

DOI: 10.1002/zaac.202200141

# Protonation of Hydrido-Tetrylenes: H<sub>2</sub> Elimination vs. Tetrylium Cation Formation

Philip M. Keil<sup>[a]</sup> and Terrance J. Hadlington<sup>\*[a]</sup>Dedicated to Prof. Cameron Jones on the occasion of his 60<sup>th</sup> birthday

We describe the reactions of amido-E<sup>II</sup> hydride complexes, <sup>PhIP</sup>DippEH (<sup>PhIP</sup>Dipp = {[Ph<sub>2</sub>PCH<sub>2</sub>Si<sup>i</sup>Pr<sub>2</sub>](Dipp)N}<sup>-</sup>; Dipp = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; E = Ge (5), Sn (6)), towards the oxonium complex [(Et<sub>2</sub>O)<sub>2</sub>H][BAR<sup>F</sup><sub>4</sub>] (Ar<sup>F</sup> = 3,5-CF<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>). For 5, formation of the dihydro-tetrylium complex (*i.e.* [<sup>PhIP</sup>DippGeH<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>], (7)) is favoured, in contrast to the same reaction for 6 which selectively leads to H<sub>2</sub> elimination, furnishing the novel tetryliumylidene [<sup>PhIP</sup>DippSn][BAR<sup>F</sup><sub>4</sub>] (4). The related cationic Ge<sup>II</sup>

complex (*i.e.* [<sup>PhIP</sup>DippGe][BAR<sup>F</sup><sub>4</sub>] (3)) could be accessed *via* the often utilised chloride abstraction route with Na[BAR<sup>F</sup><sub>4</sub>]. The high Lewis acidity of this species has been demonstrated through the reaction of 3 towards the nitrogen bases, NH<sub>3</sub> and 4-dimethylaminopyridine. In the latter case, a classic donor-acceptor complex is formed. Conversely, for NH<sub>3</sub>, the [DippN] fragment of the ligand is intriguingly displaced by [HN], presumably through double proton-transfer in loss of DippNH<sub>2</sub>.

## Introduction

Carbocations have been considered as some of the most reactive carbon species since the discovery of the first carbocation in 1901.<sup>[1]</sup> The chemistry of the heavier Group 14 cations ER<sub>3</sub><sup>+</sup> (E = Si, Ge or Sn) has been of growing interest in the last two decades, and has proved to display similar reactivity, but a much richer coordination chemistry due to their progressively larger coordination sphere and more diffuse valence orbitals.<sup>[2]</sup> Closely related cationic tetrylenes, where E has an oxidation state of +2, are of particular interest, possessing a nucleophilic lone pair of electrons as well as two vacant *p*-orbitals, making them highly Lewis acidic ambiphilic compounds.<sup>[3]</sup> Their isolation can be achieved by utilising a weakly coordination anion (WCA), so forming highly reactive systems which typically require additional thermodynamic and/or kinetic stabilization. Nevertheless, remarkable examples of quasi one-coordinate amido E<sup>II</sup> cations (E = Ge, Sn) have been isolated by Jones et al., stabilized by the extremely bulky (aryl)(silyl)amide ligand, L\* (L\* = {[2,6-(Ph<sub>2</sub>CH)<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub>](SiMe<sub>3</sub>)N}<sup>-</sup>). These species were accessed through chloride abstraction from (amido)(chloro)tetrylene precursors with the metal-aluminate salts, M[Al{OC(CF<sub>3</sub>)<sub>3</sub>]<sub>4</sub>] (M = Li, Ag),

eliminating LiCl or AgCl (Figure 1).<sup>[4]</sup> These are considered to be quasi one-coordinate cations since they bear only weak intramolecular arene stabilization.<sup>[5]</sup> Other examples of E<sup>II</sup> cations include the use of cyclopentadienyl,<sup>[6]</sup> N-donor,<sup>[7]</sup> carbodiphosphorane,<sup>[8]</sup> carbene,<sup>[9]</sup> and phosphine ligands for additional stabilization.<sup>[10]</sup> Most commonly, these E<sup>II</sup> cations are formed *via* halide abstraction from halo-tetrylene precursors (Figure 1(a)). Utilising an alternative route, Driess et al. showed that protonation of the unsaturated ligand scaffold of a diamino silylene with [(Et<sub>2</sub>O)<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] results in Nacnac-stabilized Si<sup>II</sup> cations (Figure 1(b)).<sup>[11]</sup> The group of Wesemann have more recently shown that H<sub>2</sub> elimination from aryl tin trihydride species is also a promising method for the generation of Sn<sup>II</sup> cations (Figure 1(c)).<sup>[5]</sup>

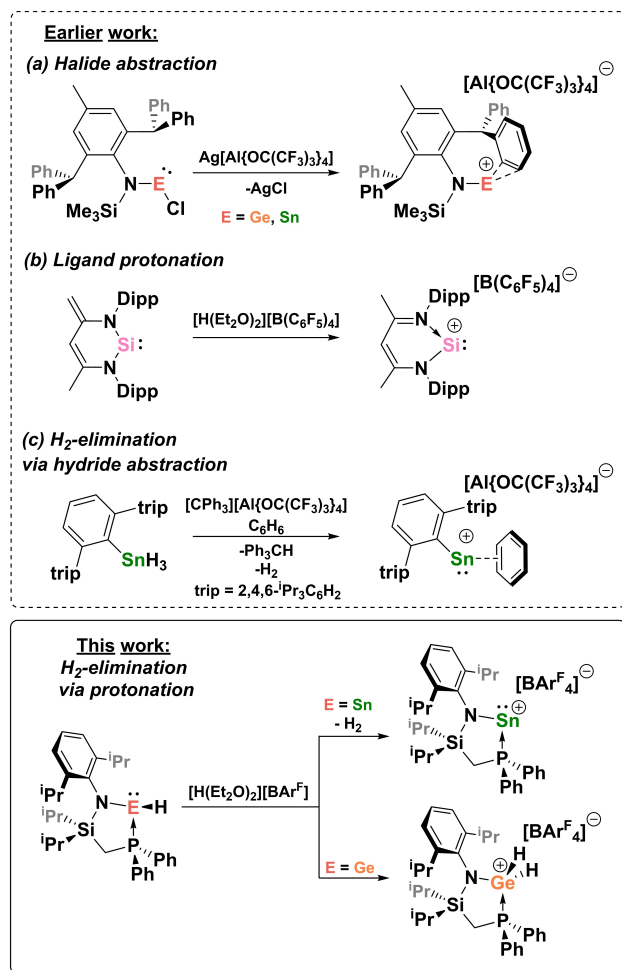
The further chemistry of tetryliumylidenes has demonstrated the activation of challenging chemical bonds in ammonia, silanes, boranes, and dihydrogen.<sup>[7d,9f,10]</sup> It was shown by Inoue et al. that a simple NHC-stabilized Ge<sup>II</sup> cation is even an effective catalyst for challenging processes such as the hydrosilylation of CO<sub>2</sub>, showing the great potential of this compound class.<sup>[12]</sup>

In our own work, we have recently reported the synthesis of (amido)(chloro)tetrylenes, featuring both mono-dentate and phosphine-functionalised bidentate amide ligands, which were utilized in the synthesis of cationic E<sup>II</sup>-Ni<sup>0</sup> complexes (E = Ge, Sn).<sup>[13]</sup> In these cases, the tetrylenes were combined with Na[BAR<sup>F</sup><sub>4</sub>] *in situ* in order to obtain cationic Ni<sup>0</sup> complexes. Given that our developed bidentate ligand systems led to Ni<sup>0</sup> complexes having a rich chemistry, such as hydrosilylation catalysis and reversible ammonia binding, we wished to develop synthetic routes to the free E<sup>II</sup> cations, to investigate their chemistry and make them available as ligands towards TM complexes beyond those which we have already reported. Herein, we describe the successful synthesis of these phosphine stabilized E<sup>II</sup> cations *via* two routes, including the novel

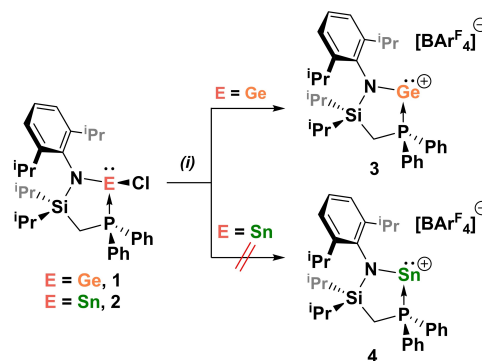
[a] P. M. Keil, T. J. Hadlington  
Fakultät für Chemie  
Technische Universität München  
Lichtenbergstraße 4  
E-mail: terrance.hadlington@tum.de

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/zaac.202200141>

© 2022 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.



**Figure 1.** Selected known examples of low coordinate E<sup>II</sup> cationic synthesis and the new synthetic route of H<sub>2</sub>-elimination via protonation presented in this work.

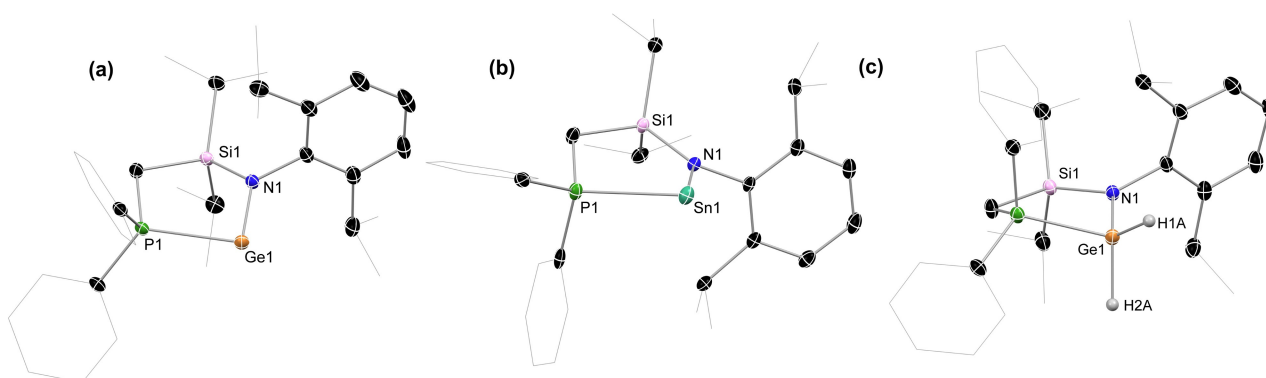


**Scheme 1.** Reaction of 1 with Na[BARF<sub>4</sub>] to give 3, and unsuccessful conversion of 2 to 4. (i) Na[BARF<sub>4</sub>], DCM, 30 min.

protonation-H<sub>2</sub> elimination route. The further reactivity of the Ge<sup>II</sup> cation is also described.

## Results and Discussion

We first attempted to access the cations *via* simple chloride abstraction from the reported phosphine-stabilized (amido)(chloro)tetrylenes, <sup>Ph<sup>i</sup>P</sup>DippGeCl (1) and <sup>Ph<sup>i</sup>P</sup>DippSnCl (2) (<sup>Ph<sup>i</sup>P</sup>Dipp = {Ph<sub>2</sub>PCH<sub>2</sub>Si<sup>i</sup>Pr<sub>2</sub>}(Dipp)N<sup>-</sup>) with Na[BARF<sub>4</sub>] in DCM (Scheme 1). The reaction between 1 and Na[BARF<sub>4</sub>] immediately became deep yellow after addition of DCM, with concomitant formation of a white precipitate. Workup afforded a yellow powder of cationic complex [<sup>Ph<sup>i</sup>P</sup>DippGe][BARF<sub>4</sub>] (3) in good yields of up to 86%. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 3 in THF-*d*<sub>6</sub> shows one singlet at 7.0 ppm, and a considerably more symmetrical <sup>1</sup>H NMR spectrum than the chloro-germylene precursor.<sup>[13a]</sup> Layering DCM solutions of 3 with pentane led to formation of large yellow crystalline blocks of this species, which confirmed the successful synthesis of 3 through X-ray diffraction analysis (Figure 2(a)).



**Figure 2.** The molecular structures of (a) 3, (b) 4, and (c) 7, with thermal ellipsoids at 25% probability. [BARF<sub>4</sub>]<sup>-</sup> anions and hydrogen atoms omitted for clarity, aside from hydrogen atoms of the GeH<sub>2</sub> moiety in 7. Selected bond distances (Å) and angles (°) for 3: Ge1-P1 2.461(1); Ge1-N1 1.822(3); N1-Ge1-P1 86.71(8) (1); For 5: Sn1-P1 2.668(1); Sn1-N1 2.060(3); N1-Sn1-P1 81.22(8); for 7: Ge1-P1 2.336(1); Ge1-N1 1.829(2); N1-Ge1-P1 92.60(8).

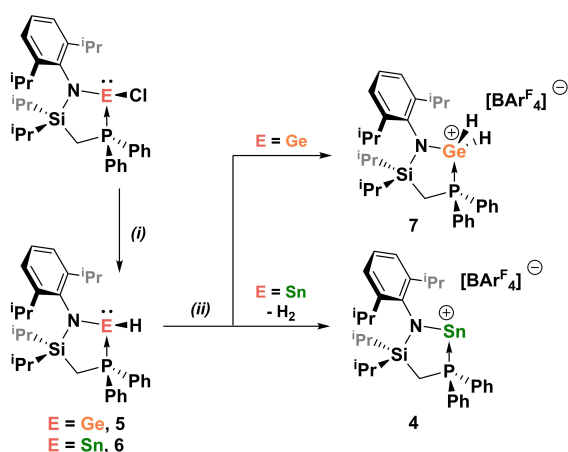
Utilising the same route with **2**, we were not able to access the cationic species  $[\text{P}^{\text{hip}}\text{DippSn}][\text{BAR}^{\text{F}}_4]$  (**4**). That is, the reaction of the Sn<sup>II</sup> analogue **2** with  $\text{Na}[\text{BAR}^{\text{F}}_4]$  in DCM did not result in a color change, although it did appear to form a single new species as ascertained from crude  $^{31}\text{P}$  NMR spectra (Figure S41 in ESI). However, from these reactions only an oily residue could be isolated, which provided no crystalline species in our hands. Varying the solvent (e.g. to PhF or Et<sub>2</sub>O) did not improve this. Nevertheless, as integrations in  $^1\text{H}$  NMR spectra of these oily residues did not match the potential Sn<sup>II</sup> cation, we concluded that **4** did not form in this reaction.<sup>[14]</sup>

We have recently shown that the related hydrido, amido, and hydroxy Ge<sup>II</sup>-Ni<sup>0</sup> complexes can be reacted with  $[(\text{Et}_2\text{O})_2\text{H}][\text{BAR}^{\text{F}}_4]$  in the elimination of dihydrogen, ammonia, and water, respectively, to yield cationic Ge<sup>II</sup>-Ni<sup>0</sup> complexes.<sup>[13b]</sup> Wesemann et al. have also shown that hydride abstraction from aryl tin trihydrides leads to dihydrogen elimination, resulting in the corresponding stannylene cations.<sup>[5]</sup> Therefore, we were curious as to whether the synthesis of the cationic tetrylenes (viz. **3** and **4**) could be possible via the analogous hydrido-tetrylenes,  $\text{P}^{\text{hip}}\text{DippEH}$  (E = Ge (**5**) and Sn (**6**)), which would then be protonated with  $[(\text{Et}_2\text{O})_2\text{H}][\text{BAR}^{\text{F}}_4]$ , in the loss of H<sub>2</sub>. Hydride complexes **5** and **6** were readily accessed through reaction of **1** and **2** with  $\text{K}[\text{HB}^{\text{s}}\text{Bu}_3]$  at  $-78^\circ\text{C}$  (Scheme 2). The Ge<sup>II</sup> derivative **5** is particularly straight forward to isolate, after simply filtering the reaction mixture, removing all volatiles, and washing with pentane. The Ge-H signal can be seen in the  $^1\text{H}$  NMR spectrum of **5**, at 7.45 ppm, as a doublet through coupling to the phosphine moiety. It is also clearly visible in the IR spectrum as an intense stretching band at  $1758\text{ cm}^{-1}$ . For the Sn<sup>II</sup> system, some decomposition can be seen upon warming crude reaction mixtures to ambient temperatures, indicated by dark brown reaction mixtures. Nevertheless, extracting these reaction mixtures with a combination of toluene and pentane precipitates the dark impurities, giving a colourless filtrate from which **6** crystallizes after storage at  $-32^\circ\text{C}$  overnight. The  $^1\text{H}$  NMR

spectrum of **6** reveals a very low-field shift for the Sn-H moiety, as a doublet at 12.09 ppm, shifted lower than all but one reported Sn<sup>II</sup> hydride systems.<sup>[15]</sup> One set of Sn-satellites can also clearly be observed as doublets, with a  $^1\text{J}_{\text{SnH}}$  coupling of 27.7 Hz, presumably with both  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  satellites overlapping. Clear  $^1\text{J}_{\text{SnP}}$  satellites are observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of this species ( $\delta = -1.1$  ppm;  $^1\text{J}_{117\text{SnP}} = 1184$  Hz;  $^1\text{J}_{119\text{SnP}} = 1240$  Hz). The IR spectrum of **6** has a sharp signal at  $1619\text{ cm}^{-1}$  which can be attributed to the Sn-H stretching frequency.<sup>[15b]</sup> The X-ray crystal structures of **5** and **6** (Figure S42 in ESI) indicate three-coordinate E<sup>II</sup> centres, with pseudo-tetrahedral geometry due to the presence of stereoactive lone pairs of electrons at these centres. Remaining metrical parameters are in keeping with our previously reported halo-tetrylenes bearing the same phosphine-functionalised amide ligands.<sup>[13a]</sup>

With these hydride complexes in hand, we attempted the synthesis of the cationic tetrylenes **3** and **4** by addition of fluorobenzene solutions of  $[(\text{Et}_2\text{O})_2\text{H}][\text{BAR}^{\text{F}}_4]$  to fluorobenzene solutions of **5** or **6** at  $-40^\circ\text{C}$  (Scheme 2). For the Ge<sup>II</sup> complex **5** no color change or gas evolution could be observed, but crude  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra clearly suggested formation of one new species, with a singlet resonance at  $\delta = -0.8$  ppm. After addition of pentane and storing the mixture at ambient temperature for three days, large colourless crystals could be isolated, revealing that the amido-germylium dihydride complex **7** had formed (Figure 2(c)). The  $^1\text{H}$  NMR spectrum of **7** reveals a distinct shift of the Ge-H resonance, observed at  $\delta = 7.45$  ppm in **5**, now appearing as a doublet at  $\delta = 6.37$  ppm with a considerably larger  $^2\text{J}_{\text{PH}}$  coupling of 35.1 Hz, and integrating to 2H. This is in keeping with the structure as determined by X-ray crystallography, featuring a cationic GeH<sub>2</sub> moiety, which apparently does not eliminate H<sub>2</sub> to form **3**. The formally Ge<sup>IV</sup> centre in **5** contains a tetrahedral, four coordinate cationic germanium centre, which electronically bears resemblance to the related (carbene)(boryl)germylium dihydride reported by Aldridge et al.<sup>[16]</sup> as well as the terphenyl-ligated germylium complex recently reported by Wesemann et al.<sup>[5]</sup> The reactivity of the latter compound, which features a lower coordinate Ge centre, is seemingly amplified relative to **5**, represented by its C-H and arene activation reactions above  $0^\circ\text{C}$ . Indeed, closely related E<sup>IV</sup> cations (E = Si-Pb) are also known to strongly interact with C-C  $\pi$ -systems.<sup>[17]</sup> This would suggest that the flanking phosphine arm in **5** aids greatly in stabilizing this species. The IR spectrum of **5** confirms the presence of hydride ligands, featuring two Ge-H stretching bands at  $1759$  and  $1611\text{ cm}^{-1}$  (Figure S17 in ESI). Notably, attempts to thermally drive elimination of H<sub>2</sub> were unsuccessful, only resulting in decomposition.

In contrast to these findings, the reaction of the related Sn<sup>II</sup> system, **6**, with  $[(\text{Et}_2\text{O})_2\text{H}][\text{BAR}^{\text{F}}_4]$  resulted in an immediate colour change to yellow, concomitant with gas evolution. Addition of pentane and storage at  $4^\circ\text{C}$  led to formation of yellow crystals of **4** in a moderate yield. X-ray diffraction analysis of these crystals confirmed the formation of the Sn<sup>II</sup> cation **4** (Figure 2(b)), presumably in a similar H<sub>2</sub> reductive elimination to known neutral and cationic Sn<sup>IV</sup> poly-hydrides.<sup>[5,18]</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** in THF-*d*<sub>6</sub> contains a single singlet signal at  $\delta = 16.5$  ppm, with distinct  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  satellites ( $^1\text{J}_{117\text{Sn}} =$



**Scheme 2.** Conversion of the tetrylene chlorides **1** and **2** to the tetrylenes hydrides **5** and **6** with K-Selectride followed by protonation to get the cationic complexes **7** and **4**. (i) K-Selectride, toluene,  $-78^\circ\text{C}$ ; (ii)  $[(\text{Et}_2\text{O})_2\text{H}][\text{BAR}^{\text{F}}_4]$ , PhF,  $-40^\circ\text{C}$ .

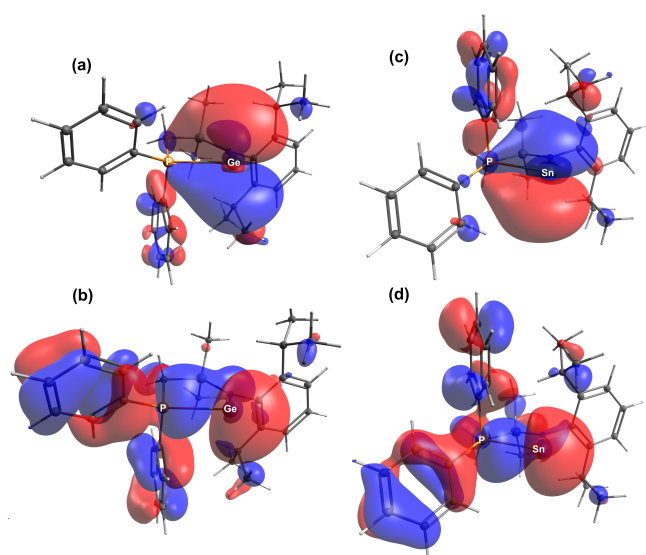
1552 Hz;  $^1J_{119\text{SnP}}=1630$  Hz). A doublet at  $\delta=31.6$  ppm can be observed in the  $^{119}\text{Sn}$  NMR, with a  $^1J_{119\text{SnP}}$  coupling matching that observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum.

The crystal structures of **3** and **4** show that the tetrel element centres are two-coordinate, bound by the amido ligand's N- and P-centres. A considerable contraction of the Ge–N and Sn–N bond distances ( $d_{\text{GeN}}=1.822(3)$  Å,  $d_{\text{SnN}}=2.060(3)$  Å) of roughly 0.1 Å and 0.06 Å, compared to the corresponding chloro-tetrelenes ( $d_{\text{GeN}}=1.925(3)$  Å,  $d_{\text{SnN}}=2.122(3)$  Å), can be observed.<sup>[13a,b]</sup> This can be attributed to the enhancement of the Lewis acidity leading to stronger electron donation of the N-centre to the vacant *p*-orbitals of the tetrel element centres. Interestingly, the Ge–P and Sn–P distances ( $d_{\text{GeP}}=2.461(1)$  Å,  $d_{\text{SnP}}=2.668(1)$  Å) are slightly elongated compared to the distances in the corresponding chloro-

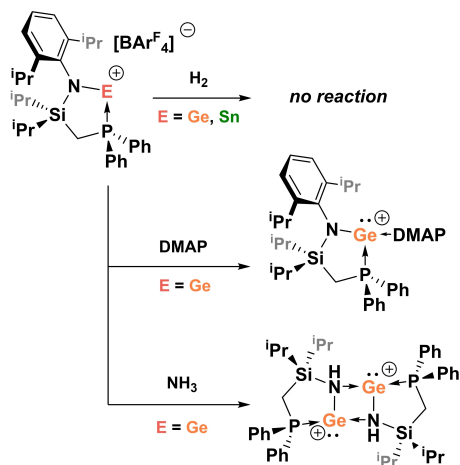
tetrelenes ( $d_{\text{GeP}}=2.472(1)$  Å,  $d_{\text{SnP}}=2.657(1)$  Å), despite the now cationic  $\text{E}^{\text{II}}$  centres, most likely caused by the increased  $\text{N}\rightarrow\text{E}^{\text{II}}$  donation. The lowest energy conformation and the related frontier orbitals of the full molecules of **3** and **4** were calculated using Density Functional Theory (DFT).<sup>[19]</sup> For both systems, a large HOMO-LUMO gap was found (**3**: 7.28 eV; **4**: 6.87 eV), which would typically indicate that these species are not reactive towards relatively inter small molecules such as  $\text{H}_2$ .<sup>[20]</sup> Nevertheless, the Lewis acidity of these compounds is borne out by the LUMOs, which represent vacant *p*-orbitals localized at the  $\text{E}^{\text{II}}$  centres (Figure 3(a) and (c)). Lone electron pairs localized at the same centres can be found at the HOMO-2 level (Figure 3, (b) and (d)).

Following the successful isolation of the cations **3** and **4** via different routes, they were briefly screened in their reactivity in small molecule activation (Scheme 3), given that two-coordinate neutral tetrelenes, with which **3** and **4** are isoelectronic, are known to react with  $\text{H}_2$ ,<sup>[21]</sup>  $\text{NH}_3$ ,<sup>[22]</sup>  $\text{CO}_2$ ,<sup>[23]</sup> and even  $\text{CO}$ .<sup>[24]</sup> As suggested by their wide HOMO-LUMO separations, neither of these cations showed any reaction towards  $\text{H}_2$ , despite the stability of the germylium dihydride **7**, which would represent the formal  $\text{H}_2$  addition product of **3**. Reactions with  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  also did not proceed. The reaction of this  $\text{Ge}^{\text{II}}$  cation with DMAP, however, did proceed, leading to discoloration of the reaction solution. Following work-up, colorless crystals could be isolated, which were found to be the three-coordinate  $\text{Ge}^{\text{II}}$  cation **8** through single-crystal X-ray diffraction analysis. Compound **8** is essentially isostructural with hydride complex **5**, with a *pseudo*-tetrahedral  $\text{Ge}^{\text{II}}$  centre. That is, DMAP coordination reduces the  $\text{DippN}\rightarrow\text{Ge}$  donation, leading to an elongation of this bond ( $d_{\text{NGe}}=1.916(3)$  Å). A concomitant contraction of the P–Ge bond is also seen ( $d_{\text{PGe}}=2.487(1)$  Å).

Reaction of **3** towards the protic N-base, ammonia, gave quite different results. Whilst our previously reported  $\text{Ni}^0$  complex,  $[\text{P}^{\text{Hipp}}\text{DippGe}]^+ \cdot [\text{Ni}(\text{PPh}_3)_2]$ , reversibly binds ammonia at the  $\text{Ge}^{\text{II}}$  centre,<sup>[13b]</sup> addition of ammonia to solutions of **3** irreversibly leads to colorless solutions after carefully agitating the solution for 5 min. Remarkably, an X-ray diffraction analysis of crystals isolated from such reactions revealed the unexpected product **9** formed through complete elimination of the  $[\text{NDipp}]$  fragment of the ligand, now replaced by an  $[\text{NH}]$  unit (Figure 4(b)). Due to the reduced steric bulk, the cationic complex **9** forms a dimeric structure where the  $[\text{NH}]$  functionalities bridge the two cationic  $\text{Ge}^{\text{II}}$  centres, which has a crystallographic plane of symmetry cutting the central  $[\text{Ge}_2\text{N}_2]$  ring. A degree of delocalization in this central unit can be assumed, given the two very similar Ge–N bond lengths of 2.021(1) and 2.053(9) Å. The P–Ge bond distances are in keeping with those observed in DMAP adduct **8** ( $d_{\text{PGe}}=2.472(3)$  Å), as one might expect given the similar coordination nature at  $\text{Ge}^{\text{II}}$  in these compounds. The N–H unit in **9** can be seen as a doublet in the  $^1\text{H}$  NMR spectrum of this species, at  $\delta=5.01$  ppm, coupling to the two chelating phosphine arms in a symmetrical manner, giving further evidence for a delocalized bonding model in the central  $[\text{Ge}_2\text{N}_2]$  ring system. The loss of the characteristic Dipp signals, e.g. those of the isopropyl CH and  $\text{CH}_3$  groups, is in keeping with the observed solid-state structure whereby the  $\text{DippNH}_2$  frag-

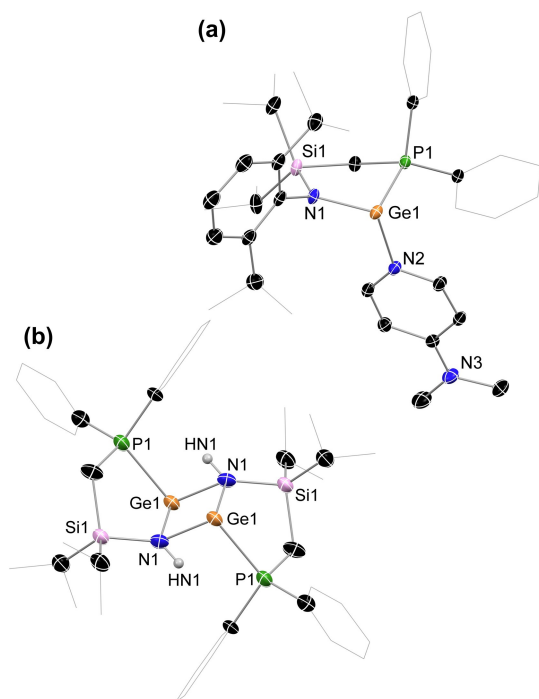


**Figure 3.** (a) The calculated LUMO of **3**; (b) the calculated HOMO-2 of **3**; (c) the calculated LUMO of **4**; (d) the calculated HOMO-2 of **4**.



**Scheme 3.** Reaction of **3** with DMAP and ammonia giving the DMAP adduct **8** and the dimeric activation product **9**.





**Figure 4.** The molecular structures of the cation parts in (a) **8**, and (b) **9**, with thermal ellipsoids at 25% probability, and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angle (°) for **8**: Ge1–P1 2.487(1); Ge1–N1 1.916(3); Ge1–N2 2.096(3); N1–Ge1–P1 86.99(8); For **9**: Ge1–P1 2.472(3); Ge1–N1 2.021(1); Ge1–N1' 2.053(9); Ge1...Ge1' 3.064(2); N1–N1' 2.686(1); P1–Ge1–N1 86.2(3); P1–Ge1–N1' 90.3(3); Ge1–N1–Ge1' 97.5(4); N1–Ge1–N1' 82.5(3); P1–Ge1–Ge1' 87.63(8).

ment has been entirely eliminated. A similar phosphine stabilized amido Ge<sup>II</sup> cation reported by Aldridge et al. also insights reactive non-innocence of the neighboring N-Dipp unit, the ammonia adding across the Ge–N bond resulting in a GeNH<sub>2</sub> unit and a cationic nitrogen atom.<sup>[10]</sup>

## Conclusions

As a whole, we have shown that the cations **3** and **4** can be synthesized from their chloro-tetrylenes **1** and **2**. This can either be done by chloride abstraction in the case of Ge<sup>II</sup> to isolate **3** or by H<sub>2</sub> elimination *via* protonation of the Sn<sup>II</sup> hydride **6** to get **4**. When the protonation was attempted with the Ge<sup>II</sup> hydride **5**, H<sub>2</sub> elimination was not observed, resulting in the cationic Ge<sup>IV</sup> dihydride **7**. The reactivity and Lewis acidity of the cationic tetrylenes **3** and **4** was analyzed by reacting **3** with DMAP and ammonia. Whilst the reaction with DMAP results in the expected DMAP adduct **8**, ammonia is cooperatively activated in an unusual manner leading to the elimination of DippNH<sub>2</sub> in exchange for an [NH] fragment, forming novel cationic tetrylene **9**. For future research, the cationic tetrylenes **3** and **4** can be employed as ligands directly, avoiding *in situ* generation, allowing for more controlled synthesis of transition metal

complexes, in contrast to our previously utilized 'uncontrolled' one pot synthesis of Ni<sup>0</sup> complexes.

## Experimental Section

**General considerations.** All experiments and manipulations were carried out under dry oxygen free argon atmosphere using standard Schlenk techniques or in a MBraun inert atmosphere glovebox containing an atmosphere of high purity argon. C<sub>6</sub>D<sub>6</sub> was dried, degassed and stored over a potassium mirror. All other solvents were dried over activated 4 Å mol sieves. <sup>PhIP</sup>DippGeCl<sub>2</sub>,<sup>[13a]</sup> <sup>PhIP</sup>DippSnCl<sub>2</sub>,<sup>[13b]</sup> Na[BAr<sup>F</sup><sub>4</sub>] ([BAr<sup>F</sup><sub>4</sub>]<sup>−</sup> = [B(3,5-CF<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>])<sup>[25]</sup> and [(Et<sub>2</sub>O)<sub>2</sub>H[BAr<sup>F</sup><sub>4</sub>]]<sup>[26]</sup> were synthesized according to known literature procedures. All other reagents were used as received. NMR spectra were recorded on a Bruker AV 400 Spectrometer. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to the residual solvent signals as internal standards. <sup>29</sup>Si{<sup>1</sup>H} NMR spectra were externally calibrated with SiMe<sub>4</sub>. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were externally calibrated with H<sub>3</sub>PO<sub>4</sub>. <sup>119</sup>Sn{<sup>1</sup>H} NMR spectra were externally calibrated with SnMe<sub>4</sub>. Liquid Injection Field Desorption Ionization Mass Spectrometry (LIFDI-MS) was measured directly from an inert atmosphere glovebox with a Thermo Fisher Scientific Exactive Plus Orbitrap equipped with an ion source from Linden CMS.<sup>[27]</sup> For the ammonia experiments ammonia 5.0 was used. Elemental analyses (C, H, N) were performed with a combustion analyzer (elementar vario EL, Bruker). Infrared spectra were measured with the Alpha FT IR from Bruker containing a platinum diamond ATR device.

**[<sup>PhIP</sup>DippGe][BAr<sup>F</sup><sub>4</sub>], **3**.** A solid mixture of **1** (2.50 g, 4.19 mmol) and Na[BAr<sup>F</sup><sub>4</sub>] (3.71 g, 4.19 mmol) was dissolved in DCM at ambient temperature and stirred for 30 min. The resulting light-yellow suspension was filtered, and all volatiles removed *in vacuo*. The resulting yellow residue was washed with pentane twice and dried *in vacuo* yielding analytically pure **3** (5.12 g, 86%) as a pale yellow powder. Yellow crystals suitable for X-ray diffraction were obtained from a concentrated DCM solution layered with pentane stored for 4 days at ambient temperature.

**<sup>1</sup>H NMR** (THF-*d*<sub>8</sub>, 400 MHz, 298 K): δ = 0.81 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.06 (m, 8H, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>, Si-Pr<sup>i</sup>-CH), 1.13 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.24 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 2.54 (d, 2H, <sup>2</sup>J<sub>HP</sub> = 16.1 Hz, CH<sub>2</sub>-PPh<sub>2</sub>), 3.04 (hept, 2H, <sup>2</sup>J<sub>HP</sub> = 6.5 Hz, Dipp-Pr<sup>i</sup>-CH), 7.18 (s, 3H, Ar-CH), 7.58 (s, 4H, Ar<sub>BAr<sup>F</sup><sub>4</sub></sub>-H<sub>para</sub>), 7.68 (m, 6H, Ar-CH), 7.80 (s, 8H, Ar<sub>BAr<sup>F</sup><sub>4</sub></sub>-H<sub>ortho</sub>), 7.97 (m, 4H, Ar-CH).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (THF-*d*<sub>8</sub>, 162 MHz, 298 K): δ = 7.0 (s, PPh<sub>2</sub>)

**<sup>13</sup>C{<sup>1</sup>H} NMR** (THF-*d*<sub>8</sub>, 101 MHz, 298 K): δ = 2.3 (CH<sub>2</sub>-PPh<sub>2</sub>), 17.0 and 17.0 (Si-Pr<sup>i</sup>-CH), 19.0 and 20.2 (Si-Pr<sup>i</sup>-CH<sub>3</sub>), 22.9 and 28.9 (Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 29.2 (Dipp-Pr<sup>i</sup>-CH), 118.4, 121.6, 124.3, 125.4, 127.0, 127.7, 128.1, 128.5, 129.7, 130.1, 130.3, 130.7, 131.1, 131.2, 133.0, 133.1, 134.1, 134.1, 135.8, 148.0, 162.2, 162.7, 163.2 and 163.7 (Ar-C).

**<sup>29</sup>Si{<sup>1</sup>H} NMR** (THF-*d*<sub>8</sub>, 99 MHz, 298 K): δ = 24.4 (d, <sup>2</sup>J<sub>SiP</sub> = 10.8 Hz, CH<sub>2</sub>-Si-Pr<sup>i</sup>).

**MS/LIFDI-HRMS** found (calcd.) m/z: 562.2057 (562.2114) for [M-BAr<sup>F</sup><sub>4</sub>]<sup>+</sup>.

**Anal. calcd.** for C<sub>21</sub>H<sub>38</sub>ClNSiSn: C, 53.12%; H, 3.89%; N, 0.98%; found: C, 53.07%; H, 3.85%; N, 1.21%.

**[<sup>PhIP</sup>DippSn][BAr<sup>F</sup><sub>4</sub>], **4**.** A solution of [(Et<sub>2</sub>O)<sub>2</sub>H[BAr<sup>F</sup><sub>4</sub>]] (250 mg, 0.247 mmol) in PhF was added dropwise to a solution of **6** (150 mg, 0.247 mmol) in PhF at −40 °C with stirring, resulting in a light yellow solution. This was allowed to warm to ambient temperature, leading to dark brown suspension which was filtered and concentrated *in vacuo* to ~2 mL. Addition of 10 mL of pentane led

to a light yellow solution formation of some dark droplets of oil. The solution was separated from the oil *via* canula transfer, and placed at 4 °C overnight yielding light yellow crystals of **4** (130 mg, 36%), which were suitable for X-ray diffraction analysis.

<sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz, 298 K): δ = 0.81 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.04 (m, 8H, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>, Si-Pr<sup>i</sup>-CH), 1.11 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.23 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 2.50 (d, 2H, <sup>2</sup>J<sub>HP</sub> = 15.2 Hz, CH<sub>2</sub>-PPh<sub>2</sub>), 3.18 (hept, 2H, <sup>2</sup>J<sub>HP</sub> = 6.8 Hz, Dipp-Pr<sup>i</sup>-CH), 7.13 (m, 3H, Ar-CH), 7.58 (s, 4H, Ar<sub>BARF</sub>-H<sub>para</sub>), 7.65 (m, 6H, Ar-CH), 7.80 (s, 8H, Ar<sub>BARF</sub>-H<sub>ortho</sub>), 7.91 (m, 4H, Ar-CH).

<sup>31</sup>P{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 162 MHz, 298 K): δ = 16.5 (s, PPh<sub>2</sub>, <sup>1</sup>J<sub>117SnP</sub> = 1552 Hz, <sup>1</sup>J<sub>119SnP</sub> = 1630 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 101 MHz, 298 K): δ = 4.3 (CH<sub>2</sub>-PPh<sub>2</sub>), 17.2 and 17.2 (Si-Pr<sup>i</sup>-CH), 18.9 and 20.1 (Si-Pr<sup>i</sup>-CH<sub>3</sub>), 23.3 and 28.6 (Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 29.2 (Dipp-Pr<sup>i</sup>-CH), 118.4, 121.6, 124.3, 125.3, 126.4, 127.0, 129.3, 129.7, 130.0, 130.4, 130.6, 131.0, 131.1, 133.2, 133.3, 133.6, 133.7, 135.7, 141.1, 141.2, 147.3, 162.2, 162.7, 163.2 and 163.7 (Ar-C).

<sup>29</sup>Si{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 99 MHz, 298 K): δ = 18.6 (d, <sup>2</sup>J<sub>SIP</sub> = 6.9 Hz, CH<sub>2</sub>-Si-Pr<sup>i</sup>).

<sup>119</sup>Sn NMR (THF-d<sub>8</sub>, 149 MHz, 233 K): δ = 31.6 (d, <sup>1</sup>J<sub>SnP</sub> = 1630 Hz, Sn-PPh<sub>2</sub>).

MS/LIFDI-HRMS found (calcd.) m/z: 608.1860 (608.1924) for [M-BARF<sub>4</sub>]<sup>+</sup>.

Anal. calcd. for C<sub>21</sub>H<sub>38</sub>ClNSiSn: C, 51.45%; H, 3.77%; N, 0.95%; found: C, 52.27%; H, 3.86%; N, 1.08%.

<sup>PhIP</sup>DippGeH, **5**. A solution of **1** (1.28 g, 2.14 mmol) in toluene was cooled to -78 °C, and a solution of K-Selectride (1 M in THF, 2.14 mL, 2.14 mmol) slowly added. The mixture was subsequently allowed to warm to ambient temperature. The light orange mixture was filtered, and all volatiles were removed *in vacuo*. The oily residue was extracted in pentane, filtered, and concentrated to ~20 mL. The solution was placed at -32 °C overnight leading to a crop of light yellow crystals. The solution was decanted with a canula, the crystals washed with pentane (1 x 5 mL), and dried *in vacuo* to afford **5** (0.53 g, 44%) as a light yellow crystalline solid. Crystals suitable for X-ray diffraction analysis were obtained from a concentrated pentane solution at ambient temperature after 1 day.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 298 K): δ = 0.74 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 0.89 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.00 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.07 (m, 1H, Si-Pr<sup>i</sup>-CH), 1.16 (m, 6H, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.36 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.42 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.46 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.77 (m, 3H, Si-Pr<sup>i</sup>-CH, CH<sub>2</sub>-PPh<sub>2</sub>), 2.87 (hept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, Dipp-Pr<sup>i</sup>-CH), 4.11 (hept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, Dipp-Pr<sup>i</sup>-CH), 6.95 (m, 3H, Ar-CH), 7.07 (m, 6H, Ar-CH), 7.45 (d, 1H, <sup>2</sup>J<sub>HP</sub> = 5.8 Hz, Ge-H), 7.50 (m, 2H, Ar-CH), 7.65 (m, 2H, Ar-CH).

<sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz, 298 K): δ = 9.2 (s, PPh<sub>2</sub>)

<sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 101 MHz, 298 K): δ = 9.2 (CH<sub>2</sub>-PPh<sub>2</sub>), 15.9 and 16.1 (Si-Pr<sup>i</sup>-CH), 18.0, 19.7, 20.4 and 20.7 (Si-Pr<sup>i</sup>-CH<sub>3</sub>), 23.0, 23.3, 26.9 and 27.2 (Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 28.0 and 28.6 (Dipp-Pr<sup>i</sup>-CH), 123.3, 123.9, 124.1, 129.0, 129.0, 129.1, 129.1, 130.6, 130.7, 130.8, 130.9, 132.0, 132.3, 132.5, 132.6, 132.7, 132.8, 134.4, 134.6, 146.3, 146.3, 147.1, 147.2, 148.5 and 148.5 (Ar-C).

<sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 99 MHz, 298 K): δ = 10.1 (d, <sup>2</sup>J<sub>SIP</sub> = 10.2 Hz, CH<sub>2</sub>-Si-Pr<sup>i</sup>).

MS/LIFDI-HRMS found (calcd.) m/z: 562.2086 (562.2114) for [M-H]<sup>+</sup>.

Anal. calcd. for C<sub>21</sub>H<sub>38</sub>ClNSiSn: C, 66.21%; H, 7.89%; N, 2.49%; found: C, 66.20%; H, 8.15%; N, 2.59%.

IR, ν/cm<sup>-1</sup> (ATR): 1758 (s, m, Ge-H).

<sup>PhIP</sup>DippSnH, **6**. A solution of **2** (2.51 g, 3.90 mmol) in toluene was cooled to -78 °C and a solution of K-Selectride (1 M in THF, 3.90 mL, 3.90 mmol) was slowly added. The mixture was subsequently allowed to warm to ambient temperature, during which time the color of the mixture changed from orange to dark brown. The mixture was concentrated, and pentane was added until a dark precipitate had formed. The mixture was filtered and placed at -32 °C overnight, leading to a crop of colorless crystals. The solution was removed *via* canula, the crystals washed with pentane (~5 mL) and dried *in vacuo* to yield **6** (1.85 g, 3.04 mmol, 78%) as an off-white crystalline solid. Crystals suitable for X-ray diffraction analysis were obtained from a concentrated pentane solution stored at ambient temperature, after 1 day.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 298 K): δ = 0.77 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 0.93 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.00 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.06 (m, 1H, Si-Pr<sup>i</sup>-CH), 1.14 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.23 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.38 (m, 9H, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.75 (m, 2H, Si-Pr<sup>i</sup>-CH, CH<sub>2</sub>-PPh<sub>2</sub>), 2.00 (m, 1H, CH<sub>2</sub>-PPh<sub>2</sub>), 3.01 (hept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Dipp-Pr<sup>i</sup>-CH), 4.19 (hept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, Dipp-Pr<sup>i</sup>-CH), 6.96 (m, 3H, Ar-CH), 7.05 (m, 5H, Ar-CH), 7.16 (m, 1H, Ar-CH), 7.56 (m, 4H, Ar-CH), 12.09 (d, 1H, <sup>2</sup>J<sub>HP</sub> = 4.5 Hz, Sn-H; Sn-satellites (d, <sup>1</sup>J<sub>Hsn</sub> = 14.1 Hz) and (d, <sup>1</sup>J<sub>Hsn</sub> = 14.1 Hz)).

<sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz, 298 K): δ = -1.1 (s, PPh<sub>2</sub>, <sup>1</sup>J<sub>117SnP</sub> = 1184 Hz, <sup>1</sup>J<sub>119SnP</sub> = 1240 Hz).

<sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 101 MHz, 298 K): δ = 11.4 (CH<sub>2</sub>-PPh<sub>2</sub>), 16.1 and 16.7 (Si-Pr<sup>i</sup>-CH), 18.2, 19.6, 20.2 and 20.9 (Si-Pr<sup>i</sup>-CH<sub>3</sub>), 23.1, 23.6, 26.9 and 27.0 (Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 27.7 and 28.3 (Dipp-Pr<sup>i</sup>-CH), 123.1, 123.3, 124.1, 129.1, 129.1, 129.2, 129.2, 130.6, 130.6, 130.9, 130.9, 131.8, 132.1, 132.8, 132.9, 132.9, 133.0, 134.9, 135.1, 145.4, 145.4, 147.6, 147.7, 148.4 and 148.4 (Ar-C).

<sup>29</sup>Si{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 99 MHz, 298 K): δ = 7.72 (d, <sup>2</sup>J<sub>SIP</sub> = 9.2 Hz, CH<sub>2</sub>-Si-Pr<sup>i</sup>).

<sup>119</sup>Sn NMR (C<sub>6</sub>D<sub>6</sub>, 149 MHz, 233 K): δ = -86.5 (d, <sup>1</sup>J<sub>SnP</sub> = 1240 Hz, Sn-PPh<sub>2</sub>).

MS/LIFDI-HRMS found (calcd.) m/z: 608.1893 (608.1924) for [M-H]<sup>+</sup>.

Anal. calcd. for C<sub>21</sub>H<sub>38</sub>ClNSiSn: C, 61.19%; H, 7.29%; N, 2.30%; found: C, 60.70%; H, 7.01%; N, 2.44%.

IR, ν/cm<sup>-1</sup> (ATR): 1619 (s, m, Sn-H).

<sup>PhIP</sup>DippGeH<sub>2</sub>[BARF<sub>4</sub>], **7**. A solid mixture of **5** (200 mg, 0.36 mmol) and [(Et<sub>2</sub>O)<sub>2</sub>H][BARF<sub>4</sub>] (360 mg, 0.36 mmol) was dissolved in PhF at ambient temperature and stirred for 30 min. All volatiles were removed from the solution *in vacuo*, and pentane (10 mL) added. The solution was placed at 4 °C overnight yielding colorless crystals of **7** (352 mg, 0.25 mmol, 69%), which were suitable for X-ray diffraction analysis.

<sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz, 298 K): δ = 0.83 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.05 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 1.11 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, Si-Pr<sup>i</sup>-CH<sub>3</sub>), 1.28 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, Dipp-Pr<sup>i</sup>-CH<sub>3</sub>, Si-Pr<sup>i</sup>-CH), 2.48 (d, 2H, <sup>2</sup>J<sub>HP</sub> = 16.8 Hz, CH<sub>2</sub>-PPh<sub>2</sub>), 3.19 (hept, 2H, <sup>2</sup>J<sub>HP</sub> = 6.8 Hz, Dipp-Pr<sup>i</sup>-CH), 6.37 (d, 2H, <sup>2</sup>J<sub>HP</sub> = 35.1 Hz, PPh<sub>2</sub>-GeH<sub>2</sub>), 7.18 (s, 3H, Ar-CH), 7.58 (s, 4H, Ar<sub>BARF</sub>-H<sub>para</sub>), 7.78 (m, 14H, Ar-CH/ Ar<sub>BARF</sub>-H<sub>ortho</sub>), 7.96 (m, 4H, Ar-CH).

<sup>31</sup>P{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 162 MHz, 298 K): δ = -0.8 (s, PPh<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 101 MHz, 298 K): δ = 5.6 (CH<sub>2</sub>-PPh<sub>2</sub>), 15.7 (Si-Pr<sup>i</sup>-CH), 17.8 and 19.0k (Si-Pr<sup>i</sup>-CH<sub>3</sub>), 23.9 and 26.9 (Dipp-Pr<sup>i</sup>-CH<sub>3</sub>), 29.3 (Dipp-Pr<sup>i</sup>-CH), 116.7, 118.4, 121.6, 122.8, 123.5, 124.3, 125.9, 127.1, 127.7, 129.8, 130.1, 130.4, 130.7, 130.9, 131.6, 131.7, 133.9, 134.0, 135.8, 147.8, 162.3, 162.8, 163.2 and 163.7 (Ar-C).

$^{29}\text{Si}\{^1\text{H}\}$  NMR (THF- $d_8$ , 99 MHz, 298 K):  $\delta = 15.0$  (d,  $^2J_{\text{SiP}} = 2.5$  Hz, Si-Pr).

MS/LIFDI-HRMS found (calcd.) m/z: 562.2106 (562.2114) for  $[\text{M}-2\text{H}-\text{BARF}_4]^+$ .

Anal. calcd. for  $\text{C}_{21}\text{H}_{38}\text{ClNSiSn}$ : C, 53.04%; H, 4.03%; N, 0.98%; found: C, 53.02%; H, 3.70%; N, 1.04%.

IR,  $\nu/\text{cm}^{-1}$  (ATR): 1759 (s, w, Ge-H), 1611 (s, w, Ge-H).

$[\text{Ph}^{\text{IP}}\text{DippGe-DMAP}][\text{BARF}_4]$ , **8**. A solid mixture of **3** (200 mg, 0.36 mmol) and DMAP (360 mg, 0.36 mmol) was dissolved in PhF at ambient temperature and stirred for 30 min. All volatiles were removed from the solution *in vacuo*, and pentane added (5 mL). The solution was placed at 4 °C overnight yielding colorless crystals of **8** (352 mg, 0.25 mmol, 69%), which were suitable for X-ray diffraction analysis.

$^1\text{H}$  NMR (THF- $d_8$ , 400 MHz, 298 K):  $\delta = 0.55$  (d, 3H,  $^3J_{\text{HH}} = 7.3$  Hz, Si-Pr- $\text{CH}_3$ ), 0.65 (d, 3H,  $^3J_{\text{HH}} = 6.6$  Hz, Dipp-Pr- $\text{CH}_3$ ), 0.75 (m, 1H, Si-Pr-CH), 0.94 (d, 3H,  $^3J_{\text{HH}} = 6.9$  Hz, Dipp-Pr- $\text{CH}_3$ ), 1.09 (d, 3H,  $^3J_{\text{HH}} = 7.4$  Hz, Si-Pr- $\text{CH}_3$ ), 1.20 (m, 6H, Dipp-Pr-CH/Si-Pr- $\text{CH}_3$ ), 1.30 (d, 3H,  $^3J_{\text{HH}} = 6.7$  Hz, Dipp-Pr- $\text{CH}_3$ ), 1.37 (d, 3H,  $^3J_{\text{HH}} = 7.3$  Hz, Si-Pr- $\text{CH}_3$ ), 1.52 (m, 1H, Si-Pr-CH), 2.06 (m, 1H,  $\text{CH}_2\text{-PPh}_2$ ), 2.80 (m, 2H,  $\text{CH}_2\text{-PPh}_2/\text{Dipp-Pr-CH}$ ), 3.10 (s, 6H, DMAP-N- $\text{CH}_3$ ), 3.68 (m, 1H, Dipp-Pr-CH), 6.76 (d,  $^3J_{\text{HH}} = 6.6$  Hz,  $\text{Ar}_{\text{DMAP-CH}}$ ), 7.10 (s, 3H, Ar-CH), 7.32 (m, 4H, Ar-CH), 7.43 (m, 1H, Ar-CH), 7.58 (s, 4H,  $\text{Ar}_{\text{BARF-H}_{\text{para}}}$ ), 7.72 (m, 3H, Ar-CH), 7.80 (s, 8H,  $\text{Ar}_{\text{BARF-H}_{\text{ortho}}}$ ), 8.10 (m, 4H, Ar-CH).

$^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ , 162 MHz, 298 K):  $\delta = -1.1$  (s,  $\text{PPh}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 101 MHz, 298 K):  $\delta = 4.7$  ( $\text{CH}_2\text{-PPh}_2$ ), 17.3 and 17.3 (Si-Pr-CH), 19.2, 20.3, 20.8 and 20.9 (Si-Pr- $\text{CH}_3$ ), 21.0, 22.3, 27.6, and 29.1 (Dipp-Pr- $\text{CH}_3$ ), 29.5 and 29.6 (Dipp-Pr-CH), 39.6 (DMAP-N- $\text{CH}_3$ ), 108.6, 116.0, 116.2, 118.4, 121.6, 124.3, 124.4, 125.6, 126.7, 127.1, 129.8, 130.0, 130.3, 130.4, 130.7, 130.8, 130.9, 131.0, 131.1, 132.0, 132.6, 134.2, 134.3, 135.8, 145.4, 147.9, 148.5, 157.5, 162.3, 162.8, 163.2 and 163.7 (Ar-C).

$^{29}\text{Si}\{^1\text{H}\}$  NMR (THF- $d_8$ , 99 MHz, 298 K):  $\delta = 19.0$  (d,  $^2J_{\text{SiP}} = 12.3$  Hz,  $\text{CH}_2\text{-Si-Pr}_2$ ).

MS/LIFDI-HRMS found (calcd.) m/z: 684.2890 (680.2958) for  $[\text{M}-\text{BARF}_4]^+$ .

Anal. calcd. for  $\text{C}_{21}\text{H}_{38}\text{ClNSiSn}$ : C, 54.36%; H, 4.24%; N, 2.72%; found: C, 54.18%; H, 4.04%; N, 2.81%.

$[(\text{Ph}_2\text{PCH}_2\text{Si}^{\text{IP}}\text{Pr}_2\text{N}(\text{H})\text{Ge})_2[\text{BARF}_4]_2$ , **9**. A solution of **3** (250 mg, 0.18 mmol) in PhF was cooled to  $-40^\circ\text{C}$ . Addition of  $\text{NH}_3$  (8 mL, 0.36 mmol) led to a colorless solution, which was swirled for 5 min at  $-40^\circ\text{C}$ . Then the mixture was subjected to vacuum to remove excess ammonia. The solution was subsequently allowed to warm to ambient temperature, and the solution concentrated to  $\sim 5$  mL *in vacuo*. Pentane (5 mL) was added, and the solution placed at 4 °C for 7 days, leading to colorless crystals of **9** (132 mg, 0.11 mmol, 59%), which were suitable for X-ray diffraction analysis.

$^1\text{H}$  NMR (THF- $d_8$ , 400 MHz, 298 K):  $\delta = 0.97$  (m, 14H, Si-Pr-CH/Si-Pr- $\text{CH}_3$ ), 1.99 (d, 2H,  $^3J_{\text{HP}} = 16.5$  Hz,  $\text{CH}_2\text{-PPh}_2$ ), 5.01 (d, 1H,  $^3J_{\text{HP}} = 35.0$  Hz, Ge-N-H), 7.09 (m, 2H, Ar-CH), 7.34 (m, 1H, Ar-CH), 7.59 (m, 8H, Ar-CH), 7.79 (m, 11H, Ar-CH).

$^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ , 162 MHz, 298 K):  $\delta = 13.5$  (s,  $\text{PPh}_2$ ).

2.35 ( $\text{CH}_2\text{-PPh}_2$ ), 16.2 and 16.2 (Si-Pr-CH), 18.1 and 18.3 (Si-Pr- $\text{CH}_3$ ), 116.0, 116.2, 118.4, 121.6, 124.3, 125.1, 125.1, 127.0, 128.6, 129.0, 129.8, 130.1, 130.4, 130.8, 130.9, 131.0, 131.1, 133.4, 133.5, 133.6, 133.6, 135.8, 162.3, 162.7, 163.7, 163.7 and 165.3 (Ar-C).

$^{29}\text{Si}\{^1\text{H}\}$  NMR (THF- $d_8$ , 99 MHz, 298 K):  $\delta = 31.2$  (d,  $^2J_{\text{SiP}} = 18.0$  Hz, Si-Pr).

Anal. calcd. for  $\text{C}_{21}\text{H}_{38}\text{ClNSiSn}$ : C, 48.45%; H, 3.11%; N, 1.11%; found: C, 50.03%; H, 3.14%; N, 1.24%.

N.B. The acquisition of mass spectrometry data was not successful due to repeated strong fragmentation and instability of the compound.

## Acknowledgements

TJH thanks the Fonds der Chemischen Industrie (FCI) for generous funding of this research through a Liebig Stipendium, the DFG for an Independent Research grant (Project No. 470323245), and the Technical University Munich for the generous endowment of TUM Junior Fellow Funds. We also acknowledge the Gauss Centre for Supercomputing e. V. for providing computing time on the GCS Super computer Super MUC at Leibniz Supercomputing Centre. We also thank M. Muhr, and A. Heidecker for aiding in the measurement of LIFDI-MS and IR spectra. Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** tetryliumylidenes · single-centre ambiphiles · ammonia activation ·  $\text{H}_2$ -elimination · low-valent

- [1] a) J. F. Norris, W. W. Sanders, *Am. Chem. J.* **1901**, *25*, 54–62; b) J. F. Norris, *Am. Chem. J.* **1901**, *25*, 117–122; c) F. Kehrman, F. Wentzel, *Chem. Ber.* **1901**, *34*, 3815–3819.
- [2] a) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354–396; b) H. Fang, Z. Wang, X. Fu, *Coord. Chem. Rev.* **2017**, *344*, 214–237; H. F. T. Klare, L. Albers, L. Süsse, S. Keess, T. Müller, M. Oestreich, *Chem. Rev.* **2021**, *121*, 5889–5985.
- [3] a) V. S. V. S. N. Swamy, S. Pal, S. Khan, S. S. Sen, *Dalton Trans.* **2015**, *44*, 12903–12923; b) P. Frisch, S. Inoue, *Dalton Trans.* **2020**, *49*, 6176–6182.
- [4] J. Li, C. Schenk, F. Winter, H. Scherer, N. Trapp, A. Higelin, S. Keller, R. Pöttgen, I. Krossing, C. Jones, *Angew. Chem. Int. Ed.* **2012**, *51*, 9557–9561.
- [5] A quasi-one coordinate  $\text{Sn}^{\text{II}}$  cation: F. Diab, F. S. W. Aicher, C. P. Sindlinger, K. Eichele, H. Schubert, L. Wesemann, *Chem. Eur. J.* **2019**, *25*, 4426–4434.
- [6] a) P. Jutzi, F. Kohl, P. Hoffmann, C. Krüger, Y. Tsay, *Chem. Ber.* **1980**, *113*, 757–769. A related example with neutral arene donor stabilization: b) T. Probst, O. Steigelmann, J. Riede, H. Schmidbaur, *Angew. Chem. Int. Ed.* **1990**, *29*, 1397–1398.
- [7] a) H. V. R. Dias, Z. Wang, *J. Am. Chem. Soc.* **1997**, *119*, 4650–4655; b) M. Stender, A. D. Phillips, P. P. Power, *Inorg. Chem.* **2001**, *40*, 5314–5315; c) A. E. Ayers, H. V. R. Dias, *Inorg. Chem.* **2002**, *41*, 12, 3259–3268; d) F. Cheng, J. M. Dyke, F. Ferrante,

- A. L. Hector, W. Levason, G. Reid, M. Webster, W. Zhang, *Dalton Trans.* **2010**, 39, 847–856; e) Y. Xiong, S. Yao, S. Inoue, A. Berkefeld, M. Driess, *Chem. Commun.* **2012**, 48, 12198–12200; f) T. Ochiai, D. Franz, E. Irran, S. Inoue, *Chem. Eur. J.* **2015**, 21, 6704–670; g) D. C. H. Do, A. V. Protchenko, M. Á. Fuentes, J. Hicks, P. Vasko, S. Aldrige, *Chem. Commun.* **2020**, 56, 4684–4687.
- [8] S. Khan, G. Gopakumar, W. Thiel, M. Alcarazo, *Angew. Chem. Int. Ed.* **2013**, 52, 5644–5647.
- [9] a) P. A. Rugar, V. N. Staroverov, P. J. Ragogna, K. M. Baines, *J. Am. Chem. Soc.* **2007**, 129, 15138–15139; b) Y. Xiong, S. Yao, G. Tan, S. Inoue, M. Driess, *J. Am. Chem. Soc.* **2013**, 135, 5004–5007; c) K. Inomata, T. Watanabe, H. Tobita, *J. Am. Chem. Soc.* **2014**, 136, 14341–14344; d) K. Inomata, T. Watanabe, Y. Miyazaki, H. Tobita, *J. Am. Chem. Soc.* **2015**, 137, 11935–11937; e) A. Rit, R. Tirfoin, S. Aldridge, *Angew. Chem. Int. Ed.* **2016**, 55, 378–382; f) M. Roy, S. Fujimori, M. Ferguson, R. McDonald, N. Tokitoh, E. Rivard, *Chem. Eur. J.* **2018**, 24, 14392–14399; g) R. J. Mangan, A. Rit, C. P. Sindlinger, R. Tirfoin, J. Campos, J. Hicks, K. E. Christensen, H. Niu, S. Aldridge, *Chem. Eur. J.* **2020**, 26, 306–315.
- [10] Y. Zhou, P. Vasko, J. Hicks, M. Á. Fuentes, A. Heilmann, E. L. Kolychev, S. Aldrige, *Dalton Trans.* **2020**, 49, 9495–9504.
- [11] M. Driess, S. Yao, M. Brym, C. van Wüllen, *Angew. Chem. Int. Ed.* **2006**, 45, 6730–6733.
- [12] D. Sarkar, S. Dutta, C. Weetman, E. Schubert, D. Koley, S. Inoue, *Chem. Eur. J.* **2021**, 27, 13072–13078.
- [13] a) P. M. Keil, T. Szilvási, T. J. Hadlington, *Chem. Sci.* **2021**, 12, 5582–5590; b) P. M. Keil, T. J. Hadlington, *Angew. Chem. Int. Ed.* **2022**, 61, e202114143; *Angew. Chem.* **2022**, 134, e202114143; c) P. M. Keil, T. J. Hadlington, *Chem. Commun.* **2022**, 58, 3011–3014.
- [14] A possible product might be two Sn-atoms being linked by a Cl atom, which would result in a mono cationic complex and fits the <sup>1</sup>H NMR (Figure S40 in ESI).
- [15] a) T. J. Hadlington, M. Hermann, J. Li, G. Frenking, C. Jones, *Angew. Chem. Int. Ed.* **2013**, 52, 10199–10203; *Angew. Chem.* **2013**, 125, 10389–10393; b) T. J. Hadlington, M. Driess, C. Jones, *Chem. Soc. Rev.* **2018**, 47, 4176–4197.
- [16] R. J. Mangan, A. Rit, C. P. Sindlinger, R. Tirfoin, J. Campos, J. Hicks, K. E. Christensen, H. Niu, S. Aldridge, *Chem. Eur. J.* **2020**, 26, 306–315.
- [17] a) T. Müller, C. Bauch, M. Ostermeier, M. Bolte, N. Auner, *J. Am. Chem. Soc.* **2003**, 125, 2158–2168; b) Y. Yang, R. Panisch, M. Bolte, T. Meller, *Organometallics* **2008**, 27, 4847–4853.
- [18] a) C. P. Sindlinger, L. Wesemann, *Chem. Sci.* **2014**, 5, 2739–2746; b) C. P. Sindlinger, A. Stasch, H. F. Bettinger, L. Wesemann, *Chem. Sci.* **2015**, 6, 4737–4751.
- [19] Calculated at the ωB97XD/def2-SVP(Ge, Sn: def2-TZVPP) level.
- [20] a) A. V. Protchenko, J. I. Bates, L. M. A. Saleh, M. P. Blake, A. D. Schwarz, E. L. Kolychev, A. L. Thompson, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2016**, 138, 4555–4564; b) M. V. Zabalov, M. A. Syroeshkin, B. N. Mankaev, S. V. Timofeev, M. P. Egorov, S. S. Karlov, *Russ. Chem. Bull. Int. Ed.* **2021**, 70, 1075–1079.
- [21] a) Y. Peng, B. D. Ellis, X. Wang, P. P. Power, *J. Am. Chem. Soc.* **2008**, 130, 12268–12269; b) A. V. Protchenko, K. H. Birjukumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, 134, 6500–6503.
- [22] a) Y. Peng, J.-D. Guo, B. D. Ellis, Z. Zhu, J. C. Fettinger, S. Nagase, P. P. Power, *J. Am. Chem. Soc.* **2009**, 131, 16272–16282; b) T. J. Hadlington, M. Hermann, G. Frenking, C. Jones, *Chem. Sci.* **2015**, 6, 7249–7257; c) T. J. Hadlington, J. A. B. Abdalla, R. Tirfoin, S. Aldridge, C. Jones, *Chem. Commun.* **2016**, 52, 1717–1720.
- [23] F. Hanusch, L. Groll, S. Inoue, *Chem. Sci.* **2021**, 12, 2001–2015.
- [24] a) Y. Wang, A. Kostenko, T. J. Hadlington, M.-P. Luecke, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2019**, 141, 626–634; b) D. Reiter, R. Holzner, A. Porzelt, P. Frisch, S. Inoue, *Nat. Chem.* **2020**, 11, 1131–1135; c) S. Fujimori, S. Inoue, *J. Am. Chem. Soc.* **2022**, 144, 2034–2050.
- [25] A. J. Martínez-Martínez, A. S. Weller, *Dalton Trans.* **2019**, 48, 3351–3354.
- [26] F. K. Scharnagl, M. F. Hertrich, G. Neitzel, R. Jackstell, M. Beller, *Adv. Synth. Catal.* **2019**, 361, 374–379.
- [27] M. Muhr, P. HeiB, M. Schütz, R. Bühler, C. Gemel, M. H. Linden, H. B. Linden, R. A. Fischer, *Dalton Trans.* **2021**, 50, 9031–9036.

---

 Manuscript received: April 4, 2022

Revised manuscript received: May 9, 2022

Accepted manuscript online: May 10, 2022