Dalton Transactions

PAPER

View Article Online
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Cite this: *Dalton Trans.*, 2019, **48**, 125

Tetrazastannoles *versus* distannadiazanes – a question of the tin(II) source†

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Received 26th October 2018,
Accepted 16th November 2018

DOI: 10.1039/c8dt04295k

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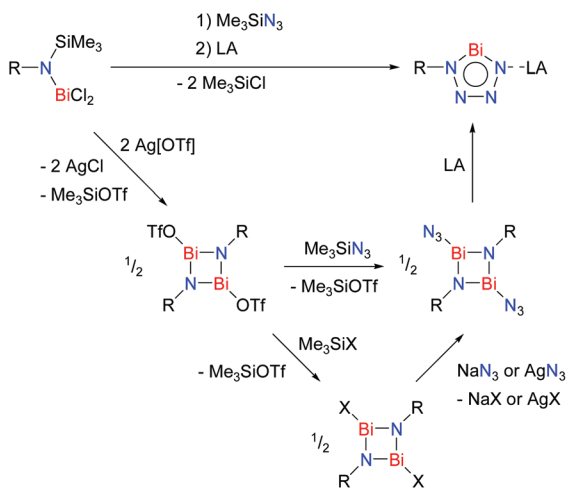
Various tin(II) compounds such as Mes^*_2Sn (Mes^* = 2,4,6-tri-*tert*-butylphenyl), $Sn[N(SiMe_3)_2]_2$ and TerSnCl (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl) could be readily oxidised by organic azides to release N_2, forming nitrogen-tin compounds. Depending on the used Sn(II) compound, the reactions with two equivalents of azide led to the formation of tetrazastannoles ($R_2N_4SnR'_2$) or cyclo-distannadiazanes $[R_2Sn(\mu\text{-}NR')]_2$. The reactivity was independent of the electronic situation of the organic azide. Additionally, Mes^*_2Sn formed an amido-azido compound of the type $R(R')Sn(N(SiMe_3)_2)N_3$ in the presence of Me_3SiN_3. Presumably, the corresponding tetrazastannole was formed in the first step followed by a ring opening reaction. The same holds true for the reaction of $Sn[N(SiMe_3)_2]_2$ with Me_3SiN_3 while TerSnCl showed no reaction in the presence of Me_3SiN_3, even after prolonged heating.

Introduction

In recent years we have been interested in pnictogen-rich ring systems such as neutral tetrazapnictoles (R-N_4Pn; Pn = P, As, Sb, and Bi), of which the corresponding phosphorus,[1] arsenic[2,3] and antimony[4] derivatives could be successively prepared. So far, however, the related bismuth compound is unknown, although several synthesis attempts have been made. This includes experiments for generating a bismadiazonium salt (R-NBi^+) by Lewis acid induced elimination of Me_3SiCl[5–7] or Me_3SnCl[8] and attempted [3 + 2] cycloadditions with azides (Scheme 1). But all these attempts proved unfruitful and a new strategy had to be considered. For this reason, we attempted [4 + 1] cycloadditions rather than [3 + 2] cycloadditions, thus avoiding the *in situ* generation of highly reactive and sensitive bismuthenium or bismadiazonium cations. For this purpose, a suitable N_4 transfer reagent had to be identified. Tetrazastannoles, consisting of a SnN_4 heterocycle, appeared to be ideal since SnN compounds are known to be mild transfer reagents of nitrogen-containing groups.[8–14] Therefore, we were interested in the synthesis of tetrazastannoles (tetrazenides of tin) as starting materials for the generation of BiN_4 ring system. A convenient method for the synthesis of tetrazenides or tetrazabutadienes is the oxidation of an element such as tin in a formal low oxidation state by azides. In fact, the first compound with a stable tetrazabutadiene fragment was observed utilizing such a reaction pathway.[15] Today, many tetrazenides and tetrazabutadienes are known, synthesised by the oxidation route as depicted in Scheme 2 (pathway A).[15–17]

Indeed, the oxidation of tin(II) compounds with organic azides is a useful technique to generate SnN_4 compounds. For example, Weidenbruch's group was able to synthesize a tetrazastannole in the reaction of Mes^*_2Sn with two equivalents of 1-azido-3,5-bis(trifluoromethyl)benzene (**1b**).[18] An interesting product of this oxidation reaction was the isolation of a stannaimine from the reaction of $Sn[N(SiMe_3)_2]_2$ with one equi-



Scheme 1 Previously attempted syntheses of tetrazabismutholes.

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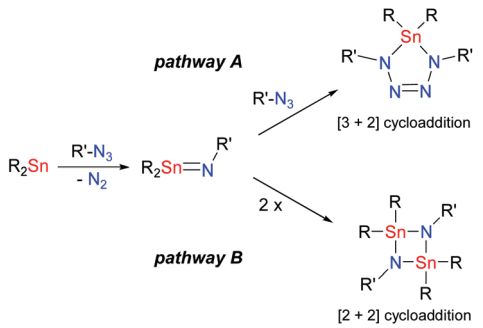
†Electronic supplementary information (ESI) available: X-ray data, synthesis of all starting materials and discussed tin species along with all spectra and analytical details. CCDC 1872841–1872847. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt04295k



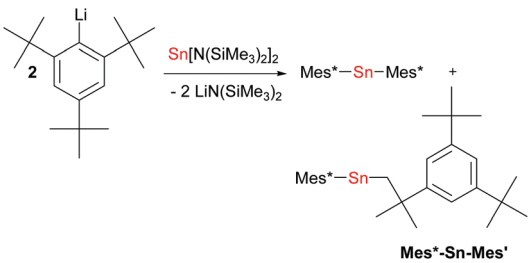
Scheme 2 Reaction of tin(II) compounds with organic azides (pathway A: +R-N_3; pathway B: dimerization) yielding nitrogen–tin(IV) species.

valent of $DippN_3$ (Dipp = 2,6-diisopropylphenyl), a compound with a N–Sn double bond that is stable towards dimerization in the solid state.[19] In the event that two equivalents of the less sterically encumbered 1-azido-2,6-diethylbenzene were used, the reaction led to the respective tetrazastannole. Based on the oxidation of Lappert's stannylene ($Sn[N(SiMe_3)_2]_2$) with different organic azides, a whole series of tetrazastannoles was already synthesised.[20] The observed reactivity hinted at a two-step reaction: in the first step a stannaimine was formed under N_2 evolution, which reacted in the second step with a second equivalent azide in a [3 + 2]-cycloaddition to give a tetrazastannole (Scheme 2, pathway A). Or, if no second equivalent of azide was available for the cycloaddition, the stannaimine dimerized to a cyclo-distannadiazane (Scheme 2, pathway B).[20] The competition between reaction pathway A and B was already discussed by Wiberg *et al.*[21] and the group of Grützmacher.[22]

Results and discussion

Synthesis

Mes*$_2$Sn. In a first series of experiments, Weidenbruch's stannylen Mes*$_2$Sn was used as tin(II) source. The synthesis of Mes*$_2$Sn, however, turned out to be more complicated than expected. At first, Mes*Br was transferred into Mes*Li in a metal–halide-exchange reaction with *n*-BuLi followed by a reaction with $Sn[N(SiMe_3)_2]_2$. The two main difficulties of this synthesis were to remove $LiN(SiMe_3)_2$ and the occurrence of the isomerization product Mes*SnMes′ (Scheme 3).



Scheme 3 Synthesis of Mes*$_2$Sn along with Mes*-Sn-Mes′ as side products.

Because it was impossible to isolate pure Mes*$_2$Sn, the crude product was used in the further reactions with azides. Adding a solution of 1-azido-4-dimethylaminobenzen (p-$(CH_3)_2N$–C_6H_4–N_3, **1a**) in toluene to a Mes*$_2$Sn solution in the same solvent resulted in a moderate gas evolution. In contrast to the Weidenbruch reaction of 1-azido-3,5-di(trifluoromethyl)benzene (m,m-$(CF_3)_2$–C_6H_3–N_3, **1b**) with Mes*$_2$Sn, a four-membered ring system – a cyclo-distannadiazan (**2**, Fig. 1) – was formed in small yields amongst other unidentified products. However, one of the Mes* groups attached to the tin was isomerized as discussed before in the synthesis of Mes*$_2$Sn (Scheme 2). As we started from a mixture Mes*$_2$Sn/Mes*-Sn-Mes′, it could not be determined whether the isomerization occurred due to the reaction with the azide. Obviously, in the reaction mixture of Mes*$_2$Sn (or Mes*SnMes′) and **1a**, the [2 + 2] cycloaddition (dimerization) of the *in situ* formed stannaimine (Scheme 2, pathway B) is preferred over the [3 + 2] cycloaddition with another equivalent of azide.

Besides aryl azides, we were also interested in the reaction of Mes*$_2$Sn with readily available Me_3SiN_3. In this case, also isomerization of one of the Mes* scaffolds was observed but neither a tetrazastannole nor a cyclo-distannadiazane could be identified. X-ray diffraction of a single crystal obtained from this reaction revealed the formation of the azido-disilylamido compound **3** (Fig. 2). It can be assumed that the formation of **3** occurred *via* the desired tetrazastannole. It is known that Me_3Si moieties can easily migrate. A similar behaviour was already observed for zirconium,[23] thorium[24] and tin compounds.[20] In all these cases a ring opening mechanism was proposed leading to the formation of open-chain like *trans*-bent azido ligands and in our case to **3** after migration of one Me_3Si group.

$Sn[N(SiMe_3)_2]_2$. Since the synthesis of Mes*$_2$Sn was rather hindered due to the formation of side products that could not be completely removed, another tin(II) compound, $Sn[N(SiMe_3)_2]_2$, was utilized. There are already some examples in the literature of tetrazastannoles synthesized from Lappert's

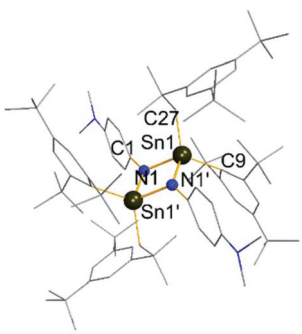


Fig. 1 Molecular structure of **2**. H atoms omitted for clarity. Selected bond length (Å) and angles (°): Sn1–N1a 2.111(5), Sn1–N1a′ 2.013(4), Sn1–C9 2.199(2), Sn1–C27 2.173(2), N1a–C1a 1.404(3), N1a′–Sn1–N1a 80.0(2), N1a–Sn1–C9 118.1(2), N1a–Sn1–C27 105.6(2), C27–Sn1–C9 117.88(8), Sn1′–N1a–Sn1 100.0(2), C1a–N1a–Sn1 122.4(2), C1a–N1a–Sn1′ 135.5(2), C2a–C1a–N1a–Sn1–122.4(4).

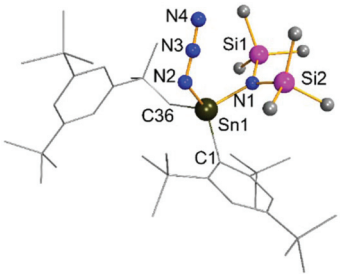


Fig. 2 Molecular structure of **3**. H atoms omitted for clarity. Selected bond length (Å) and angles (°): Sn1–N1 2.068(2), Sn1–N2 2.101(2), Sn1–C1 2.167(2), Sn1–C36 2.169(2), N2–N3 1.198(3), N3–N4 1.147(3), N1–Si1 1.749(2), N1–Si2 1.771(2), N1–Sn1–N2 98.51(7), N1–Sn1–C1 105.88(7), N2–Sn1–C1 106.56(7), N1–Sn1–C36 118.92(7), C1–Sn1–C36 118.23(7), Si1–N1–Sn1 123.77(9), Si1–N1–Si2 116.95(9), Si2–N1–Sn1 117.59(8), N2–N3–N4 175.5(3), N3–N2–Sn1 122.3(2).

stannylene.[19,20] As shown by Meller *et al.*, the synthesis of tetrazastannoles can be started from relatively small phenyl azides and the readily available $Sn[N(SiMe_3)_2]_2$. With regard to the results with Mes^*_2Sn, it was interesting to see if the electronic situation in the azide has an influence on the product formed. For this purpose, $Sn[N(SiMe_3)_2]_2$ was reacted with both the electron rich azide **1a** (formation of **4a**, Fig. 3) as well with the electron poor azide **1b** (formation of **4b**, Fig. 4). In both case the corresponding tetrazastannole was formed (Scheme 4) and could be isolated in reasonable yields (**4a** 60%, **4b** 45%) as pure substances.

In another experiment, the aryl azide 1-azido-4-nitrobenzene (p-O_2N–C_6H_4–N_3, **1c**) was also reacted with $Sn[N(SiMe_3)_2]_2$, however, only decomposition was observed (no formation of **4c**). Hence, it can be concluded that the nitro group is not stable under the applied reaction conditions. In the reaction of $Sn[N(SiMe_3)_2]_2$ with an excess of Me_3SiN_3, an azido-tri-bis(trimethylsilyl)amidostannane (**4d**) was obtained in almost quantitative yield (Scheme 5), similar to the reaction of Mes^*_2Sn with Me_3Si-N_3 (Fig. 2). Presumably, in the first step a stannaimine is formed upon release of molecular nitrogen and

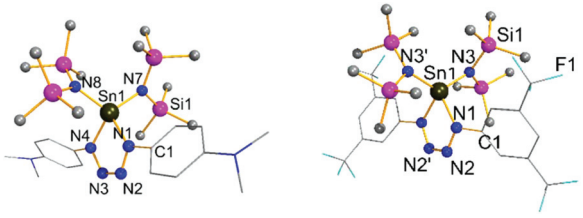


Fig. 3 Molecular structure of **4a** and **4b** in the crystal. H atoms omitted for clarity. Selected bond length (Å) and angles (°), **4a**: N1–Sn1 2.044(2), N4–Sn1 2.045(2), N7–Sn1 2.036(2), N8–Sn1 2.028(2), N1–N2 1.375(3), N2–N3 1.272(3), N3–N4 1.384(3), N8–Sn1–N7 113.2(1), N8–Sn1–N1 126.6(1), N7–Sn1–N1 105.0(1), N8–Sn1–N4 103.8(1), N7–Sn1–N4 129.19(9), N1–Sn1–N4 76.66(9). **4b**: N3–Sn1 2.003(1), N1–Sn1 2.062(1), N1–N2 1.381(2), N2–N2′ 1.264(2), N3–Sn1–N3′ 123.76(6), N3–Sn1–N1 116.99(5), N3′–Sn1–N1 106.91(4), N1–Sn1–N1′ 75.65(6), N2–N1–C1 114.4(1), N2–N1–Sn1 114.88(8), C1–N1–Sn1 128.81(8).

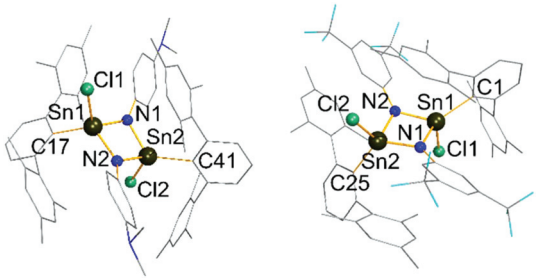
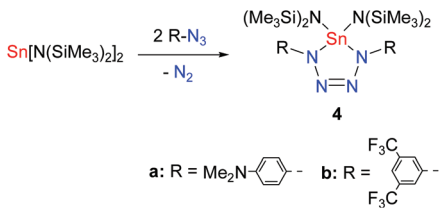
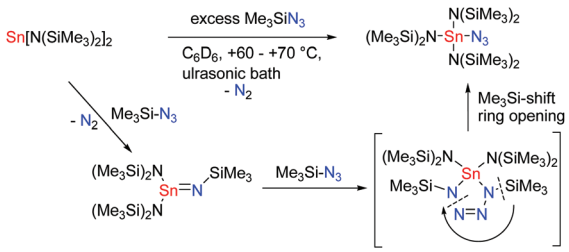


Fig. 4 Molecular structure of **5a** and **5b**. H atoms omitted for clarity. Selected bond length (Å) and angles (°), **5a**: Sn1–N1 2.032(2), Sn2–N2 2.039(2), Sn1–C17 2.138(3), Sn1–Cl1 2.3499(8), Sn2–N1 2.031(2), Sn2–N2 2.035(2), Sn2–C41 2.153(3), Sn2–Cl2 2.3591(8); N1–Sn1–N2 81.61(9), N2–Sn1–C17 119.2(1), C17–Sn1–Cl1 107.96(8), N1–Sn2–N2 81.74(9), N2–Sn2–C41 125.7(1), C41–Sn2–Cl2 113.46(8), Sn2–N1–Sn1 97.9(1). **5b**: Sn1–N1 2.042(2), Sn1–N2 2.049(2), Sn1–C1 2.145(3), Sn1–Cl1 2.3471(7), Sn2–N1 2.043(2), Sn2–N2 2.046(2), Sn2–C25 2.128(3), Sn2–Cl2 2.3354(3), N1–C49 1.391(3), N2–C57 1.395(3); N1–Sn1–N2 81.10(9), N1–Sn1–C1 121.88(9), N2–Sn1–C1 131.6(1), N1–Sn1–C1 102.19(6), N2–Sn1–Cl1 100.19(6), C1–Sn1–Cl1 113.29(8), N1–Sn2–N2 81.14(8), N1–Sn2–C25 121.59(9), N2–Sn2–C25 117.56(9), N1–Sn2–Cl2 109.82(7), N2–Sn2–Cl2 111.33(6), C25–Sn2–Cl2 111.91(7), C49–N1–Sn1 130.2(2), C49–N2–Sn2 130.7(2), Sn1–N1–Sn2 98.41(9), C57–N2–Sn2 128.9(2), C57–N2–Sn1 130.7(2), Sn2–N2–Sn1 98.10(9).



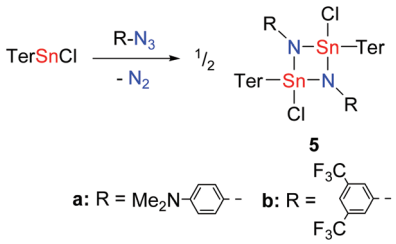
Scheme 4 Reaction of $Sn[N(SiMe_3)_2]_2$ with **1a** and **1b**.



Scheme 5 Reaction of $Sn[N(SiMe_3)_2]_2$ with an excess of Me_3Si-N_3 yielding azido-tri-bis(trimethylsilyl)amidostannane (**4d**) in a formal 2-step synthesis.

then a formal oxidative addition of a second equiv. of Me_3SiN_3 along with a 1.4 shift of the Me_3Si^+ ion occurs as shown in Scheme 5. Amido-azido-stannane **4d** was already reported by Ruzicka *et al.*[20] Unfortunately, the tetrazastannoles **4a** and **4b** are so well kinetically protected by the $N(SiMe_3)_2$ groups that it was impossible to generate a corresponding BiN_4 heterocycle by using these tetrazastannoles as R_2N_4 transfer reagent.

TerSnCl. Other interesting tin(II) compounds related to the synthesis of tetrazastannoles are Power's TerSnCl and



Scheme 6 Reaction of synthesis of **5a** and **5b**.

Ter_2Sn.[25] Prior to the synthesis, we modelled a hypothetical tetrazastannole by quantum chemical methods starting from Ter_2Sn, but the terphenyl substituent proved to be too bulky to allow the formation of a terphenyl-substituted tetrazastannoles. For this reason, all experiments were performed only with TerSnCl as starting material. In contrast to the reactions with $Sn[N(SiMe_3)_2]_2$, four-membered ring systems with an Sn_2N_2 skeleton could be isolated in reactions with the aryl azides **1a** and **1b**, respectively (Scheme 6 and Fig. 4). The corresponding tetrazastanoles were not observed.

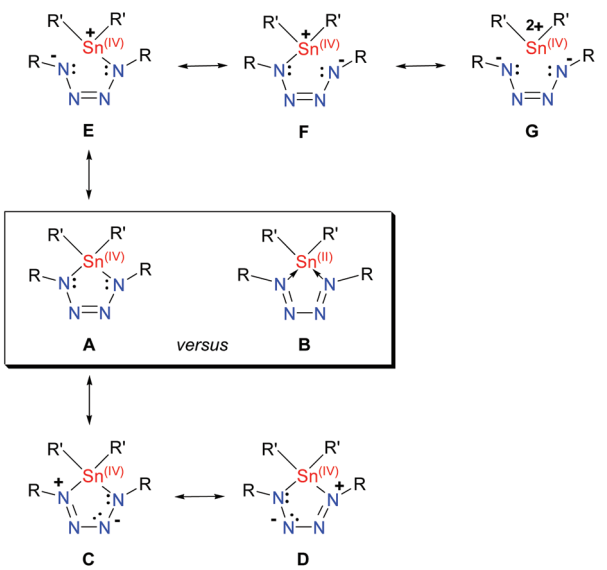
To complete the studies on TerSnCl, at first the reactivity to Me_3SiN_3 was also investigated at ambient temperatures. Since no reaction was observed after 24 hours, we performed temperature-variable NMR studies. For this reason, TerSnCl was added to an NMR tube and dissolved in C_6D_6. After addition of Me_3SiN_3, the reaction was monitored by ^1H and ^{29}Si INEPT NMR spectroscopy. Even after heating the reaction mixture at 60° C for 6 hours, no reaction between TerSnCl and Me_3SiN_3 was observed.

Structure and bonding

Compound **2** crystallized in the triclinic space group $P\bar{1}$ as centrosymmetric dimer. The centre of inversion is in the middle of the planar Sn_2N_2 scaffold (Fig. 1). There is a shorter (Sn1–N1a′ 2.013(4) Å) and one slightly longer (Sn1–N1a 2.111(5) Å) N–Sn distance within the Sn_2N_2 ring system, but both distances are in the expected range for a (polarized) single bond ($\sum r_{cov}$(N–Sn) = 2.11 Å).[26] As shown in Fig. 1, the C–Sn distance to the Mes* moiety (Sn1–C9 2.199(2) Å) as well as to the methylene carbon atom of the Mes′ moiety (Sn1–C27 2.173(2) Å) are in the typical range of C–Sn single bonds ($\sum r_{cov}$(C–Sn) = 2.15 Å).[26] Interestingly, the C–Sn bond to the methylene carbon atom (C27) is slightly shorter than to the aryl carbon (C1) hinting at a larger steric strain of the Mes* compared to the Mes′ moiety. Both tin atoms exhibit a distorted tetrahedral environment with rather short N–Sn–N angles (80.0(2)°) and significantly larger Sn–N–Sn′ angles (100.0(2)°).

The amido–azido compound **3** also crystallized in the space group $P\bar{1}$ with two molecules per unit cell (Fig. 2). Although both N–Sn bonds are in the expected range for polarized single bonds, the distance to the amido ligand (Sn1–N1 2.068(2) Å) is slightly shorter than to the azido ligand (Sn1–N2 2.101(2) Å). The amido nitrogen N1 is nearly trigonal-planar coordinated ($\sum\measuredangle$(N1) = 358°), which is typical for $(Me_3Si)_2N$ moieties due to hyperconjugation effects.[20,27–30] As expected for a covalently bonded azide, it exhibits a *trans*-bent arrangement (N2–N3–N4 175.5(3)°, N3–N2–Sn1 122.3(2)°). As in compound **2**, there was an isomerization of one of the Mes* groups leading to a tin bond with one carbon atom of a methylene group (Sn1–C36 2.169(2) Å) besides a bond between the tin and an aryl carbon bond (Sn1–C1 2.167(2) Å). These two different C–Sn bond lengths are equal within the standard deviation.

4a and **4b** could be crystallised from toluene (Fig. 3). While **4a** crystallises in the triclinic space group $P\bar{1}$ with a complete molecule in the asymmetric unit, **4b** crystallises in the monoclinic space group $C2/c$ with only half a molecule in the asymmetric unit. All N–Sn distances are similar for **4a** and **4b**. (**4a:** N1–Sn1 2.044(2) Å, N4–Sn1 2.045(2) Å, N7–Sn1 2.036(2) Å, N8–Sn1 2.028(2) Å; **4b:** N3–Sn1 2.003(1) Å, N1–Sn1 2.062(1) Å) and in the expected range for polarised N–Sn bonds ($\sum r_{cov}$(N–Sn) = 2.11 Å).[26] The structure parameters of the N_4 unit can be used as indicators to determine whether a tetrazenide or a tetrazabutadiene is present in the solid state.[16,17,24,31–37,38,39] It should be noted that there are other spectroscopic methods to distinguish between these forms,[40] but in some cases no unambiguous determination is possible. The most prominent structural feature is the planar 5-membered ring with a formal double bond in the backbone and two formal single bonds, as shown by the comparison of the experimentally determined N–N bond lengths with the sum of the covalent radii (**4a:** N1–N2 1.375(3) Å, N2–N3 1.272(3) Å, N3–N4 1.384(3) Å; **4b:** N1–N2 1.381(2) Å, N2–N2′ 1.264(2) Å, *cf.* $\sum r_{cov}$(N–N) = 1.42 Å; $\sum r_{cov}$(N=N) = 1.20 Å).[26] In this regard, the compounds can be discussed as tetrazastannoles with a formal $Sn^{(IV)}$ (Scheme 7, **A**) rather than tetrazabutadiene complexes with a formal $Sn^{(II)}$ center (Scheme 7, **B**, *vide infra*).



Scheme 7 Lewis representations of tetrazastannole(IV) (**A**) and a tetrazabutadiene tin(II) complex (**B**). Not all ionic representations are shown. Only lone pairs, which are part of the π bonding system within the heterocycle are depicted.

The cyclo-distannadazanes **5a** and **5b** crystallized in monoclinic space groups (Fig. 4). But while **5a** crystallized in $P2_1/n$ with one independent molecule in the asymmetric unit, **5b** crystallized in $C2/c$ with two independent molecules. Both independent molecules show the same structural parameters within the standard deviation. Therefore, only one of the two independent molecules is considered in structure discussions. In the four-membered ring systems of **5a** and **5b**, the N–Sn distances are all equal within the standard deviation (**5a:** Sn1–N1 2.032(2), Sn2–N2 2.039(2), Sn2–N1 2.031(2), Sn2–N2 2.035(2); **5b:** Sn1–N1 2.042(2), Sn1–N2 2.049(2), Sn2–N1 2.043(2), and Sn2–N2 2.046(2) Å). Intriguingly, there is no inversion centre in the middle of the Sn_2N_2 scaffold as in the closely related Mes* compound **3**. This is because the two terphenyl groups are twisted by approximately 90° in both compounds.

In order to better understand the structure and bonding of compounds **2–5** and to determine whether they are formal $Sn^{(II)}$ or $Sn^{(IV)}$ species, in particular compounds **4a** and **4b**, density functional calculations along with NBO analyses (NBO = natural bond analysis)[41–43] were performed at the PBE1PBE/def2svp utilizing the X-ray structural data (single point computations). A summary of selected NBO charges are listed in Table 1. For all considered tin species, NBO analysis finds a Lewis representation with tetravalent tin(IV) atoms as the most favoured Lewis formula. All Sn–N bonds are highly polar and usually only localized with *ca.* 10–15% at the tin atoms. Therefore, a rather large partial charge is found for the tin atoms ranging between +2.0 and +2.3*e*. In accord with our structural data for **4a** and **4b** (*vide supra*), NBO analysis finds as best Lewis representation a structure with four highly polar Sn–N single bonds and one N–N double bond as depicted in formula **A** (Scheme 7), clearly indicating the preference of a tetrazastannole over a tetrazabutadiene complex (**B**). Additionally, a closer look at the delocalisation effects within the SnN_4 5-ring (hyperconjugation), clearly indicates resonance between structures **A**, **C**, and **D** that describes delocalisation of the π bonds within the N_4 frangment (*e.g.* **4a:** $n_{N1} \rightarrow \pi^*_{N2-N3}$ and $n_{N4} \rightarrow \pi^*_{N2-N3}$, E = 50.6 kcal mol^{-1}). Moreover, also ionic resonance (**E**, **F** and **G**) plays an important role, in accord with the electron localization function (Fig. 5) which displays a formal Sn^{4+} center and a $[RNNNNR]^{2-}$ and two $[NR_2]^-$ ligands.

Table 1 Selected NBO data of all tin compounds, partial charges in e, charge of a specific molecular fragment (Q_{frag}) in e[a]

	q(Sn)	q(N1)	q(N2)	q(N3)	q(N4)	Q_{frag}
2	2.10	−1.32	−1.32	—	—	—
3	2.08	−0.70	0.24	−0.18	−1.75	−0.65[b]
4a	2.28	−0.71	−0.06	−0.06	−0.72	−1.16[c]
4b	2.31	−0.69	−0.04	−0.04	−0.69	−1.26[c]
5a	2.03	−1.28	−1.27	—	—	—
5b	2.04	−1.27	−1.26	—	—	—

[a] Only N atoms of the heterocycle are listed. [b] Fragment = azido ligand. [c] Fragment = RNNNNR.

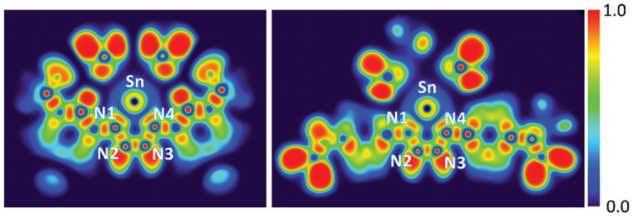


Fig. 5 Two-dimensional cross section through the Sn–N1–N2 plane of the electron localization function (ELF). Left: **4a** and right: **4b**.

Conclusions

In the oxidation reaction of tin(II) compounds with various azides, the nature of the product formed, strongly depends on the tin compound used as starting material. With Mes^*_2Sn several difficulties arose, starting with the isolation of the pure compound and the problem of the isomerization reactions of the Mes* units. The reaction of $Sn[N(SiMe_3)_2]_2$ with two equivalents of aryl azides led, on the one hand, to the formation of the desired five-membered SnN_4 ring system, a tetrazastanole. On the other hand, the same reaction with TerSnCl as the tin(II) source led to the formation of four-membered ring systems, cyclo-distannadiazanes, which contain a Sn_2N_2 skeleton. Regardless of whether the azide was added to the tin compound (local excess of TerSnCl) or whether the tin compound was given to the azide (local excess of azide), the formation of cyclo-distannadiazanes was always observed. The use of only one equivalent of azide in the reaction with TerSnCl is a convenient method for the synthesis of compounds of the type $[TerSn(Cl)NR]_2$ (R = aryl). Since the by-product is N_2, the work-up of the reaction mixture is easily achieved. Furthermore, there is still a chlorine atom present at the tin atom allowing further functionalisation. The bulky terphenyl group at tin is also helpful in the synthesis of highly sensitive compounds. In addition, the electronic situation within the Sn_2N_2 ring can be adjusted by using differently substituted aryl groups. Tetrazastannoles could be easily synthesised from $Sn[N(SiMe_3)_2]_2$ and their use as N_4 transfer reagents has yet to be demonstrated. In particular, we want to test the use of tetrazastannoles in the synthesis of PnN_4 species (Pn = P, As, Sb, Bi) in the future. It could be shown that Me_3SiN_3 is not suitable for the synthesis of tetrazastannoles because the Me_3Si group can migrate easily. This behavior causes a ring-opening reaction and the formation of amido-azido compounds. Although all attempts to generate a BiN_4 heterocycle by using the discussed tetrazastannoles as transfer reagent failed, because of the high kinetic stability of the tetrazastannoles, many new interesting aspects of tin-nitrogen chemistry are reported in this work (see above).

Experimental

All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or

drybox techniques. Full experimental (including the synthesis and full characterization of all starting materials, spectra *etc.*) and computational data are available in the ESI.† ‡

Synthesis of 4a

$Sn[N(SiMe_3)_2]_2$ (1.758 g, 4.00 mmol) was dissolved in toluene (10 mL) and cooled to −40 °C. A solution of **1a** (1.298 g, 8.00 mmol) in toluene (10 mL) was added dropwise, which resulted in an immediate gas evolution. The reaction mixture was stirred in the cold for 45 min and then warmed to room temperature. After stirring the reaction mixture at this temperature for another 45 min, the gas evolution ceased and the solution was filtered (F4). The filtrate was concentrated to induce crystallization. Yield: 1.741 g (2.37 mmol, 59.1%) of **4a** as yellow crystalline needles in three crops.

Mp.: 104 °C (decomp.). **CHN** calc (found) in %: 45.70 (45.362), H 7.67 (6.564), N 15.23 (15.324). **^{1}H NMR** (298.2 K, benzene-d_6, 300.13 MHz): 0.30 (s, 36 H, $^2J\{^1H–^{29}Si\}$ = 6.2 Hz, Si(CH_3)$_3$), 2.52 (s, 12 H, N(CH_3)$_2$), 6.74 (m, 4 H, arom. C*H*), 7.68 (m, 4 H, arom. C*H*). **^{13}C{^{1}H} NMR** (299.0 K, benzene-d_6, 75.48 MHz): 5.8 (s, Si(CH_3)$_3$), 41.2 (s, N(CH_3)$_2$), 114.1 (s, arom. *C*H), 122.9 (s, arom. *C*H), 138.6 (s, arom **C**), 148.3 (s, arom. **C**). **^{29}Si-INEPT NMR** (298.2 K, benzene-d_6, 59.63 MHz): 8.5 (dec, $^2J\{^1H–^{29}Si\}$ = 6.5 Hz, *Si*(CH_3)$_3$). **^{119}Sn{^{1}H} NMR** (298.3 K, benzene-d_6, 111.85 MHz): −215 (s, N_4*Sn*($N(SiMe_3)_2$)$_2$). **IR** (ATR-IR, 32 scans, cm^{-1}): 3074 (w), 3045 (w), 2949 (w), 2893 (w), 2883 (w), 2837 (w), 2791 (w), 1610 (w), 1566 (w), 1510 (s), 1477 (w), 1441 (m), 1406 (w), 1342 (w), 1277 (m), 1265 (m), 1252 (s), 1217 (m), 1188 (w), 1161 (w), 1122 (w), 1057 (w), 1020 (m), 997 (m), 960 (m), 949 (m), 895 (s), 877 (s), 835 (s), 818 (s), 796 (s), 756 (s), 719 (s), 673 (s), 634 (m), 619 (m), 592 (m), 534 (m). Crystals obtained from toluene were suitable for X-ray diffraction. As **4a** was sensitive towards light, no Raman spectra could be collected.

Synthesis of 4b

To a stirred solution of $Sn[N(SiMe_3)_2]_2$ (0.149 g, 0.34 mmol) in toluene (5 mL) was added a solution of **1b** (0.173 g, 0.68 mmol) in toluene (3 mL) dropwise at −40 °C. The golden, clear solution was warmed to room temperature over a period of 30 min (slight gas evolution) and stirred at this temperature for additional 30 min. The reaction mixture was filtered (F4) and concentrated until the crystallization started (*ca.* 3 mL). Fractionated crystallization yielded 0.140 g (0.15 mmol, 44.6%) **4b** as yellowish crystals in two crops. Crystals obtained from toluene were suitable for single crystal diffraction.

Mp.: 181.0 °C. **CHN** calc. (found): C 36.49 (36.353), H 4.59 (4.378), N 9.12 (9.357). **^{1}H NMR** (298.2 K, C_6D_6, 300.13 MHz): 0.07 (s, 36 H, $^2J\{^1H–^{29}Si\}$ = 6.4 Hz, [N(Si(CH_3)$_3$)$_2$]$_2$), 7.52 (m, 2 H, *p*-C*H*), 8.04 (m, 4 H, *o*-C*H*). **^{13}C{^{1}H} NMR** (298.2 K, C_6D_6, 75.47 MHz): 5.4 (s, $^1J\{^{13}C–^{29}Si\}$ = 56.7 Hz), 116.7 (m, *p*-C*H*), 119.4 (m, *o*-C*H*), 124.3 (q, $^1J\{^{13}C–^{19}F\}$ = 273 Hz, CF_3), 133.5 (q, $^2J\{^{13}C–^{19}F\}$ = 33 Hz, *C*CF_3), 148.5 (s, arom. i-**C**). **^{19}F{^{1}H} NMR** (298.2 K, C_6D_6, 282.40 MHz): −62.4 (s, C*F*$_3$). **^{29}Si-INEPT NMR** (298.2 K, C_6D_6, 59.63 MHz): 10.8 (m, *Si*(CH_3)$_3$). **^{119}Sn{^{1}H} NMR** (298.2 K, C_6D_6, 111.92 MHz): −227.5 (s, N_4*Sn*N_2). **IR** (ATR-IR, 32 scans, cm^{-1}): 3104 (w), 2966 (w), 1764 (w), 1620 (w), 1608 (w), 1461 (w), 1420 (w), 1377 (m), 1274 (s), 1253 (s), 1181 (m), 1165 (s), 1140 (m), 1125 (s), 1043 (w), 975 (s), 860 (s), 839 (s), 796 (s), 752 (m), 719 (s), 701 (s), 680 (s), 620 (m), 598 (w), 573 (w), 526 (w), 497 (w), 478 (w), 441 (w), 429 (m). **Raman** (laser: 633 nm, accumulation time: 10 s, 20 scans, cm^{-1}): 3105 (1), 3059 (1), 2976 (1), 2971 (1), 2911 (2), 2645 (1), 2595 (1), 1623 (2), 1611 (3), 1474 (1), 1423 (5), 1385 (4), 1323 (1), 1252 (2), 1184 (1), 1169 (1), 1144 (1), 1134 (1), 1111 (1), 1093 (1), 1042 (2), 999 (10), 896 (1), 875 (1), 845 (1), 800 (1), 754 (1), 729 (1), 682 (4), 672 (1), 638 (2), 619 (1), 597 (1), 526 (1), 497 (1), 428 (1), 391 (1), 362 (1), 354 (1), 342 (2), 321 (1), 286 (1), 254 (1), 225 (1), 202 (1).

Synthesis of 5a

A solution of TerSnCl (0.234 g, 0.50 mmol) in toluene (4 mL) was cooled to −40 °C resulting in an orange suspension. **1a** (0.162 g, 1.00 mmol) was dissolved in toluene (3 mL) and added to the TerSnCl suspension dropwise. The now dark red, clear solution was stirred in the cold for 1 h. After concentration to approximately 1 mL, the solution was stored at +5 °C for 10 h. The supernatant was removed from the precipitate and discarded. The precipitate was washed with *n*-hexane (1 mL) and recrystallized from hot benzene (*ca.* +50 °C). Two crops of crystals yielded 0.080 g (0.06 mmol, 25.0%) of X-ray quality crystals.

Mp.: 228 °C. **CHN** calc. (found) in %: C 63.87 (63.294), H 5.86 (5.638), N 4.65 (4.354). **^{1}H NMR** (298.2 K, thf-d_8, 300.13 MHz): 1.73 (s, 24 H, *o*-CH_3), 2.16 (s, 12 H, *p*-CH_3), 2.88 (s, 12 H, N(CH_3)$_2$), 6.12 (m, 4 H, arom. C*H* from 4-dimethylaminophenyl), 6.31 (m, 4 H, arom. C*H* from 4-dimethylaminophenyl), 6.50 (s, 8 H, $C_6H_2(CH_3)_3$), 6.87 (m, 4 H, *m*-C*H*), 7.30 (s, 3 H, $\frac{1}{2}C_6H_6$), 7.42 (m, 2 H, *p*-C*H*). **^{13}C{^{1}H}-NMR** (298.2 K, thf-d_8, 75.48 MHz): 21.7 (s, *C*H_3), 21.9 (s, *C*H_3), 42.3 (s, N(CH_3)$_2$), 114.9 (arom. *C*H from 4-dimethylaminophenyl), 124.1 (arom. *C*H from 4-dimethylaminophenyl), 129.2 (s, C_6H_6), 129.6 (s, $C_6H_2(CH_3)_3$), 130.8 (s, *m*-*C*H), 132.4 (s, *p*-*C*H), 136.7 (s, arom. **C**), 138.1 (s, arom. **C**), 139.3 (s, arom. **C**), 144.1 (s, arom. **C**), 145.2 (s, arom. **C**), 146.5 (s, arom. **C**), 150.2 (s, arom. **C**). **^{119}Sn{^{1}H}-NMR** (298.2 K, thf-d_8, 111.89 MHz): −151 (s, N_2*Sn*$_2$(Cl)$_2$Ter$_2$). **IR** (ATR-IR, 32 scans, cm^{-1}): 3088 (w), 3059 (w), 3018 (w), 2974 (w), 2947 (w), 2912 (m), 2875 (w), 2850 (w), 2831 (w), 2785 (w), 2733 (w), 1610 (w), 1568 (w), 1502 (s), 1477 (m), 1444 (s), 1377 (m), 1325 (w), 1315 (w), 1294 (w), 1263 (s), 1209 (m), 1180 (m), 1161 (m), 1132 (m), 1088 (w), 1055 (m), 1032 (m), 1011 (w), 987 (w), 945 (m), 912 (w), 881 (s), 847 (s), 810 (s), 802 (s), 775 (m), 731 (s), 704 (m), 692 (s), 679 (s), 625 (m), 590 (m), 573 (m), 548 (m). **Raman** (633 nm, accumulation time: 20 s, 10 scans, cm^{-1}): 3066 (1), 3043 (1), 2914 (2), 2855 (1), 2834 (1), 2821 (1), 2788 (1), 2734 (1), 1607 (3), 1508 (1), 1479 (1), 1441 (1), 1395 (1), 1382 (1), 1328 (1), 1303 (3), 1291 (3), 1265 (1),

‡ Experimental and spectral data, as well as crystallographic data are given in the ESI.†

1230 (1), 1193 (2), 1179 (1), 1162 (1), 1133 (1), 1100 (2), 1011 (1), 1003 (1), 990 (1), 943 (6), 804 (0), 739 (6), 701 (1), 663 (1), 621 (1), 575 (4), 557 (6), 521 (1), 509 (1), 502 (1), 475 (1), 464 (1), 422 (1), 417 (1), 337 (2), 220 (10).

Synthesis of 5b

To a stirred solution of TerSnCl (0.234 g, 0.50 mmol) in toluene (3 mL) was added a solution of **1b** (c = 0.2 M, V = 1 mL, 1.00 mmol) in toluene dropwise at −40 °C. The resulting clear, yellow solution was stirred for 1 h (gas evolution) in the cold and warmed to room temperature afterward. The solvent was removed *in vacuo* and recrystallization from a minimum amount of hot benzene resulted in the deposition of pale-yellow to colorless crystals of **5b** (0.165 g, 0.09 mmol, 37.5%).

Mp.: 315 °C (decom.). **CHN** calc. (found): C 55.32 (55.437), H 4.06 (3.834), N 2.02 (2.647). **^{1}H NMR** (298.2 K, thf-d_8, 300.13 MHz): 1.72 (s, 24 H, *o*-C$\boldsymbol{H}_3$), 2.13 (s, 12 H, *p*-C$\boldsymbol{H}_3$), 6.57 (s, 8 H, $C_6\boldsymbol{H}_2(CH_3)_3$), 6.79 (broad, 4 H, *o*-$C_6\boldsymbol{H}_3(CF_3)_2$), 6.96 (m, 4 H, m-C***H***), 7.28 (broad, 2 H, *p*-$C_6\boldsymbol{H}_3(CF_3)_2$), 7.55 (m, 2 H, *p*-C***H***). **^{13}C{^{1}H} NMR** (298.2 K, thf-d_8, 75.47 MHz): 20.9 (s, *o*-***C***H_3), 21.7 (s, *p*-***C***H_3), 114.1 (s, *p*-$\boldsymbol{C}_6H_3(CF_3)_2$), 122.4 (s, *o*-$\boldsymbol{C}_6H_3(CF_3)_2$), 124.8 (q, $^1J\{^{13}C\text{-}^{19}F\}$ = 272 Hz, ***C***F_3), 129.9 (arom. ***C***H), 131.6 (s, *p*-***C***H), 132.3 (q, $^2J\{^{13}C\text{-}^{19}F\}$ = 32 Hz, **C**(CF_3)), 134.1 (s, arom. **C**), 137.0 (s, arom. **C**), 138.6 (arom. **C**), 139.2 (arom. **C**), 141.6 (arom. **C**), 150.0 (s, arom. **C**), 154.3 (s, arom. **C**). **^{19}F{^{1}H} NMR** (298.2 K, thf-d_8, 282.40 MHz): −65.4 (s, C***F***$_3$). **^{119}Sn{^{1}H} NMR** (298.2 K, thf-d_8, 111.92 MHz): −144.4 (s, $N_4\boldsymbol{Sn}N_2$). **IR** (ATR-IR, 32 scans, cm^{-1}): 3030 (w), 2982 (w), 2951 (w), 2920 (w), 2856 (w), 2737 (w), 1610 (w), 1601 (w), 1568 (w), 1462 (m), 1448 (m), 1363 (s), 1271 (s), 1171 (s), 1124 (s), 1032 (w), 997 (m), 966 (s), 912 (w), 870 (m), 849 (s), 804 (m), 769 (w), 735 (s), 723 (s), 698 (s), 679 (s), 640 (m), 625 (w), 596 (m), 573 (m), 548 (w). **Raman** (laser: 633 nm, accumulation time: 10 s, 20 scans, cm^{-1}): 3122 (1), 3083 (1), 3065 (1), 3040 (1), 3016 (1), 2922 (2), 2859 (1), 2737 (1), 1613 (1), 1563 (1), 1486 (1), 1441 (1), 1383 (2), 1306 (3), 1286 (1), 1273 (1), 1228 (1), 1181 (1), 1168 (1), 1109 (1), 1100 (1), 1011 (1), 1002 (3), 947 (1), 742 (1), 705 (1), 661 (3), 576 (3), 560 (2), 523 (1), 504 (1), 466 (1), 424 (1), 420 (1), 405 (1), 353 (2), 348 (3), 284 (1), 221 (10), 192 (1), 170 (2), 142 (4), 123 (3).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the University of Rostock for financial support.

Notes and references

1 A. Villinger, P. Mayer and A. Schulz, *Chem. Commun.*, 2006, 1236–1238.
2 A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2008, **47**, 603–606.
3 M. Kuprat, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2013, **52**, 7126–7130.
4 M. Lehmann, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2011, **50**, 5221–5224.
5 C. Hering-Junghans, M. Thomas, A. Villinger and A. Schulz, *Chem. – Eur. J.*, 2015, **21**, 6713–6717.
6 C. Hering-Junghans, A. Schulz, M. Thomas and A. Villinger, *Dalton Trans.*, 2016, 6053–6059.
7 J. Bresien, C. Hering-Junghans, A. Schulz, M. Thomas and A. Villinger, *Organometallics*, 2018, **37**, 2571–2580.
8 A. Schulz, M. Thomas and A. Villinger, *Z. Anorg. Allg. Chem.*, 2017, **643**, 1406–1414.
9 M. Veith and B. Bertsch, *Z. Anorg. Allg. Chem.*, 1988, **557**, 7–22.
10 M. Veith, B. Bertsch and V. Huch, *Z. Anorg. Allg. Chem.*, 1988, **559**, 73–88.
11 K. Jones and M. F. Lappert, *J. Organomet. Chem.*, 1965, **3**, 295–307.
12 A. Kendrick, H. Nöth, B. Stalla and W. Storch, *J. Chem. Soc., Dalton Trans.*, 1989, 1311–1319.
13 T. Gasparis, H. Nöth and W. Storch, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 326–327.
14 W. Storch and H. Nöth, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 235–236.
15 B. Margaret and R. Knox, *Chem. Commun.*, 1967, 1243–1244.
16 W. C. Trogler, *Acc. Chem. Res.*, 1990, **23**, 426–431.
17 P. Overbosch, G. van Koten and O. Overbeek, *J. Am. Chem. Soc.*, 1980, **102**, 2091–2093.
18 U. Fooken, W. Saak and M. Weidenbruch, *J. Organomet. Chem.*, 1999, **579**, 280–284.
19 G. Ossig, A. Meller, S. Freitag and R. Herbst-lrmer, *J. Chem. Soc., Chem. Commun.*, 1993, 497–499.
20 P. Svec, Z. Padelkova, M. Alonso, F. De Proft and A. Ruzicka, *Can. J. Chem.*, 2014, **92**, 434–440.
21 N. Wiberg and S.-K. Vasisht, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 93–95.
22 H. Grützmacher and H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1017–1018.
23 K. E. Meyer, P. J. Walsh and R. G. Bergman, *J. Am. Chem. Soc.*, 1995, **117**, 974–985.
24 P. Yang, E. Zhou, B. Fang, G. Hou, G. Zi and M. D. Walter, *Organometallics*, 2016, **35**, 2129–2139.
25 R. S. Simons, L. Pu, M. M. Olmstead and P. P. Power, *Organometallics*, 1997, **16**, 1920–1925.
26 P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 12770–12779.
27 J. Bresien, C. Hering-Junghans, P. Kumm, A. Schulz, M. Thomas and A. Villinger, *Eur. J. Inorg. Chem.*, 2018, **018**, 647–651.
28 W. Baumann, D. Michalik, F. Reiß, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2014, **53**, 3250–3253.
29 W. Baumann, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2008, **47**, 9530–9532.

30 T. Ochiai, D. Franz, E. Irran and S. Inoue, *Chem. – Eur. J.*, 2015, **21**, 6704–6707.
31 G. A. Miller, S. W. Lee and W. C. Trogler, *Organometallics*, 1989, **8**, 738–744.
32 J. Ashley-Smith, M. Green and A. Stone, *J. Chem. Soc., Dalton Trans.*, 1972, 1805–1809.
33 J. Risse, R. Scopelliti and K. Severin, *Organometallics*, 2011, **30**, 3412–3418.
34 G. Albertin, S. Antoniutti, A. Bacchi and A. Celebrin, *Dalton Trans.*, 2007, 661–668.
35 P. Overbosch, G. van Koten, D. M. Grove, A. L. Spek and A. J. M. Duisenberg, *Inorg. Chem.*, 1982, **21**, 3253–3260.
36 F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham and D. Sutton, *J. Am. Chem. Soc.*, 1971, **93**, 1826–1827.
37 D. Sutton, *Inorg. Chem.*, 1972, **11**, 2827–2831.
38 R. J. J. Doedens, *Chem. Commun.*, 1968, 1271–1272.
39 A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1996, **6133**, 3771–3778.
40 M. J. Maroney and W. C. Trogler, *J. Am. Chem. Soc.*, 1984, **106**, 4144–4151.
41 A. E. Reed, L. a. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
42 F. Weinhold, C. R. Landis and E. D. Glendening, *Int. Rev. Phys. Chem.*, 2016, **35**, 399–440.
43 E. D. Glendening, C. R. Landis and F. Weinhold, *J. Comput. Chem.*, 2013, **34**, 1429–1437.