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Diverse Reactivity of an Electrophilic Phosphasilene towards Anionic Nucleophiles: Substitution or Metal–Amino Exchange

Philipp Willmes, Lukas Junk, Volker Huch, Cem B. Yildiz, and David Scheschkewitz**

In memory of Manfred Weidenbruch

Abstract: *The reaction of MesLi (Mes = 2,4,6-trimethylphenyl) with the electrophilic phosphasilene $R_2(NMe_2)Si\text{-}RSi{=}PNMe_2$ (**2**, R = Tip = 2,4,6-triisopropylphenyl) cleanly affords $R_2(NMe_2)Si\text{-}RSi{=}PMes$ and thus provides the first example of a substitution reaction at an unperturbed Si=P bond. In toluene, the reaction of **2** with lithium disilenide, $R_2Si{=}Si(R)Li$ (**1**), apparently proceeds via an initial nucleophilic substitution step as well (as suggested by DFT calculations), but affords a saturated bicyclo[1.1.0]butane analogue as the final product, which was further characterized as its $Fe(CO)_4$ complex. In contrast, in 1,2-dimethoxyethane the reaction of **1** with **2** results in an unprecedented metal–amino exchange reaction.*

More than 30 years after the isolation of the first stable disilene,[1] compounds with double bonds to silicon[2] (and heavier main-group elements in general)[3] remain a central topic of organoelement chemistry. More recently, functional groups in the periphery of double bonds to heavier elements have been drawing increasing attention as they allow for further manipulations without immediate loss of the unsaturated moiety.[4]

Disilenides of type **A** contain a nucleophilic reaction site that makes it possible to transfer the Si=Si moiety to a variety of organic or inorganic electrophiles (Figure 1).[5] The resulting products either contain an unperturbed Si=Si moiety or rearrange to cyclic compounds under consumption of the double bond. Potentially electrophilic disilenes of type **B** are scarce,[6] but exhibit useful reactivity: 1,2-dibromodisilenes react with various nucleophiles to give the corresponding substituted disilenes.[6c] An iododisilene can be converted into the corresponding phosphino derivative by treatment with lithium diphenylphosphide.[6d]

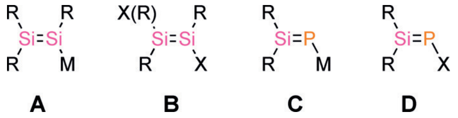

Figure 1. Nucleophilic and electrophilic disilenes **A** and **B**, nucleophilic phosphasilenes **C**, and potentially electrophilic phosphasilenes **D** (M = metal, X = anionic leaving group, R = alkyl, aryl, or silyl).

Much less is known regarding the functionalization of the heteronuclear phosphasilenes with inherently polarized Si=P bonds.[7] Although the lone pair of electrons at phosphorus readily coordinate to transition metal centers such as gold or tungsten,[8,9] covalent metal-functionalized phosphasilenes of type **C** are rare. In fact, no nucleophilic reactivity with retention of the Si=P bond is documented for the few examples reported.[10] Phosphasilenes of type **D** with typical anionic leaving groups X were unknown until we very recently reported the reactions of disilenide **1** with diaminochlorophosphanes to yield *P*-amino-functionalized phosphasilenes.[11] As dimethylamide is known to serve as a leaving group in reactions with anionic nucleophiles (e.g. carboxylic acid amides with silyllithium reagents),[12] we felt encouraged to investigate the suitability of phosphasilene **2** in this regard.

We here report the reactivity of phosphasilene **2** in toluene as the electrophile with examples for the transfer of the unperturbed P=Si bond as well as the subsequent rearrangement to a cyclic derivative. In addition, we show that **2** engages in an unprecedented lithium–amino exchange reaction when the more polar solvent 1,2-dimethoxyethane (dme) is used.

In preliminary studies, phosphasilene **2** was treated with one equivalent of either methyl- or *tert*-butyllithium. According to ^{31}P NMR spectroscopy, the reactions proceed only slowly at room temperature and various secondary products appear before full conversion of **2**. Since we were unable to unambiguously identify, let alone isolate, stable products from the reaction mixtures, we turned our attention to a sterically more demanding nucleophile. Indeed, while no discernible reaction took place at room temperature, heating mesityllithium with **2** in toluene at 60 °C for 60 h led to selective and full conversion. The quantitative formation of the *P*-mesityl-substituted phosphasilene **3** as an *E*/*Z* mixture was confirmed by multinuclear NMR spectroscopy (Scheme 1).[13]

The ^{31}P NMR resonances of *E*/*Z*-**3** at $\delta = 234.4$ and 217.9 ppm (*E*/*Z* ratio: 84:16) are in the typical range for Si=P bonds. Both signals show silicon satellites with characteristically large coupling constants (*E*-**3**: $^{1}J_{P\text{-}Si} = 193.9$ Hz,

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[*] M. Sc. P. Willmes, M. Sc. L. Junk, Dr. V. Huch,
Prof. Dr. D. Scheschkewitz
Krupp-Lehrstuhl für Allgemeine und Anorganische Chemie
Universität des Saarlandes
66125 Saarbrücken (Germany)
E-mail: scheschkewitz@mx.uni-saarland.de
Dr. C. B. Yildiz
Department of Chemistry, Faculty of Science and Letters
Aksaray University
68100 Aksaray (Turkey)
E-mail: cemburakyildiz@aksaray.edu.tr

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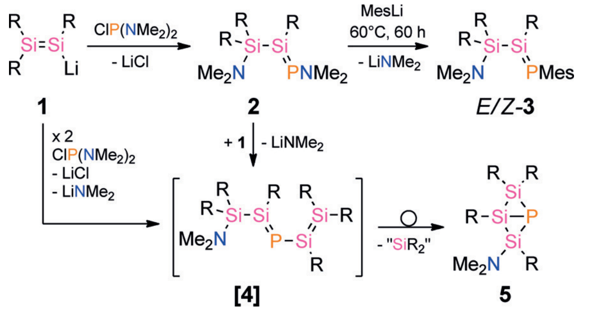


Scheme 1. Reactions of electrophilic phosphasilene **2** with nucleophiles; synthesis of *P*-mesityl-substituted phosphasilene **3** and phosphatrisila[1.1.0]bicyclobutane derivative **5** with proposed intermediacy of butadiene analogue [**4**] (R = Tip = 2,4,6-iPr$_3$C$_6$H$_2$).

$^2J_{\text{P-Si}} = 46.6$ Hz and Z-**3**:$^1J_{\text{P-Si}} = 189.0$ Hz, $^2J_{\text{P-Si}} = 26.0$ Hz).[7–10] The larger $^2J_{\text{P-Si}}$ coupling indicates a *cis* relationship of the lone pair on phosphorus with the β-silicon atom and thus supports the assignment of the major isomer as *E*-**3**.[14] Notably, the ^{31}P nuclei in *E*/*Z*-**3** exhibit a considerably stronger shielding than in *E*/*Z*-**2** (*E*-**2**: 344.8 and *Z*-**2**: 336.2 ppm)[11] and in Sekiguchi's "push–pull" phosphasilene (389.3 ppm),[15] demonstrating the "normal" polarization of the P=Si bond in **3**. The polarization towards the phosphorus atom is confirmed by the ^{29}Si NMR resonance of *E*-**3** at 193.9 ppm, which is shifted downfield by $\Delta\delta = 90$ ppm relative to that of *E*-**2** (103.5 ppm). The longest wavelength absorption in the UV/Vis spectrum of **3** at $\lambda_{\text{max}} = 374$ nm ($\varepsilon = 7700\,\text{M}^{-1}\,\text{cm}^{-1}$) is blue-shifted compared to **2** ($\lambda_{\text{max}} = 410$ nm).

Single crystals were obtained from hexane at room temperature. An X-ray diffraction study confirmed the major isomer, *E*-**3**, to be present in the solid state (Figure 2).[13] Notably, dissolving crystals of *E*-**3** results in a mixture of *E*/*Z*-**3** with ^{31}P signals in the same ratio as in the crude product. Due to the absence of the nitrogen donor substituent, the Si2=P1 bond is slightly shorter than in *E*-**2** (*E*-**3**: 2.0923(6); *E*-**2**: 2.1187(7) Å), but well within in the typical range for phosphasilenes.[7] As to be expected for "normal" polarization of the P=Si bond, the coordination environment of Si2 is perfectly planar (sum of angles at Si2: 360.0°) unlike in the case of *E*-**2** (sum of angles at Si2: 358.85°).[11]

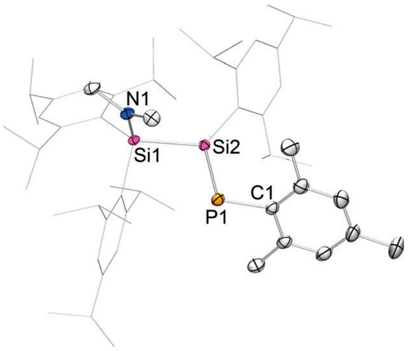


Figure 2. Molecular structure of *E*-**3** in the solid state (thermal ellipsoids at 50%, H atoms and disordered *i*Pr groups omitted for clarity). Selected bond lengths [Å]: Si2–P1 2.0923(6), Si1–Si2 2.4175(5), Si1–N1 1.736(1), P1–C1 1.846(2).

Encouraged by these results, we investigated the reactivity of **2** towards a more elaborate nucleophile, namely disilenide **1**. We anticipated the phosphatrisila-1,3-butadiene [**4**] and/or its isomers as possible products. For the related homonuclear Si$_4$R$_6$ scaffold, analogues of 1,3-butadiene,[16] bicyclo[1.1.0]butane,[17] and cyclobutene[18,19] have been reported. Of the possible P/SiR permutations, however, so far only bicyclo[1.1.0]butane analogues are known as stable derivatives: 1,3-diphospha-2,4-disilabicyclo[1.1.0]butane[20] and 1,2,3-triphospha-4-silabicyclo[1.1.0]butanes.[21]

A solution of disilenide **1** and *P*-dimethylaminophosphasilene **2** in toluene shows no reaction at room temperature. Heating to 65 °C for 3 hours, however, quantitatively affords a new product with a ^{31}P signal at $\delta = -212.3$ ppm, suggesting the absence of a Si=P bond (Scheme 1).[13] Three ^{29}Si NMR doublets at $\delta = -5.1$ ($^1J_{\text{Si-P}} = 84.7$ Hz), -39.5 ($^1J_{\text{Si-P}} = 84.7$ Hz), and -119.8 ppm ($^1J_{\text{Si-P}} = 5.2$ Hz) were observed. In particular, the strong shielding and small coupling constant of the signal at the highfield end of the spectrum are typical for bridgehead atoms in bicyclobutane derivatives.[17,20–22] Notably, the same product is obtained in a convenient one-pot synthesis starting from **1** without isolation of phosphasilene **2** (Scheme 1).[13] The X-ray analysis of single crystals of **5** confirms its identity as phoshatrisilabicyclo[1.1.0]butane (Figure 3).[13] The Si–P bridgehead bond (Si2–P1 2.4273(8) Å) is markedly longer than the single bonds in reported cyclic silicon phosphorus species.[23] The phosphorus atom in **5** is constrained to extreme pyramidalization by the bridgehead position (sum of angles at P1: 214°).

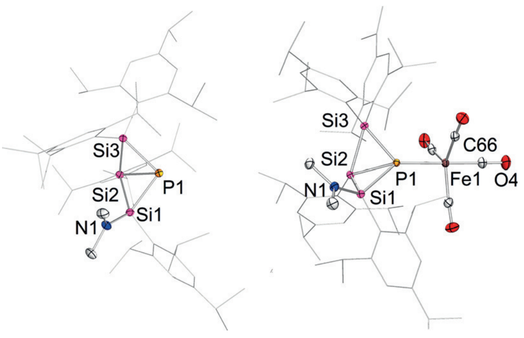
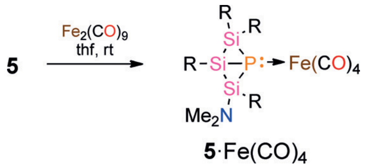
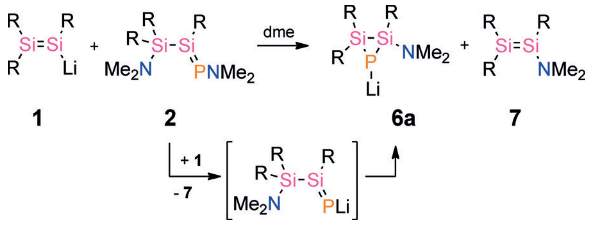


Figure 3. Structure of **5** (left) and **5**·Fe(CO)$_4$ (right) in the solid state (thermal ellipsoids at 50%, H atoms and disordered *i*Pr groups omitted). Selected bond lengths [Å] and angles [°]: **5**: Si1–P1 2.2217(8), Si2–P1 2.4273(8), Si3–P1 2.2566(8), Si1–Si2 2.2899(8), Si2–Si3 2.2915(8), Si1–N1 1.711(2); P1-Si1-Si2 65.08(3), Si1-Si2-Si3 94.58(3) P1-Si3-Si2 64.51(3). **5**·Fe(CO)$_4$: Si1–P1 2.3764(3), Si2–P1 2.3418(3), Si3–P1 2.2609(3), Si1–Si2 2.2736(3), Si2–Si3 2.3447(3), Si1–N1 1.7079(7), P1–Fe1 2.3182(3); P1-Si1-Si2 60.43(1), Si1-Si2-Si3 96.45(1), P1-Si3-Si2 61.09(1).

This strong pyramidalization should confer excellent σ-donor properties. Treatment of **5** with an excess of Fe$_2$(CO)$_9$ indeed leads to quantitative conversion to **5**·Fe(CO)$_4$ (Scheme 2).[13] The ^{31}P NMR signal of **5**·Fe(CO)$_4$ at $\delta = -92.5$ ppm is shifted downfield compared to that of the free



Scheme 2. Synthesis of tetracarbonyl iron complex **5**·Fe(CO)$_4$.



Scheme 3. Metal–amino exchange reaction of **2** with disilenide **1** in dme affording disilaphosphiranide **6a** and aminodisilene **7** with proposed intermediacy of *P*-lithiophosphasilene (R = Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$).

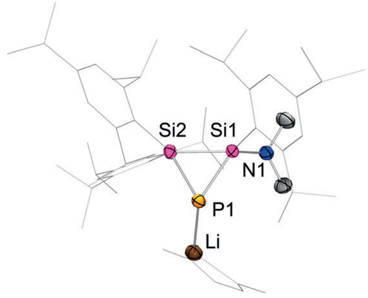


Figure 4. Molecular structure of **6a** in the solid state (thermal ellipsoids at 50%, H atoms and disordered *i*Pr groups omitted for clarity). Selected bond lengths [Å]: Si2–P1 2.2312(7), Si1–P1 2.1720(7) Si1–Si2 2.2958(7), Si1–N1 1.7405(15), P1–Li1 2.464(3).

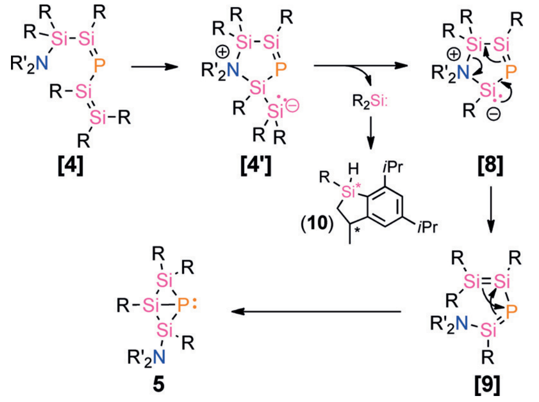
ligand (**5**: $\delta = -212.3$ ppm). An X-ray diffraction study on single crystals of **5**·Fe(CO)$_4$ (Figure 3) confirms its constitution.[13] Presumably due to steric congestion, the P–Fe bond (2.3181(3) Å) is significantly longer than those usually reported for phosphane–iron complexes (2.08–2.211 Å).[24] Nonetheless, the bridgehead P–Si bond in **5**·Fe(CO)$_4$ is shorter than that in the free ligand (**5**: 2.4273(8); **5**·Fe(CO)$_4$: 2.3418(3) Å). The apparent strengthening of the Si1–P1 bond is reflected in an increased Wiberg bond index for the computational model **5Dip**·Fe(CO)$_4$ (WBI = 0.933) compared to **5Dip** (WBI = 0.821, calculations at B3LYP/6-31+G-(d,p);[13] **5Dip**: Tip substituents replaced by 2,6-diisopropylphenyl groups). This increase is mainly due to a constructive interaction of the Fe center along the bridgehead Si–P vector in the HOMO−3 of **5Dip**·Fe(CO)$_4$. In the free ligand **5Dip**, the lone pair at phosphorus is mostly attributed to the HOMO and predominantly interacts with the other two silicon atoms (see Figures S35 and S36 in the Supporting Information). The NBO analysis indicates that the Fe–P bond in **5Dip**·Fe(CO)$_4$ (55.91%) has more p character than the lone pair of **5Dip** (36.17%). As a consequence, the s character of the bridgehead bond is increased upon coordination (**5Dip**: 4.75%; **5Dip**·Fe(CO)$_4$: 11.2%; average values for B and P). According to the IR spectrum of **5**·Fe(CO)$_4$, the ligand **5** is a somewhat stronger σ-donor than common phosphanes[25] and of similar strength as N-heterocyclic carbenes (**5**·Fe(CO)$_4$: $\tilde{\nu}(\mathrm{CO}) = 2036$, 1959, 1941, 1926 cm^{-1}; NHC$^{\mathrm{Dip}}$Fe(CO)$_4$: $\tilde{\nu}(\mathrm{CO}) = 2035$, 1947, 1928, 1919 cm^{-1};[26] NHC$^{\mathrm{Dip}}$= C{N(Ar)CH}$_2$, Ar = 2,6-diisopropylphenyl).

The high temperature required for the formation of **5** in toluene excluded the observation of any intermediate such as [**4**] (Scheme 1). We reasoned that the use of 1,2-dimethoxyethane (dme) as a more polar donor solvent may increase the nucleophilicity of disilenide **1** to an extent that the postulated intermediate [**4**] might be isolated. The ^{31}P NMR spectrum of the reaction mixture of phosphasilene **2** and disilenide **1** in dme after 48 h at room temperature indeed showed a single new resonance, albeit at very high field ($\delta = -245.9$ ppm) and thus indicative of selective conversion to a compound without a P–Si double bond. A diffraction study on single crystals obtained by crystallization from pentane revealed that an exchange between the lithium atom and the dimethylamino group had occurred to afford the lithium disilaphosphiranide **6a** (m.p. 151 °C) in 22% yield (Scheme 3, Figure 4).[13] The silicon–silicon distance (Si1–Si2 2.2958(7) Å) is rather short for a single bond as are both Si–P bonds (Si1–P1 2.1720(7) Å, Si2-P1 2.2312(7) Å). Similarly shortened Si–P bonds (2.203–2.234 Å) have been reported for open-chained disilyl phosphides which had been attributed to the electrostatic attraction between the negatively charged phosphorus and the positively polarized silicon atoms.[27] In the case of **6a**, however, the shortening is more likely due to back-donation by the anionic phosphorus into σ* orbitals at silicon. Similar shortening had been observed for a homonuclear cyclotrisilanide.[28] The ^{29}Si NMR signals of **6a** at −33.0 and −68.5 ppm are in accord with the persistence of the three-membered-ring structure of **6a** in solution. Apart from traces of **6a**, the ^{29}Si NMR spectrum of the mother liquor shows only two main resonances at 95.5 and 26.2 ppm in line with a polarized Si–Si double bond. A correlated ^{29}Si,^{1}H NMR spectrum proves the direct attachment of three Tip substituents and one dimethylamino group, thus confirming the formation of aminodisilene **7** (Scheme 3) even in the absence of an X-ray diffraction study in the solid state.[29]

While the metal–halogen exchange reaction represents a textbook case in organic chemistry, the lithium–amino exchange between **1** and **2** is unprecedented to the best of our knowledge. Typically, amino groups only exert metalation-directing effects as for example in case of the *ortho*-lithiation of *N*,*N*-dimethylaniline.[30] We assume that the separation of a lithium disilenide ion pair by 1,2-dimethoxyethane turns the initial coordination of the phosphorus lone pair of **2** to the lithium cation of **1** into a competitive process. Subsequent transfer of the NMe$_2$ group to the Si=Si moiety would explain the formation of the amino-substituted disilene **7** and a lithiated phosphasilene intermediate that rapidly cyclizes to **6a** (Scheme 3). Similar cyclizations have been reported for the reduction of related trisilaallyl chlorides.[28] It should be noted that in contrast to P$_2$Si systems, many of which have been described,[31] PSi$_2$ ring systems are relatively rare.[23,32]

Driess et al. reported that a lithium phosphadisiliranide not unlike **6a** was too reactive for isolation.[23] In solution, **6a** is protonated only slowly to give a mixture of *cis*- and *trans*-disilaphosphirane **6b**.[13]

In order to test their possible transient occurrence during the formation of bicycle **5** in a nondonor solvent, a mixture of **6a** and **7** in C_6D_6 was heated to 65 °C for three hours, but apart from a certain amount of protonation leading to **6b** no significant conversion was detected by NMR spectroscopy. Under identical conditions **1** and **2** convert quantitatively to **5**, plausibly via the transient occurrence of the substitution product [**4**] (Scheme 1). According to DFT calculations at the B3LYP/6-31+G(d,p) level of theory on a simplified model (Scheme 4, methyl and NH_2 instead of Tip and $N(CH_3)_2$ groups, respectively; for details see Supporting Information),[13] the intramolecular coordination of the amino group of [**4**]-**Me** to the newly introduced Si=Si moiety to give cyclic [**4′**]-**Me** is only mildly endergonic with $\Delta G = 0.5$ kcal mol^{-1}. The reversible coordination of Lewis bases to Si=Si bonds has been demonstrated recently.[33] The extrusion of SiR_2 from the five-membered ring [**4′**]-**Me** with an exocyclic SiR_2 moiety is strongly endergonic with $\Delta G = +21.9$ kcal mol^{-1}. This value is still compatible with the reaction conditions and could be lower in the experimental case due to the much more pronounced steric congestion imposed by the Tip substituents. As shown by Okazaki, Tokitoh, and co-workers, steric strain can indeed lead to the dissociation of Si=Si double bonds into two silylene fragments either with or without trapping by coordination of an external base.[34] The ring opening of the resulting ylide [**8**]-**Me** to give an unstable 1-phospha-1,3,4-trisilabutadiene [**9**]-**Me** is only mildly endergonic by $\Delta G = +6.3$ kcal mol^{-1}, albeit with a substantial barrier of $\Delta G^{\neq} = +21.2$ kcal mol^{-1}. The final step of the pathway to the bicyclo[1.1.0]butane analogue **5-Me** overcompensates for this in being exergonic by $\Delta G = -28.1$ kcal mol^{-1}, which is in accordance with reported isomerizations of third row systems from 1,3-butadiene to bicyclo[1.1.0]butane.[35] An alternative mechanism via direct extrusion of SiR_2 from [**4**] is unlikely, based on the much more substantial barrier of $\Delta G^{\neq} = +38.3$ kcal mol^{-1}.



Scheme 4. Plausible mechanism for the formation of **5** and proposed byproduct **10** (Experimental case: R = Tip = 2,4,6-triisopropylphenyl, R = Me; DFT calculations: R = Me; R′ = H).

Expectedly, the $SiTip_2$ liberated in the experimental case is too short-lived for observation: in addition to the signals of the product **5**, however, the crude reaction mixture shows two additional ^{29}Si NMR signals at $\delta = -21.5$ and -25.1 ppm in a 2:3 ratio, which we assign to the diastereomeric mixture of **10** (Scheme 2).[13] The ^{29}Si,^{1}H-correlation experiment shows crosspeaks to ^{1}H resonances in the typical Si–H region ($\delta = 6.05$ ppm, $^{1}J_{\text{Si-H}} = 295.8$ Hz and $\delta = 5.77$ ppm, $^{1}J_{\text{Si-H}} = 213.3$ Hz). Silylenes (as well as germylenes) typically undergo intramolecular C–H insertion reactions especially when they are generated at elevated temperatures.[34a,36] Apparently, $SiTip_2$ inserts into a methyl group of the Tip substituents under the reaction conditions.

In summary, we have shown that the *P*-amino-functionalized phosphasilene **2** reacts as an electrophilic phosphasilene in non-donor solvents in an unprecedented functional group transformation with preservation of an uncompromised P=Si unit. The reaction of **2** with mesityllithium indeed affords the corresponding *P*-mesityl-substituted phosphasilene **3** in good yield. The treatment of **2** with disilenide **1** in toluene initially may result in formation of a transient substitution product as well, but rapid subsequent silylene extrusion yields the very stable trisilaphosphabicyclo[1.1.0]butane **5**, which was characterized as a strongly σ-donating ligand. In stark contrast, the reaction of **1** with **2** in the donor solvent dme proceeds via a unique amino–lithium exchange yielding the disilaphosphiranide **6a** and a rare example of an aminodisilene.

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