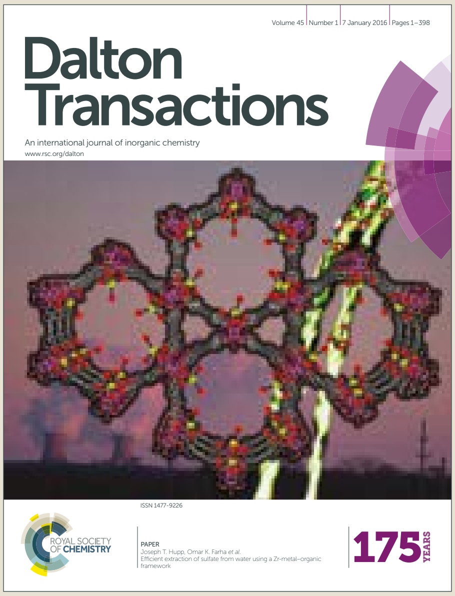
Check for updates

View Article Online
View Journal

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: N. Parvin, R. Dasgupta, S. Pal, S. S. Sen and S. Khan*, Dalton Trans.*, 2017, DOI: 10.1039/C7DT01055A.



Volume 45 | Number 1 | 7 January 2016 | Pages 1–398

Dalton Transactions

An international journal of inorganic chemistry
www.rsc.org/dalton

ISSN 1477-9226

ROYAL SOCIETY OF CHEMISTRY

PAPER
Joseph T. Hupp, Omar K. Farha *et al.*
Efficient extraction of sulfate from water using a Zr-metal–organic framework

175 YEARS

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/dalton

Dalton Transactions

COMMUNICATION

View Article Online
DOI: 10.1039/C7DT01055A

Strikingly diverse reactivity of structurally identical silylene and stannylene[†]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

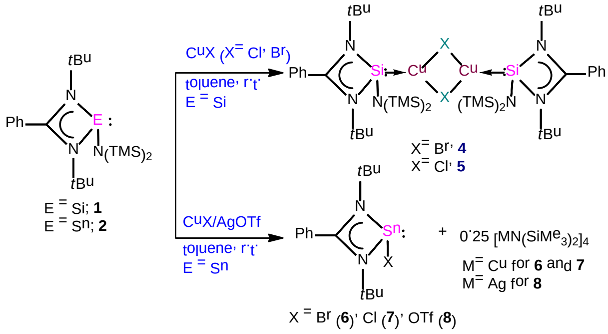
www.rsc.org/

Nasrina Parvin,[a] Rajarshi Dasgupta,[a] Shiv Pal,[a] Sakya S. Sen*[b] and Shabana Khan*[a]

Abstract: Reactivity of structurally identical silylene and stannylene $[PhC(N{\it t}Bu)_2EN(SiMe_3)_2]$ (E=Si (1) and Sn (2)) towards coinage metals have been explored. While 1 has the propensity to form adduct with coinage metals (4 and 5), 2 undergoes ligand exchange reaction with copper halides and silver triflate leading to $PhC(N{\it t}Bu)_2SnX$ (X=Br (6), Cl (7), and OSO_2CF_3 (8)) with concomitant formation of $[M\{N(SiMe_3)_2\}]$ (M = Cu, Ag). However, with $AgSbF_6$ both 1 and 2 led to ion pairs, $9^+{\cdot}SbF_6^-$ and $10^+{\cdot}SbF_6^-$ displaying weaker Ag····F interactions in the latter.

Compounds of a family of structurally similar derivatives often display similar physical and chemical properties. Silylenes and stannylenes are the heavier congener of *N*-heterocyclic carbenes (NHCs).[1] Coinage metal NHC complexes have been extensively studied for their intriguing structural properties and numerous applications.[2] Going by the mushrooming chemistry of silylene-transition metal complexes,[3] one could expect that one of the next targets would be to replace NHCs by their heavier congeners as ligands for coinage metals. Examples of complexes having silylene to group 11 dative interactions have been initially predicted by Frenking et al.[4] and subsequently realized by the groups of Iwamoto,[5] Lappert,[6] Driess,[7] Robinson,[8] as well as by us[9a,b]. On the contrary, the reaction of stannylene with copper complexes have a modicum of precedence except the recent studies by Klinkhammer, Baumgartner, and others.[10] Moreover, silylene can form a simple adduct with coinage metal halides,[8] which rely solely on the Si→TM dative bond to maintain complex stability. Comparable adduct with stannylene has a modicum of precedence.[10b] This can be rationalized by greater σ-donation ability of silylene than its heavier congener, where the lone pair of electrons has higher *s*-character.

The present study is intended to achieve two aims at once: (a) explore a new stannylene ligand for coinage metal complexes and (b) an one-to-one comparison of the reactivity study of silylenes and stannylenes towards transition metal halides. To systematically compare the reactivity, both silylene and stannylene should have exactly same ligands and substituents as subtle modifications often induce structural or chemical diversities.[11]



Scheme 1. Reactions of silylene and stannylene with copper halides

Hence, we zeroed in the previously reported $[PhC(N{\it t}Bu)_2SiN(SiMe_3)_2]$[12] (**1**) and $[PhC(N{\it t}Bu)_2SnN(SiMe_3)_2]$[13] (**2**) for the comparison study and reacted with coinage metals. While the reaction of copper halides with **1** afforded the formation of anticipated adducts, $[\{PhC(N{\it t}Bu)_2\}Si\{N(SiMe_3)_2\}]_2Cu_2X_2$ [X=Br (**4**) and Cl (**5**)], **2** underwent a σ-bond metathesis leading to formation of $[PhC(N{\it t}Bu)_2SnX]$ [X=Br (**6**) and Cl (**7**)]. In line with this observation, the reaction of **2** with AgOTf ($Tf{=}SO_2CF_3$) resulted in $[PhC(N{\it t}Bu)_2SnOTf]$ (**8**). On the contrary, the reaction of $AgSbF_6$ with **1** and **2** resulted in $\mathbf{9}^+{\cdot}SbF_6^-$ and $\mathbf{10}^+{\cdot}SbF_6^-$ complexes.

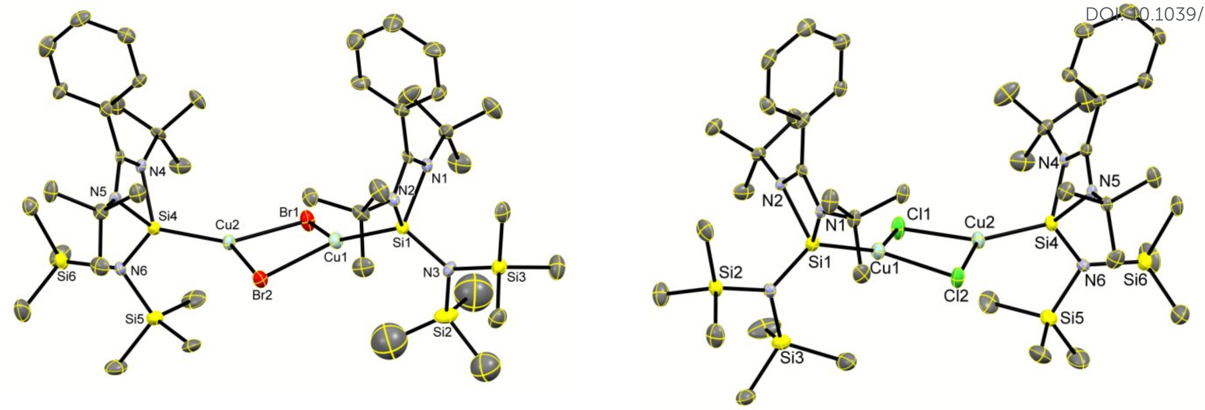
---

[a] *Department of Chemistry*
Indian Institute of Science Education and Research Pune
Dr. Homi Bhaba Road, Pashan, Pune - 411008, India
Phone: 0091-20-2590-8137
E-mail: shabana@iiserpune.ac.in
Homepage: http://www.iiserpune.ac.in/~shabana/
[b] *Inorganic Chemistry and Catalysis Division*
CSIR-National Chemical Laboratory
Dr. Homi Bhaba Road, Pashan, Pune - 411008, India
Phone: 0091-20-2590-3052
E-mail: ss.sen@ncl.res.in
Homepage: http://academic.ncl.res.in/ss.sen

[†] *Dedicated to Prof. Jai Deo Singh*

*Electronic supplementary information (ESI) available: Preparation of **4-10** and X-ray crystallographic data for **4-6**, **9**, and **10**. CCDC no. 1474385 (**4**), 1474386 (**5**), 1535769(**6**), 1535770(**9**), 1535771 (**10**).*

View Article Online
DOI: 10.1039/C7DT01055A



4

5

Figure 1. Molecular structures of **4** and **5** with anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°): **4**: Cu1–Si1 2.222(2), Cu2–Si4 2.221(2), Cu1··Cu2 3.255(1), Cu1–Br1 2.4297(12), Cu1–Br2 2.4828(12), Cu2–Br1 2.4360(12), Cu2–Br2 2.4822(11); Si1–Cu1–Br1 135.79(7), Si1–Cu1–Br2 128.08(7), Si4–Cu2–Br1 133.62(7), Si4–Cu2–Br2 130.21(7), Cu1–Br1–Cu2 83.96(4), Cu2–Br2–Cu1 81.92(4), Br1–Cu1–Br2 95.99(4), Br1–Cu2–Br2 95.84(4); **5**: Cu1···Cu2 3.1378(9), Cu1–Si1 2.1986(13), Cu1–Cl1 2.3003(11), Cu1–Cl2 2.3542(11), Cu2–Si4 2.2027(13), Cu2–Cl1 2.3022(11), Cu2–Cl2 2.3450(11); Si1– Cu1–Cl1 134.41(4), Si1–Cu1–Cl2 131.00(4), Cl1–Cu1–Cl2 94.20(4), Si4–Cu2–Cl1 136.75(4), Si4–Cu2–Cl2 128.81(4), Cl1–Cu2–Cl2 94.39(4), Cu2–Cl2–Cu1 83.79(4), Cu1–Cl1–Cu2 85.97.

Treatment of silylene **1** with one molar equivalent of CuBr and CuCl in toluene at room temperature furnished the respective silylene-copper complexes **4** and **5** (Scheme 1). As expected, the coordination of copper to the Si(II) center led to the downfield shift in the respective ^{29}Si NMR resonance (**4**: *δ* 5.72 and **5**: *δ* 4.79 ppm) in comparison to that of **1** (*δ* –8.07 ppm) but upfield with respect to that of [{PhC(N*t*Bu)$_2$}Si{N(SiMe$_3$)$_2$}]$_2$Cu$_2$I$_2$ (**3**) (*δ* 16.85 ppm).[9a] It is apparent from the ^{29}Si NMR resonances of **3**-**5** that copper halides with less electronegative substituents lead to a more downfield shift. Surprisingly, the reactions of **2** with copper halides did not lead to the formation of the anticipated adduct and instead resulted in amidinato Sn(II) bromide (**6**) and chloride (**7**), generating from the metathesis reaction. The concomitant formation of copper(I) bis(trimethylsilyl)amide, [Cu{N(SiMe$_3$)$_2$}] as a by-product was spectroscopically and structurally established (See Supporting Information). Such metathetical reaction is reminiscent of the reactivity of Sn[N(SiMe$_3$)$_2$]$_2$, which undergoes facile metathesis reactions with amines, alcohols, amides, carboxylic acids, amine hydrochloride salts, and related compounds.[14] To test the ligand exchange behaviour is an intrinsic property of **2**, we decided to investigate the reaction of **2** with silver triflate (AgOSO$_2$CF$_3$) which also undergo ligand exchange reaction leading to LSnOTf (L = PhC(N*t*Bu)$_2$) (**8**).[13]

The corresponding structural parameters of **4** and **5** are very much alike and the noticeable alterations of the bond lengths and angles are attributed to the different halides. Both **4** and **5** crystallize in the triclinic space group *P*-1[15] and consists of a four-membered Cu$_2$X$_2$ core, where each silylene ligand is coordinated to a Cu atom. A two-fold symmetry axis passes through the centroid of the four-membered Cu$_2$X$_2$ ring, which is almost planar. Each Si(II) center in **4** and **5** is four coordinate and exhibits a slightly distorted tetrahedral geometry (Figure 1). The Si–N(SiMe$_3$)$_2$ bond distances are 1.746(6) Å for **4** and 1.732(3) Å for **5**, which are in good agreement with the Si-N bond lengths in the previously reported Si(II) amides **1** (1.769(7) Å),[12] [PhC(N*t*Bu)$_2$SiNMe$_2$] (1.724(2) Å),[16] and **3** (1.731(9) Å).[8] The Si→Cu bond lengths in **4** are 2.221(2) and 2.222(2) Å, while in **5** these are 2.197(2) and 2.203(2) Å. These bond lengths are in good accordance with the Si–Cu bond lengths in **3** (2.243(3) and 2.250(3) Å)[9a] and in other reported Si–Cu bond lengths [2.1981(12)–2.289(4) Å].[5-8]

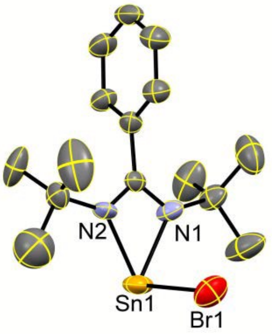
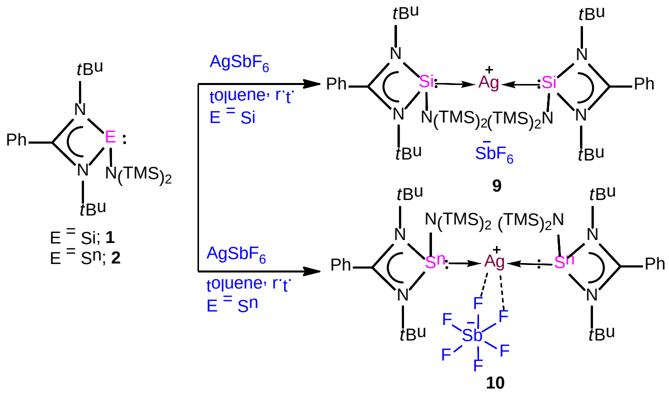


Figure 2. Molecular structure of **6** with anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°):N2-Sn1 2.171(6); N1-Sn1 2.168(6); Sn1-Br1 2.620(2); N2-Sn1-Br1 94.35(16); N1-Sn1-Br1 93.21(16); N2-Sn1-N1 60.20(2).

The structure of **6** was established by single crystal X-ray studies. The structure of **6** is very similar to those of PhC(N*t*Bu)$_2$ECl (E=Si,[17] Ge,[18] and Sn[13]) showing a distorted trigonal pyramidal geometry with a lone pair of electrons on the Sn(II) atom (Figure 2). The Sn-Br bond length is of 2.6197(13) Å, which is in good accordance with the regular Sn–Br bond lengths (ca. 2.59 Å).[19] The ^{119}Sn NMR spectrum of **6** exhibits a singlet resonance at *δ* 68.45 ppm, which is significantly downfield that of **7** (*δ* 29.6 ppm).[13] The structures of compound **7** and **8** were previously reported.[13] Hence they were only characterized by spectroscopic analyses and compared to the samples prepared by previously reported synthetic methods. Therefore, our method also provides new

DOI: 10.1039/C7DT01055A

synthetic route to access such functionalized stannylene complexes which were otherwise only accessible via salt elimination methodology.



Scheme 2. Reactions of silylene and stannylene with AgSbF$_6$.

A different reactivity pattern was observed for the coordination of **2** to Ag[SbF$_6$]. When the latter was reacted with **1** and **2**, cationic silylene-silver complex **9**$^+$·SbF$_6^-$ and stannylene-silver complex **10**$^+$·SbF$_6^-$ were obtained. The dichotomic behavior of **2** towards AgOTf and AgSbF$_6$ can be rationalized from the greater Lewis acidity of Ag atom in AgSbF$_6$ as well as the bulkier nature of the latter.

Single crystals of **9**$^+$·SbF$_6^-$ and **10**$^+$·SbF$_6^-$ suitable for X-ray analysis were obtained by recrystallization from toluene at 0 °C in a refrigerator. X-ray analysis shows that **9**$^+$·SbF$_6^-$ exists as an ion pair (Figure 4): the closest distance between the F atom in the SbF$_6^-$ moiety and the Ag atom is 6.087 Å, which is greater than the sum of the van der Waals radii of F and Ag (3.2 Å). The silicon center is tetra-coordinate and exhibits a distorted tetrahedral geometry. Two silylene moieties almost linearly coordinate to the Ag atom with the Si1–Ag1–Si1 angle of 171.85(3)°. The Si–Ag bond lengths [2.4249(13) Å and 2.4243(12) Å] significantly surpass those in our [{PhC(N*t*Bu)$_2$}Si{N(SiMe$_3$)$_2$}]$_2$Ag$_2$[OTf]$_2$ [2.337(2) Å and 2.346(2) Å][9a] and Iwamoto's dialkylsilylene-silver complex (2.4015(16) Å).[5] In the ^{29}Si NMR spectrum of **9**, signals in the form of two doublets appearing around δ 11.62 ppm with with ^{1}J ^{29}Si to ^{109}Ag = 333.05 and ^{1}J ^{29}Si to ^{107}Ag = 288.50 Hz.[20] The SiMe$_3$ substituents resonate at δ 7.17 and 8.61 ppm.

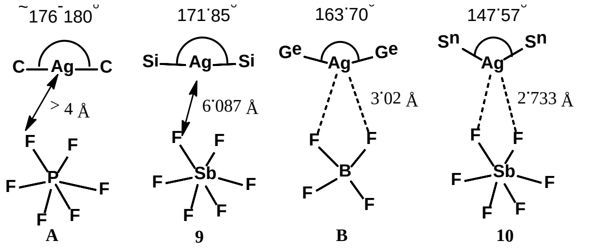


Figure 3. Schematic representation of the comparison of C(II), Si(II), Ge(II) and Sn(II) supported dimeric Ag+ cations.

Although the formulation of **9** and **10** are akin to each other but their structural parameters are significantly different (Figure 5). Most strikingly, the Sn-Ag-Sn framework is severely bent with an angle of 147.57°. Moreover, **10**$^+$ is weakly bound to the SbF$_6^-$ counter anion through the fluorine atoms with the shortest Ag–F bond distance of 2.733 Å. The ^{19}F spectrum of **9** and **10** exhibits resonances at around δ –121 (**9**) and –120 ppm (**10**), respectively. However signals in the ^{19}F NMR spectra of **9** and **10** can only be seen at low temperature which could be due to some dynamic behavior. Compound **10** shows signals in the form of two doublets appearing around δ 99.15 ppm with ^{1}J^{119}Sn to ^{109}Ag = 4176.96 and ^{1}J ^{119}Sn to ^{107}Ag = 3668.40 Hz in the ^{119}Sn NMR spectrum. The downfield shift in the latter than those in **6** and **7** can be attributed to the cationic nature of **10**. To the best of our knowledge, compound **10** is the first Ag cation stabilized by stannylene ligand with two Sn(II)→Ag dative bonds. Upon comparison of **9** and **10** with the analogous [(NHC)$_2$Ag]$^+$ (**A**)[21a] (NHC=IDipp, IMe, IEt) and [{PhC(N*t*Bu)$_2$Ge(*t*Bu)}$_2$Ag]$^+$ (**B**)[21b] complexes, it is apparent that moving from top to bottom within the group the coordination behaviour varies dramatically (Figure 3) and this can be attributed to the higher *s*-character of the lone pair of electrons down the group. These differences are indicative of weaker σ-donation of the stannylene ligand than that of silylene. Silylene may provide sufficient stabilization to attenuate the Lewis acidity of the Ag$^+$ cation and hence there is no interaction with the counter-anion in **9**. However, stannylene may not render σ-donation to that extent and thereby the Ag$^+$ cation is stabilized by further interaction with the fluorine atoms. The Sn(II)→Ag bond distance is 2.6217 Å, which is longer than that in [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgSn(Cl)[(*n*-Pr)$_2$ATI] [ATI=aminitroponiminate] [2.5863(6) Å][22] and other structurally characterized Sn-Ag bond distances such as [MeSi{Si(Me)$_2$N(*p*-Tol)}$_3$-SnAg]$_2$ (2.6567(7) Å),[23] [(thf)Ag(μ-SCN)Sn{CH(SiMe$_3$)$_2$}$_2$]$_2$ (2.598(1) Å),[24] and [HB(3,5-(CF$_3$)$_2$Pz)$_3$]AgSn(N$_3$)[(*n*-Pr)$_2$-ATI] (2.5943(6) Å).[25]

In summary, we have reported a series of reactions with structurally identical silylene and stannylene and the first one-to-one compared their reactivity. All reactions with silylene follow the same pattern either forming the neutral adduct (**3**-**5**) or ionic complex (**9**) depending the transition metal precursors. However, this is not the case with stannylene. It undergoes metathesis reaction with copper halides and silver triflate leading to the formation of different functionalized stannylenes (**6**-**8**) with simultaneous formation of corresponding metal amides. This is a new synthetic route to access various functionalities at stannylenes. However, the reaction of stannylene **2** with AgSbF$_6$ led to the first stannylene-silver ionic complex where two stannylene units donate the electron density to stabilize the Ag$^+$ cation. Our result also mirrors on the greater donor ability of silylene than that of stannylene as the former form the cationic silver complex without any interaction of the counter-anion while corresponding silver cation with stannylene is being coordinated to the counter-anion. All the isolated complexes were structurally characterized.

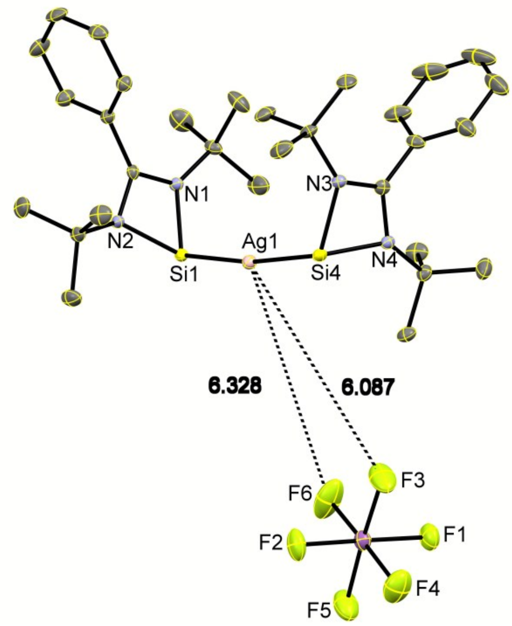


Figure 4. Molecular structure of **9** with anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms and N(SiMe$_3$)$_2$ moieties are not shown for clarity. Selected bond lengths (Å) and bond angles (°): N1-Si1 1.839(3); N2-Si1 1.842(3); Si1-Ag1 2.4249(13); Si4-Ag1 2.4243(12); Si1-Ag1-Si4 171.85(3); N1-Si1-Ag1 113.28(10); N2-Si1-Ag1 111.61(10); N3-Si4-Ag1 110.57(10); N4-Si4-Ag1 110.86(10).

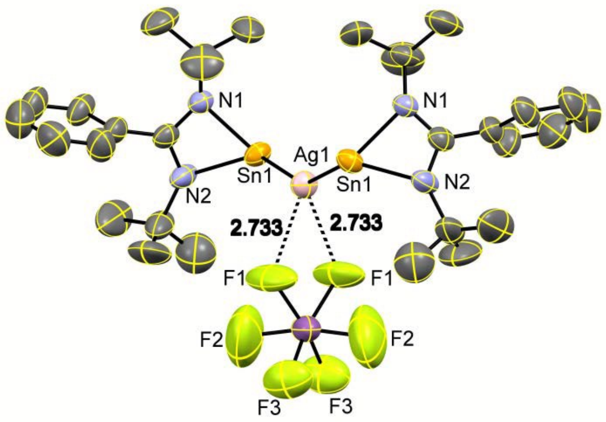


Figure 5. Molecular structure of **10** with anisotropic displacement parameters depicted at the 50 % probability level. Hydrogen atoms and N(SiMe$_3$)$_2$ moieties are not shown for clarity. Selected bond lengths (Å) and bond angles (°): N1-Sn1 2.176(6); N2 Sn1 2.153(7); Sn1-Ag1 2.6217(8); N1-Sn1-Ag1 112.17(15); N2-Sn1-Ag1 117.60(19); Sn1-Ag-Sn1 147.57(4)

Acknowledgements

SK thanks SERB (India), DST-FIST and IISER Pune for financial support. NP and SP thank UGC for providing fellowships. RDG thanks CSIR for fellowship. SSS thanks the Ramanujan research grant (SB/S1/RJN-073/2014) for financial support. We thank the reviewers for their valuable inputs to improve the quality of the manuscript.

Notes and references

View Article Online
DOI: 10.1039/C7DT01055A

1 (*a*) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457-492; (*b*) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354-396; (*c*) Y. Mizuhata, T. Sasamori and N.Tokitoh, *Chem. Rev.*, 2009, **109**, 3479-3511; (*d*) S. S. Sen. S. Khan, P. P. Samuel and H. W. Roesky, *Chem. Sci.*, 2012, **3**, 659–682; (*e*) S. Yadav, S. Saha, and S. S. Sen, *ChemCatChem*, 2016, **8**, 486–501.

2 J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561–3598.

3 (a) B. Blom, S. Enthaler, S. Inoue, E. Irran and M. Driess, *J. Am. Chem. Soc.*, 2013, **135**, 6703–6713; (b) C. I. Someya, M. Haberberger, W. Wang, S. Enthaler and S. Inoue, *Chem. Lett.,* 2013, **42**, 286–288; (c) D. Gallego, A. Brück, E. Irran, F. Meier, M. Kaupp, M. Driess and J. F. Hartwig, *J. Am. Chem. Soc.,* 2013, **135**, 15617–15626; (d) M. Stoelzel, C. Präsang, B. Blom and M. Driess, *Aust. J. Chem.,* 2013, **66**, 1163–1170; (e) A. Brück, D. Gallego, W. Wang, E. Irran, M. Driess and J. F. Hartwig, *Angew. Chem., Int. Ed.,* 2012, **51**, 11478–11482; (f) W. Wang, S. Inoue, S. Enthaler and M. Driess, *Angew. Chem., Int. Ed.,* 2012, **51**, 6167–6171; (g) W. Wang, S. Inoue, E. Irran and M. Driess, *Angew. Chem., Int. Ed.,* 2012, **51**, 3691–3694.

4 C. Boehme and G. Frenking, *Organometallics,* 1998, **17**, 5801–5809.

5 Y. Inagawa, S. Ishida and T. Iwamoto, *Chem. Lett.,* 2014, **43**, 1665–1667.

6 A. G. Avert, B. Gehrhus, P. B. Hitchcock, M. F. Lappert and H. Maciejewski, *J. Organomet. Chem.*, 2003, **686**, 321–331.

7 G. Tan, B. Blom, D. Gallego and M. Driess, *Organometallics,* 2014, **33**, 363–369.

8 M. Chen, Y. Wang, Y. Xie, P. Wei, R. J. Gilliard, Jr., N. A. Schwartz, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *Chem. Eur. J.,* 2014, **20**, 9208–9211.

9 (*a*) S. Khan, S. K. Ahirwar, S. Pal, N. Parvin and N. Kathewad, *Organometallics,* 2015, **34**, 5401-5406; (*b*) S. Khan, S. Pal, N. Kathewad, P. Parameswaran, S. De and I. Purushothaman, *Chem. Commun.*, 2016, **52**, 3880–3882.

10 (*a*) J. Klett, K. W. Klinkhammer and M. Niemeyer, *Chem. Eur. J.*, 1999, **5**, 2531 – 2536; (*b*) J. Hlina, H. Arp, M. Walewska, U. Flörke, K. Zangger, C. Marschner, and J. Baumgartner, *Organometallics*, 2014, **33**, 7069 – 7077; (*c*) U. Anandhi and P. R. Sharp, *Inorg. Chim. Acta* 2006, **359**, 3521–3526.

11 Effects of substituent in [PhC(N*t*Bu)$_2$SiX] for P$_4$ activation: (*a*) S. S. Sen, S. Khan, H. W. Roesky, D. Kratzert, K. Meindl, J. Henn, D. Stalke, J.-P. Demers and A. Lange, *Angew. Chem. Int. Ed.,* 2011, **50**, 2322–2325; (*b*) S. Khan, R. Michel, S. S. Sen, H. W. Roesky and D. Stalke, *Angew. Chem. Int. Ed.*, 2011, **50**, 11786-11789.

12 S. S. Sen, J. Hey, R. Herbst-Irmer, H. W. Roesky and D. Stalke, *J. Am. Chem. Soc.,* 2011, **133**, 12311-12316.

13 S. S. Sen, M. P. Kritzler-Kosch, S. Nagendran, H. W. Roesky, T. Beck, A. Pal and R. Herbst-Irmer, *Eur. J. Inorg. Chem.*, 2010, 5304–5311.

14 (*a*) M. Veith, *Chem. Rev.*, 1990, **90**, 3-16; (*b*) W. P. Neumann, *Chem. Rev.*, 1991, **91**, 311-334.

15 (*a*) T. Kottke and D. Stalke, *J. Appl. Crystallogr.,* 1993, **26**, 615–619; (*b*) D. Stalke, *Chem. Soc. Rev.*, 1998, **27**, 171–178; (*c*) G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64***,* 112–122.

16 C.-W. So, H. W. Roesky, P. M. Gurubasavaraj, R. B. Oswald, M. T. Gamer, P. G. Jones and S. Blaurock, *J. Am. Chem. Soc.* 2007, **129**, 12049-12054.

17 (*a*) C.-W. So, H. W. Roesky, J. Magull and R. B. Oswald, *Angew. Chem., Int. Ed.*, 2006, **45**, 3948-3950; (*b*) S. S. Sen, H. W. Roesky, D. Stern, J. Henn and D. Stalke, *J. Am. Chem. Soc.,*

View Article Online
DOI: 10.1039/C7DT01055A

2010, **132**, 1123-1126; (*c*) H.-X. Yeong, K.-C. Lau, H.-W. Xi, K. H. Lim and C.-W. So, *Inorg. Chem.* 2010, **49**, 371-373.

18 S. Nagendran, S. S. Sen, H. W. Roesky, D. Koley, H. Grubmüller, A. Pal and R. Herbst-Irmer, *Organometallics* 2008, **27**, 5459-5463.

19 B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans.*, 2008, 2832–2838.

20 T. G. Driver and K. A. Woerpel, *J. Am. Chem. Soc.*, 2004, **126**, 9993-10002.

21 (*a*) M. Kriechbaum, J.Hölbling, H.-G. Stammler, M. List, R. J. F. Berger and U. Monkowius, *Organometallics,* 2013, **32**, 2876－2884; (*b*) L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez and D. Polo, *Organometallics,* 2015, **34**, 5479－5484.

22 A. E. Ayers and H. V. R. Dias, *Inorg. Chem.*, 2002, **41**, 3259-3268.

23 B. Findeis, L. H. Gade, I. J. Scowen and M. McPartlin, *Inorg. Chem.*, 1997, **36**, 960-961.

24 P. B. Hitchcock, M. F. Lappert and L. J.-M. Pierssens, *Organometallics*, 1998, **17**, 2686-2688.

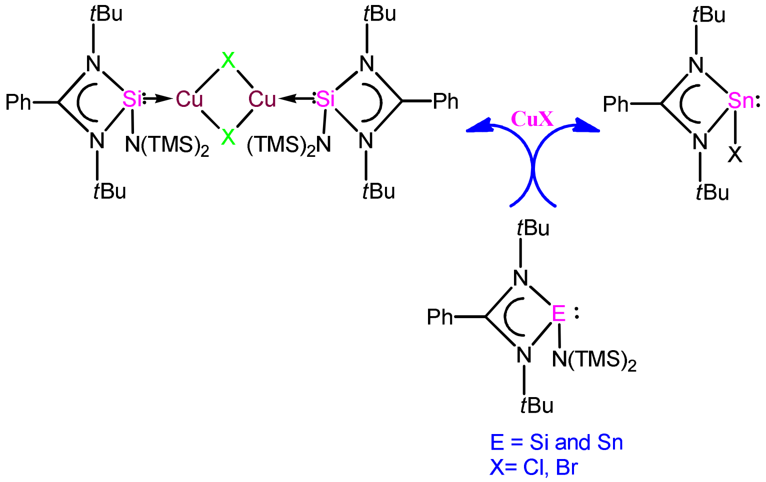
25 A. E. Ayers and H. V. R. Dias, *Polyhedron*, 2002, **21**, 611–618.

View Article Online
DOI: 10.1039/C7DT01055A

TOC

Strikingly diverse reactivity of structurally identical silylene and stannylene

Nasrina Parvin,[a] Rajarshi Dasgupta,[a] Shiv Pal,[a] Sakya S. Sen*[b] and Shabana Khan*[a]



Divergent reactivity of structurally similar silylene and stannylene was observed with coinage metal halides. While the former tends to form adduct, the latter undergoes ligand exchange reaction.