A Fully Phosphane-Substituted Disilene

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Abstract: There is growing interest in compounds containing functionalized E=E multiple bonds (E=Si, Ge, Sn, Pb) because of their potential to exhibit novel physical and chemical properties. However, compounds containing multiple functionalities are rare, with scarcity increasing with increasing degree of substitution. The first ditetrelene \( R_1E=E=R_2 \) in which the \( E=E \) bond is substituted by four heteroatoms (other than Si) is described. The tetrrophosphi-dilsilene [\{(Mes)\}P]Si=Si[\{(Mes)\}P]; \( 7 \) is readily isolated from the reaction between SiBr\(_4\) and [\{(Mes)\}P]Li, the latter of which acts as a sacrificial reducing agent. The structure of \( 7 \) is presented, while the bonding in, and stability of \( 7 \) were probed using DFT calculations.

Since Lappert’s landmark report of the distannene \([\{(Me,Sn)\}_2]_2\); \( 1 \) numerous examples of compounds containing multiple bonds between \( p \)-block elements have been reported.\(^2\) Nevertheless, there is continuing interest in these compounds and recent developments in this area have turned to functionalized species, which provide fascinating opportunities for tuning the physical and chemical properties of the \( E=E \) bond.\(^[[3–12]]\)

Typically, ditetrelenes (the heavier group 14 analogues of alkenes, \( R_1E=E=R_2 \)) require sterically demanding substituents to kinetically protect the \( E=E \) double bond.\(^[[1,2]]\) These substituents are usually drawn from bulky aryl, silyl, or occasionally alkyl groups. In contrast, ditetrelenes substituted by heteroatoms from groups 15–17 are rather scarce, since such heteroatoms usually favor the formation of the corresponding tetrelenes \( R_1E \).

Over the last few years several examples of disilenes and digermenes substituted by either one or two group 15–17 atoms have been reported. For example, Scheschkewitz and co-workers demonstrated that treatment of \([\{(Trip)\}Si\] with \( R_2PCl \) or iodine gives \([\{(Trip)\}Si=E=Si(Trip)\] (A, Figure 1) or \([\{(Trip)\}Si=Si(Trip)\] (B), respectively (\( R=PH, iPr, Cy, tBu, NR_2 \); \( R'=Me\), Et, \( iPr \)); \( \text{Trip}=2,4,6-iPr\_C_6H_{12} \)),\(^[[3,4]]\) while Sekiguchi and co-workers showed that disilynes undergo 1,2-addition with amines to give amino-substituted disilenes \([\{(Me,Sn)\}_2]_2PtSi[H(Si=Si(NR_2)]_2Si[\{(Me,Sn)\}_2]_2\] (C); \( NR_2=NEt_3, N(CH_2Me)_2, NPh_2, \) and \( NH_PBu_3 \)).\(^[[5]]\) In an alternative approach, Jutzli and co-workers demonstrated that the disilene \((Cp^*)[\{(Me,Sn)\}_2]_2Si=Si[N(SiMe_3)_2]_2(Cp^*)\] (D) may be formed (presumably via the transient silylene \([Cp^*][(Me,Sn)\_2]_2N(SiMe_3)\] by a reaction between \([Cp^*]_2Si][B(C_6F_5)_4]\) and \( Li[N(SiMe_3)_2]\).\(^[[6]]\) More recently, Roessky and co-workers independently showed that this compound is accessible from the reaction of \( Cp^*\_2SiCl_H \) and \( K[N(SiMe_3)_2]_2\).\(^[[7]]\) Perhaps the most intriguing observation is that the cyclic dianionsilylene \((C_2H_2)N(Bu)_2Si\) aggregates to an unusual amino-substituted disilene \( E \) on standing at room temperature, rather than the corresponding tetraminosilene,\(^[[8]]\) in solution a dynamic equilibrium between the silylene and \( E \) is observed (closely related digermenes have been isolated by Weidenbruch and co-workers).\(^[[9]]\) A dynamic equilibrium was also proposed for the highly sterically hindered dibromodisilene \( F \) and its bromosilylene analogue.\(^[[10]]\) Similarly, Müller, Kira, Apeloig, and co-workers have proposed a dynamic equilibrium between the digemmalenyl \((iPr,N)Si\) and its disilene dimer, based on variable-temperature UV/Vis spectroscopy; although this latter disilene has not been isolated and these studies suggest that the disilene itself is a minor component over the temperature range measured.\(^[[11]]\)

Very recently Bacereido, Kato, and co-workers reported the dimerization of heteroleptic, intramolecularly base-stabilized amino-chlorosilylenes and amino-hydrosilylenes by

![Figure 1. Disilenes substituted by group 14–17 atoms.](image-url)
insertion of one silylene fragment into the Si–X bond of another to give compounds G.[13] To date, there have been no reports of disilenes substituted by three or more group 15–17 atoms, which are isolable in the solid state.

Since the tendency for heteroatom-substituted tetrelenes to dimerize to the corresponding ditetrelenes is a function of the electronegativity and π-donor capacity of the heteroatom, diaminotetrelenes (R₂N)₂E (E = Si, Ge, Sn, Pb) typically show limited tendency towards dimerization. Phosphorus is significantly less electronegative than nitrogen and, while calculations suggest that P and N have similar inherent π-donor capabilities,[14] the large barrier to inversion at phosphorus prevents routine adoption of the planar geometry necessary for efficient πr–πr interactions. Thus, diphasphatetrelenes (R₂P)₂E represent an interesting class of compounds in which the tetrel center may not benefit from significant stabilization from the o-withdrawing/n-donating effects of the phosphorus atoms. It is perhaps unsurprising then that few diphasphatetrelenes have been reported and that, until recently, none of these compounds exhibited P–E πr–πr interactions.[15]

Recently, we reported the first examples of diphasphaphermynes and -stannylenes (H) in which phosphorus adopts a planar geometry, resulting in efficient P–E πr–πr interactions (Figure 2).[16] We now report our attempts to extend this method to the synthesis of a diphasaphsilylene and the consequent isolation of a unique disilene substituted by four phosphorus atoms.

Following on from our earlier report,[16] we initially attempted the synthesis of the crowded precursor [(Dipp)₂P]₂SiCl₂ (1), aiming to reduce this to the corresponding diphasaphsilylene. However, while we were able to isolate a few crystals of 1 (Supporting Information), the difficulty of isolating this compound cleanly in acceptable yield prevented further exploitation. Consequently, we sought a less sterically demanding substituent at phosphorus and so synthesized the dichlorosilane [(Mes)₂P]₂SiCl₂ (2), which was isolated in good yield and purity from the reaction between SiCl₄ and 2 equivalents of [(Mes)₂P]₂Li (Mes = 2,4,6-Me₃C₆H₂), as a colorless solid.

However, treatment of 2 with 2 equivalents of KC₈ did not lead to the corresponding diphasaphsilylene [(Mes)₂P]₂Si (3), but instead gave a mixture of the potassium phosphaneide [(Mes)₂P]₂K, along with a small amount of the diphasphane (Mes)₂P–P(Mes)₂, and a very small number of red crystals, which were shown by X-ray crystallography to be the triphosphasilanate complex [(Mes)₂P]₂SiK(THF) (4) (Supporting Information). The formation of 4 during this reaction clearly indicates that the Si⁰ center is reduced to Si² in this process. However, given that 4 is effectively an adduct between 2 and [(Mes)₂P]₂K, its formation suggests in situ reduction of 3 (or the corresponding disilene, see proceeding text) by the KC₈ to give [(Mes)₂P]₂K and an unidentified silicon-containing species (Scheme 1). Attempts to circumvent this over-reduction by using lithium as a milder reducing agent gave the triphosphasilanate complex [(Mes)₂P]₂SiLi(THF) (5; THF: identified by multielement NMR spectroscopy), whereas magnesium was found not to react with 2. We have not been able to synthesize 4 by a more systematic route, but 5 may be isolated in good yield and purity (see proceeding text).

It has been determined that the dehydrochlorination of chlorosilanes by strong bases is an effective route to SiII species.[7,17] Therefore, as an alternative strategy we prepared the chlorosilane [(Mes)₂P]₂SiCl₂ (6). However, reactions between 6 and a variety of strong non-nucleophilic bases (such as LiN(SiMe₃)₂, or LiN(CMe₃C₂H₅)₂) gave complex mixtures of products, as judged by ³¹P[¹H] NMR spectroscopy, from which we were not able to isolate any silicon-containing species.

Since the over-reduction of 2 by alkali metals is in direct competition with the formation of the diphasaphsilylene 3, we sought to prepare the dibromosilane [(Mes)₂P]₂SiBr₂ in the expectation that reduction of this species to a diphasaphsilylene would be more competitive with the over-reduction (P–Si cleavage) process. To our surprise, we found that the reaction between SiBr₄ and 2 equiv of [(Mes)₂P]₂Li in diethyl ether gave a dark blue solution, which slowly decolorized and deposited a small amount of dark-purple crystals; these were shown by X-ray crystallography to be the tetraphosphasilene [(Mes)₂P]₂Si–Si[(Mes)₂] (7) (see proceeding text).

This clearly indicated that the lithium phosphaneide was itself acting as a reducing agent and so we adjusted the stoichiometry accordingly.[16] Thus, the reaction between SiBr₄ and four equivalents of [(Mes)₂P]₂Li in diethyl ether yields a similar dark-blue solution. Removal of the solvent and extraction of the residue into light petroleum gave a brown solution after removal of the LiBr side-product (Scheme 2). A ³¹P[¹H] NMR spectrum of this crude solution exhibits a singlet at ~31.4 ppm that is due to (Mes)₂P–P(Mes)₂ and a broad singlet at ~41.3 ppm, which we
tentatively assign to the silylene 3 (although we have not yet been able to isolate this species), along with a 1:1:1:1 quartet at $-62.5$ ppm corresponding to 5, and a singlet at $-90.8$ ppm that is due to an unknown species (approximate ratio of peaks 1:0:2:2:1:3:1:0). We were unable to locate a signal corresponding to 3 in the $^{29}$Si NMR spectrum of this crude solution; this may be due to extensive signal broadening for this species, as noted for the analogous diphostastannylene G for which no $^{113}$Sn NMR signal could be found at room temperature either in the solid state or solution. On standing at room temperature for several days, this brown solution deposits dark-purple crystals of 7 in reasonable yield; heating the solution under reflux accelerates deposition such that it is complete within 4 hours.

Compound 7 has limited solubility in common organic solvents, preventing characterization by solution-state NMR spectroscopy. However, the solid-state cross-polarization magic angle spinning (CP-MAS) $^{31}$P($^1$H) NMR spectrum of 7 consists of a pair of singlets at $-55.9$ and $-77.9$ ppm, consistent with the two distinct phosphorus environments observed by X-ray crystallography (see proceeding text), while the solid-state CP-MAS $^{29}$Si($^1$H) NMR spectrum of 7 consists of a broad singlet at $111.7$ ppm; $^{29}$P–$^{29}$Si coupling is not resolved. The $^{29}$Si chemical shift of 7 is in the typical range for disilenes; the observed $^{31}$P($^1$H) and $^{29}$Si($^1$H) chemical shifts correlate reasonably well with those obtained from DFT calculations (Supporting Information).

Single crystals suitable for X-ray crystallography were grown from n-hexane solutions of 3 that were left to stand at room temperature for several days. The structure of 7 is shown in Figure 3, along with selected bond lengths and angles. Compound 7 crystallizes as a discrete molecular species in which the silicon atoms are disordered over two positions with 92.8 occupancy, with a center of inversion midway along each of the two Si–Si vectors. The major disorder component has a strongly trans-bent geometry (40.6° deviation of the SiP$_2$ mean plane from the Si–Si vector). This contrasts with the near-planar geometries adopted by most silicon-substituted disilenes, although a few carbon-substituted disilenes do exhibit large trans-bending angles. The trans-bending angle in the major disorder component of 7 is similar to those observed in a few heteroatom-substituted systems; for example in (Trip)$_2$Si=Si(Trip)$_2$ the trans-bending angle at the phosphorus-substituted silicon center is 30.8°, while the trans-bending angles in (Bbt)BrSi=SiBr(Bbt) are 32.4 and 39.8° (Bbt = 2,6-[(Me$_3$Si)$_2$C]$_2$H). The phosphorus atoms adopt a pyramidal configuration (sum of angles at P(1) 325.62°, P(2) 337.94°), and the Si–P distances are 2.2666(8) and 2.2392(8) Å, which are comparable to Si–P distances reported for the few other compounds with a direct bond between P and Si; for example, the Si–P distances in (Trip)$_2$Si=Si(Trip)(PCy$_3$)$_2$ and [PhC(NiBu)$_2$]$_2$Si=Si(PiPr$_3$)$_2$ are 2.2367(12) and 2.307(8) Å, respectively. The relatively short Si–P distances in 7 may suggest a degree of conjugation between the phosphorus lone pairs and the Si–Si bond. The plane of one aromatic ring on each phosphorus center lies parallel to the corresponding ring in the opposite Si(PiPr$_3$)$_2$ moiety with an interplane separation of 3.6 Å, consistent with an offset π–π interaction. This interaction may contribute to the overall stability of the disilene.

As a consequence of the restraints used in solving the crystal structure, any discussion of the minor disorder

**Scheme 2.** Synthesis of complexes 5 and 7 from SiBr$_4$. 

**Figure 3.** Molecular structure of the major disorder component of 7 viewed a) above and b) along the Si–Si vector (H atoms omitted for clarity). c) The core of 7, showing the relationship of the two disorder components (minor component shown with dashed lines). Selected bond lengths [Å] and angles [°] for the major disorder component:

| Bond | Length [Å] | Angle [°] |
|------|-----------|----------|
| Si=Si | 2.2392(8) | 115.03(5) |
| Si(1A)-Si(1B) | 3.6 | 40.6 |

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component of 7 must necessarily be more circumspect; however this disorder component appears to have a trans-bending angle of 23.8°, while the Si(1B)–Si(1C) distance of 2.109(11) Å appears identical to that in the major disorder component. The minor disorder component was not observed in the solid-state $^3$Si$^1$H NMR spectrum of 7, but a small peak is present at −67.4 ppm in the corresponding CP-MAS $^3$P$^1$H NMR spectrum, which we tentatively ascribe to this component.

Treatment of 7 with either lithium or KC$_8$ yields the phosphinides [(Mes)$_2$P]M (M = Li, K) as the sole identifiable phosphorus-containing products. We also find that treatment of a slurry of 7 in THF with two equivalents of [(Mes)$_2$P]Li-(THF) cleanly yields the triphosphasilane complex 5.THF. The foregoing is consistent with our premise that the triphosphasilane anions result from cleavage of a P–Si bond in 3 (or its dimer 7), to generate [(Mes)$_2$P]Li (or [(Mes)$_2$P]K), followed by adduct formation with another molecule of 3 (or 7) to give 4 or 5.

To better understand the bonding in and stability of 7 we have undertaken a density functional theory (DFT) study. Since the X-ray crystal structure of 7 contains two distinct disorder components, which differ chiefly in the degree of trans-bending, we have modeled both of these molecules using the crystallographic coordinates as a starting point for the optimization; these are referred to hereafter as $7_{\text{maj}}$ and $7_{\text{min}}$ for the minimum energy geometries corresponding to the major and minor disorder components, respectively (Table 1). Additionally, we have located a minimum energy geometry for the alternative phosphanide-bridged dimer [(Mes)$_2$P]Si[μ-$\text{P}$(Mes)$_2$]$\ldots$Si(P(Mes)$_2$)] ($7_{\text{ab}}$).

The minimum energy geometry of $7_{\text{maj}}$ is similar to the crystallographically determined structure, but exhibits a twist between the two SiP$_2$ units (14.75° dihedral angle between the two normals of the SiP$_2$ planes). The calculated trans-bending angles of 38.42 and 40.04° are close to that determined crystallographically, but the calculated Si–Si bond distance of 2.2386 Å is somewhat longer than that observed in the solid state; this is likely a consequence of the twisted geometry of $7_{\text{maj}}$ which would reduce the Si–Si $\pi$-overlap. The calculated trans-bending angle of $7_{\text{min}}$ (6.22°) differs significantly from that in the solid-state structure (23.8°), although the calculated Si–Si distance (2.182 Å) is close to that determined crystallographically (2.190(11) Å). The DFT calculations reveal that $7_{\text{min}}$ and $7_{\text{maj}}$ are almost isoenergetic, with the former just 9.0 kJ mol$^{-1}$ less stable than the latter. In comparison, the alternative dimeric form $7_{\text{ab}}$, containing a P$_2$Si$_2$ core, lies 82.7 kJ mol$^{-1}$ higher in free energy than $7_{\text{maj}}$.

Inspection of the molecular orbitals of both $7_{\text{maj}}$ and $7_{\text{min}}$ reveals that the HOMO and LUMO are essentially the Si=Si $\pi$ and $\pi^*$ orbitals, although in both cases there is a significant component of these orbitals on the phosphorus atoms (Supporting Information). Natural Bond Orbital (NBO) analysis yields Wiberg Bond Indices (WBI) for the Si=Si bonds in $7_{\text{maj}}$ and $7_{\text{min}}$ of 1.411 and 1.551, respectively, consistent with substantial double bond character. The WBI for the Si–P bonds in $7_{\text{maj}}$ and $7_{\text{min}}$ range from 0.934 to 1.016, significantly greater than we calculate for a straightforward P–Si$^\text{IV}$ $\sigma$-bond (see proceeding text), again suggesting some interaction between the phosphorus lone pairs and the Si=Si bond.

To explore the dimerization energy of the putative diphosphasilylene 3 to the tetraphosphasilene 7 we have calculated the minimum energy geometries of the two extreme forms of the silyne. These are $3_{\text{plan}}$, in which the two phosphorus centers approach planarity, and $3_{\text{pris}}$, in which both phosphorus centers adopt a pyramidal configuration (Table 1); all attempts to obtain a minimum energy geometry for a molecule possessing one planar and one pyramidal phosphorus center, as observed in the diphosphagermynes and -stannylenes H, converged to $3_{\text{plan}}$. For $3_{\text{pris}}$, both phosphorus centers are close to planar (sum of angles at P = 352.71 and 352.76°) and the Si–P distances (2.208 and 2.207 Å) are shorter than is typical for a Si–P single bond; however, the Si–P distances are longer than previously reported Si–P bonds in phosphasilenes such as (Bu)-Ttrip)Si=P-Si(Pr)$_2$, (Si-P 2.062(1), Si-P 2.255(1) Å$^{[23]}$, although we note that the latter involves Si$^\text{IV}$ rather than Si$^\text{III}$ and fully sp$^2$-hybridized and hence smaller phosphorus and silicon centers. The foregoing, along with Si–P WBI of 1.221 and 1.222, suggest a significant Si–P $\pi$-interaction in $3_{\text{pris}}$, despite the slight variation from a planar geometry of the phosphorus centers. In contrast, the Si–P distances in $3_{\text{pris}}$ are both 2.337 Å and the WBI for these bonds are both 0.804, consistent with Si–P single bonds.

Our calculations reveal that $3_{\text{plan}}$ is more stable than $3_{\text{pris}}$ by 16.4 kJ mol$^{-1}$. These calculations also show dimerization to the disilene $7_{\text{pris}}$ is strongly favored; the difference in Gibbs free energy between the disilene $7_{\text{pris}}$ and two equivalents of $3_{\text{plan}}$ is +71.0 kJ mol$^{-1}$. This is in marked contrast to recent calculations on the putative tetramino-substituted ditetrelenes [(Me$_2$Si)$_2$N]$_2$E=E[N(SiMe$_3$)$_2$], which suggests that dissociation to the corresponding tetrelene monomers [(Me$_2$Si)$_2$N]$_2$E: is strongly favored (E=Ge, $\Delta G$ = −69 kJ mol$^{-1}$; E=Sn, $\Delta G$ = −75 kJ mol$^{-1}$; E=Pb, $\Delta G$ = −45 kJ mol$^{-1}$)$^{[24]}$

In summary, we have shown that a unique tetraphosphasilene is accessible by reduction of a simple Si$^\text{III}$ starting material, using sacrificial lithium phosphanide as the reducing agent. This is the first example of a structurally characterized ditetrelene substituted by more than two heteroatoms from groups 15–17.

Table 1: Calculated geometries for $7_{\text{maj}}$, $7_{\text{min}}$, $7_{\text{ab}}$, $3_{\text{plan}}$, and $3_{\text{pris}}$. 

| Geometry | Si-Si Bond Distance (Å) | Si-Si Bond Angle (°) |
|----------|------------------------|----------------------|
| $7_{\text{maj}}$ | 2.2386 | 6.22 |
| $7_{\text{min}}$ | 2.182 | 23.8 |
| $3_{\text{plan}}$ | 2.337 | 71.0 |
| $3_{\text{pris}}$ | 2.062 | 16.4 |

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Conflict of interest

The authors declare no conflict of interest.

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[1] a) P. I. Davidson, M. F. Lappert, J. Chem. Soc. Chem. Commun. 1973, 317; b) D. E. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thomas, J. Chem. Soc. Chem. Commun. 1976, 261.
[2] For comprehensive reviews, see: a) P. P. Power, Chem. Rev. 1999, 99, 3463; b) R. C. Fischer, P. P. Power, Chem. Rev. 2010, 110, 3877.
[3] For a recent review, see: C. Prasang, D. Scheschkewitz, Chem. Soc. Rev. 2016, 45, 900.
[4] a) M. Hartmann, A. Haji-Abdi, A. Abserfelder, P. R. Haycock, A. J. P. White, D. Scheschkewitz, Dalton Trans. 2010, 39, 9288; b) D. Scheschkewitz, Angew. Chem. Int. Ed. 2004, 43, 2965; Angew. Chem. 2004, 116, 3025; c) P. Willmes, M. J. Cowley, M. Hartmann, M. Zimmer, V. Huch, D. Scheschkewitz, Angew. Chem. Int. Ed. 2014, 53, 2216; Angew. Chem. 2014, 126, 2248.
[5] a) K. Takeuchi, M. Ikosho, M. Ichinohe, A. Sekiguchi, J. Am. Chem. Soc. 2010, 132, 930; b) K. Takeuchi, M. Ikosho, M. Ichinohe, A. Sekiguchi, J. Organomet. Chem. 2011, 696, 1156.
[6] P. Jutzi, A. Mix, B. Neumann, B. Rummel, W. W. Schoeller, H.-G. Stammler, A. B. Rozenken, J. Am. Chem. Soc. 2009, 131, 12137.
[7] S. Khan, S. S. Sen, H. W. Roesky, D. Kratzer, R. Michel, D. Staltek, Inorg. Chem. 2010, 49, 9689.
[8] T. A. Schmedake, M. Haaf, Y. Apeloig, T. Muller, S. Bukalov, R. West, J. Am. Chem. Soc. 1999, 121, 9471.
[9] a) A. Schäfer, W. Saak, M. Weidenbruch, Z. Anorg. Allg. Chem. 1998, 624, 1405; b) A. Schäfer, W. Saak, M. Weidenbruch, H. Marsmann, G. Henkel, Chem. Ber. 1997, 130, 1733.
[10] K. Suzuki, T. Matsuoi, D. Hashizume, K. Tamao, J. Am. Chem. Soc. 2011, 133, 19710.
[11] M. Takahashi, S. Tsutsui, K. Sakamoto, M. Kira, T. Muller, Y. Apeloig, J. Am. Chem. Soc. 2001, 123, 347.
[12] T. P. Robinson, M. J. Cowley, D. Scheschkewitz, J. Moiccochea, Angew. Chem. Int. Ed. 2015, 54, 683; Angew. Chem. 2015, 127, 693.
[13] R. Rodriguez, Y. Contie, Y. Mao, N. Saffon-Merceron, A. Bacereido, V. Branchadell, T. Kato, Angew. Chem. Int. Ed. 2015, 54, 15276; Angew. Chem. 2015, 127, 15491.
[14] J. Kapp, C. Schade, A. M. El-Nahasa, P. V. R. Schleyer, Angew. Chem. Int. Ed. Engl. 1996, 35, 2236; Angew. Chem. 1996, 108, 2373.
[15] K. Izod, Coord. Chem. Rev. 2012, 256, 2972.
[16] a) K. Izod, D. G. Rayner, S. M. El-Hamruni, R. W. Harrington, U. Baisch, Angew. Chem. Int. Ed. 2014, 53, 3636; Angew. Chem. 2014, 126, 3710; b) K. Izod, P. Evans, P. G. Waddell, M. R. Probert, Inorg. Chem. 2016, 55, 10510.
[17] R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Staltek, Angew. Chem. Int. Ed. 2009, 48, 5683; Angew. Chem. 2009, 121, 5793.
[18] Related spontaneous E1β–E1α reduction has been observed previously in the isolation of a diboryl)silylene and an aryl-phosphagermymylene and -phosphastannylene: a) M. Usher, A. V. Protchenko, A. Rit, J. Campos, E. Kolychev, R. Tirfoin, S. Aldridge, Chem. Eur. J. 2016, 22, 11685; b) B. P. Johnson, S. Almstatter, F. Dielmann, M. Bodenstein, M. Scheer, Z. Anorg. Allg. Chem. 2010, 636, 1275.
[19] For examples, see: a) I. Bejan, D. Scheschkewitz, Angew. Chem. Int. Ed. 2007, 46, 5783; Angew. Chem. 2007, 119, 5885; b) J. Jeck, I. Bejan, A. J. P. White, D. Nied, F. Brecher, D. Scheschkewitz, J. Am. Chem. Soc. 2010, 132, 17306; c) R. Tanaka, T. Iwamoto, M. Kira, Angew. Chem. Int. Ed. 2006, 45, 6371; Angew. Chem. 2006, 118, 6519.
[20] C. W. So, H. W. Roesky, P. M. Gurubasavaranj, R. B. Oswald, M. T. Gamer, P. G. Jones, S. Blaurock, J. Am. Chem. Soc. 2007, 129, 12049.
[21] M. Driess, S. Rell, H. Pritzkov, Chem. Commun. 1995, 253.
[22] J.-D. Guo, D. J. Liptrot, S. Nagase, P. P. Power, Chem. Sci. 2015, 6, 6235.

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