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A neutral low-coordinate heterocyclic bismuth-tin species†

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The reaction of distannadiazane bearing bulky ^{R}Ar*-groups (^{R}Ar* = $C_6H_2\{C(H)Ph_2\}_2R$-2,6,4; R = iPr, *t*Bu) with ECl_3 (E = Sb, Bi) was studied resulting in the isolation of previously unknown *N,N*-bis-(dichloropnictino)amines (3) and a novel heterocyclic carbenoid bismuth species (4) bearing a $Bi^{(III)}$ and a $Sn^{(IV)}$ center. The structure and bonding was investigated by means of X-ray structure elucidations and DFT calculations.

Pnictogen–nitrogen heterocycles of the type $[XE(\mu\text{-}NR)]_2$ (E = P, As, Sb, Bi; species I in Fig. 1) are valuable starting materials for preparative E–N chemistry.[1] Usually, $[ClE(\mu\text{-}NR)]_2$ (E = P, As) is prepared from $RN(ECl_2)H$ in a base-assisted (*e.g.* NEt_3) cyclization,[2] however, for the heavier analogs this strategy works poorly. For example, $[ClBi(\mu\text{-}NTer)]_2$ (Ter = terphenyl = 2,6-bis-(2,4,6-trimethylphenyl)phenyl) was initially obtained in moderate yields of 45% besides large amounts of $ClBi(N(H)Ter)_2$.[3] In analogy to Veith's synthesis of $[Me_2SiE(\mu\text{-}NtBu)_2]^+$ (II in Fig. 1),[4] our group succeeded in establishing a straightforward route towards the synthesis of $[ClE(\mu\text{-}NTer)]_2$ (E = Sb, Bi), based on the *trans*-metalation of the respective tin precursor.[5] Now highly reactive *cyclo*-1,3-dipnicta-2,4-diazenium salts of the type $[E(ClE)(\mu\text{-}NTer)_2]^+$ (E = P, As,[6] Sb, Bi;[5] III in Fig. 1) can be obtained by chloride abstraction from $[ClE(\mu\text{-}NTer)]_2$ by means of Lewis acids such as $GaCl_3$. A new area of research opened up with the isolation of thermally stable biradicaloids of the type $[E(\mu\text{-}NTer)]_2$ (E = P, As; IV in Fig. 1) which can easily be accessed by reduction of $[ClE(\mu\text{-}NTer)]_2$ with activated magnesium chips.[7]

Just recently, we described the synthesis of stable acyclic chloropnictenium ion salts, with an exceedingly bulky ^{R}Ar*-group (Ar* = $C_6H_2\{C(H)Ph_2\}_2R$-2,6,4; R = Me, *t*Bu) attached to the nitrogen atom.[8] This sterically demanding moiety offers two flanking phenyl groups for arene-interactions with the low-coordinate reactive site of the molecules. Jones and co-workers realized new bonding situations with the aid of the ^{R}Ar*-moiety,[9] such as mono-coordinate Ge or Sn cations,[10] singly bonded distannyene and Ge and Sn hydride complexes,[11,12] that showed magnificent activity as a catalyst in hydroboration reactions.[13] Just recently, the first example of an amido-distibene in $[^{iPr}Ar*N(SiiPr_3)Sb]_2$ was reported.[14] Herein we describe the synthesis of an unprecedented distannadiazane $[Sn(\mu\text{-}N^{R}Ar*)]_2$ with a planar N_2Sn_2-core and its *trans*-metalation with ECl_3 (E = Sb, Bi), resulting in the isolation of the first *N,N*-bis(dichlorostibino)amine and an elusive four-membered ring system with a $N_2Bi^{(III)}Sn^{(IV)}$ unit.

In analogy to a procedure described by Power *et al.*, leading to the first isolable distannadiazane $[Sn(\mu\text{-}NTer)]_2$,[15] the exceedingly bulky amine ^{tBu}Ar*NH_2 and $Sn\{N(SiMe_3)_2\}_2$ were combined in a Schlenk flask without solvent and heated to 160 °C over a period of 45 min, affording a deep red solid. $HN(SiMe_3)_2$ and excess $Sn\{N(SiMe_3)_2\}_2$ were removed *in vacuo* and the crude product was recrystallized from C_6H_5F to obtain red crystals of $[Sn(\mu\text{-}N^{tBu}Ar*)]_2$ (**1R**, R = *t*Bu) in moderate yields (64%). The synthesis of **1Me** and **1iPr** suffered from low solubility of the products in common organic solvents, however, minimal amounts of X-ray quality crystals of **1iPr** were obtained from C_6H_6. In the ^{13}C and ^{1}H NMR spectrum **1iPr** and **1*t*Bu** can be easily identified by the signals of the *para*-substituent of the inner phenyl group and their diagnostic ^{119}Sn NMR shifts

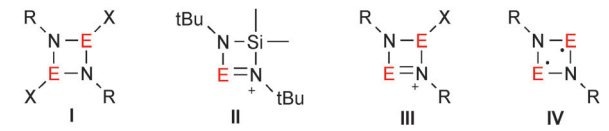

Fig. 1 Selected known four-membered E–N heterocycles.[4–7]

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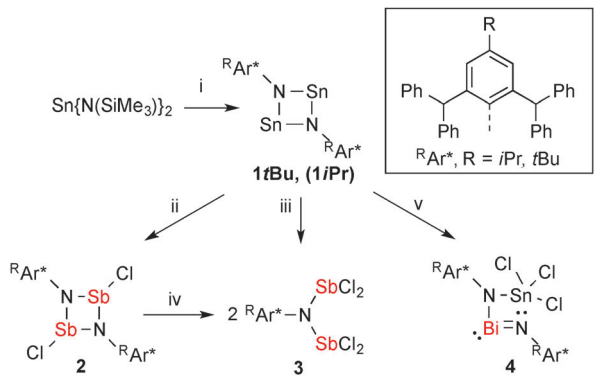
(**1iPr** 783.1 ppm, **1*t*Bu** 789.2 ppm; *cf.* [Sn(μ-NTer)]$_2$ 738.9 ppm). **1iPr** and **1*t*Bu** crystallize as solvates of C_6H_6 or C_6H_5F (see Fig. S1 and S4 in the ESI†), respectively, in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit, which lies on a crystallographically imposed centre of inversion. In contrast to [Sn(μ-NTer)]$_2$, in which the Sn_2N_2 ring is characterized by a folding about the Sn···Sn axis of 148°, the Sn_2N_2-core is planar with slightly different N1–Sn1 and N1′–Sn1′ distances (**1iPr** 2.076(2), 2.086(2); **1*t*Bu** 2.075(2), 2.090(2) Å; *cf.* [Sn(μ-NTer)]$_2$ 2.09, 2.11 Å), a transannular Sn1···Sn1′ separation of 3.2304(4) (**1iPr**) and 3.2318(3) Å (**1*t*Bu**) and rather acute angles at the tin center (**1iPr** 78.27(7), **1*t*Bu** 78.22(6)°, *cf.* [Sn(μ-NTer)]$_2$ 77.6°).[15] The nitrogen atoms are in a planar environment as expected for a formal sp^2-hybridized center with a p-type lone pair (LP) of electrons. Hence, the planarity of the core is imposed by the increasing bulkiness of the *t*BuAr*-moieties, as a bend core would result in pyramidalization about the N atoms to fit both ^{R}Ar*-groups in. Just recently, the bonding in [E(μ-NTer)]$_2$ (E = Ge, Sn, Pb) was studied in detail by Ziegler *et al.*, who analysed the interaction of the monomeric units E(μ-NTer) in the dimeric structure, with the result that the dimer is kept together by two σ- and π-bonds.[16]

Combining red **1*t*Bu** with two equivalents of $SbCl_3$ in CH_2Cl_2 resulted in an immediate decolourisation, accompanied by a colourless precipitate (Scheme 1, reaction (ii)), which was removed by filtration and from the filtrate X-ray quality crystals of *trans*-[ClSb(μ-NTer)]$_2$ (**2**) were grown overnight at room temperature. This metathesis route gives **2** reproducibly in good yields, while using the elimination of $SnCl_2$ as the driving force, which dates back to the seminal work of Veith,[17] who established this route to prepare [$Me_2SiECl(\mu\text{-}N\textit{t}Bu)_2$] ring systems (*vide supra*, Fig. 1 species II).[18]

Pale yellow crystals of **2** are moisture-sensitive, but indefinitely stable in an inert gas atmosphere and can be heated above 270 °C without decomposition. **2** crystallizes solvent-free in the triclinic space group $P\bar{1}$ with one molecule in the unit cell and displays a *trans*-substituted centrosymmetric dimer with a planar Sb_2N_2 core protected by two bulky ^{tBu}Ar* groups similar to the molecular structures of [XSb(μ-NMes*)]$_2$ X = F, Cl, Br, I; *trans*-[ClSb(μ-N*t*Bu)]$_2$.[19,20] As expected the Sb atoms are trigonal



Scheme 1 Preparation of **1R-4**: (i) 2 ^{R}Ar*NH$_2$, −2 HN(SiMe$_3$)$_2$, (ii) 2 SbCl$_3$, −2 SnCl$_2$, (iii) 4 SbCl$_3$, −2 SnCl$_2$, (iv) 2 SbCl$_3$, and (v) BiCl$_3$, −Sn.

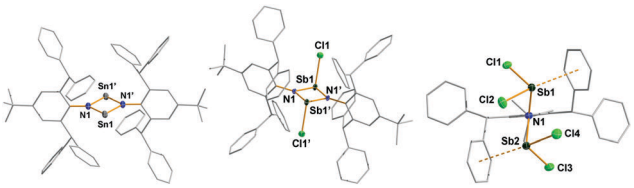


Fig. 2 Molecular structures of **1*t*Bu** (left), **2** (middle) and **3** (right). Thermal ellipsoids drawn at 50% probability and −100 °C. ^{tBu}Ar* substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°) of **1*t*Bu**: Sn1–N1 2.0752(16), 2.0897(16); N1–Sn1–N1′ 78.22(6); **2**: Sb1–N1 2.033(2), Sb1–N1′ 2.034(2), Sb1–Cl1 2.4327(7), Sb1Sb1 3.1749(3), N1–C1 1.430(3) Å, ∑(<Sb) 273.05; ∑(<N) 359.83, C1–C2–N1–Sb1 77.6(2); **3**: Sb1–N1 2.030(2), Sb1–Cl1 2.3709(7), Sb1–Cl2 2.4338(7), Sb2–N1 2.039(2), Sb2–Cl3 2.3731(7), Sb2–Cl4 2.4199(7), N1–C1 1.434(3), ∑(<Sb1) 280.08, ∑(<Sb2) 281.47, Sb1–N1–C1–C6 80.0(2).

pyramidally coordinated, with an s-type LP located on Sb and a trigonal planar coordination environment about the N atom. Additionally, one rather weak dipolar interaction between Sb and a flanking phenyl group (Sb···C$_{Ct}$ = 3.29 Å, C$_{Ct}$ = centroid) is detected (Fig. 2, left).[21] The formation of **2** can be reproduced, however, if an excess of $SbCl_3$ is used, a new product ^{tBu}Ar*N(SbCl$_2$)$_2$ (**3**) was isolated. Consequently, we reasoned that **3** was accessible directly from **1*t*Bu** (reaction (iii) in Scheme 1) when combined with four equiv. of $SbCl_3$, which yielded pure **3**. Moreover, treatment of **2** with two additional equiv. of $SbCl_3$ also afforded (reaction (iv) in Scheme 1) **3** in good yields (78%). **3** is thermally stable and melts without decomposition at 236 °C and also shows distinct ^{1}H NMR shifts for the *p*-*t*Bu, the CHPh$_2$ and the inner phenyl H atoms. Furthermore, **3** belongs to the family of *N*,*N*-bis(dichloropnictino)amines, which are well documented for phosphorus (RN(PCl$_2$)$_2$, R = Dipp, Trip, Ph).[2] Compound **3** was found to be monoclinic ($P2_1/n$) with one molecule of **3** and two disordered C_6H_5F solvents molecules in the asymmetric unit. The Sb–N distances of 2.030(2) and 2.039(2) Å are shorter than the sum of the covalent radii for Sb and N (*cf.* $\sum r_{cov}$(N–Sb) = 2.11 Å)[22] representing highly polarized Sb–N single bonds. The trigonal planar N atom lies between both pyramidal $SbCl_2$ units, which adopt a *trans* configuration with respect to the $SbCl_2$ moieties (Fig. 2 right). Interestingly, two intramolecular Sb···Cl contacts (Sb1···Cl4, Sb2···Cl2 *ca.* 3.35 Å; *cf.* $\sum r_{vdW}$(N–Sb) = 3.81 Å),[23] stabilizing this *trans* configuration, but no intermolecular contacts are observed.

In addition, the reaction of **1*t*Bu** with two equiv. of $BiCl_3$ was studied in CH_2Cl_2, resulting in a black reaction mixture (reaction (v) in Scheme 1). After multiple filtrations a clear orange solution was obtained. Recrystallization yielded small amounts of orange crystals that were identified as the hitherto unknown [BiSnCl$_3$(μ-N$^{t\text{Bu}}$Ar*)$_2$] (**4**). The black residue could not be conclusively identified and we assume that elemental tin is formed in a complex redox process that might also involve the formation of elemental bismuth (*vide infra*). It has been shown before that the Sn(II) center in [Me_2SiSn(μ-N*t*Bu)$_2$] acts as a chloride acceptor in the coupling of phosphaalkenes[24] and in the reaction with chlorophosphanes.[25]

Revision of the reaction conditions prompted us to repeat the experiment in C_6H_5F with one equivalent of $BiCl_3$

(with respect to **1*t*Bu**), to exclude a chloride-shift from CH_2Cl_2. This again resulted after filtration over a celite-padded frit and concentration of the filtrate in the deposition of orange crystals of **4** as a C_6H_5F solvate. Only small amounts of pure **4** could be isolated, therefore we cannot provide a comprehensive characterization. Nevertheless, the ^{119}Sn NMR spectrum of these isolated crystals revealed a signal at 115.5 ppm (Fig. S13, ESI†), which is in the expected range for a hypercoordinate $N_2Sn^{(IV)}Cl_3$ moiety (*cf.* $Me_3SnCl_2^-$: 47.7, $Me_2SnCl_3^-$: 128 ppm, $MeSnCl_4^-$: 274 ppm).[26] It should be noted that ^{119}Sn NMR data strongly depend on substitution, coordination number and solvent giving rise to large chemical shift differences (*cf.* [$SnCl_3${κ^2-DippN(H)C_2H_4N(Dipp)}] −303 ppm).[27] According to MO and NBO analyses of the truncated model [$BiSnCl_3(\mu$-NPh)$_2$], **4** can either be described as zwitterionic bismaallyl species (Lewis representation A/C in Fig. 4), as a bismuthenium species (E) or as an iminobismutane (B and D), and therefore represents the first neutral compound with a **4e–3c** double bond delocalized along N–Bi–N (Fig. 4). In addition, an s-type lone pair (93%, see Fig. S14 and S15, ESI†) is located at the Bi center. Lewis representations A/C represent the best Lewis structures according to NBO analysis. Along with structures of type E/F, which also possess a rather large weight, since the π bonds are dominantly located at the N atoms (81%), this situation resembles that of N-heterocyclic carbenes (NHC),[28] which are stabilized by intramolecular π-donor–π-acceptor interactions (population of the p_z(Bi) = 0.47e) to stabilize the dicoordinate carbene C atom. It should be noted that also Bi–N σ bonds (78%) are highly polar, as well as the Sn–Cl or Sn–N bonds (N, Cl: *ca.* 80%). The computed large positive charges at the Bi and Sn centers are very similar with values of +1.67 and 1.77e supporting the picture of highly polarized Bi–N and Sn–Y (Y = Cl, N) bonds.

4 crystallizes as CH_2Cl_2 solvate (**4**·$(CH_2Cl_2)_2$) in the triclinic space group $P\bar{1}$ with two molecules of **4** and four CH_2Cl_2 molecules (disordered on their positions) in the cell. Moreover, from C_6H_5F species **4** crystallizes as a solvate of fluorobenzene solvate (**4**·C_6H_5F) in the orthorhombic space group $Pna2_1$ (the discussion is led for **4**·CH_2Cl_2). The most prominent structural feature is the planar 4-membered Sn–N–Bi–N heterocycle featuring two different heavy main group metals (deviation from planarity < 2.3°, Fig. 3). Both Bi–N bond lengths are rather short with 2.106(3) and 2.108(3) Å (*cf.* $\sum r_{cov}$(N–Bi) = 2.22, (N═Bi) = 2.01 Å;[22] [$Me_2SiBi(\mu$-N*t*Bu)$_2$]$^+$ 2.08 Å, [Bi(IBi)(μ-NTer)$_2$]$^+$ 2.13 Å, and [$Me_2SiBi(\mu$-NDipp)$_2$] 2.12 Å, where Dipp = 2,6-$iPrC_6H_3$)[4,5,29] clearly displaying some Bi–N double bond character in accord with our computation (Fig. 4). Interestingly, both Sn–N bond lengths (2.094(3) and 2.107(3) Å, *cf.* $\sum r_{cov}$(N–Sn) = 2.11, (N═Sn) = 1.90 Å) are in the similar range like the Bi–N distances, however, describing typical highly polarized $Sn^{(IV)}$–N single bonds. Both the N–Bi–N angle and N–Sn–N angles are rather acute with *ca.* 78° (*cf.* [$Me_2SiBi(\mu$-N*t*Bu)$_2$]$^+$ 72.9, [Bi(IBi)(μ-NTer)$_2$]$^+$ 77.4°, and [$Me_2SiBi(\mu$-NDipp)$_2$]$^+$ 73.7),[4,5,29] while the two Bi–N–Sn angles are much larger with 101–102°. A closer look at the secondary interactions revealed that the Sn–N–Bi–N heterocycle is well protected inside the pocket formed by the two $^{t\mathrm{Bu}}$Ar*-phenyl substituents. However, the dicoordinate bismuth is stabilized by strong secondary interactions (Menshutkin type π complexes)[21]

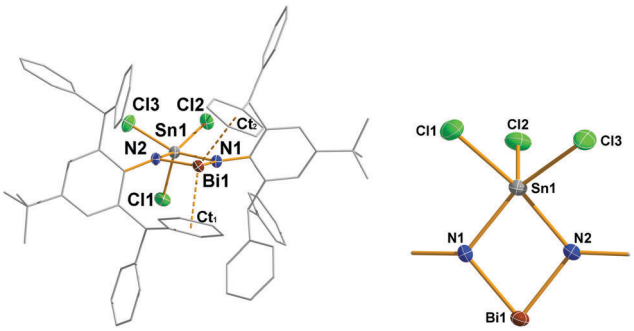


Fig. 3 Molecular structures of **4**. Thermal ellipsoids drawn at 50% probability and −100 °C. $^{t\mathrm{Bu}}$Ar* substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths (Å) and angles (°) of **4**: Sn1–N1 2.094(3), Sn1–N2 2.107(3), Sn1–Cl1 2.353(1), Sn1–Cl3 2.387(1), Sn1–Cl2 2.403(1), Sn1···Bi1 3.2631(4), Bi1–N1 2.106(3), Bi1–N2 2.108(3), N1–C37 1.425(5), N2–C1 1.426(5), N1–Sn1–N2 78.41(12), N1–Bi1–N2 78.10(12), ∑(<N1) 358.0, ∑(<N2) 353.4, Bi1–C_{Ct_1} 2.891, Bi1–C_{Ct_2} 2.978 Å.

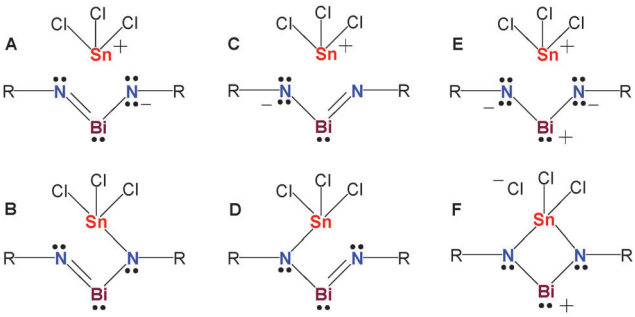


Fig. 4 Selected Lewis representations of **4**.

with two phenyl groups as indicated by very short Bi···centroid distances (2.891/2.978 Å; *cf.* [$^{\mathrm{Me}}$Ar*N($SiMe_3$)BiCl][$Al(OR^F)_4$]$^+$ 2.86/2.94 Å)[8] which are well within the range of van-der-Waals radii ($\sum r_{vdW}$(C···Bi) = 3.77 Å).[23]

In conclusion, we succeeded in the preparation of the first *N*,*N*′-bis(dichlorostibinino)amine and an unusual heterocycle containing $Sn^{(IV)}$ and a dicoordinate Bi-center, which is protected by arene-interactions to flanking phenyl groups of the bulky Ar* moiety. These species might be useful starting materials for the preparation of pnictadiazonium salts of Sb and Bi. In comparison to stable N-heterocyclic carbenes,[28] the dicoordinated Bi species **4** can be regarded as a heavy atom analog of NHCs.

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Notes and references

1 (*a*) G. He, O. Shynkaruk, M. W. Lui and E. Rivard, *Chem. Rev.*, 2014, **44**, 7815–7880; (*b*) M. S. Balakrishna, D. J. Eisler and T. Chivers, *Chem. Soc. Rev.*, 2007, **36**, 650–664.
2 (*a*) F. Reiß, A. Schulz, A. Villinger and N. Weding, *Dalton Trans.*, 2010, **39**, 9962; (*b*) C. Ganesamoorthy, M. S. Balakrishna, J. T. Mague and H. M. Tuononen, *Inorg. Chem.*, 2008, **47**, 7035–7047; (*c*) N. Burford, C. T. Stanley, K. D. Conroy, B. Ellis, C. L. B. MacDonald, R. Ovans,

A. D. Phillips, P. Ragogna and D. Walsh, *Can. J. Chem.*, 2002, **80**, 1404–1409; (*d*) V. D. Romanenko, A. B. Drapailo, A. N. Chernega and L. N. Markovskii, *Zh. Obshch. Khim.*, 1991, **61**, 2434–2441; (*e*) S. Goldschmidt and H.-L. Krauß, *Liebigs Ann. Chem.*, 1955, **595**, 193–202.
3 D. Michalik, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2010, **46**, 7575–7577 (*Angew. Chem.*, 2010, **122**, 7737–7740).
4 M. Veith, B. Bertsch and V. Huch, *Z. Anorg. Allg. Chem.*, 1988, **559**, 73–88.
5 M. Lehmann, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2012, **51**, 8087–8091 (*Angew. Chem.*, 2012, **124**, 8211–8215).
6 (*a*) D. Michalik, A. Schulz, A. Villinger and N. Weding, *Angew. Chem., Int. Ed.*, 2008, **47**, 6465–6468 (*Angew. Chem.*, 2008, **120**, 6565–6568); (*b*) A. Schulz and A. Villinger, *Inorg. Chem.*, 2009, **48**, 7359–7367.
7 (*a*) T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2011, **50**, 8974–8978 (*Angew. Chem.*, 2011, **123**, 9136–9140); (*b*) S. Demeshko, C. Godemann, R. Kuzora, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2013, **52**, 2105–2108 (*Angew. Chem.*, 2013, **125**, 2159–2162); (*c*) A. Hinz, A. Schulz and A. Villinger, *Chem. – Eur. J.*, 2014, **20**, 3913–3916; (*d*) A. Hinz, R. Kuzora, A. Schulz and A. Villinger, *Chem. – Eur. J.*, 2014, **20**, 14659–16673; (*e*) A. Hinz, A. Schulz and A. Villinger, *Chem. Commun.*, 2015, **51**, 1363–1366.
8 C. Hering-Junghans, M. Thomas, A. Schulz and A. Villinger, *Chem. – Eur. J.*, 2015, **21**, 6713–6717.
9 J. Li, A. Stasch, C. Schenk and C. Jones, *Dalton Trans.*, 2011, **40**, 10448–10456.
10 J. Li, C. Schenk, F. Winter, H. Scherer, N. Trapp, A. Higelin, S. Keller, R. Pöttgen, I. Krossing and C. Jones, *Angew. Chem., Int. Ed.*, 2012, **51**, 9557–9561 (*Angew. Chem.*, 2012, **124**, 9695–9699).
11 J. Li, C. Schenk, C. Goedecke, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, 2011, **133**, 18622–18625.
12 T. J. Hadlington and C. Jones, *Chem. Commun.*, 2014, **50**, 2321.
13 (*a*) T. J. Hadlington, M. Hermann, J. Li, G. Frenking and C. Jones, *Angew. Chem., Int. Ed.*, 2013, **52**, 10199–10203 (*Angew. Chem.*, 2013, **125**, 10389–10393); (*b*) T. J. Hadlington, M. Hermann, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, 2014, **136**, 3028–3031.
14 D. Dange, A. Davey, J. A. B. Abdalla, S. Aldridge and C. Jones, *Chem. Commun.*, 2015, **51**, 7128–7131.
15 W. A. Merrill, R. J. Wright, C. S. Stanciu, M. M. Olmstead, J. C. Fettinger and P. P. Power, *Inorg. Chem.*, 2010, **49**, 7097–7105.
16 M. Brela, A. Michalak, P. P. Power and T. Ziegler, *Inorg. Chem.*, 2014, **53**, 2325–2332.
17 M. Veith, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 265–266 (*Angew. Chem.*, 1975, **87**, 287–288).
18 M. Veith and B. Bertsch, *Z. Anorg. Allg. Chem.*, 1988, **557**, 7–22.
19 M. Lehmann, A. Schulz and A. Villinger, *Eur. J. Inorg. Chem.*, 2010, 5501–5508.
20 D. J. Eisler and T. Chivers, *Inorg. Chem.*, 2006, **45**, 10734–10742.
21 H. Schmidbaur and A. Schier, *Organometallics*, 2008, **27**, 2361–2395.
22 P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 12770–12779.
23 M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. A*, 2009, **113**, 5806–5812.
24 E. Niecke, H. J. Metternich and R. Streubel, *Eur. J. Inorg. Chem.*, 1990, 67–69.
25 J. K. West and L. Stahl, *Organometallics*, 2012, **31**, 2042–2052.
26 (*a*) P. J. Smith and A. P. Tupciauskas, *Annu. Rep. NMR Spectrosc.*, 1978, **8**, 291; (*b*) G. F. Hewitson, Master thesis, Durham University, 1980; (*c*) J. Ortera, *J. Org. Chem.*, 1981, **221**, 57.
27 S. M. Mansell, C. A. Russell and D. F. Wass, *Dalton Trans.*, 2015, **44**, 9756–9765.
28 (*a*) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39–92; (*b*) N. Marion and S. P. Nolan, *Acc. Chem. Res.*, 2008, **41**, 1440–1449; (*c*) D. Bézier, J.-B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2013, **355**, 19–33.
29 R. J. Schwamm, B. M. Day, M. P. Coles and C. M. Fitchett, *Inorg. Chem.*, 2014, **53**, 3778.