_2]$ ($\text{L} = \text{PPh}_3$, NCMe) and SnCl_4 provides the novel tetrabicyclo[3.3.3.3.0] lantern compound $[\text{PdSn}(\mu\text{-mt})_4\text{Cl}_2]$ (**1**) in which a dative $\text{Pd}^{\text{II}} \rightarrow \text{Sn}^{\text{IV}}$ bond is housed within the cage structure. Single-crystal X-ray diffraction analysis reveals a Pd–Sn separation of 2.605(1) Å in this compound, and the cation $[\text{PdSn}(\text{mt})_4\text{Cl}]^+$

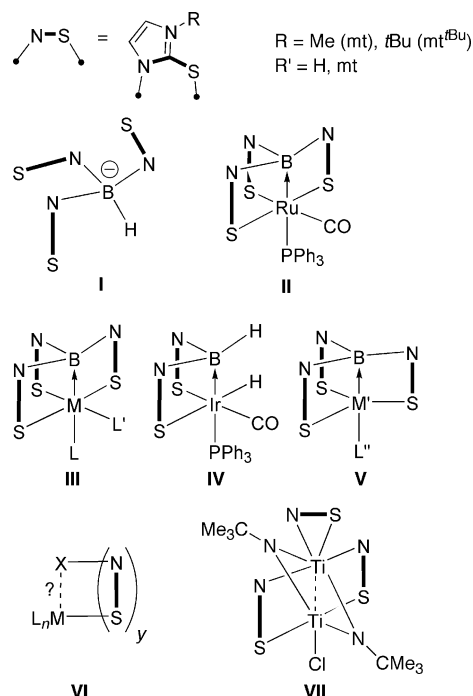
was detected by ESI-MS analysis of an acetonitrile solution of $[\text{PdSn}(\mu\text{-mt})_4\text{Cl}_2]$. Quantum chemical analysis of the Pd–Sn bonding situation revealed predominant electrostatic interactions between the positively charged Sn and the negatively charged Pd atom.

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Introduction

One of the more unusual aspects of the coordination chemistry of Reglinski's tris(methimazolyl)borato ligand (**I**)^[1] is the facility with which it may undergo B–H activation upon coordination to a late transition metal.

The first example of such a process provided the archetypal “metallaboratrane” $[\text{Ru}(\text{CO})(\text{PPh}_3)\{\text{B}(\text{mt})_3\}]$ (**II**, $\text{mt} = 1\text{-methyl-2-mercaptoimidazole}$),^[2a] which also confirmed for the first time the viability of metal–boron dative bonding.^[3] Compound **II** proved to be not an isolated curiosity, but rather the forerunner to a wide range of such metallaboratranes (accommodating *metalla*→*bora* *trans-annular* interactions), including examples based on all the metals of groups 8–10 in which the *trans-annular* $\text{M} \rightarrow \text{B}$ dative bond is buttressed by two or three *mt* groups or related heterocycles (**III–V**, Scheme 1).^[2] The question therefore arises as to what other types of unusual bonding, dative or otherwise, might be supported by methimazolyl bridges (**VI**). An encouraging illustration of this potential is provided by the recently reported dititanium complex $[\text{Ti}_2(\mu\text{-mt})_2(\mu\text{-N}t\text{Bu})_2(\kappa^2\text{-mt})\text{Cl}]$ (**VII**) in which two titanium atoms are held in close proximity by two *mt* buttresses in spite of the absence of a formal Ti–Ti bond.^[4]



Scheme 1. Methimazolyl-derived ligands and cages. $\text{MLL}' = \text{Ru}(\text{CO})(\text{PPh}_3)$, $\text{Ru}(\text{CO})(\text{CNR})$, $\text{Ru}(\text{CS})(\text{PPh}_3)$, $\text{Os}(\text{CO})(\text{PPh}_3)$, $\text{Fe}(\text{CO})_2$, $\text{RhCl}(\text{PPh}_3)$, $\text{Rh}(\text{cod})^+$, $\text{Rh}(\text{PMe}_2)_2^+$, $\text{Rh}(\text{S}_2\text{CNMe}_2)$, $\text{RhH}(\text{PPh}_3)$, $\text{Rh}(\text{PPh}_3)(\text{CNR})^+$, $\text{PtH}(\text{PR}'_3)^+$; $\text{M}'\text{L}'' = \text{Pt}(\text{PPh}_3)$, NiCl , $\text{Pd}(\text{PMe}_3)$, $\text{Co}(\text{PPh}_3)^+$ ($\text{R} = t\text{Bu}$, $\text{C}_6\text{H}_3\text{Me}_2$ -2,6, $\text{C}_6\text{H}_2\text{Me}_3$ -2,4,6, $\text{R}' = \text{Ph}$, Me , Et).

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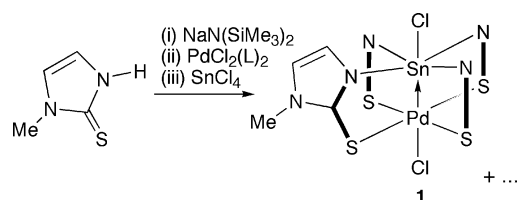
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Despite the increasing number of examples of metallaboratranes that establish the diversity of this class of compounds, this inverse complex building pattern, in which the transition metal is a “ligand” to a main group element supported by methimazolyl bridges, remains limited to boron that serves the role of Lewis acid. Herein we report the

straightforward synthesis and crystal structure of a metallastannatane, the first metalla→metallatane with a non-boron Lewis acid centre.

Results and Discussion

The ambident methimazole anion proved to be an effective buttressing ligand to clamp together thiophilic soft transition-metal atoms with characteristically harder boron(III) atoms. Whereas softer main-group-element atoms, e.g. Ge^{IV} or Sn^{IV} , show significant thiophilicity, they can still cope very well with sp^2 hybridised nitrogen donor atoms. Therefore, the sodium salt of methimazole [from Hmt and $\text{NaN}(\text{SiMe}_3)_2$] was treated subsequently with a Pd^{II} source and SnCl_4 which resulted in the formation, inter alia, of palladastannatane **1** (Scheme 2). The precipitate which results from the reaction performed in thf contained small amounts of **1**, and this novel paddle-wheel-like compound was extracted with chloroform to yield some crystals suitable for single-crystal X-ray diffraction analysis (Figure 1).^[5]



Scheme 2. For clarity reasons only one of the four methimazolyl chelates is drawn as such (without defining the multiple bonding character of the C–S and C–N bonds). The remaining three chelates are abbreviated as S–N.

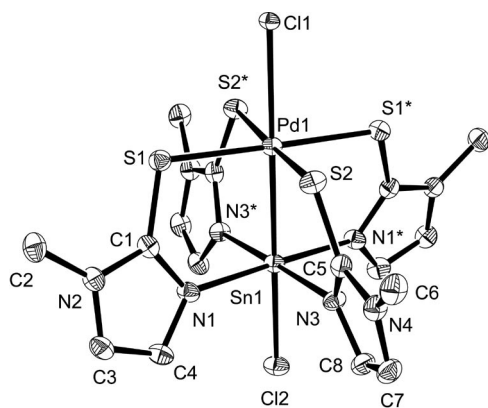


Figure 1. Molecular structure of **1** in the crystal of $\mathbf{1} \cdot (\text{CHCl}_3)_2$ (50% displacement ellipsoids, hydrogen atoms and chloroform molecules omitted, asterisk indicates symmetry generated atoms).

Unlike metallaboratranes, which bear two or three buttressing methimazolyl moieties, in **1** the Pd^{II} and Sn^{IV} atoms are bridged by four methimazole groups in a lantern-like fashion. This tetracyclo-[3.3.3.3.0] motif is commonly encountered in studies of metal–metal multiple bonding, supporting M–M covalent bonds of multiplicities

1–4,^[6] but not generally associated with dative bonding or situations where one of the metals is a main group element. This arrangement has also been found in some group 10 homodinuclear complexes with dipalladium or diplatinum cores supported by four bidentate ligands.^[7] In the case of ambident bridges, however, each metal atom has bonds to both kinds of donor atoms. Unlike these homobimetallic compounds, the heterobimetallic nature of **1** is supported by the four ambident ligands in such an arrangement as to accommodate the greater thiophilicity of Pd^{II} and the predisposition of the hard Sn^{IV} atom towards the hard nitrogen donors. Sn1 and Pd1 adopt almost octahedral coordination geometries. The atoms Cl1, Pd1, Sn1 and Cl2 are situated on a crystallographically imposed twofold axis, such that the asymmetric unit comprises two independent methimazolyl groups. Sn1 and Pd1 are displaced slightly [–0.030(2) and 0.042(1) Å] from the least-squares planes defined by the N1,N2,N1*,N2* and S1,S2,S1*,S2* donor sets, respectively, such that the Sn–Pd separation [2.605(1) Å] is significantly shorter than the distance between these two planes [2.678(2) Å] (Figure 2, left). This Sn–Pd distance indicates an attractive electronic interaction between these two atoms, accommodated by a propeller-like tilting of the four methimazolyl groups, the least-squares-plane of the heterocycles based on N1 and N3 subtending angles of 14.7(1) and 10.9(1)° with the Pd–Sn vector, respectively. The geometric parameters for the two independent methimazolyl moieties are similar, as can be seen from the bond lengths Sn1–N1 2.160(2) Å, Sn1–N3 2.168(2) Å, Pd1–S1 2.362(1) Å, Pd1–S2 2.350(1) Å.

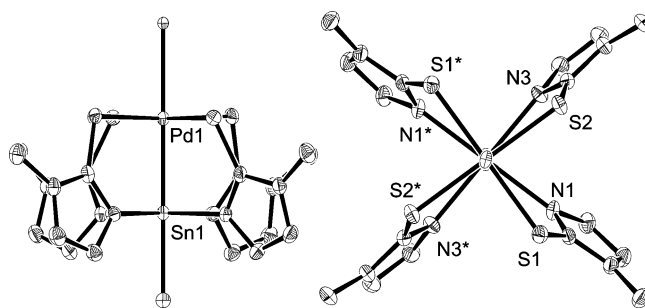
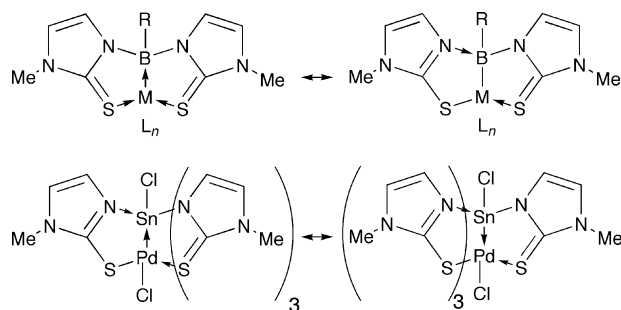


Figure 2. Views perpendicular (left) and parallel (right) to the two-fold axis Sn1–Pd1.

The octahedral coordination sphere of the formally Pd^{II} d^8 -centre allows for electron donation towards the Lewis acid Sn^{IV} atom. In the case of metallaboratranes various resonance structures of N-donor-stabilised boryl–metal complexes may be considered to also contribute when interpreting their molecular structures (Scheme 3 top).

For palladastannatane **1**, not only the contribution of the methimazolyl resonance structures but also two combinations of oxidation states of the metal atoms have to be considered. Tin(II) is an effective reductant whilst Pd^{IV} is an extremely strong oxidant, features which support the $\text{Pd}^{\text{II}} \rightarrow \text{Sn}^{\text{IV}}$ model rather than that involving a Pd^{IV} stannylene complex (Scheme 3, bottom). As a result of the similar

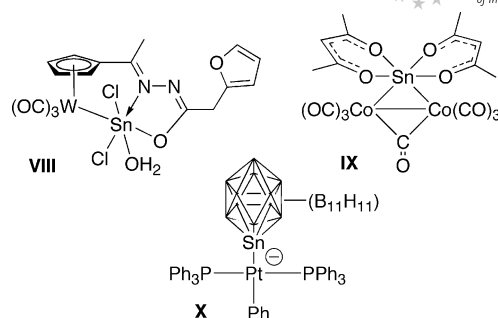


Scheme 3. Selected resonance structures of metallaboratranes (top) and palladastannatranes **1** (bottom).

electronegativities of Pd and Sn the final bond between them may also be regarded as covalent, which is accounted for by suitable methimazolyl resonance structure combinations.

The Pd–Sn bond length [2.605(1) Å] is within the range observed for Pd–Sn bonds in various stannyl and stannylene complexes with tetracoordinate tin and palladium atoms.^[8] Despite the increased coordination number of both metal atoms in **1**, their interatomic distance is surprisingly short, which is accommodated by or indeed imposes tilting of the methimazolyl moieties, the absence of which would allow for Pd–Sn bond length extension. The alternative oxidation state description would only invert the dative bond assignment from Pd^{II}→Sn^{IV} to Pd^{IV}←Sn^{II}. However, three effects should still favour a short Sn–Pd separation: (i) the four buttressing methimazolyl bridges, (ii) formal Pd→Sn donation *trans* to a very polar Sn–Cl bond, (iii) covalent bonding properties due to similar electronegativities of Sn and Pd (which also apply for Pd-stannyl and Pd-stannylene complexes). There are currently no structural data available for hexacoordinate tin complexes bearing one short Sn–(late transition metal) bond and five conventional donors around the tin atom. The class of complexes reported by Wang et al. and Tang et al. (**VIII**, Scheme 4)^[9] bear a conventional covalent bond between hexacoordinate tin and an early transition metal (Mo or W). Compounds with hexacoordinate tin bound to late transition metals are limited to μ -stannylene complexes (**IX**) or complexes of the [H₁₁B₁₁Sn]^{2–} ligand, the Sn atom of which is part of a *clos*-heteroboronate (**X**).^[10]

Regarding the contributions of the methimazolyl groups to various resonance structures within **1**, the Sn–N bond lengths suggest contributions from both formal covalent and formal dative interactions. They are slightly longer than those found in hexacoordinate Sn^{IV}Cl₂ complexes bearing phthalocyanine- and porphyrin-related ligands.^[11] Compared with other hexacoordinate tin(IV) complexes which allow for distinction between short (covalent) bonds and notably longer (dative) N→Sn bonds within bidentate chelates,^[12] the Sn–N bonds in **1** are significantly shorter than those described as dative. The C–S bond lengths [1.721(3) and 1.727(3) Å] are in the same range as those found in metallaboratranes.^[2] The Pd–S separations are slightly longer than those reported for some examples of Pd^{II} methimazolyl and methimazole (Hmt) compounds.^[13]



Scheme 4. Transition-metal complexes bearing a hexacoordinate tin atom.

1 was prepared from either [PdCl₂(PPh₃)₂] or [PdCl₂(NCMe)₂] as the palladium source. In both cases only small amounts (ca. 1%) of **1** could be obtained from the thf-insoluble product mixture by extraction with chloroform. This material was still contaminated by other Pd complexes, one of them being Pd(methimazole)₄Cl₂,^[13a] which is also only slightly soluble in chloroform. Although NMR spectroscopic investigation of **1** was precluded by its poor solubility in solvents such as chloroform, acetonitrile or thf, the solubility in acetonitrile was sufficient for ESI-MS analysis (cation mode). One of the M–Cl bonds ionises under the ESI-MS conditions employed such that the isotopic mass distribution pattern of the cation [PdSn(mt)₄Cl]⁺ was observed. There was no mass spectroscopic indication for the formation of the acetonitrile solvate of this cation, [PdSn(mt)₄(NCMe)Cl]⁺.

In order to gain deeper insight into the Pd–Sn bonding situation of compound **1** (in spite of the lack in accessibility of larger amounts of pure complex **1**, which precluded us from recording ¹¹⁹Sn NMR and Mössbauer spectra), quantum chemical calculations were performed. The gas phase conformation of **1** (optimised with DFT methods) revealed close similarity to the molecular shape found in the crystal structure. In particular, the Pd–Sn separation remains nearly constant [2.605(1) Å in the crystal, 2.629 Å optimised for the gas phase]. The most striking difference is found for the Sn–Cl and Pd–Cl bonds, which are 2.409(1) and 2.628(1) Å, respectively, in the crystal and adjust to 2.501 and 2.518 Å, respectively, upon optimisation. This behaviour can clearly be seen as a result of chloroform molecules in the crystal structure, two of which establish C–H⋯Cl contacts (H⋯Cl separation ca. 2.6 Å) to the Pd-bound chlorine atom, thus giving rise to a Pd–Cl bond lengthening accompanied by a Sn–Cl bond shortening. In view of the same outcome with respect to the intramolecular Pd–Sn separation, the crystallographically determined structure was employed for further computational analyses.

Natural charges and occupations of the metal atoms and chlorine atoms are given in Table 1. The chlorine atoms exhibit similar electronic situations regardless of the pivot atom (Sn vs. Pd), i.e. partially donating their chloride ionic charge towards the respective metal atom. Whereas the tin atom is positively charged, thus representing a Lewis acid centre in this system, the palladium atom carries a notable

negative charge. These results support both the existence of strong attractive interactions between the metal atoms due to the opposite sign of the charges and the applicability of a resonance model in which Pd has a noticeably lower formal oxidation state than that of the Sn atom (hence supporting the Pd^{II}→Sn^{IV} model).

Table 1. Natural charge, Mulliken charge and natural configuration of selected atoms of compound **1**.

Atom	Natural charge	Mulliken charge	Natural electronic configuration ^[a]
Cl (@Sn)	−0.59	−0.34	[Ne] 3s ^{1.89} 3p ^{5.70}
Sn	+2.31	+1.07	[Kr] 5s ^{0.68} 4d ¹⁰ 5p ^{0.99}
Pd	−0.72	−0.89	[Kr] 5s ^{0.42} 4d ^{9.05} 5p ^{1.22}
Cl (@Pd)	−0.53	−0.49	[Ne] 3s ^{1.90} 3p ^{5.63}

[a] The configuration of the Sn atom involves a contribution of 5d^{0.02} 6p^{0.01}, the configuration of the Pd atom involves a contribution of 5d^{0.03}.

In addition to the strong electrostatic Pd–Sn attraction, analysis of the molecular orbitals and the electron density profile along the Cl–Pd–Sn–Cl axis revealed the existence of bond critical points between Cl and Pd, Cl and Sn as well as Pd and Sn, the latter of which supports covalent contributions to the Pd–Sn interaction. [Natural bond orbital (NBO) analysis, however, does not identify a Pd–Sn bond. Higher-energy molecular orbitals are responsible for the metal–ligand bonds and do not show any bonding or antibonding contributions between Pd and Sn.] Finally, the predominantly ionic character of the Pd–Sn interaction in **1** corresponds well with the description of “ordinary” donor–acceptor interactions as “dative bonds” (e.g., in hexacoordinate silicon complexes), which also exhibit noticeable ionic contributions to the overall bonding situation.^[14]

Conclusions

The isolation of **1**, whilst not in synthetically useful amounts, nevertheless demonstrates that the methimazolyl group is capable of supporting novel bonding situations beyond the original metallaboratrane motif, an aspect the potential of which we are currently exploring.

Experimental Section

All calculations have been carried out by using density-functional theory (DFT) with gradient corrections (PBE functional,^[15] DZVP-GGA basis set^[16] using deMon 2 K^[17]). Charges and electron configurations have been estimated by using natural atomic orbital occupancies with the Gaussian NBO software as implemented in Gaussian03.^[18]

Preparation of 1·(CHCl₃)₂: Bis(triphenylphosphane)palladium(II) chloride (0.35 g, 0.50 mmol) was stirred in thf (5 mL) at room temperature. In a second flask methimazole (0.23 g, 2.0 mmol) was dis-

solved in thf (5 mL), a solution of sodium bis(trimethylsilyl)amide (1.0 M) in thf (2.0 mL, 2.0 mmol) was added and the resulting clear solution stirred at room temperature for 5 min, then this solution was added dropwise to the suspension of [PdCl₂(PPh₃)₂] to provide a dark red solution and colourless precipitate (NaCl). A solution of SnCl₄ (0.13 g, 0.50 mmol) in hexane (3.5 mL) was then added dropwise while stirring, resulting in the deposition of an orange precipitate. After 30 min being stirred at room temperature, the precipitate was filtered off, washed with thf (3 × 3 mL) and dried in vacuo. This solid (ca. 450 mg) contained some milligrams of compound **1**. In order to crystallise **1**, 125 mg of this precipitate were stirred in chloroform (20 mL) at 60 °C, then filtered through diatomaceous earth. The solvent was allowed to evaporate slowly from the filtrate to provide some brown crystals of **1**·(CHCl₃)₂ (ca. 1 mg) which were separated manually under a microscope.

Alternatively, this procedure was carried out by using [PdCl₂(NCMe)₂] (0.13 g, 0.50 mmol) instead of [PdCl₂(PPh₃)₂]. The precipitate thus obtained had a brownish colour; however, even repeated extraction with chloroform did not yield more than a few milligrams of **1**·(CHCl₃)₂. The poor solubility of **1** in various organic solvents prevented solution NMR spectroscopic studies. The yield of **1** from the above-mentioned synthesis was not sufficient for further solid-state analyses, such as ¹¹⁹Sn NMR or Mössbauer spectroscopy.

Supporting Information (see footnote on the first page of this article): Cartesian coordinates of the molecular structures of compound **1** in the crystal and its optimised gas-phase structure as well as an electron-density map for a cross-section along the Cl–Pd–Sn–Cl axis.

Acknowledgments

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- [5] Crystal structure analysis of **1**·(CHCl₃)₂: A suitable single crystal was mounted in inert oil (Paratone) on a glass fibre and then transferred to the cold nitrogen gas stream of the diffractometer (Nonius KappaCCD, graphite-monochromated Mo-*K*_α radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on *F*² for all unique reflections (SHELXL-97). For hydrogen atoms, a riding model was employed. CCDC-658154 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Selected data for **1**·(CHCl₃)₂: single crystal of dimensions $0.17 \times 0.09 \times 0.07$ mm obtained by slow evaporation of a solution in chloroform, C₁₈H₂₂Cl₈N₈PdS₄Sn, *M*_r = 987.37, *T* = 100(2) K, monoclinic, space group *C2/c*, *a* = 15.3578(4), *b* = 12.0492(3), *c* = 17.7516(4) Å, $\beta = 90.409(2)^\circ$, *V* = 3284.84(14) Å³, *Z* = 4, $\rho_{\text{calcd.}}$ = 1.997 Mg m⁻³, $\mu(\text{Mo-}K_{\alpha}) = 2.241$ mm⁻¹, *F*₍₀₀₀₎ = 1928, $2\theta_{\text{max}}$ = 60.0°, 32184 collected reflections, 4786 unique reflections (*R*_{int} = 0.0511), 203 parameters, *S* = 1.052, *R*₁ = 0.0346 [*I* > 2σ(*I*)], *wR*₂(all data) = 0.0834, max./min. residual electron density +1.891/−1.067 e Å⁻³.
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