

Molecular structures, solid-state aggregation and redox transformations of low-valent amido-thallium compounds †

Lutz H. Gade

Laboratoire de Chimie Organométallique et de Catalyse (UMR 7513), Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg, France.
E-mail: gade@chimie.u-strasbg.fr

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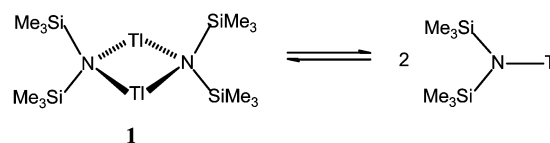
Thallium(I) amides, almost unknown a decade ago, have been a recent focus of main group amide chemistry yielding a large variety of unprecedented structural motifs and patterns of reactivity. The structural chemistry in the solid state was found to be characterised by a clustering of weakly attractive metal–metal interactions as well as metal–arene interactions giving rise to finite or infinite aggregates. Controlled redox disproportionation of thallium(I) amides has provided access the mixed valent compounds including covalently metal–metal bonded Tl^I-Tl^II complexes while stepwise metal exchange reactions have given mixed metal derivatives.

Introduction

A large number of solid state structures of alkali metal (in particular lithium) amides were determined throughout the 1980s and 1990s. Our knowledge and understanding of the underlying structural principles has been considerably advanced by a systematic combination of theoretical and experimental studies. The basic principles of their molecular aggregation and structural motifs have been discussed in several

review articles in recent years.¹ While alkali metal amides thus represent a well established class of molecular inorganic compounds, the corresponding amido metal compounds of monovalent thallium—in its aqueous solution chemistry frequently related to the heavier alkali metals!—were almost unknown until very recently. The structural characterization of thallium(I) amides by X-ray diffraction only began in the 1990s.² Progress was slow initially due to their extreme air sensitivity and thermal lability and lagged considerably behind the development of the organometallic and Werner-type coordination chemistry of thallium(I).³

Among the first amido compounds to be studied in this context was $[(Me_3Si)_2NTl^I]_2$ (**1**) which was found to be dimeric in the solid state but dissociates upon sublimation.⁴



In this unique case of a structure determination by electron diffraction in the gas phase and by X-ray diffraction in the solid state a remarkable change in the metric parameters was observed. Upon dissociation of the dimeric amido compound the Tl–N bonds contract by *ca.* 0.4 Å from 2.581(7) to 2.148(12) Å indicating the strong dependence of such interatomic distances on the detailed structural environment of the metal centres concerned. We will therefore place the emphasis in the discussions of the amide structures on the general topographical characteristics.

The structurally characterized thallium(I) amides known to date are not well described by the electrostatic model which works so well in the structural chemistry of the lighter alkali metal amides. As a heavy Group 13 metal thallium has a pseudo-closed shell $6s^2$ electron configuration and a contracted ionic radius as a consequence of the d- and f-block contraction of the valence shell. The monocation Tl^+ therefore is of approximately the same size as Na^+ and it is due to this combination of properties that Tl compounds have similar chemistry to alkali metals in aqueous solution.

Instead, and in contrast to the alkali metals, molecular thallium(I) compounds display attractive intermolecular heavy metal–metal contacts⁵ which appear to arise from weak dispersion forces (*vide infra*), a pronounced interaction with arene rings and low-coordinate metal centres. Another significant difference is the tendency for solvation of the metal atoms, with alkali metal cations being most readily coordinated by donor solvents while monovalent thallium appears to be more resistant to increasing its coordination number by donor solvation.⁶

The aim of this Perspective is to highlight the aspects of thallium(I) amide chemistry which distinguish it from the corresponding alkali metal chemistry. This includes the accessibility of the oxidation states II and III and thus the propensity of thallium(I) compounds to undergo redox transformations.⁷

† Dedicated to Lord Lewis, a mentor and friend, on the occasion of his 75th birthday.

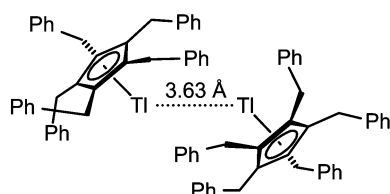
Lutz H. Gade is a professor of chemistry at the Université Louis Pasteur, Strasbourg and the Head of the Laboratory of Organometallic Chemistry and Catalysis. After completing his undergraduate studies at the University of Bonn and the Technical University of Munich, he went to Cambridge to work for his Ph.D. with Jack Lewis. Having returned to Germany after completing his thesis in 1991, he joined the Chemistry Department at the University of Würzburg where he finished his habilitation in 1996 and where he subsequently worked as a lecturer. In 1998 he moved to Strasbourg to take up his present position, and in summer 2000 he was elected a member of the Institut Universitaire de France. His research interests lie in the fields of coordination chemistry, organometallic chemistry and homogeneous catalysis.



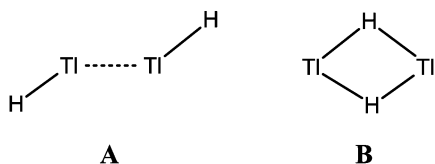
Lutz H. Gade

Closed shell interactions between thallium(I) centres: a brief summary

The possibility of bonding interactions between closed shell thallium(I) centres attracted much attention about a decade ago due to the controversy concerning their nature. The original object of study was pentabenzylcyclopentadienylthallium(I) which was found to aggregate in the form of dimers in the solid.⁸ In the crystal structure of the compound pairs of monomers were oriented in such a way that the thallium(I) centres in two such molecules were located at a distance of 3.63 Å.



Whereas Janiak and Hoffmann initially postulated relatively strong bonding interactions, based on an extended Hückel MO study of the TlH-dimer,⁹ this view was later qualified.¹⁰ Notably, essentially the same methodological approach applied by Budzelaar and Boersma indicated that the metal-metal interaction was at best weak.¹¹



This view was confirmed by a theoretical study of the TlH-dimer performed at the SCF-CI level which led to the conclusion that attractive interactions between the molecules through metal-metal contacts are weak correlation effects, of probably less than 20 kJ mol⁻¹.¹² Moreover, Schwerdtfeger found that the previously discussed “*trans*-bent” arrangement (A) only represented a local minimum on the energy hypersurface of the molecule while the total energetic minimum of the thallium(I) hydride dimer corresponded to the hydride-bridged ring structure (B).^{13,14} The interpretation in terms of a weak “metallophilic contact” (*vide infra*) rather than a strong bonding interaction has offered support for alternative explanations for the observed aggregates in the solid. A most suggestive picture was put forward by von Schnering, aptly termed “umbrella effect”,¹⁵ which relates the packing of molecules in the crystal primarily to their shape, thus generating close metal-metal contacts as a *secondary* effect. The competition (or cooperation) between the interaction of the metal centres and the influence of the periphery (shape) of the molecule therefore has to be considered in all cases.¹⁶

The work of Pyykkö and his co-workers has only recently led to a clarification of the nature of these “metallophilic” interactions between formally closed shell metal centres. As was shown in a series of detailed theoretical studies, they represent a correlation effect which at long intermetallic distances is essentially a “classical” dispersion force.^{17,18} This dispersive (van der Waals) attraction is frequently reinforced by electrostatic components as well as a charge-transfer-type dispersion contribution.¹⁹

Whereas the “metallophilic” attraction between d¹⁰ metal centres is enhanced by the relativistic contraction of the s and p electron shells (along with the destabilization of the d-orbitals),¹⁵ the relativistic contribution to the closed shell interaction between s² metal centres such as Tl^I actually

weakens their dispersive attraction.²⁰ It is thus not surprising that the observation of “metallophilic” attraction between thallium(I) centres strongly depends upon the absence of competing intra- and inter-molecular interactions such as electrostatic attraction or repulsion or the van der Waals interactions with aromatic rings.

Finite “clustering” of thallium(I) amides

In view of the potential ambiguity in the interpretation of the Tl...Tl contacts between mononuclear molecular species due to the weakness of the interaction, the fixation of several Tl-centres at close proximity in polynuclear thallium(I) complexes was thought to offer the opportunity of a higher intermolecular metal-metal “connectivity” and thus enhanced intermetallic attraction.

Such a situation was observed in the dimeric aggregate of a completely metalated triaminosilane, [CH₃Si{N(Tl)*t*Bu}₃]₂ (1), reported by Veith *et al.* which represents a unique structural array in amide chemistry (Fig. 1).²¹ In contrast to the almost

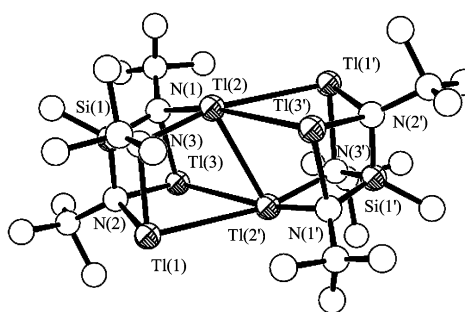


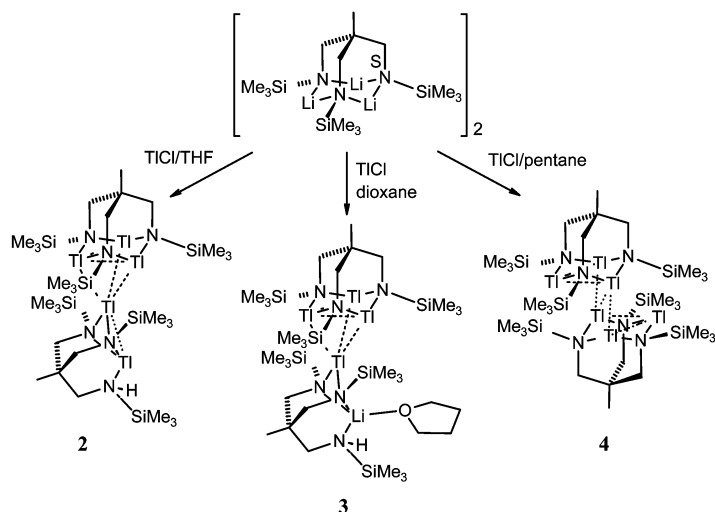
Fig. 1 Dimeric molecular structure of [CH₃Si{N(Tl)*t*Bu}₃]₂ (1), reported by Veith *et al.*

spheroidal cage formed by the lithium analogue which is based mainly on ionic amido-N-metal interactions, the thallium compound aggregates *via* metal-metal contacts generating a structure in which the disposition of the six metal atoms may be viewed as defining a pair of edge-sharing tetrahedra.

This molecular structure is distinguished from the other thallium(I) aggregates by the extremely short Tl...Tl contact Tl(2)–Tl(2') of 3.146(7) and 3.189(7) Å for the two independent molecules in the unit cell. This is to be seen in comparison with Tl^I–Tl^I contacts which are usually found in the type of structures discussed in this article which lie in the range of 3.3–3.7 Å. Regarding the detailed geometry of the {diamide-Tl}₂ unit, a pronounced *trans*-bent arrangement is apparent, the angle between the Tl(2)–N(1)–N(3) plane and the Tl(2)–Tl(2') vector being 100° (96° for the second independent molecule). This is reminiscent of the *trans*-bent structures found in tin(II) chemistry and may indicate a bonding situation in between the generally observed van der Waals type attraction and that described by the Carter–Goddard–Malrieu–Trinquier model.¹⁴

The interesting cluster-type structure reported by Veith *et al.* led us to synthesize polynuclear thallium(I) amides containing the tripodal amido ligands we had previously introduced to the coordination chemistry of the early transition metals.²² These were thought to be slightly more flexible than the triamido-silane derivatives and, in view of the different orientation of the amido N-functions to give alternative structural motifs.

The result of the transmetalation of the tripodal lithium amide [H₂CC{CH₂N(Li)SiMe₃}]₂²³ with TlCl was found to depend sensitively on the solvent used.^{24,25} Whereas the reaction in ether solvents such as thf or dioxane led to relatively rapid metal exchange with concomitant partial redox decomposition, the use of a saturated hydrocarbon suppressed the redox-chemical side reactions and led to slow but complete transmetalation. Using tetrahydrofuran and dioxane, respectively, it was



Scheme 1 Solvent dependence of the products isolated from the metal exchange of $[\text{H}_3\text{CC}\{\text{CH}_2\text{N}(\text{Li})\text{SiMe}_3\}_3]_2$ with TlCl giving the structurally characterized amidothallium species 2–4.

possible to isolate and crystallize the partially demetallated compounds $[\{\text{H}_3\text{CC}(\text{CH}_2\text{NSiMe}_3)_2(\text{H})\text{Tl}\}_3]$ (2) and $[\text{H}_3\text{CC}\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}_3][\text{H}_3\text{CC}\{\text{CH}_2\text{NSiMe}_3\}_3(\text{H})(\text{Tl})(\text{Li}-\text{thf})]$ (3), while the metal exchange carried out in pentane selectively gave the completely metallated derivative $[\text{H}_3\text{CC}\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}_3]_2$ (4) (Scheme 1).

The molecular structure of 3 is displayed in Fig. 2a along with

The close structural relationship between 2 and 3 raised the question whether it was possible to convert 3 to 2 by using the standard metal exchange procedure with TlCl. Although some decomposition is observed upon performing the metal exchange in THF, compound 2 could indeed be isolated from the product mixture in 60–70% yield based on 3 (Scheme 2).

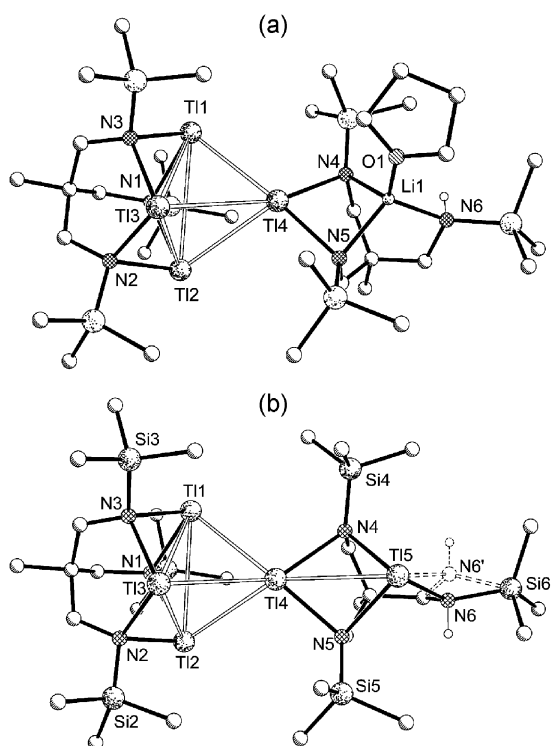
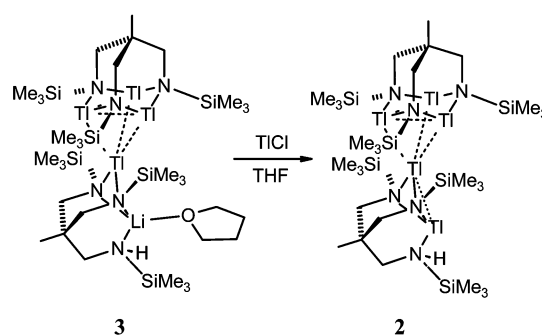


Fig. 2 Comparative representation of the molecular structures of compounds 3 (a) and 2 (b).

the molecular structure of 2 in Fig. 2b. The relationship between the structures of 2 and 3 is immediately apparent, the most striking feature being in both cases the central tetrahedral arrangement of the thallium atoms. In the structure of 3 there are three amido-bridged Tl–Tl contacts [Tl(1)–Tl(2) 3.8535(7), Tl(2)–Tl(3) 3.5180(7), Tl(1)–Tl(3), 3.9037(7) Å] and three unsupported metal–metal contacts [Tl(1)–Tl(4) 3.3150(6), Tl(2)–Tl(4) 3.4611(9), Tl(3)–Tl(4) 3.6759(7) Å] which are close to the shortest Tl–Tl distances observed in α -thallium metal (3.408 and 3.457 Å).



Scheme 2 Conversion of 3 to 2 by reaction with TlCl in THF.

The isolation and characterization of the partially metallated 3 showed that redox disproportionation inducing partial demetalation of the amides already occurs during the course of the metal exchange reactions, thus constituting two competitive reaction pathways. It is therefore not the result of a subsequent thermal decomposition of the fully metallated product. This latter aspect will be discussed below in more detail.

A single crystal X-ray structure analysis of the fully metallated amide 4 established its molecular structure in the solid state (Fig. 3).²⁵ The structural centrepiece of the dimeric aggregate

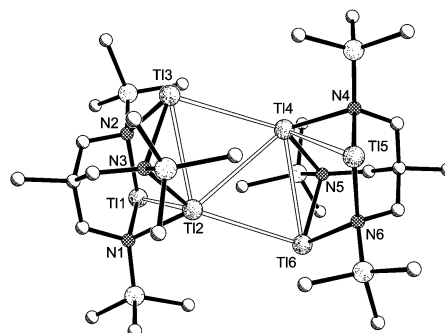


Fig. 3 Molecular structure of the dimeric unit in the crystal structure of 4.

gates is the array of the six Tl atoms, joined by amido bridges within the molecular units and by Tl...Tl contacts between the two tripodal amides [$d_{av}(\text{Tl}-\text{Tl}) = 3.768 \text{ \AA}$]. In this way an open ladder type structure of the dimeric units emerges in which each half is distorted considerably with respect to the almost ideally threefold symmetric trithallium-units in **2** and **3** which are "capped" by the linking Tl atom [Tl(4)] in the latter. This appears to imply that in a supramolecular aggregate based on attractive metal-metal interactions the "best fit" through such contacts may be achieved by combination of non-equal, *i.e.* complementary building blocks, generating polyhedral metal arrays with maximum Tl...Tl connectivity. This is not the case in the structure of **4** in which two Tl atoms [Tl(2) and Tl(4) in Fig. 3] are bent towards each other to come into contact; a situation which is most apparent when viewing the trithallium amido units of **2,3** and **4** along an axis defined by the bridge-head C-CH₃ axis of the tripodal ligands (Fig. 4).

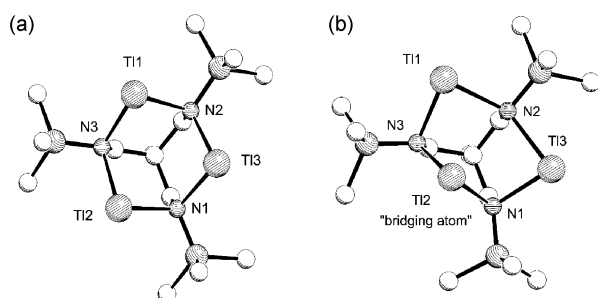


Fig. 4 Comparison of the Tl₃-building blocks in **2** and **3** (a) and in **4** (b) showing the distortion of the latter from the almost trigonal symmetry found for the centrally "capped" Tl₃-triangles.

Whereas the symmetrically capped Tl₃ unit in **2** and **3** displays almost ideal threefold symmetry, one of the Tl atoms in **4**, Tl(2), protrudes out of the plane otherwise spanned by the metal atoms of the monomeric unit in **4** pushing the other two Tl atoms, Tl(1) and Tl(3) further apart (4.61 Å).

A closer inspection of the way these dimeric units are packed in the crystal (Fig. 5) revealed no significant intermolecular metal-metal interactions, the shortest Tl-Tl distance being larger than 4.3 Å and thus outside of the range of significant intermolecular contacts.

A comparison of the crystal structure of Veith's [H₃CSi{N(Tl)*t*Bu}₃]₂ with that established for compound **4** is instructive. In both cases an aggregation through Tl...Tl contacts is observed with the two (distorted) Tl₃-triangles adopting a "slipped" arrangement with respect to each other. However, **4** aggregates to form a more open Tl₆-array, possibly as a consequence of a greater degree of steric demand of the ligand periphery operating in the latter.

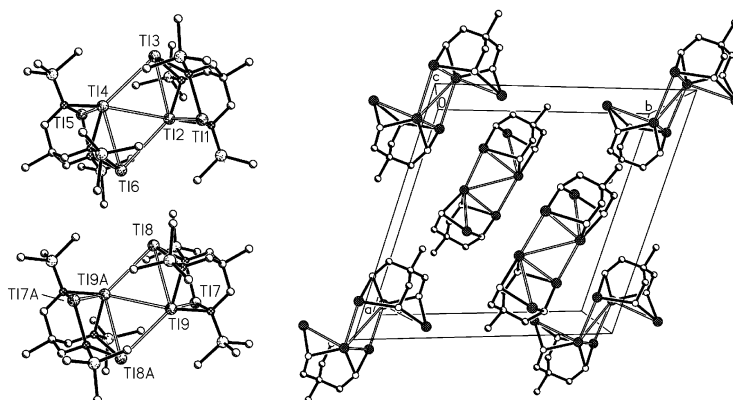


Fig. 5 Packing of the dimers in the crystal structure of **4**. For clarity, the SiMe₃-groups of the amide units are not shown in the view of the unit cell.

A remarkable structural arrangement in a thallium amide aggregate has been reported by Lappert and co-workers.²⁶ During the course of their systematic study into the coordination chemistry of tetraazaheptatrienyl ligands they synthesized and characterized the 1,3,5,7-tetraazaheptatrienyl-lithium (**5a**), -sodium (**5b**) and -thallium (**5c**) derivatives. For the latter they found a tetrameric aggregate in the solid state structure comprising four units each of which consists of two thallium atoms and two [Me₃SiNCHN]₂CH⁻ which is displayed in Fig. 6.

Internuclear Tl(1)-Tl(2), Tl(1)-Tl(3) and Tl(3)-Tl(4) contacts (with interatomic distances of 3.76, 3.65 and 3.89 Å), which are at the long distance limit of such dispersive interactions lead to the formation of the cluster depicted in Fig. 6. From the point of view of the structural systematics proposed in this article, this type of structure represents a borderline case between clustering and (ring) chain formation (*vide infra*).

Infinite (Tl^I)_n chain structures

The crystal structure of **5c** revealed a pattern of aggregation which may be classified as a ring, *i.e.* closed chain structure. Aggregation to give infinite chains is to be expected for thallium amides containing isolated, exposed Tl^I-centres. This was the case in the monomeric unit of the difunctional thallium amide CH₂{CH₂N(Tl)SiMe₃}₂ (**6**).²⁷ This simple amido complex was found to have a molecular structure in which the two amido-N atoms and the two thallium(i) centres form a puckered four membered ring, the metal atoms occupying rather exposed positions thus generating the potentially "sticky ends" for aggregation (Fig. 7a).

In the solid the molecular units of **6** aggregate *via* Tl...Tl contacts to form infinite, double-stranded bands (Fig. 7b,c). The two strands consist of monomers facing each other and occupying translationally displaced positions which generate a one dimensional grid consisting of distorted hexagons of metal-metal contacts. In the resulting planar bands one of the two metal atoms in the monomers not only forms a direct contact to its neighbour within a strand [Tl...Tl 3.775(3) Å] but also across to the opposite strand [Tl...Tl 3.697(3) Å].

In order to assess the importance of the relative exposure of the thallium(i) centres in the structure of **6** for the aggregation in the solid, the structurally analogous Tl-amide CH₂{CH₂N(Tl)Si*t*BuMe₂}₂ (**7**) containing the bulkier silyl substituent *t*BuMe₂Si at the amido functionalities was synthesized. The crystal structure of **7** revealed a packing in the solid which appears to be entirely dictated by the molecular shape rather than metal-metal contacts as found for **6** (Fig. 8).

The shortest intermolecular Tl...Tl distances of over 4.7 Å are testimony to the absence of significant metal-metal interaction in the crystal. With the exception of the somewhat greater shielding of the Tl₂N₂-unit in the molecule the overall molecular shapes of **6** and **7** are closely related. This is to be

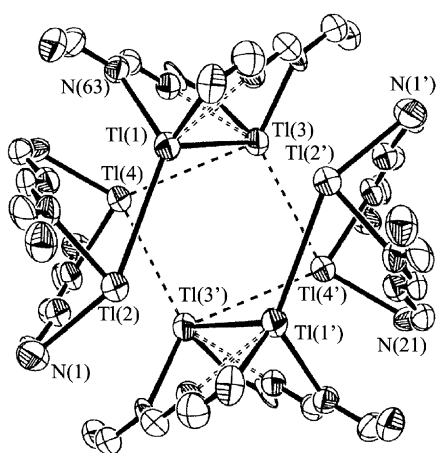


Fig. 6 The molecular structure of the tetrameric aggregate of bis(1,3,5,7-tetraazaheptatrienyl)dithallium (**5c**) reported by Lappert *et al.* (from ref. 26).

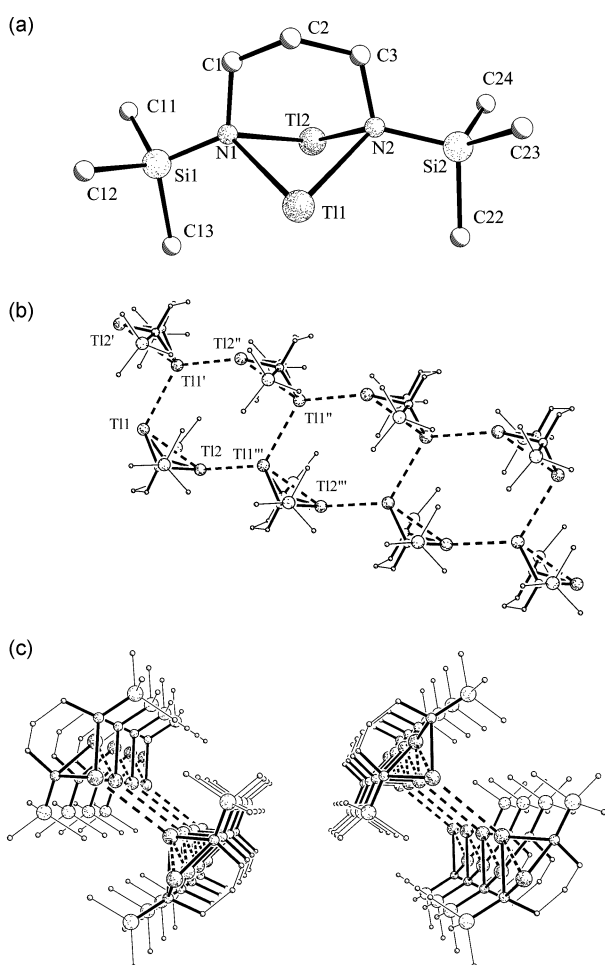


Fig. 7 (a) The monomeric unit of the difunctional thallium amide $\text{CH}_2\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}_2$ (**6**). (b) and (c) Aggregation of the molecular units of **6** via $\text{Tl} \cdots \text{Tl}$ contacts to form infinite, double-stranded bands.

seen in the context of the “umbrella effect” proposed by von Schnering which was mentioned in the Introduction.¹⁵ The fact that the molecules containing the more exposed metal atoms display structural motifs characterized by metal–metal contacts, while those less favoured in doing so by nature of their more shielded molecular structure do not, supports the relevance of such weak interactions between the heavy metals in the structure of compound **6**.

Another type of thallium(I) chain formation has been reported by Peters *et al.* Metallation of bis(8-quinoliny)amine

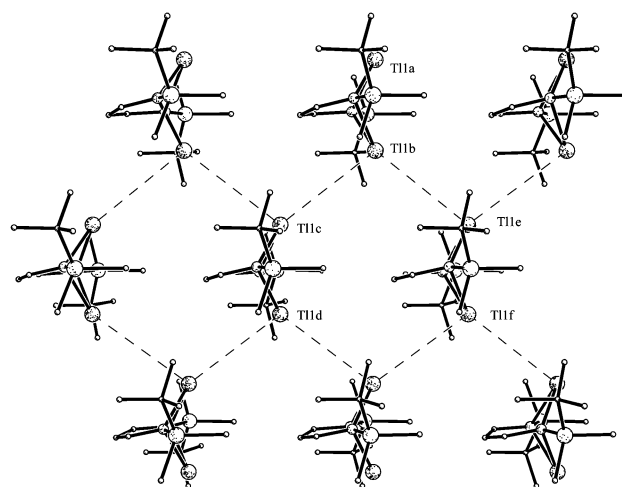


Fig. 8 Crystal structure of the difunctional thallium amide **7**.

by the same reaction sequence as described for the previous examples, *via* the lithium amide and subsequent metal exchange, yielded the thallium(I) amide **8**.²⁸ The crystal structure of this compound revealed a $(\text{Tl}^{\text{I}})_n$ zigzag chain with a $\text{Tl} \cdots \text{Tl}$ distance of 3.5336(5) Å, *i.e.* within the range of the intermetallic contacts discussed above (Fig. 9). This arrange-

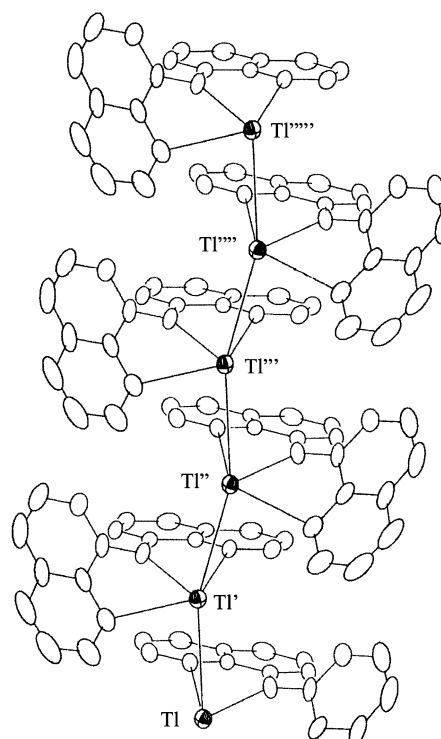


Fig. 9 Chain structure of the thallium bis(8-quinoliny)amide **8** reported by Peters *et al.* (from ref. 28).

ment is probably additionally supported by weak arene π -stacking interactions between the quinoline rings.

Finally, an example of thallium(I) chain formation in which metal–metal interactions appear to distort a molecular amide structure is provided by the tripodal thallium amide $[\text{MeSi}\{\text{SiMe}_2\text{N}(\text{Tl})\text{tBu}\}_3]$ (**9**).²⁹ In contrast to the structure of the corresponding lithium amide, the tripodal amido ligand in **1** experiences considerable distortion and bears little resemblance to the adamantanoid arrangement of the former (Fig. 10a). The structure is polymeric (Fig. 10b) and in the monomer two Tl-atoms and two amido-N atoms form a four-membered ring $[\text{Tl}(1)\text{--N}(2)\text{--Tl}(2)\text{--N}(3)]$ in which the two thallium atoms are 3.653(2) Å apart, while the remaining amido-Tl group appears

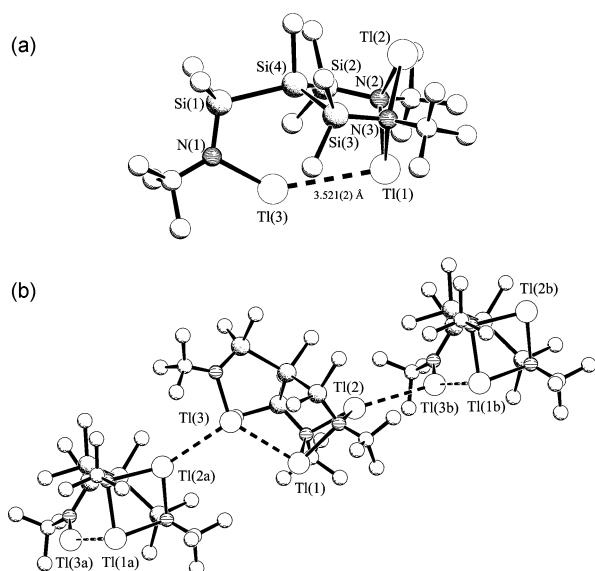


Fig. 10 (a) Molecular structure of the tripodal thallium amide $[\text{MeSi}\{\text{SiMe}_2\text{N}(\text{Tl})\text{tBu}\}_3]$ (**9**). (b) Polymeric chain structure of compound **9** in the crystal.

to be “pendant” on the ligand framework. In the solid, molecular units related by a glide plane are connected *via* intermolecular Tl–Tl contacts $[\text{Tl}(2)\text{--}\text{Tl}(3')] 3.673(2) \text{ \AA}]$ to form infinite chains of amidothallium molecules.

Metal–metal vs. thallium(I)–arene attraction

As has been found for many other low-valent p-block metal cations, Tl^+ forms stable π -arene complexes with a variety of aromatic ring compounds. A prerequisite for their formation appears to be the use of weakly coordinating anions which do not interfere with the arene–metal donor–acceptor interaction. First structurally characterized by Amma and Turner in the 1960s,³⁰ this field was significantly advanced more recently by Schmidbaur,³¹ Frank³² and others.³³ Arene–thallium interactions were also found in thallium compounds containing heteroatom donor ligands which possess arene functions in their ligand periphery. An early example of such a secondary arene–Tl interaction was reported by Strähle and Beck who determined the crystal structures of the complexes $[\text{Tl}(\text{ArNNAr})_2]$ (Ar = Ph, Tol).³⁴

One of the first amidothallium(I) complexes to be structurally characterized, Roesky’s $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3(\text{Me}_3\text{Si})\text{NTl}]_4$, aggregates as a tetramer which is held together by four attractive Tl–arene interactions (Fig. 11).³⁵ The thallium atoms in this compound are each located approximately centrally above the phenyl ring of a neighbouring molecule, the mean thallium–centroid distance being 3.11 \AA . This distance is somewhat greater than those found for the “simple” arenethallium complexes referred to above ($2.9\text{--}3.0 \text{ \AA}$).

In view of this firmly established propensity of monovalent thallium to interact with arene rings we were interested to find out how the introduction of an arene group in the ligand backbone of the tripodal thallium amides, which had been investigated by us, would affect their solid state structure. It was conceivable that a combination of $\text{Tl} \cdots \text{Tl}$ and $\text{Tl} \cdots$ arene interactions would lead to structural arrangements which were significantly different from the previously studied system. In order to simply “perturb” a known thallium(I) amide, we employed the tripodal amido ligand $[\text{C}_6\text{H}_5\text{C}(\text{CH}_2\text{NSiMe}_3)_3]^{3-}$ which is entirely analogous to the neopentane derived tripod employed in compounds **2–4**.

An X-ray diffraction study established the remarkable structural arrangement for compound **10** shown in Fig. 12.³⁶ Instead

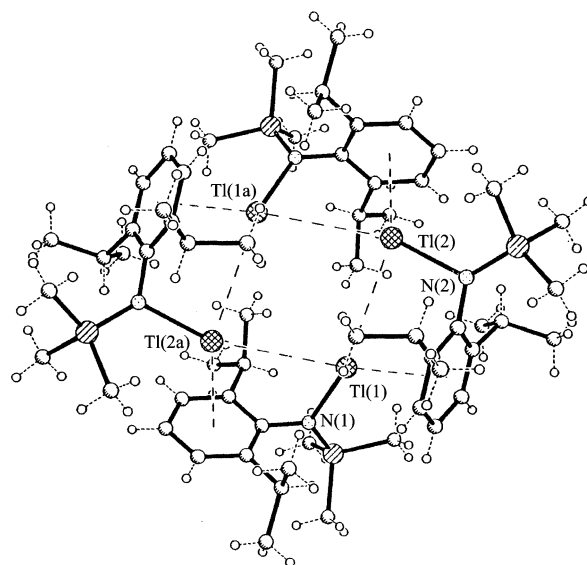


Fig. 11 The tetrameric aggregate in the crystal structure of $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3(\text{Me}_3\text{Si})\text{NTl}]_4$ reported by Roesky *et al.* (from ref. 35).

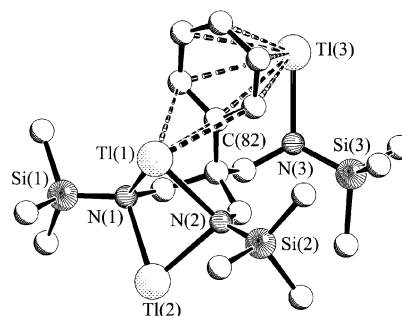


Fig. 12 Molecular structure of the monomeric unit of **10** showing the thallium– π -arene interaction of the apical phenyl group.

of the claw-like conformation normally observed for the tripodal amides the metallated amido-claws bend upwards bringing two of the three thallium atoms into close contact with the apical phenyl group. Whereas Tl(3) adopts a slightly slipped six-coordination of the aryl ring with $\text{Tl} \cdots \text{C}$ distances lying in the range of $3.34\text{--}3.75 \text{ \AA}$, Tl(1), which is part of an intramolecular Tl_2N_2 four-membered ring, is located very close to the *ipso*-phenyl carbon atom C(82). In fact, the distance $\text{Tl}\text{--}\text{C}(82)$ of 2.88 \AA is significantly shorter than usually observed for π -bonding in heavy main group element chemistry and approaches the regime found in covalent Tl–C interactions. Only the *ipso*-C-atom as well as the two *ortho*-carbons lie within a range of potential bonding interaction with respect to Tl(1) [$d\{\text{Tl}(1)\text{--}\text{C}(\text{ortho})\} = 3.23, 3.20 \text{ \AA}$], formally making this arrangement a three-coordination.

In the solid the amidothallium units are dimeric, and the apparently pendant amido-Tl(3) unit in Fig. 12 is in fact part of a Tl_2N_2 four-membered ring structure the centre of which coincides with a crystallographic centre of symmetry. In the crystal structure these dimers form infinite chains which are defined by intermolecular thallium–thallium contacts (Fig. 13). The intermolecular metal–metal distance of $d\{\text{Tl}(1)\text{--}\text{Tl}(5)\} = 3.75 \text{ \AA}$ lies at the extreme end of such metal–metal contacts and the attractive interaction therefore is thought to be rather weak.

A rare example of a metal–heteroarene π -interaction was found in the crystal structure of $[(2\text{-C}_5\text{H}_4\text{N})\text{C}(\text{CH}_3)\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}_2]$ (**11**).³⁷ This compound is monomeric in the solid state with the pyridyl ring being disordered between two orientations. In one of the components of this disorder the pyridyl

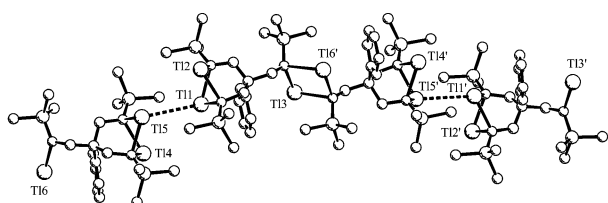


Fig. 13 The infinite chain structure of compound **10** in the crystal.

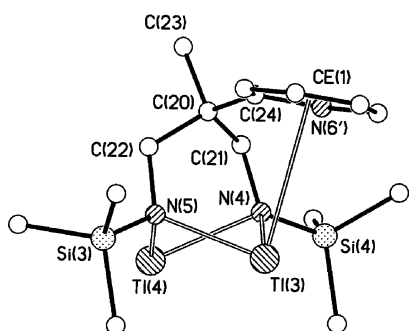
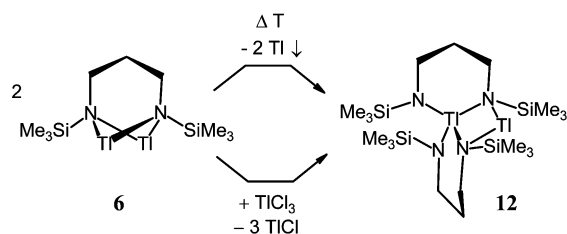


Fig. 14 A metal-heteroarene π -interaction in the disordered crystal structure of $[(2\text{-C}_5\text{H}_4\text{N})\text{C}(\text{CH}_3)\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}_2]_2$ (**11**).

ring is engaged in a π -interaction with a thallium atom [Tl(3)–centroid: 3.524 Å] (Fig. 14).

Redox disproportionation of thallium(i) amides: the synthesis and structural characterization of $\text{Tl}^{\text{I}}\text{Tl}^{\text{II}}$ and $\text{Tl}^{\text{I}}\text{Tl}^{\text{III}}$ mixed valent amido complexes

As discussed in the Introduction, thallium(i) amides are prone to thermally induced redox-chemical transformations which may either lead to non-specific degradation of a compound or its selective conversion. While the former alternative is more frequently encountered, these redox processes have led to a variety of interesting amidothallium complexes containing the metal in a higher oxidation state (Scheme 3).



Scheme 3 Controlled thermal degradation of compound **6** to the mixed valent compound **12** and the rational synthesis of the latter by reaction of **6** with TiCl_3 .

A simple example of such a selective transformation takes place if the dinuclear thallium(i) amide **6** is carefully heated in a hydrocarbon solvent. This leads to the precipitation of one molar equivalent of thallium metal and the concomitant formation of the mixed valent compound $[\{\text{CH}_2\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}_2\}_2\text{Tl}^{\text{I}}\text{Tl}^{\text{III}}]$ (**12**) (Scheme 3). The same compound was obtained upon reaction of **6** with TiCl_3 .³⁸ The molecular structure was determined by X-ray diffraction (Fig. 15). Both thallium atoms in **12** are part of a tricyclic structure consisting of the six-membered chelate rings as well as the adjacent four-membered dimetallacycle. The trivalent metal atom resides in the centre of the complex and adopts a distorted tetrahedral coordination geometry while the Tl^{I} atom is dicoordinated and located in an exposed position on the outside.

Compound **12** displays dynamic behaviour in solution as reflected in the NMR spectra recorded at variable temperature

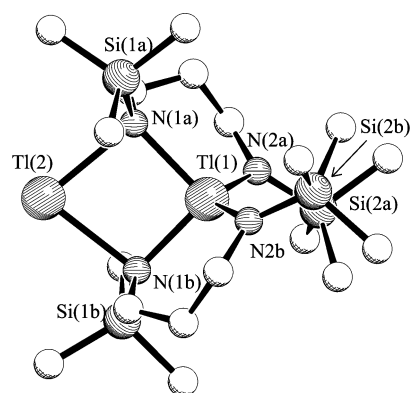


Fig. 15 Molecular structure of the mixed valent compound $[\{\text{CH}_2\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}_2\}_2\text{Tl}^{\text{I}}\text{Tl}^{\text{III}}]$ (**12**).

which indicated a rapid “rotation” of the thallium(i) atom around the tetraamidothallium(III) core. Such a “rotation” of a monovalent metal atom coordinated to an amido tripod is reminiscent of the dynamic behaviour of the tripodal lithium triamidostannates(III) investigated previously by us³⁹ and a similar dynamic behaviour was also observed by Veith and co-workers for a range of mixed Li–Group 13 metal amido complexes.⁴⁰

The low temperature limit spectrum representing the static structure could be obtained at $T \leq 220$ K (Fig. 16). The doublet

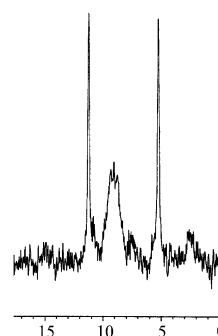
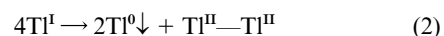


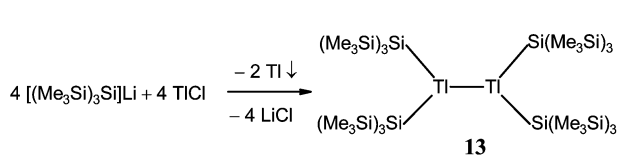
Fig. 16 The low temperature limit ^{29}Si NMR spectrum of the $\text{Tl}^{\text{I}}\text{Tl}^{\text{III}}$ compound **12** representing the static structure could be obtained at $T \leq 220$ K.

resonance at $\delta = 8.2$ with the large $^2J(^{203/205}\text{Tl}-^{29}\text{Si})$ coupling of 238 Hz is assigned to the SiMe_3 -groups at the N-donor which are not bridged by the Tl^{I} -atom. The second resonance is observed as an unresolved multiplet due to coupling to both the Tl^{III} and Tl^{I} nuclei. We frequently observed that coupling to monovalent thallium leads to considerable resonance broadening probably due to rapid relaxation of the metal nucleus.

The disproportionation of monovalent thallium giving metallic thallium(0) and thallium(III) species [eqn. (1)] is the most frequently observed pattern of redox reactivity. A second possible reaction pathway has led to the isolation of metal–metal bonded thallium(II) complexes [eqn. (2)] and currently represents the only known access to this fascinating and previously elusive class of molecular compounds.



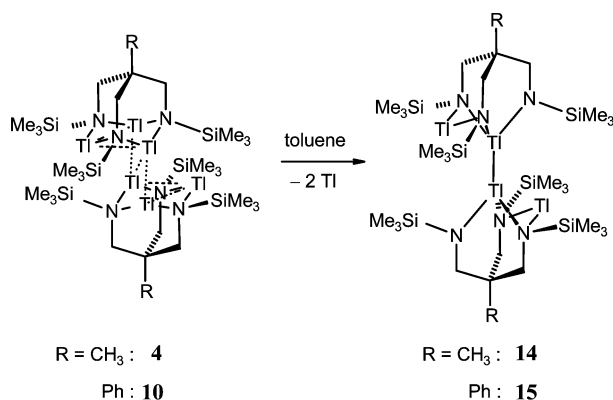
The field was opened up by Klinkhammer in 1994 who reported the synthesis and structural characterization of the first molecular $\text{Tl}^{\text{II}}\text{—Tl}^{\text{II}}$ compound, $[\{(\text{Me}_3\text{Si})_3\text{Si}\}\text{Tl}^{\text{II}}\text{—Tl}^{\text{II}}\{\text{Si}(\text{SiMe}_3)_3\}]$ (**13**) (Scheme 4).⁴¹



Scheme 4 Klinkhammer's synthesis of the first thallium(II)–Tl–Tl amide **13**.

The Tl–Tl bond length in this complex was found to be 2.9142(5) Å. Since this first report, a few analogous redox-degradation products containing covalent thallium–thallium bonds have been isolated and characterized by X-ray diffraction.⁴²

At the early stages of our investigation into the preparative chemistry of Tl^I-amides, we discovered a similar type of redox chemical formation of Tl^{II}–Tl^{II} species.²⁴ Upon stirring [CH₃C(CH₂N(Tl)SiMe₃)₃]₂ (**4**) and [C₆H₅C(CH₂N(Tl)SiMe₃)₃]_{*n*} (**10**) in toluene at ambient temperature for 24 h, both compounds are selectively (and completely) converted to the mixed-valent species [{CH₃C(CH₂NSiMe₃)₃}(Tl^I)Tl^{II}–Tl^{II}(Tl^I){CH₃–C(CH₂NSiMe₃)₃}] (**14**) and [{C₆H₅C(CH₂NSiMe₃)₃}(Tl^I)Tl^{II}–Tl^{II}(Tl^I){C₆H₅C(CH₂NSiMe₃)₃}] (**15**), respectively (Scheme 5). A single crystal X-ray structure analysis of **14** confirmed the presence of a covalent Tl^{II}–Tl^{II} bond (Fig. 17).



Scheme 5 Controlled thermal conversion of the tripod thallium(I) amides **4** and **10** to the mixed valent Tl–Tl bonded compounds **14** and **15**, respectively.

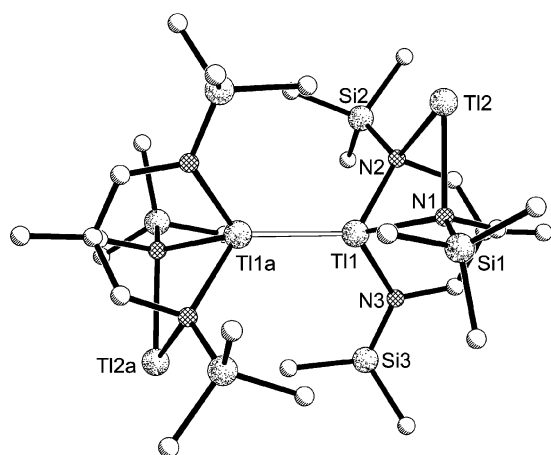


Fig. 17 Molecular structure of the mixed valent Tl^ITl^{II} compound **14** containing a covalent Tl^{II}–Tl^{II} metal–metal bond.

The most prominent structural feature of **14** is the directly metal–metal bonded Tl₂⁴⁺ fragment which is effectively shielded by the ligand framework and the peripheral *N*-bonded SiMe₃-groups. The Tl–Tl distance of 2.734(2) Å is remarkably short in comparison to those found in the previously reported molecular Tl–Tl bonded compounds [{(Me₃Si)₃Si}Tl–Tl{Si(SiMe₃)₃}] (**13**) [*d*(Tl–Tl) = 2.9142(5) Å]⁴¹ and [(*t*Bu)₃Si}Tl–Tl{Si(*t*Bu)₃}]

[*d*(Tl–Tl) = 2.966(2) Å],^{42a} as well as the value of 2.840(3) Å found by Dronskowski and Simon for the Tl₂⁴⁺ cations in the solid state structure of Tl_{0.8}Sn_{0.6}Mo₇O₁₁.⁴³ The length of the metal–metal bond observed in **14** is close to that calculated at the HF-SCF level for *D*_{2d} Tl₂H₄ by Treboux and Barthelat (2.775 Å),¹³ however, in view of the well known wide variations of covalent M–M bond lengths in heavy metal chemistry and their dependence upon the sets of ligands associated with them such comparisons should be treated with care. The large body of data obtained for the isoelectronic “neighbour” in the periodic table, Hg₂²⁺, serves as a *caveat* in this context!⁴⁴

As Schnöckel *et al.* have pointed out in a review, thallium is the only Group 13 metal for which an “ethane-analogue” of the form [X₂(D)E–E(D)X₂] (X = anionic ligand, D = neutral donor ligand, E = Group 13 element in the formal oxidation state II) has remained elusive.⁴⁵ Compounds **14** and **15** are closely related to this missing link in the structural systematics of the divalent elements of this group. The indium(I/II)-analogue of **14**, [{CH₃C(CH₂NSiMe₃)₃}(In^I)In^{II}–In^{II}(In^I){CH₃–C(CH₂NSiMe₃)₃}] (**16**) was directly obtained by reaction of the lithium amide of the tripod ligand with indium(I) chloride. The metal–metal bond length of 2.807(1) Å is greater than the Tl(1)–Tl(1′) distance in **14** but lies in the range previously found for covalent In–In bonds.⁴⁶

In the examples cited above, the disproportionation of monovalent thallium (and indium) compounds may be employed for the controlled and systematic synthesis of mixed-valent species. In many cases, this redox chemical activity is an unwanted (or rather unintended) side reaction. Nevertheless, several structurally interesting compounds could be serendipitously isolated and characterized from these preparations. An example of such a reaction product was obtained upon addition of three molar equivalents first of butyl lithium and then of thallium(I) chloride to the tripodal amine HC{SiMe₂}NH(*p*-Tol)₃ at –78 °C and subsequent slow warming to ambient temperature.⁴⁵ This gave, apart from the precipitation of thallium metal, a bright yellow solution from which yellow–orange crystals were obtained. A single crystal X-ray structure analysis established the molecular structure of a Tl(III)/Tl(I) mixed metal complex **17** in which a butylthallium(III) unit is coordinated by the tripodal amido ligand while two of the donor atoms are bridged by a thallium(I) atom (Fig. 18a).

Compound **17** was the first example of a structurally characterized long chain alkyl thallium complex in contrast to the considerable number of methylthallium derivatives reported in the literature. Such non-functionalized long chain alkylthallium species are thought to be thermally labile, and it seems to be this particular coordination environment which renders **17** sufficiently stable to allow its isolation and characterization. NMR spectroscopic studies carried out in solution suggest that compound **17** is fluxional with the “external” Tl(I) atom exchanging between the different bridging positions which is similar to the dynamic behaviour discussed above for compound **12**.

A closer inspection of the crystal structure of **17** revealed that the complex is aggregated in the form of weakly associated dimers (Fig. 18b). This type of association occurs through weak *π*-arene–Tl(I)-contacts^{30–33} with, respectively one tolyl group of the neighbouring molecule: Tl(2)–C(Ar′) = 3.26–3.51 Å; Tl(2)–centroid: 3.093 Å. The intermetallic contact of Tl(2)–Tl(2′) 3.7615(13) Å is rather long and therefore thought to play a secondary role.

Metal–ligand vs. metal–metal redox chemistry: thallium(I)-induced synthesis of 4,9-diaminoperylene-quinone-3,10-diimine derivatives

As discussed in the previous section the redox-transformations of the monovalent heavy Group 13 metal amido compounds

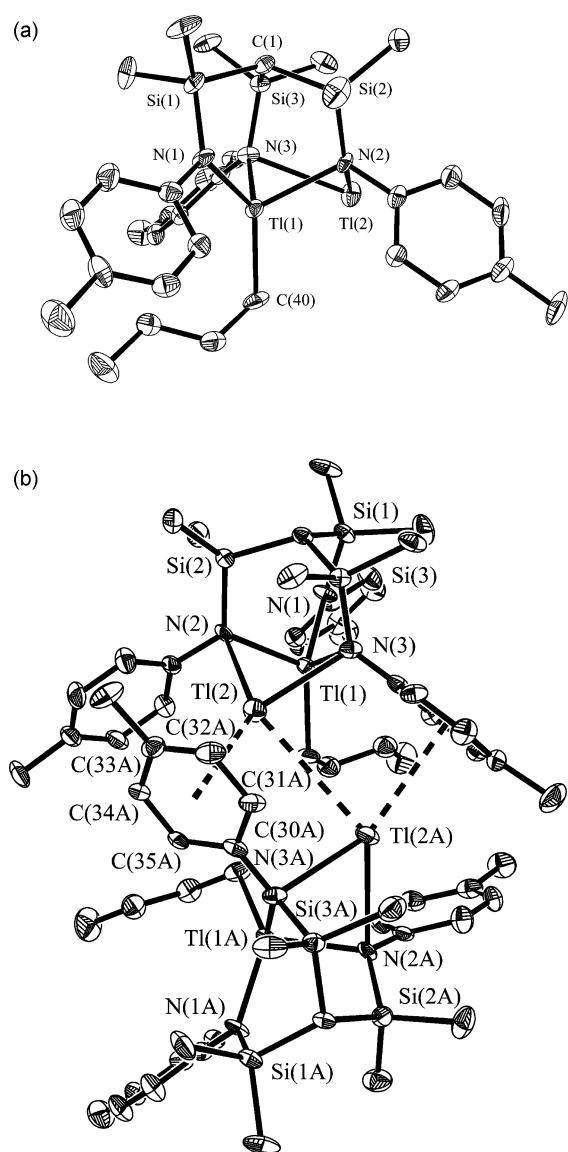
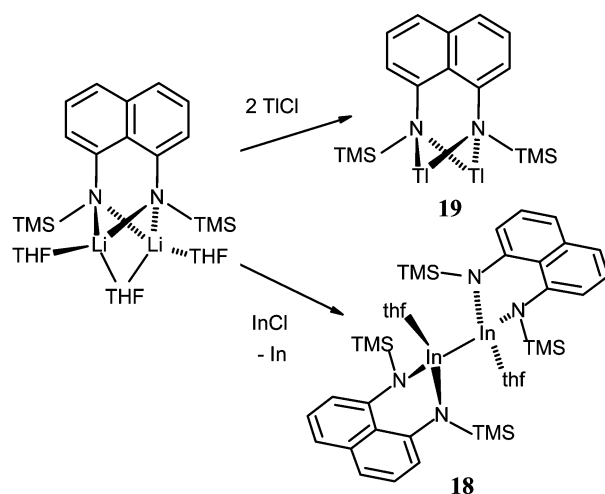


Fig. 18 (a) Molecular structure of $[\text{HC}\{\text{SiMe}_2\text{N}(p\text{-Tol})\}_3(\text{TlBu})(\text{Tl})]$ (**17**). (b) Dimeric aggregate of **17** in the solid state through π -arene-thallium contacts [Tl(2)–Tl(2A): 3.7615(13) Å].

may either lead to the mixed-valent $\text{M}^{\text{I}}\text{M}^{\text{II}}$ and $\text{M}^{\text{I}}\text{M}^{\text{III}}$ complexes ($\text{M} = \text{In}, \text{Tl}$). Alternatively, the products of partial or complete thermal demetallation are frequently isolated.^{29,48} In the latter case the corresponding amines are probably formed *via* nitrogen radical intermediates.

In the course of our work on thallium(I) and indium(I) amides, we selected such ligands which upon thermal demetallation would give intermediates of greater stability and lifetime. Instead of the immediate abstraction of hydrogen atoms from the solvent they were thought to undergo C–C-coupling and related reactions. To this end we chose a bidentate amido-ligand derived from 1,8-diaminonaphthalene which—given the known redox-chemistry of arylamines—offered the opportunity of directing the redox chemically induced conversions into pathways other than simple demetallations.⁴⁹

In contrast to the immediate disproportionation of the In^{I} species during the course of the metal exchange, giving the $\text{In}^{\text{II}}\text{–In}^{\text{II}}$ species **18** (Scheme 6) the corresponding reaction of $[\text{1,8-}\{\text{Me}_3\text{SiN}\}\text{Li}(\text{thf})\}_2\text{C}_{10}\text{H}_6](\text{thf})$ with TlCl exclusively led to the monovalent synthetic target $[\text{C}_{10}\text{H}_6(\text{NSiMe}_3)_2\text{Tl}]_2$ (**19**). Heating compound **19** in 1,4-dioxane for 17 h led to complete conversion to a 1 : 1 mixture of diamine starting material and the new 4,9-bis(trimethylsilylamino)perylenequinone-3,10-bis-



Scheme 6 Synthesis and of the indium(II)–In–In amide **18** and thallium(I) amide **19**.

(trimethylsilylimine) **20**. Detailed mechanistic studies support a reaction pathway as outlined in Scheme 7.⁵⁰

The analogous transformation was found to be viable for a whole range of silylated 1,8-diaminonaphthalene derivatives giving the corresponding quinoidal perylenes. Apart from a fundamental interest in this unusual reactive behaviour of a class of thallium(I) amides we have developed this into an efficient preparative method for the synthesis of tetraaminoperylenequinones and their derivatives. These are of interest in a variety of applications as fluorescent dyes.⁵¹

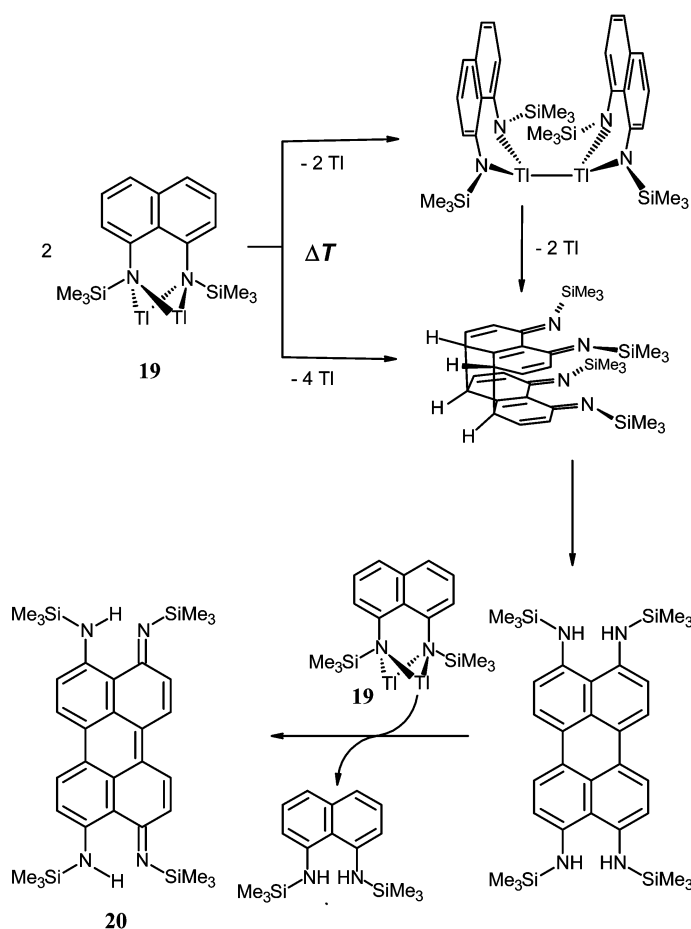
Mixed thallium–main group metal amides

A number of mixed metal thallium amides have been synthesized in recent years. These are either prepared by stepwise metal exchange of an alkali metal amide with TlCl giving rise to mixed alkali metal–thallium compounds or by reaction of the thallium(I) amides with other metal halides.

Stepwise metal exchange was possible with the silylated 1,8-diaminonaphthalene derivatives discussed in the previous section. Upon transmetalation of $[\text{1,8-}\{\text{Me}_3\text{SiN}\}\text{Li}(\text{thf})\}_2\text{C}_{10}\text{H}_6](\text{thf})$ with only one molar equivalent of TlCl , the corresponding mixed Li–Tl amide $[\text{1,8-}\{\text{Me}_3\text{SiN}\}\text{Li}(\text{thf})\}\{\text{Me}_3\text{SiN}\}\text{Tl}\}\text{C}_{10}\text{H}_6]$ (**21**) was isolated which crystallized as the dimeric aggregate displayed in Fig. 19.⁵²

This dimeric structure nicely combines the typical structural motifs of lithium amide chemistry and those of thallium(I) chemistry which we highlighted above. The two halves of the dimer, in which a Tl^{I} atom and a $(\text{thf})_2\text{Li}^+$ cation bridge the amido-N-atoms, are related by a crystallographic centre of symmetry. The $\text{Tl} \cdots \text{Tl}$ distance of 3.982(2) Å does not indicate a significant metal–metal interaction. Instead, the interaction between the Tl-centres and one of the naphthalene arene rings appears to provide the driving force for the dimeric aggregation in the solid. The distance between the Tl atom and the centroid of the η^6 -coordinated arene ring of 3.510(6) Å is somewhat greater than many of the previously reported Tl–arene contacts, but clearly within the range expected for heavy metal arene coordination.^{30–33}

A second and related example of partial metal exchange was isolated serendipitously from the reaction of the dilithium diamidopyridine $[(2\text{-C}_5\text{H}_4\text{N})\text{C}(\text{CH}_3)\{\text{CH}_2\text{N}(\text{Li})\text{SiMe}_3\}_2]_2$ with two molar equivalents of TlCl (per monomeric unit) in pentane.³⁷ After work up, two types of crystalline solids were identified, one of which was the yellow dithallium(I) diamide $[(2\text{-C}_5\text{H}_4\text{N})\text{C}(\text{CH}_3)\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}_2]_2$ (**11**) while the colourless product was found to be a mixed lithium–thallium amide and identified as $[(2\text{-C}_5\text{H}_4\text{N})\text{C}(\text{CH}_3)\{\text{CH}_2\text{N}(\text{Li})\text{SiMe}_3\}\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}]_2$ (**22**) (Fig. 20).



Scheme 7 Proposed mechanistic scheme for the interconversion of the thallium amide **19** to the corresponding perylenequinone **20**.

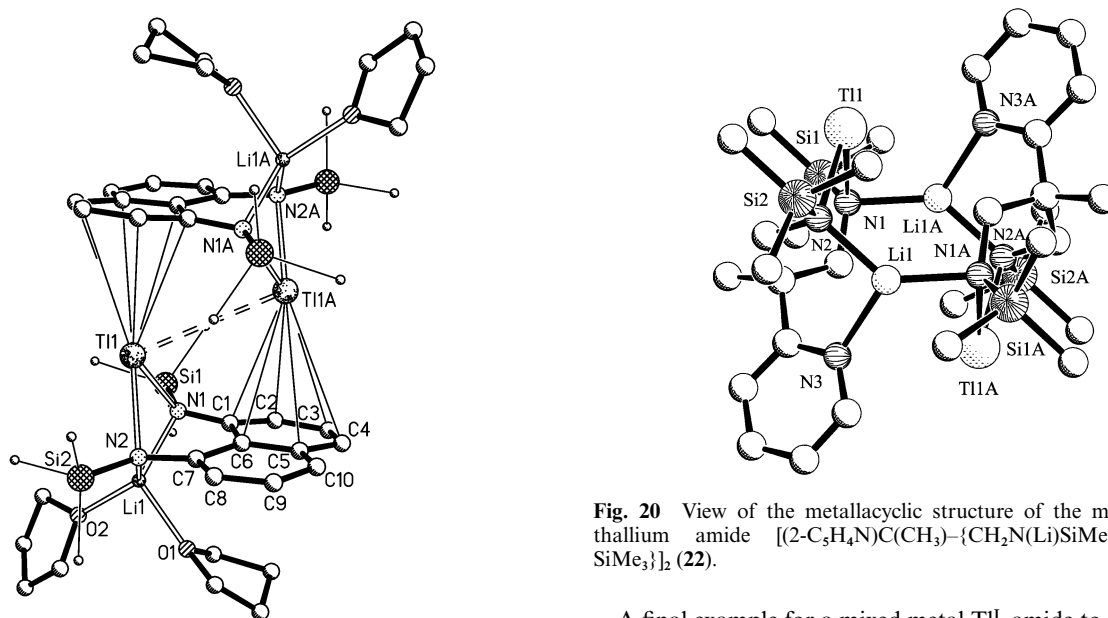


Fig. 19 The dimeric aggregation of the lithium-thallium amide $[1,8\text{-}\{(\text{Me}_3\text{SiN})\text{Li}(\text{thf})\}_2\{(\text{Me}_3\text{SiN})\text{Tl}\}_2\text{C}_{10}\text{H}_6]$ (**21**) in the crystal.

The structural centrepiece of **22** is a $\text{Li}_2\text{Tl}_2\text{N}_4$ macrocycle in which the thallium atoms occupy intramolecular bridging positions and the lithium atoms link the two metallated diamido-pyridine ligands. The centre of this cyclic structure coincides with a crystallographic centre of inversion which relates the two halves of the molecule. Whereas the dicoordinate thallium centres adopt the typically exposed positions, the lithium atoms are three-coordinate due to additional bonding of the pyridyl units.

Fig. 20 View of the metallacyclic structure of the mixed lithium-thallium amide $[(2\text{-C}_5\text{H}_4\text{N})\text{C}(\text{CH}_3)\text{-}\{\text{CH}_2\text{N}(\text{Li})\text{SiMe}_3\}\{\text{CH}_2\text{N}(\text{Tl})\text{SiMe}_3\}]_2$ (**22**).

A final example for a mixed metal Tl^{I} -amide to be discussed in this section is a mixed Group 13-Group 13 compound we isolated from a reaction attempting to synthesize the In^{I} -amide corresponding to the Tl^{I}_2 -diamide **6**.³⁸ The latter itself was employed as an amide transfer reagent in the reaction with two molar equivalents of InCl . Instead of the desired In^{I} analogue, the $\text{Tl}^{\text{I}}\text{In}^{\text{III}}$ amide $[\{\text{CH}_2(\text{CH}_2\text{NSiMe}_3)_2\}_2\text{In}^{\text{III}}\text{Tl}^{\text{I}}]$ (**23**) was isolated and characterized by X-ray diffraction. The indium and thallium atoms in the dinuclear complex **7** are part of a tricyclic structure which is entirely analogous to that of the $\text{Tl}^{\text{I}}\text{Tl}^{\text{III}}$ compound **12** (Fig. 21).

The expected tetrahedral coordination geometry of the tetraamidoindate(III) is significantly distorted by the bridging

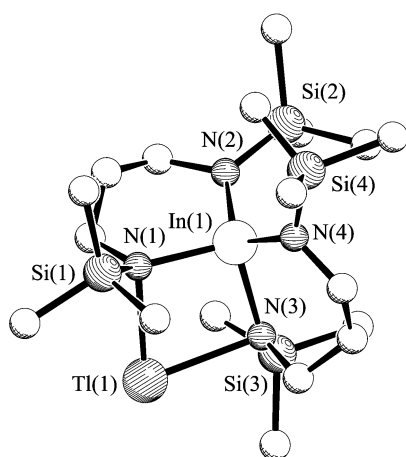


Fig. 21 Molecular structure of the $Tl^I In^{III}$ amide $[(CH_2(CH_2-NSiMe_3)_2)_2 In^{III} Tl^I]$ (**23**).

Tl^I -atom which occupies the characteristic peripheral position and was found by variable temperature NMR spectroscopy to be highly fluxional in solution. Compound **23** could be obtained in better yield by direct synthesis from **6** and $InCl_3$, as confirmed by the identical analytical and spectroscopic data.

Conclusions and outlook

The investigation of the amide chemistry of monovalent thallium has uncovered a large variety of novel structural patterns in molecular inorganic chemistry and given rise to some unprecedented chemical transformations. Based on the structural data accumulated over the years, it is fair to say that for this class of compounds the dispersive attraction between thallium(I) atoms plays a significant role in the determination of their solid state aggregation. In the absence of competing intermolecular interactions this (albeit weak) metallophilic attraction may become the dominating factor in their structural chemistry.

The use of thallium amides as ligand transfer reagents for the synthesis of redox-active main group or transition metal amido complexes has been successfully attempted in a few cases but remains largely unexplored. So far, research in this field has been entirely curiosity-driven and in most respects of purely fundamental interest. However, such projects may yield interesting "side products", such as the efficient preparative route to tetraaminoperylene, which transcend the original frame of such a research program. Given the current state of this field, more such discoveries are to be expected in the future.

Acknowledgements

Our own research described in this Perspective was carried out by two exceptionally able PhD students; Konni Hellmann opened up this field and developed the preparative methods while Christian Galka, who took over the project, made many important subsequent contributions. Annina Bergner temporarily joined the research effort. I would like to acknowledge the fruitful and indispensable collaborations with Dietmar Stalke (Würzburg) and Mary McPartlin (London) and their co-workers. Our own work was supported by the Deutsche Forschungsgemeinschaft within the Schwerpunktprogramm Polyeder and the Sonderforschungsbereich 347.

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