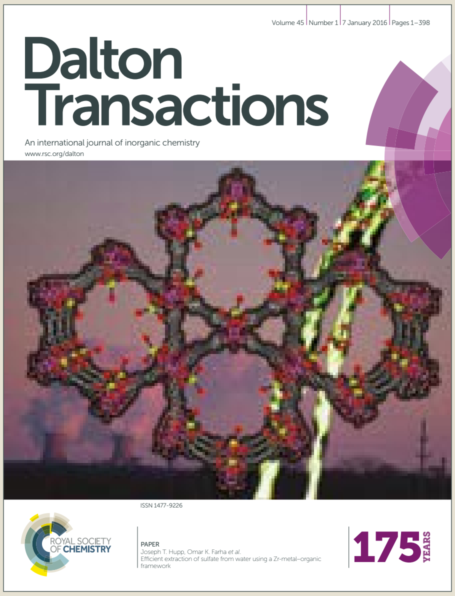
Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. So, Y. Shan, B. X. Leong, H. Xi, R. Ganguly, Y. Li and K. Lim, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT00051K.



ROYAL SOCIETY OF CHEMISTRY

rsc.li/dalton

View Article Online
DOI: 10.1039/C7DT00051K

Journal Name

ARTICLE

Reactivity of an Amidinato Silylene and Germylene toward Germanium(II), Tin(II) and Lead(II) Halides

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yu-Liang Shan,[†a] Bi-Xiang Leong,[†a] Hong-Wei Xi,[†b] Rakesh Ganguly,[§a] Yongxin Li,[§a] Kok Hwa Lim[b] and Cheuk-Wai So*[a]

The coordination chemistry of an amidinato silylene and germylene toward group 14 element(II) halides is described. The reaction of the amidinato silicon(II) amide [$LSiN(SiMe_3)_2$] (**1**, L = PhC(N*t*Bu)$_2$) with $SnCl_2$ and $PbBr_2$ afforded the amidinato silylene-dichlorostannylene and -dibromoplumbylene adducts [$L\{(Me_3Si)_2N\}SiEX_2$] (E = Sn, X = Cl (**2**); E = Pb, X = Br (**3**)), respectively, in which there are a lone pair of electrons on the Sn(II) and Pb(II) atoms. X-ray crystallography, NMR spectroscopy and theoretical studies show conclusively the Si(II)-E(II) bonds being donor-acceptor interaction. Similar electronic structures were found in the amidinato germylene-dichlorogermylene and -dichlorostannylene adducts [$L\{(Me_3Si)_2N\}GeECl_2$] (E = Ge (**5**), Sn (**6**)), which were prepared by the treatment of the amidinato germanium(II) amide [$LGeN(SiMe_3)_2$] (**4**) with $GeCl_2$.dioxane and $SnCl_2$, respectively.

Introduction

Stable tetrylenes of composition [L_2E:] (E = Si, Ge, Sn, Pb; L = supporting ligand) have attracted much attention in the past two decades due to their unique structures and reactivities.[1] They comprise a lone pair of electrons and vacant p orbital on the low valent group 14 atoms. These electronic structures enable tetrylenes being both donors and acceptors. As such, they are capable of being ancillary ligands and activating small molecules.[2] In recent years, several research groups utilized silylenes and germylenes, which are supported by amidinate, β-diketiminate and other chelate ligands, to coordinate with transition metal complexes.[3] The resulting complexes were catalytic intermediates or able to catalyse organic transformations.[4-8]

The coordination chemistry of silylenes and germylenes toward group 14 elements in the oxidation state of II has also been exploring. Silylenes and germylenes are able to donate their lone pair electrons to vacant p orbitals of tetrylenes. First, aryl- and silyl-substituted silylenes and germylenes undergo dimerization through synergic donor-acceptor interactions to form corresponding disilenes and digermenes, which comprise Si=Si and Ge=Ge double bonds, respectively.[9] Moreover, the N-heterocyclic silylene [$\{H_2CN(t\mathrm{Bu})\}_2Si$:] reacted with the N-heterocyclic germylene [$\{H_2CN(t\mathrm{Bu})\}_2Ge$:], which may proceed through the formation of a $\mathrm{Si}\rightleftarrows\mathrm{Ge}$ synergic donor-acceptor intermediate, to form the (Z)-1,2-diamino-1,2-disilyldigermene via a ring insertion reaction mechanism.[10] In addition, the N-heterocyclic silylene :Si[$(NCH_2t\mathrm{Bu})_2$-1,2-C_6H_4] underwent insertion reactions with the bis(amido)stannylene and plumbylene $E\{N(SiMe_3)_2\}_2$ (E = Sn, Pb) to form [$RSi\{N(SiMe_3)_2\}ESi\{N(SiMe_3)_2\}R$] (R = C_6H_4-1,2-$(NCH_2t\mathrm{Bu})_2$), respectively.[10] Furthermore, the N-heterocyclic silylene [$\{HCN(t\mathrm{Bu})\}_2Si$:] reacted with $SnCl_2$ to form disproportionation products [$\{HCN(t\mathrm{Bu})\}_2SiCl]_3SnCl$ and Sn.[11] Besides, the cyclic disilylated germylene [$\{Me_2Si(Me_3Si)_2Si\}_2(Et_3P)Ge$:] underwent an oxidation with $GeCl_2$.dioxane to form [$\{Me_2Si(Me_3Si)_2Si\}_2Ge(Cl)Ge(PEt_3)Cl$] and [$\{Me_2Si(Me_3Si)_2Si\}_2(Et_3P)GeCl_2$].[12] On the basis of the abovementioned examples, it seems that the formation of a stable Si(II)→E(II) and Ge(II)→E(II) adduct, which comprise a donor-acceptor single bond, is a synthetic challenge.

This synthetic difficulty has been tackling by different research groups in recent years and a handful of examples was reported. Rivard et al. utilized the NHC-dichlorogermylene [$I_{Ar}GeCl_2$] (NHC = N-heterocyclic carbene, I_{Ar} = :C{N(Ar)CH}$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) to coordinate with $GeCl_2$.dioxane to form the NHC-Ge(II)-Ge(II) adduct [$I_{Ar}Ge(Cl)_2GeCl_2$], which further underwent an insertion reaction with two equivalents of $GeCl_2$.dioxane to form [$I_{Ar}Ge(Cl)_2Ge(GeCl_3)_2$].[13] Leung et al. reported the synthesis of the asymmetric bisgermavinylidene adduct [$(Me_3SiN{=}PPh_2)_2C{=}Ge{\rightarrow}Ge{=}C(Ph_2P{=}NSiMe_3)_2$] by the reaction of [$LiC(PPh_2{=}NSiMe_3)_2$] with $GeCl_2$.dioxane.[14] Moreover, Schneider and Holthausen et al. used the hexachlorodisilane Si_2Cl_6 as a Si(II) halide source, which

---

[a] *Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, 637371 Singapore*

[b] *Singapore Institute of Technology, 10 Dover Drive, 138683 Singapore*

† Y.-L.S., B.-X.L. and H.-W.X. contributed equally: Y.-L.S. synthesized compounds **2** and **3**, B.-X.L. prepared compounds **5** and **6**, H.-W.X. carried out DFT calculations.

§ R.G. and Y.L. performed X-ray crystallography of compounds **2**, **3**, **5**, and **6**.

Electronic Supplementary Information (ESI) available: Selected crystallographic and DFT calculation data of **2**, **3**, **5**, and **6**. See DOI: 10.1039/x0xx00000x

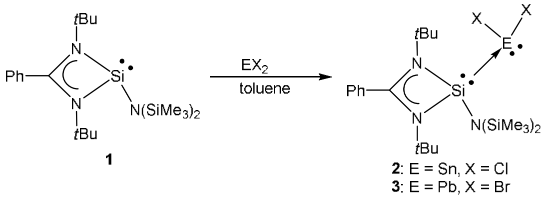
DOI: 10.1039/C7DT00051K

underwent a disproportionation and multi-step Si-Si bond heterolysis with the amine NMe_2Et to form the amine-Si(II)-Si(II) adduct $[Me_2EtNSi(Cl)_2Si(SiCl_3)_2]$.[15] In contrast, Schnepf et al. illustrated that the reaction of the metastable dichlorosilylene solution with I_{iPr} (I_{iPr} = :C{N(*i*Pr)CH}$_2$) did not afford an NHC-stabilized Si(II)-Si(II) adduct, instead two $SiCl_2$ molecules inserted into the Si-Cl bonds of another $SiCl_2$ molecule, along with the coordination of I_{iPr}, to form the NHC-silylene adduct $[I_{iPr}Si\{Si(I_{iPr})Cl_3\}\{Si(I_{iPr})Cl_2\}]Cl$.[16] Furthermore, the heavier Sn(II)-Sn(II) adducts [{1-[N(*t*Bu)C(SiMe$_3$)C(H)]-2-[N(*t*Bu)(SiMe$_3$)-CC(H)]C$_6$H$_4$}Sn→:Sn{1,2-[N(*t*Bu)(SiMe$_3$)CC(H)]$_2$C$_6$H$_4$}],[17] [{2,6-(Me$_2$N)$_2$C$_6$H$_3$}$_2$Sn→:Sn{1,8-(NCH*t*Bu)$_2$C$_{10}$H$_6$}],[18] and [{C$_9$H$_6$N-8-(Me$_3$Si)HC}$_2$Sn→:SnX$_2$] (X = Cl, Br) were also reported.[19] Besides, Müller et al. showed that the plumbylene [{Me$_2$Si(Me$_3$Si)$_2$Si}$_2$Pb:] underwent a dimerization to form the corresponding Pb(II)-Pb(II) adduct.[20]

In contrast, heterobinuclear E(II)→E'(II) adducts, which comprise two different group 14 element(II) centres (E and E'), are rare. The only structural characterized example, which is the amidinato silylene-germylene adduct [L{(Me$_3$Si)$_2$N}Si→GeCl$_2$] (L = PhC(N*t*Bu)$_2$) being formed by coordinating the corresponding silylene with GeCl$_2$.dioxane, was reported by us.[21] Moreover, Lappert et al. demonstrated the existence of the Ge(II)-Sn(II) adduct [{2,6-(Me$_2$N)$_2$C$_6$H$_3$}$_2$Ge→:Sn{1,8-(NCH$_2$*t*Bu)$_2$C$_{10}$H$_6$}] by NMR spectroscopy.[18] In continuation of our studies, we are interested in investigating whether other heterobinuclear E(II)→E'(II) adducts can be synthesized in a similar manner. Herein, we report the coordination chemistry of an amidinato silylene toward $SnCl_2$ and $PbBr_2$. The coordination chemistry of an amidinato germylene toward $GeCl_2$ and $SnCl_2$ is also described.

Results and Discussion

The reaction of the amidinato silicon(II) amide [LSiN(SiMe$_3$)$_2$] (**1**) with $SnCl_2$ in toluene at room temperature for 16 hours afforded a brown reaction suspension. It was filtered to remove unreacted $SnCl_2$ and the filtrate was concentrated to afford the amidinato silylene-dichlorostannylene adduct [L{(Me$_3$Si)$_2$N}SiSnCl$_2$] (**2**) as air- and moisture-sensitive colorless crystals in moderate yield (55.2%). The colorless crystals are soluble in toluene and THF. They are stable in solution and the solid state. Similar reaction conditions were used in the reaction of **1** with $PbBr_2$ to afford the amidinato silylene-dibromoplumbylene adduct [L{(Me$_3$Si)$_2$N}SiPbBr$_2$] (**2**) as air- and moisture-sensitive colorless crystals in low yield (36.4%) as they are not stable in solution and decompose to give a black precipitate within two days. Freshly prepared solution of compound **3** is essential for NMR spectroscopy. The electronic structures of **2** and **3** were elucidated by NMR spectroscopy and X-ray crystallography.



Scheme 1. Synthesis of **2** and **3**

The ^1H NMR spectra of **2** and **3** display one set of resonances due to the amidinate ligands and SiMe$_3$ substituents. Their ^{29}Si NMR resonances for the Si(II) atom (**2**: δ 25.6 ppm, **3**: δ 10.3 ppm) show a downfield shift compared with that of **1** (δ - 8.07 ppm) as the lone pair electrons on the Si(II) centres are donated to the vacant orbitals on the Sn(II) and Pb(II) atoms. In addition, they are downfield shifted in comparison with that of the NHC and tungsten-stabilized heavier ethylene analogue [I$_{Ar}$Si(H)$_2$Sn(H)$_2$W(CO)$_5$] (δ -91.1 ppm).[22] Moreover, compound **2** has a downfield ^{119}Sn NMR resonance (δ 77.2 ppm) in comparison with that of the NHC-dichlorostannylene adduct [I$_{Ar}$SnCl$_2$] (δ -68.7 ppm),[23] which indicates that the amidinato silylene [L{(Me$_3$Si)$_2$N}Si:] is a weaker Lewis base compared with the N-heterocyclic carbene I_{Ar} toward $SnCl_2$. Besides, the ^{119}Sn NMR signal of **2** is upfield shifted in comparison with that of the silastannene [(*t*Bu$_2$MeSi)$_2$Si=SnTip$_2$] (δ 516.7 ppm, Tip = 2,4,6-triisopropylphenyl)[24] and of compounds comprising sp^2 Sn atoms (above δ +400 ppm).[25] Hence, the ^{119}Sn NMR signal implies that compound **2** is not a silastannene. Furthermore, the ^{207}Pb NMR spectrum of **3** displays a signal at δ 2864 ppm, which is an intermediate value between those of the base-stabilized low valent lead complexes [Pb{C(SiMe$_3$)$_2$(SiMe$_2$OMe)}Cl]$_2$ (δ 4249 ppm)[26] and [2,6-(HCNAr)$_2$C$_6$H$_3$Pb]$_2$ (δ 1684 ppm).[27]

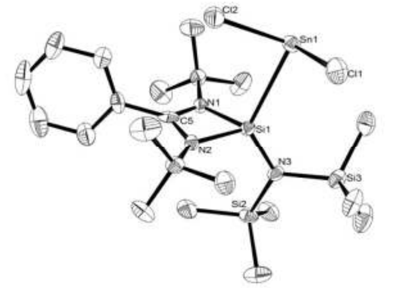


Figure 1. Molecular structure of compound **2** (ellipsoids set at 50% probability). There are two independent molecules in the asymmetric unit with slightly different bond lengths and angles. Only one independent molecule is discussed here for clarity. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-Sn1 2.7325(18), Si1-N1 1.829(5), Si1-N2 1.818(5), Si1-N3 1.708(5); Cl1-Sn1-Cl2 94.04(7), Cl1-Sn1-Si1 98.57(6), Cl2-Sn1-Si1 88.98(6), Sn1-Si1-N1 100.81(17), Sn1-Si1-N2 114.97(17), Sn1-Si1-N3 125.21(19), N1-Si1-N2 72.4(2), N1-Si1-N3 115.1(3), N2-Si1-N3 114.6(2).

The X-ray crystal structures of **2** and **3** (Figures 1 and 2) show that the amidinate ligands are bidentate coordinated to the Si1 atoms. The Si1 atoms also coordinate to the N3 atoms of the amido substituents and the E1 (E = Sn, Pb) atoms to adopt a

View Article Online
DOI: 10.1039/C7DT00051K

tetrahedral geometry. The E1 atoms display a distorted trigonal pyramidal geometry (the sum of bond angles of Sn: 281.6; Pb: 283.3°), which indicate the presence of a lone pair at the group 14 elements E. The Si1-Sn1 bond (2.7325(18) Å) in **2** is significantly longer than typical Si-Sn single bonds (2.60 Å),[1] the Si-Sn bond in the NHC and tungsten-stabilized heavier ethylene analogue [I_{Ar}Si(H)$_2$Sn(H)$_2$W(CO)$_5$] (2.5808(5) Å)[22] and the Si=Sn double bond in the silastannene [(*t*Bu$_2$MeSi)$_2$Si=SnTip$_2$] (2.4188(14) Å).[24] Similarly, the Si1-Pb1 bond (2.8051(13) Å) in **3** is significantly longer than the Si-Pb single bonds in the tris(trimethylsilyl)silyllead(IV) [{(Me$_3$Si)$_3$Si}Pb(Ph)$_2$]$_2$ (2.648(2) Å) and the Si-Pb(II) bond in the bis(hypersilyl)plumbylene [{(Me$_3$Si)$_3$Si}$_2$Pb:] (2.700(3), 2.704(3) Å).[28]

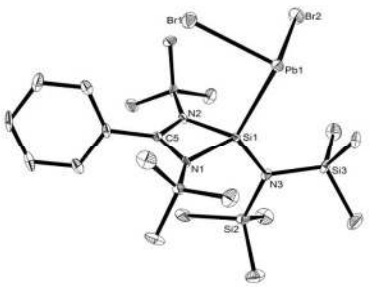


Figure 2. Molecular structure of compound **3** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1-Pb1 2.8051(13), Si1-N1 1.829(4), Si1-N2 1.839(4), Si1-N3 1.707(4); Br1-Pb1-Br2 96.847(18), Br1-Pb1-Si1 93.61(3), Br2-Pb1-Si1 92.85(3), Pb1-Si1-N1 107.62(13), Pb1-Si1-N2 112.69(12), Pb1-Si1-N3 123.32(13), N1-Si1-N2 71.65(17), N1-Si1-N3 113.52(18), N2-Si1-N3 116.13(19).

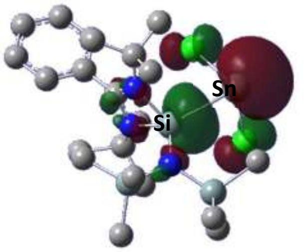
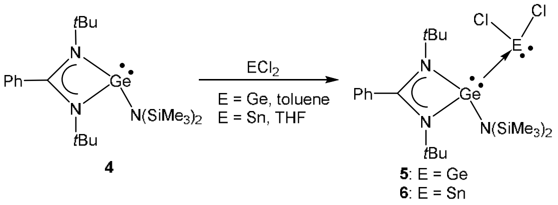


Figure 3. HOMO of compound **2** showing the donor–acceptor interaction between the Si(II) and Sn(II) centres (isovalue = 0.04)

DFT analyses at the M06-2X level (LanL08d basis set for Sn, Pb and 6-311+g(d) for other atoms) were carried out for compounds **2** and **3** to understand bonding situations. The donor–acceptor interaction Si→E: (**2**: E = Sn; **3**: E = Pb) is shown in the HOMO of each complex (Figure 3 and Figure S3), where it also shows the lone pair orbital on the E^{II} (E = Sn, Pb) centre. Accordingly, the NBO analyses show that the Si→E: bonds (**2**: E= Sn; **3**: E = Pb) are highly polarized (Table S1) and formed by the overlapping of the sp^2 hybridized lone pair orbitals on the Si(II) atoms (**2**: sp$^{2.13}$; **3**: sp$^{2.13}$) with the vacant p orbitals on the Sn(II) and Pb(II) atoms, respectively. The lone pair orbitals on the Sn and Pb centres in **2** and **3** are rich in s-character with some directionality (**2**: sp$^{0.17}$; **3**: sp$^{0.09}$). In addition, the group charges on the SnCl$_2$ (-0.40 e) and PbBr$_2$ moieties (-0.38 e) in **2** and **3** indicate a net charge flow from the amidinato silylenes [L{(Me$_3$Si)$_2$N}Si:] to them. Consequently, the Wiberg bond indices (WBI) show that the Si-E bonds are labile (WBI of **2**: 0.70 and **3**: 0.68) and their donor–acceptor bond strengths decrease from Sn to Pb. Moreover, the bond dissociation energies (**2**: 43.9, **3**: 42.0 kcal/mol) of [L{(Me$_3$Si)$_2$N}SiEX$_2$] into [L{(Me$_3$Si)$_2$N}Si:] and EX$_2$ (**2**: E = Sn, X = Cl; **3**: E = Pb, X = Br) are consistent with the WBI. They are smaller than the bond dissociation energies of H$_3$Si-EH$_3$ into H$_3$Si$^•$ and H$_3$E$^•$ (E = Sn, 68.3 kcal/mol; E = Pb, 62.0 kcal/mol).

On the basis of NMR spectroscopic, X-ray crystallographic and theoretical data, the Si-E bonding situation in **2** and **3** should be described as donor-acceptor single bonds and there are lone pairs of electrons on the E centres.

The treatment of the amidinato germanium(II) amide [LGeN(SiMe$_3$)$_2$] (**4**)[29] with one equivalent of GeCl$_2$.dioxane and SnCl$_2$ in toluene and THF for 16 hours afforded yellow suspensions, respectively. The reaction mixtures were filtered and the filtrates were concentrated to afford the amidinato germylene-dichlorogermylene and -dichlorostannylene adducts [L{(Me$_3$Si)$_2$N}GeECl$_2$] (E = Ge (**5**), Sn (**6**), Scheme 2) as air- and moisture-sensitive colorless crystalline solids in good yield (**5**: 68 %, **6**: 88 %), respectively. Compounds **5** and **6** are soluble in toluene and THF. They are stable in solution and the solid state. In contrast, there is no reaction between **4** and PbCl$_2$.



Scheme 2. Synthesis of **5** and **6**

The ^{1}H NMR spectra of **5** and **6** display one set of resonances due to the amidinate ligands and SiMe$_3$ substituents. In addition, the ^{119}Sn NMR signal of **6** (δ -184.4 ppm) is an intermediate value between that of the Lewis acidic Sn(II) centre in the Sn(II)-Sn(II) adduct [{C$_9$H$_6$N-8-(Me$_3$Si)HC}$_2$Sn→:*Sn*Cl$_2$] (δ -388 ppm)[19] and the Ge(II)-Sn(II) adduct [{2,6-(Me$_2$N)$_2$C$_6$H$_3$}$_2$Ge→:*Sn*{1,8-(NCH$_2$*t*Bu)$_2$C$_{10}$H$_6$}] (δ -58 ppm).[18] The ^{119}Sn NMR signal of **6** is also upfield shifted in comparison with the germastannenes [Tip$_2$Ge=SnTip$_2$] (δ 268 ppm)[30] and [(*t*Bu$_2$MeSi)$_2$Ge=SnTip$_2$] (δ 525 ppm).[31] These indicate that the Ge-Sn bond in compound **6** does not comprise any multiple bond character.

Single crystals of **5** (Figure 4) and **6** (Figure 5) suitable for X-ray crystallography were grown in toluene and THF solution, respectively. Their structures are comparable to the amidinato silylene-dichlorogermylene adduct [L{(Me$_3$Si)$_2$N}SiGeCl$_2$][21] and **2**, respectively. They show a four-coordinate Ge1 centre exhibiting a distorted tetrahedral geometry. The three-coordinate Ge2 atom in **5** and Sn1 atom in **6** display a distorted trigonal pyramidal geometry (the sum of bond angles, Ge2:

View Article Online
DOI: 10.1039/C7DT00051K

279.6^{o} in **5**, Sn1: 274.19^{o} in **6**) attributable to the presence of a stereochemically active lone pair of electrons.

The Ge1-Ge2 bond length in **5** (2.5868(4) Å) is longer than the Ge=Ge double bond length in the digermene [(2,5-*t*$Bu_2C_6H_3)_2$Ge=Ge(C_6H_3-2,5-*t*$Bu_2)_2$] (2.3643(4) Å).[32] It is also longer than the Ge-Ge single bond lengths in typical digermanes (ca. 2.393 – 2.437 Å),[33] and the Ge→Ge donor acceptor bond length in the asymmetric bisgermavinylidene adduct [(Me_3SiN=$PPh_2)_2$C=Ge→Ge=C(Ph_2P=NSi$Me_3)_2$] (2.4827(13) Å).[14] It is comparable with that of the NHC-Ge(II)-Ge(II) adduct [I_{Ar}Ge(Cl)$_2$GeCl_2] (2.6304(9) Å).[13]

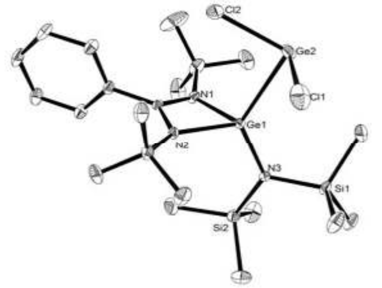


Figure 4. Molecular structure of **5** (thermal ellipsoids set at 50 % probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–Ge2 2.5868(4), Ge1–N1 1.9460(16), Ge1–N2 1.9541(16), Ge1–N3 1.8440(17); Cl1-Ge2-Cl2 99.10(3), Cl1-Ge2-Ge1 91.031(19), Cl2-Ge2-Ge1 89.488(18), N1-Ge1-N2 67.53(7), N1-Ge1-N3 110.90(7), N2-Ge1-N3 112.28(7), N1-Ge1-Ge2 109.38(5), N2-Ge1-Ge2 114.69(5), N3-Ge1-Ge2 126.60(5).

Moreover, the Ge1-Sn1 bond (2.8520(3) Å) in **6** is longer than the Ge=Sn double bond in the germastannene [Tip_2Ge=SnTip_2] (2.5065(5) Å),[30] the Ge(II)–Sn(IV) bond in the bis(stannyl)germylene-NHC adduct [I_{iPrMe}Ge{Sn(Si$Me_3)_3\}_2$] (2.703(1), 2.686(1) Å, I_{iPrMe} = :C{N(*i*Pr)C(Me)}$_2$),[34] the Ge(II)–Sn(IV) bond in the amidinato stannylgermylene [PhC{N(SiMe_3)}$_2$Ge{Sn(Si$Me_3)_3$}] (2.746(1) Å),[35] the Ge(I)-Sn(I) bond in [{C(Me)C(H)C(Me)N(Ar)}Ge-Sn{N(Ar)C(Me)}$_2$CH] (2.7210(4) Å),[36] and the zwitterionic Ge^+-Sn^- bonds in the digermadistannacyclobutadiene [(LGe)$_2$Sn]$_2$ (2.6863(6), 2.6799(6) Å).[37]

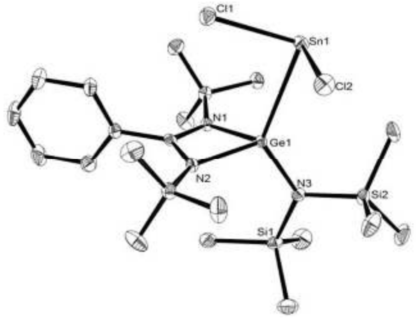


Figure 5. Molecular structure of **6** (thermal ellipsoids set at 50 % probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–Sn1 2.8520(3), Ge1–N1 1.961(2), Ge1–N2 1.970(2), Ge1–N3 1.856(2); Cl1-Sn1-Cl2 95.69(3), Cl1-Sn1-Ge1 88.751(19), Cl2-Sn1-Ge1 89.76(2), N1-Ge1-N2 66.81(9), N1-Ge1-N3 110.75(10), N2-Ge1-N3 110.36(10), N1-Ge1-Sn1 107.11(7), N2-Ge1-Sn1 117.38(7), N3-Ge1-Sn1 127.50(7).

DFT analyses at the same level as at compounds **2** and **3** were carried out for compounds **5** and **6**. Similar to compounds **2** and **3**, donor-acceptor interactions Ge→E: (**5**: E = Ge; **6**: E = Sn) are shown in their HOMOs (Figures S5 – S7), where they also show the lone pair orbitals on the E^{II} (E = Sn, Pb) centres. Accordingly, the NBO analyses show that the Ge→Sn: bond in **6** is more polarized than the Ge→Ge: bond in **5** (Table S1) due to the difference in electronegativity between the Ge and Sn centres in **6**. The Ge→E: (**5**: E= Sn; **6**: E = Pb) bonds are formed by the overlapping of the sp^2-hybridized lone pair orbitals on the Ge(II) atoms (**5**: $sp^{2.23}$; **6**: $sp^{2.19}$) with the vacant p orbitals on the E atoms. The lone pair orbitals on the E centres of the Ge→E: bonds in **5** and **6** are rich in s-character with some directionality (**5**: $sp^{0.20}$; **6**: $sp^{0.16}$). In addition, the group charge on the GeCl_2 moiety in **5** (-0.54 e) is more than that on the SnCl_2 moiety (-0.36 e) in **6**, which indicates stronger σ-donating ability of the amidinato germylene [L{(Me_3Si)$_2$N}Ge:] toward GeCl_2 in **5** than SnCl_2 in **6**. Consequently, the Ge→Ge: bond in **5** (WBI: 0.85) shows a higher Wiberg bond index in comparison with the Ge→Sn: bond in **6** (WBI: 0.70). Moreover, the bond dissociation energies (**5**: 34.7, **6**: 35.9 kcal/mol) of [L{(Me_3Si)$_2$N}GeECl_2] into [L{(Me_3Si)$_2$N}Ge:] and :ECl_2 (**5**: E = Ge; **6**: E = Sn) are smaller than those of H_3Ge-EH_3 into $H_3Ge^{\bullet}$ and $H_3E^{\bullet}$ (E = Ge: 64.3 kcal/mol; E = Sn: 64.6 kcal/mol). They are also smaller than those of compounds **2** and **3**, which illustrate [L{(Me_3Si)$_2$N}Ge:] being weaker donor than [L{(Me_3Si)$_2$N}Si:]. It is noteworthy that the bond dissociation energy of **6** is larger than that of **5**, while the covalency of the Ge→E: bonds appears to decrease from the Ge to Sn centre. This may be due to the increment of ionic contribution in the Ge→Sn: bond, resulting a more stable bonding interaction in comparison with the Ge→Ge: bond. Similar observation can be found in the N-heterocyclic germylene-alkaline earth metal complexes [{HCN(*t*Bu)}$_2$Ge→AeCp*$_2$] on descending the group (Ae = Ca, Sr, Ba).[38]

On the basis of NMR spectroscopic, X-ray crystallographic and theoretical data, the Ge-E bonding situation in **5** and **6** should be described as donor-acceptor single bonds and there are lone pairs of electrons on the E centres.

Experimental Section

General Procedure: All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. Solvents were dried by MBraun SPS-800. [LEN(SiMe_3)$_2$] (**1**: E = Si, **4**: E = Ge; L = PhC(N*t*Bu)$_2$) were prepared according to the literatures.[29,39] The ^{1}H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR spectra were recorded on a JEOL ECA 400 and Bruker Advance III 400 spectrometer. The chemical shifts δ are relative to external references SiMe_4 for ^{1}H , ^{13}C, ^{29}Si; SnMe_4 for ^{119}Sn and PbMe_4 for ^{207}Pb. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[L{(Me_3Si)$_2$N}SiSnCl_2] (**2**). Toluene (30 mL) was added to a mixture of **1** (1.26 g, 3.00 mmol) and SnCl_2 (0.57 g, 3.00 mmol) at ambient temperature. The resulting brown mixture was stirred for 16 hours. The reaction mixture was filtered and the

View Article Online
DOI: 10.1039/C7DT00051K

filtrate was concentrated to afford colorless crystals of compound **2**. Yield: 1.01 g (55.2 %). M.p.: 217.5 °C (decomposed). Elemental analysis calcd for $C_{21}H_{41}Cl_2SnN_3Si_3$: C 41.41; H 6.78; N 6.90. Found: C 41.25; H 6.56; N 6.73. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.29 (s, 9H, $SiMe_3$), 0.46 (s, 9H, $SiMe_3$), 1.22 (s, 18H, *t*Bu), 6.87 - 6.93 (m, 3H, Ph), 7.18 - 7.20 (m, 1H, Ph), 8.57 - 8.59 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 4.7 ($SiMe_3$), 5.7 ($SiMe_3$), 31.2 (C*Me*$_3$), 55.7 (*C*Me$_3$), 127.7, 128.2, 130.6, 133.4 (Ph), 171.9 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 25°C): δ = 8.3 ($SiMe_3$), 9.5 ($SiMe_3$), 25.6 (*Si*N($SiMe_3$)$_2$). ^{119}Sn{^{1}H} NMR (147.6 MHz, C_6D_6, 25°C): δ = 77.2 ppm.

[L{(Me_3Si)$_2$N}SiPbBr$_2$] (**3**). Toluene (30 mL) was added to a mixture of **1** (1.26 g, 3.00 mmol) and $PbBr_2$ (1.10 g, 3.00 mmol) at ambient temperature. The resulting yellow mixture was stirred for 16 hours. The reaction mixture was filtered and the filtrate was concentrated to afford yellow crystals of compound **3**. Yield: 0.86 g (36.4 %). M.p.: 143.1 °C (decomposed). Elemental analysis calcd for $C_{21}H_{41}Br_2N_3PbSi_3$: C 32.07; H 5.25; N 5.34. Found: C 31.98; H 5.11; N 5.07. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.28 (s, 9H, $SiMe_3$), 0.35 (s, 9H, $SiMe_3$), 1.24 (s, 18H, *t*Bu), 6.89 - 6.92 (m, 3H, Ph), 7.18 - 7.21 (m, 1H, Ph), 8.88 - 8.89 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 4.7 ($SiMe_3$), 5.7 ($SiMe_3$), 31.2 (C*Me*$_3$), 55.7 (*C*Me$_3$), 127.7, 128.2, 130.6, 133.4 (Ph), 171.9 (NCN) ppm. ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 25°C): δ = 9.6 ($SiMe_3$), 9.7 ($SiMe_3$), 10.3 (*Si*N($SiMe_3$)$_2$) ppm. ^{207}Pb{^{1}H} NMR (82.6 MHz, C_6D_6, 25°C): δ = 2864 ppm.

[L{(Me_3Si)$_2$N}GeGeCl$_2$] (**5**)**:** Toluene (50 mL) was added to a mixture of **4** (0.93 g, 2.00 mmol) and $GeCl_2$·dioxane (0.46 g, 2 mmol) at ambient temperature. The resulting light yellow mixture was stirred for 16 hours. The reaction mixture was filtered and the filtrate was concentrated to afford colorless crystals of compound **5**. Yield: 1.64 g (67.6 %). M.p.: 124 °C (decomposed). Elemental analysis (%) calcd for $C_{21}H_{41}Cl_2Ge_2N_3Si_2$: C 41.49; H 6.80; N 6.91. Found: C 40.80; H 6.88; N 6.69. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.39 (s, 9H, $SiMe_3$), 0.47 (s, 9H, $SiMe_3$), 1.16 (s, 18H, *t*Bu), 6.88 - 6.93 (m, 3H, Ph), 7.19 - 7.21 (m, 1H, Ph), 8.07 - 8.09 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 4.98 ($SiMe_3$), 5.73 ($SiMe_3$), 31.70 (C*Me*$_3$), 55.03 (*C*Me$_3$), 127.52, 127.67, 128.47, 130.34, 131.98, 132.42 (Ph), 171.08 (NCN) ppm.

[L{(Me_3Si)$_2$N}GeSnCl$_2$] (**6**): THF (50 mL) was added to a mixture of **4** (0.93 g, 2.00 mmol) and $SnCl_2$ (0.38 g, 2.00 mmol) at ambient temperature. The resulting yellow mixture was stirred for 16 hours. The reaction mixture was filtered. The filtrate was concentrated and kept at 0°C to afford colorless crystals of compound **6**. Yield: 1.214 g (88.1 %). M.p.: 157 °C (decomposed). Elemental analysis (%) calcd for $C_{21}H_{41}Cl_2GeN_3Si_2Sn$: C 38.58; H 6.32; N 6.43. Found: C 38.61; H 6.85; N 6.12. ^{1}H NMR (399.5 MHz, C_6D_6, 25°C): δ = 0.39 (s, 9H, $SiMe_3$), 0.44 (s, 9H, $SiMe_3$), 1.16 (s, 18H, *t*Bu), 6.90 - 6.96 (m, 3H, Ph), 7.20 - 7.23 (m, 1H, Ph), 8.02 - 8.04 (m, 1H, Ph) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 25°C): δ = 4.98 ($SiMe_3$), 5.93 ($SiMe_3$), 31.79 (C*Me*$_3$), 54.88 (*C*Me$_3$), 127.48, 127.61, 128.51, 130.14, 132.44, 133.14 (Ph), 170.43 (NCN) ppm. ^{119}Sn{^{1}H} NMR (147.6 MHz, C_6D_6, 25°C): δ = -184.38 ppm.

X-ray data collection and structural refinement: Intensity data for compounds **2**, **3**, **5**, and **6** were collected using a Bruker APEX II diffractometer. The crystals of **2**, **3**, **5**, and **6** were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least squares methods on F^2.[40] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. Selected X-ray crystallographic data refinements are written in ESI. CCDC-1451912 (**2**), -1451913 (**3**), -1518437 (**5**) and -1518438 (**6**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical studies.[41] Compounds **2**, **3**, **5** and **6** were investigated with DFT, by using the M06-2X hybrid functional with the 6-311G(d)+LANL08d mixed basis set. All calculations were carried out using the Gaussian 09 packages. The NBO analyses were performed using the NBO 5.0 program. The optimized geometries are in good agreement with their X-ray crystallographic data.

Conclusions

Heterobinuclear amidinato group 14 E(II)-E'(II) adducts **2**, **3**, **5**, and **6** were prepared using a simple procedure by reacting the amidinato silylene or germylene with group 14 element(II) halides. Their X-ray crystallography, NMR spectroscopy and DFT calculations show conclusively the E(II)-E'(II) bonds being donor-acceptor interaction. Their reactivity is currently under investigation.

Acknowledgements

This work is supported by AcRF Tier 1 grant (RG 06/14) and ASTAR SERC PSF grant.

Notes and references

1 V. Y. Lee and A. Sekiguchi, *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, Wiley, Chichester, U.K., 2010.
2 (a) K. Izod, *Coord. Chem. Rev.*, 2012, **256**, 2972-2993; (b) Y. Xiong, S. Yao and M. Driess, *Angew. Chem., Int. Ed.*, 2013, **52**, 4302-4311; (c) S. K. Mandal and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 298-307; (d) S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748-1767; (e) Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479-3511; (f) R. S. Ghadwal, R. Azhakar and H. W. Roesky, *Acc. Chem. Res.*, 2013, **46**, 444-456; (g) M. Asay, C. Jones and M. Driess,

View Article Online
DOI: 10.1039/C7DT00051K

Chem. Rev., 2011, **111**, 354-396; (h) S. K. Mandal and H. W. Roesky, *Chem. Commun.*, 2010, **46**, 6016-6041; (i) M. Kira, *Chem. Commun.*, 2010, **46**, 2893-2903; (j) A. V. Zabula and F. E. Hahn, *Eur. J. Inorg. Chem.*, 2008, 5165-5179; (k) W.-P. Leung, K.-W. Kan and K.-H. Chong, *Coord. Chem. Rev.*, 2007, **251**, 2253-2265.

3 (a) J. A. Cabeza, P. García-Álvarez and D. Polo, *Eur. J. Inorg. Chem.*, 2016, 10-22; (b) L. Alvarez-Rodriguez, J. A. Cabeza, P. Garcia-Alvarez and D. Polo, *Coord. Chem. Rev.*, 2015, **300**, 1-28; (c) B. Blom, D. Gallego and M. Driess, *Inorg. Chem. Front.*, 2014, **1**, 134-148; (d) B. Blom, M. Stoelzel and M. Driess, *Chem. – Eur. J.*, 2013, **19**, 40-62; (e) R. Waterman, P. G. Hayes and T. D. Tilley, *Acc. Chem. Res.*, 2007, **40**, 712-719; (f) M. Okazaki, H. Tobita and H. Ogino, *Dalton Trans.*, 2003, 493-506; (g) S. Schäfer, R. Köppe and P. W. Roesky, *Chem. – Eur. J.*, 2016, **22**, 7127-7133; (h) H. P. Hickox, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer III and G. H. Robinson, *J. Am. Chem. Soc.*, 2016, **138**, 9799-9802; (i) N. C. Breit, C. Eisenhut and S. Inoue, *Chem. Commun.*, 2016, **52**, 5523-5526; (j) J. A. Cabeza, P. García-Álvarez, R. Gobetto, L. González-Álvarez, C. Nervi, E. Pérez-Carreño and D. Polo, *Organometallics*, 2016, **35**, 1761-1770; (k) L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez and D. Polo, *Organometallics*, 2015, **34**, 5479-5484; (l) S. Khoo, H.-X. Yeong, Y. Li, R. Ganguly and C.-W. So, *Inorg. Chem.*, 2015, **54**, 9968-9975; (m) D. Yadav, R. Kumar Siwatch, S. Sinhababu, S. Karwasara, D. Singh, G. Rajaraman and S. Nagendran, *Inorg. Chem.*, 2015, **54**, 11067-11076.

4 (a) D. Gallego, S. Inoue, B. Blom and M. Driess, *Organometallics*, 2014, **33**, 6885-6897; (b) B. Blom, S. Enthaler, S. Inoue, E. Irran and M. Driess, *J. Am. Chem. Soc.*, 2013, **135**, 6703-6713.

5 W. Wang, S. Inoue, S. Enthaler and M. Driess, *Angew. Chem., Int. Ed.*, 2012, **51**, 6167-6171.

6 A. Brück, D. Gallego, W. Wang, E. Irran, M. Driess and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2012, **51**, 11478-11482.

7 (a) D. Gallego, A. Brück, E. Irran, F. Meier, M. Kaupp, M. Driess and J. F. Hartwig, *J. Am. Chem. Soc.*, 2013, **135**, 15617-15626; (b) C. I. Someya, M. Haberberger, W. Wang, S. Enthaler and S. Inoue, *Chem. Lett.*, 2013, **42**, 286-288.

8 L. Álvarez-Rodríguez, J. A. Cabeza, J. M. Fernández-Colinas, P. García-Álvarez and D. Polo, *Organometallics*, 2016, **35**, 2516-2523.

9 (a) K. K. Milnes, L. C. Pavelka and K. M. Baines, *Chem. Soc. Rev.*, 2016, **45**, 1019-1035; (b) J. Hlina, J. Baumgartner, C. Marschner, L. Albers, T. Müller and V. V. Jouikov, *Chem. - Eur. J.*, 2014, **20**, 9357-9366; (c) J. Hlina, J. Baumgartner, C. Marschner, L. Albers and T. Müller, *Organometallics*, 2013, **32**, 3404-3410; (d) T. Sasamori and N. Tokitoh, *Bull. Chem. Soc. Jpn.*, 2013, **86**, 1005; (e) R. C. Fischer and P. P. Power, *Chem. Rev.*, 2010, **110**, 3877; (f) T. Matsuo, M. Kobayashi and K. Tamao, *Dalton Trans.*, 2010, **39**, 9203; (g) D. Scheschkewitz, *Chem. – Eur. J.*, 2009, **15**, 2476; (f) M. Kira and T. Iwamoto, *Adv. Organomet. Chem.*, 2006, **54**, 73; (h) M. Kira, *J. Organomet. Chem.*, 2004, **689**, 4475; (i) V. Y. Lee and A. Sekiguchi, *Organometallics*, 2004, **23**, 2822; (j) M. Weidenbruch, *Organometallics*, 2003, **22**, 4348; (k) N. Takeda, N. Tokitoh and R. Okazaki, in *Science of Synthesis*, ed. M. G. Moloney, Thieme, Stuttgart, 2003, ch. 5.1.2; (l) N. Takeda, N. Tokitoh and R. Okazaki, in *Science of Synthesis*, ed. M. G. Moloney, Thieme, Stuttgart, 2003, ch. 5.1.6.; (m) N. Tokitoh and R. Okazaki, in *The Chemistry of Organic Germanium, Tin, and Lead Compounds*, ed. Z. Rappoport, John Wiley and Sons Ltd, Chichester, 2002, ch. 13, vol. 2; (n) M. Weidenbruch, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley and Sons Ltd, New York, 2001, ch. 5, vol. 3; (o) R. Okazaki and R. West, *Adv. Organomet. Chem.*, 1996, **39**, 231.

10 (a) C. Drost, B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1997, 1845-1846; (b) B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2514-2516; (c) A. Schaefer, W. Saak, M. Weidenbruch, H. Marsmann and G. Henkel, *Chem. Ber./Recl.*, 1997, **130**, 1733-1737; (d) A. Schaefer, W. Saak and M. Weidenbruch, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1405-1408.

11 B. Gehrhus, P. B. Hitchcock and H. Jansen, *J. Organomet. Chem.*, 2006, **691**, 811-816.

12 M. Walewska, J. Hlina, J. Baumgartner, T. Müller and C. Marschner, *Organometallics*, 2016, **35**, 2728-2737.

13 S. Al-Rafia, M. R. Momeni, R. McDonald, M. J. Ferguson, A. Brown and E. Rivard, *Angew. Chem., Int. Ed.*, 2013, **52**, 6390-6395.

14 W. P. Leung, Z. X. Wang, H. W. Li and T. C. W. Mak, *Angew. Chem., Int. Ed.*, 2001, **40**, 2501-2503.

15 J. I. Schweizer, M. G. Scheibel, M. Diefenbach, F. Neumeyer, C. Würtele, N. Kulminskaya, R. Linser, N. Auner, S. Schneider and M. C. Holthausen, *Angew. Chem., Int. Ed.*, 2016, **55**, 1782-1786.

16 A. B. Schnepf and F. Uhlemann, *Chem. - Eur. J.*, 2016, **22**, 10748-10753.

17 W.-P. Leung, H. Cheng, R.-B. Huang, Q.-C. Yang and T. C. W. Mak, *Chem. Commun.*, 2000, 451-452.

18 C. Drost, P. B. Hitchcock and M. F. Lappert, *Angew. Chem., Int. Ed.*, 1999, **38**, 1113-1116.

19 W.-P. Leung, W.-H. Kwok, F. Xue and T. C. W. Mak, *J. Am. Chem. Soc.*, 1997, **119**, 1145-1146.

20 H. Arp, J. Baumgartner, C. Marschner, P. Zark and T. Müller, *J. Am. Chem. Soc.*, 2012, **134**, 6409-6415.

21 Y. L. Shan, W. L. Yim and C. W. So, *Angew. Chem., Int. Ed.*, 2014, **53**, 13155-13158.

22 S. Al-Rafia, A. C. Malcolm, R. McDonald, M. J. Ferguson and E. Rivard, *Angew. Chem., Int. Ed.*, 2011, **50**, 8354-8357.

23 K. C. Thimer, S. I. Al-Rafia, M. J. Ferguson, R. McDonald and E. Rivard, *Chem. Commun.*, 2009, 7119-7121.

24 A. Sekiguchi, R. Izumi, V. Y. Lee and M. Ichinohe, *J. Am. Chem. Soc.*, 2002, **124**, 14822-14823.

25 K. M. Baines and W. G. Stibbs, *Adv. Organomet. Chem.*, 1996, **39**, 275-324.

26 C. Eaborn, P. B. Hitchcock, J. D. Smith and S. E. Sözerli, *Organometallics*, 1997, **16**, 5653-5658.

27 S. P. Chia, H. W. Xi, Y. Li, K. H. Lim and C. W. So, *Angew. Chem., Int. Ed.*, 2013, **52**, 6298-6301.

28 (a) S. Mallela and R. Geanangel, *Inorg. Chem.*, 1993, **32**, 602-605. (b) K. W. Klinkhammer and W. Schwarz, *Angew. Chem., Int. Ed. in Engl.*, 1995, **34**, 1334-1336.

29 P. P. Samuel, A. P. Singh, S. P. Sarish, J. Matussek, I. Objartel, H. W. Roesky and D. Stalke, *Inorg. Chem.*, 2013, **52**, 1544-1549.

30 A. Schaefer, W. Saak and M. Weidenbruch, *Organometallics*, 2003, **22**, 215-217.

31 A. Sekiguchi, R. Izumi, V. Y. Lee and M. Ichinohe, *Organometallics*, 2003, **22**, 1483-1486.

32 B. Pampuch, W. Saak and M. Weidenbruch, *J. Organomet. Chem.*, 2006, **691**, 3540-3544.

33 K. M. Baines and W. G. Stibbs, *Coord. Chem. Rev.*, 1995, **145**, 157-200.

34 N. Katir, D. Matioszek, S. Ladeira, J. Escudié and A. Castel, *Angew. Chem., Int. Ed.*, 2011, **50**, 5352-5355.

35 D. Matioszek, N. Katir, S. Ladeira and A. Castel, *Organometallics*, 2011, **30**, 2230-2235.

36 W. Wang, S. Inoue, S. Yao and M. Driess, *Chem. Commun.*, 2009, 2661-2663.

37 H. X. Yeong, H. W. Xi, Y. Li, S. B. Kunnappilly, B. Chen, K. C. Lau, H. Hirao, K. H. Lim and C. W. So, *Chem. – Eur. J.*, 2013, **19**, 14726-14731.

View Article Online
DOI: 10.1039/C7DT00051K

38 B. Blom, A. Said, T. Szilvasi, P. W. Menezes, G. Tan, J. Baumgartner and M. Driess, *Inorg. Chem.*, 2015, **54**, 8840-8848.

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

40 G. M. Sheldrick, *SHELXL-97*; Universität Göttingen, Göttingen, Germany, 1997.

41 For the details of DFT and NBO calculations and references, see the supporting information.