

# Phosphide Delivery to a Cyclotrisilene\*\*

Thomas P. Robinson, Michael J. Cowley, David Scheschkewitz,\* and Jose M. Goicoechea\*

Dedicated to Professor Gerhard Roewer on occasion of his 75th birthday

**Abstract:** The reactivity of the 2-phosphaethynolate anion ( $\text{PCO}^-$ ) towards a cyclic trisilene ( $c\text{Si}_3(\text{Tip})_4$ ) is reported. The result is the net activation of the P–C and Si–Si multiple bonds of the precursors affording a heteroatomic bicyclo-[1.1.1]pentan-2-one analogue ( $[\text{P}(\text{CO})\text{Si}_3(\text{Tip})_4]^-$ ; **1**). This reaction can be interpreted as the formal addition of a phosphide and a carbonyl across the Si–Si double bond. Photolytic decarbonylation of **1** results in the incorporation of the phosphide vertex into the cyclotrisilene scaffold, yielding a congener of the cyclobutene anion with considerable allylic character.

Unsaturated silicon species are transient intermediates during the gas-phase deposition of elemental silicon from molecular precursors.<sup>[1]</sup> Cyclotrisilene,  $c\text{Si}_3\text{H}_4$ , is the simplest unsaturated cyclic silane, and to date it has only been observed in the gas phase. Kinetic and thermodynamic stabilization of cyclotrisilenes using bulky silyl substituents was initially achieved by the groups of Kira<sup>[2]</sup> and Sekiguchi<sup>[3]</sup> (Scheme 1). More recently, Scheschkewitz and co-workers reported the synthesis of the first aryl substituted cyclotrisilenes and their reactivity towards N-heterocyclic carbenes.<sup>[4]</sup>



**Scheme 1.** Reported cyclotrisilenes.  $\text{R} = t\text{Bu}_2\text{MeSi}$ ,  $\text{R}' = \text{Si}(t\text{Bu}_2\text{MeSi})_3$ ;<sup>[2]</sup>  $\text{R} = \text{R}' = t\text{Bu}_2\text{MeSi}$ ;<sup>[3]</sup>  $\text{R} = \text{R}' = \text{Tip}$  (2,4,6-triisopropylphenyl);  $\text{R} = \text{Tip}$ ,  $\text{R}' = \text{Cp}^*$ .<sup>[4]</sup>

In view of the importance of phosphorus as an n-dopant for silicon-based semiconductors,<sup>[5]</sup> its incorporation into stable silicon compounds is both of theoretical and practical interest. While saturated species containing silicon and phosphorus in the same molecule are abundant,<sup>[6]</sup> unsaturated species featuring both elements are relatively rare. Notable examples include phosphasilenes ( $\text{P}=\text{Si}$ )<sup>[7]</sup> and phosphino disilenes.<sup>[7b,8]</sup> In particular the transfer of phosphorus to unsaturated silicon rings and clusters without concomitant incorporation of additional organic substituents is an attractive prospect for the introduction of an n-dopant at the molecular level.

Cyclotrisilenes have been shown to undergo ring expansion with isocyanides<sup>[9]</sup> and carbon monoxide.<sup>[10]</sup> Consequently, the use of unsaturated phosphorus-containing small molecules appeared to be a viable strategy for the desired incorporation of phosphorus into an unsaturated silicon scaffold. Grützmacher and co-workers have recently employed 2-phosphaethynolate ( $\text{PCO}^-$ ; a phosphorus-containing analogue of cyanate) as a phosphide source for the synthesis of a base-coordinated phosphinidene.<sup>[11]</sup> We therefore decided to explore the reactivity of  $c\text{Si}_3(\text{Tip})_4$  towards the 2-phosphaethynolate anion. The latter species was first reported by Becker and co-workers,<sup>[12]</sup> and has received significant attention following the development of new methods for its formation.<sup>[13–15]</sup> A handful of studies have already shown that  $\text{PCO}^-$  reacts with unsaturated substrates including heteroallenes, such as carbodiimides, isocyanates, and  $\text{CO}_2$ .<sup>[14–17]</sup>

Reaction of  $[\text{K}(18\text{-crown-6})][\text{PCO}]$  with  $c\text{Si}_3(\text{Tip})_4$  gives rise to two products as determined by  $^{31}\text{P}$  NMR spectroscopy (each exhibiting a singlet resonance).<sup>[18]</sup> The relative ratio of these two species, and the chemical shift of the downfield resonance, are strongly dependent on solvent polarity and are also influenced by addition of different cation sequestering agents. When the reaction is carried out in a polar solvent, for example, THF, two resonances are observed in the  $^{31}\text{P}$  NMR spectrum at about  $-56$  and  $-323$  ppm in a 1:2 ratio. Conversely, in the presence of non-polar solvents (benzene and toluene), the product with the downfield  $^{31}\text{P}$  NMR

[\*] Dr. T. P. Robinson, Prof. Dr. J. M. Goicoechea  
 Department of Chemistry, University of Oxford  
 Chemistry Research Laboratory  
 12 Mansfield Road, Oxford, OX1 3TA (UK)  
 E-mail: jose.goicoechea@chem.ox.ac.uk

Dr. M. J. Cowley,<sup>[†]</sup> Prof. Dr. D. Scheschkewitz  
 Chair in General and Inorganic Chemistry  
 Saarland University, 66125 Saarbrücken (Germany)  
 E-mail: scheschkewitz@mx.uni-saarland.de

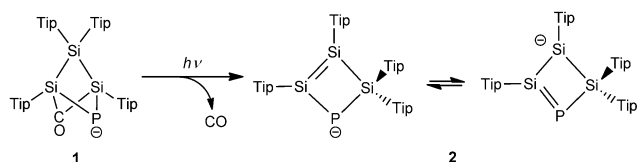
[†] New address:  
 School of Chemistry, University of Edinburgh  
 Edinburgh, EH9 3JJ (UK)

[\*\*] We thank the EPSRC (EP/K039954/1), the Royal Society (International Exchange Scheme grant), the Deutsche Forschungsgemeinschaft (SCHE 906/4-1), and the COST Action CM1302 (Smart Inorganic Polymers) for financial support, the University of Oxford for access to Chemical Crystallography facilities, C<sup>3</sup>MSaar at Saarland University for computational resources, and Elemental Microanalysis Ltd. (Devon) for elemental analyses.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201409908>.

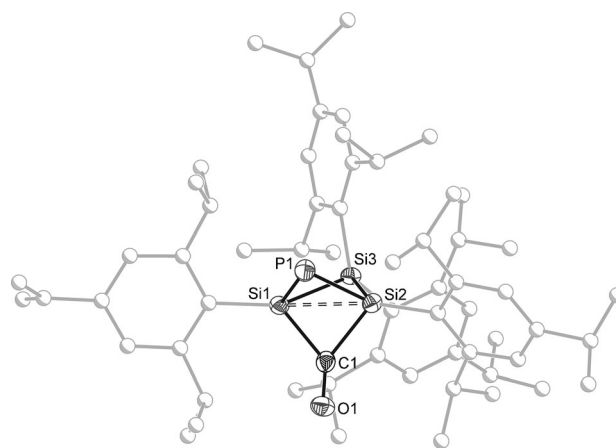
© 2014 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

resonance is favored (typically in a 4:1 ratio). It is worth noting that no interconversion between the products is observed over time or on heating the reaction mixtures. Addition of 2,2,2-cryptand to the two reagents followed by dissolution in THF further favors the formation of the product at  $-323.0$  ppm (**1**), presumably by disrupting solution phase ion-pair contacts. This species was isolated as a compositionally pure sample in moderate yields (35%) and crystallized as bright orange crystals from hot benzene. In the  $^{29}\text{Si}$  NMR spectrum, it exhibits three doublets at  $-1.8$ ,  $-10.9$ , and  $-16.1$  ppm. The chemical shifts of the resonances, and the magnitudes of the silicon–phosphorus coupling constants, indicate that the resonance at  $-1.8$  ppm corresponds to a saturated  $\text{Si}(\text{Tip})_2$  moiety at two bonds from the phosphorus atom; the more upfield resonances are consistent with  $\text{Si}(\text{Tip})$  groups with single bond coupling to a phosphorus nucleus. In the IR spectrum, a band arising from a bridging carbonyl bond stretch was observed at  $1584\text{ cm}^{-1}$ . The negative ion mode electrospray mass spectrum reveals a molecular-ion mass-envelope at  $955.80$  Da in line with a 1:1 adduct of  $\text{PCO}^-$  and cyclotrisilene (an additional, lower intensity, mass-envelope arising from the loss of a carbonyl was also observed at  $m/z$  927.75). These data firmly support the formation of  $[\text{P}(\text{CO})\text{Si}_3(\text{Tip})_4]^-$  (**1**, Scheme 2).



**Scheme 2.** Photolysis of **1** to afford **2**.

The single-crystal X-ray analysis of the product,  $[\text{K}(2,2,2\text{-crypt})]\text{1}\cdot 2\text{C}_6\text{H}_6$  reveals complete cleavage of the P–C multiple bond of the 2-phosphaethynolate anion (Figure 1). The  $\text{PCO}^-$  anion has added across the Si–Si double bond as a phosphide ( $\text{P}^-$ ) and a carbonyl moiety (CO) resulting in a bicyclo[1.1.1]pentanone-type structure. Saturated bicyclo[1.1.1]pentane units have been extensively employed as repeat units of  $[n]$ staffanes;<sup>[19]</sup> persila $[n]$ staffanes have been reported recently by Iwamoto and co-workers.<sup>[20]</sup> Of the heavier bicyclo[1.1.1]pentanones, a derivative with two silicon atoms in the scaffold has also been described which is free of any additional functionality aside of the carbonyl moiety.<sup>[21]</sup> In the case of **1**, the presence of the anionic phosphide type vertex, which is consistent with the upfield  $^{31}\text{P}$  NMR chemical shift, constitutes a potentially valuable site for further functionalization. The interatomic distance between Si1 and Si2 (formerly the double bond of the cyclotrisilene) of  $2.618(1)\text{ \AA}$  (c.f.  $2.118(1)\text{ \AA}$  in  $c\text{Si}_3(\text{Tip})_4$ )<sup>[4a]</sup> is indicative of the expected absence of a strong direct interaction between the bridgehead silicon atoms. The two remaining Si–Si bonds (both  $2.375(1)\text{ \AA}$ ) each display typical single bond lengths.<sup>[22]</sup> Greater variation is observed for the P–Si bonds, which adopt values of  $2.174(4)$  and  $2.215(4)\text{ \AA}$ . This slight asymmetry may arise from the crystallographic disorder of the phosphide and



**Figure 1.** Molecular structure of the anionic moiety in  $[\text{K}(2,2,2\text{-crypt})]\text{1}\cdot 2\text{C}_6\text{H}_6$  (ellipsoids set at 50% probability; hydrogen atoms, crystal solvent, and second component of positional disorder of phosphide vertex and carbonyl (1:1) omitted for clarity). Atoms of Tip groups shown as spheres of arbitrary radius. Selected interatomic distances [ $\text{\AA}$ ] and angles [ $^\circ$ ]: P1–Si1 2.215(4), P1–Si2 2.174(4), Si1...Si2 2.618(1), Si1–Si3 2.375(1), Si2–Si3 2.375(1), Si1–C1 2.009(15), Si2–C1 2.005(16), C1–O1 1.204(15); Si1–P1–Si2 73.22(11), Si1–C1–Si2 81.4(6), P1–Si1–Si3 94.16(9), P1–Si1–C1 82.7(4), P1–Si2–Si3 95.20(9), P1–Si2–C1 83.9(4), Si1–Si3–Si2 66.89(2).

carbonyl moieties over the two bridging positions (each at 50% occupancy). The optimized geometry of **1** calculated using a dispersion-corrected functional ( $\omega\text{B97XD}/6\text{-311g}(\text{d,p})$ ; with polarized continuum solvent model for THF) was found to be in good agreement with experimental values as were the computed NMR chemical shifts (see the Supporting Information for full details).<sup>[23]</sup> The mechanism of formation for **1** remains obscure at this time; fast reaction rates prevented us from identifying any intermediates. Previous studies on the reactivity of  $c\text{Si}_3(\text{Tip})_4$  with unsaturated compounds such as isocyanides, however, suggest that a [2+1] cycloaddition product may be involved.<sup>[9]</sup> Conversely,  $\text{PCO}^-$  has been shown to give rise to [2+2] cycloaddition products with isocyanates and ketenes, so a different reaction pathway involving the formation of a five-membered ring cannot be excluded either.<sup>[15]</sup>

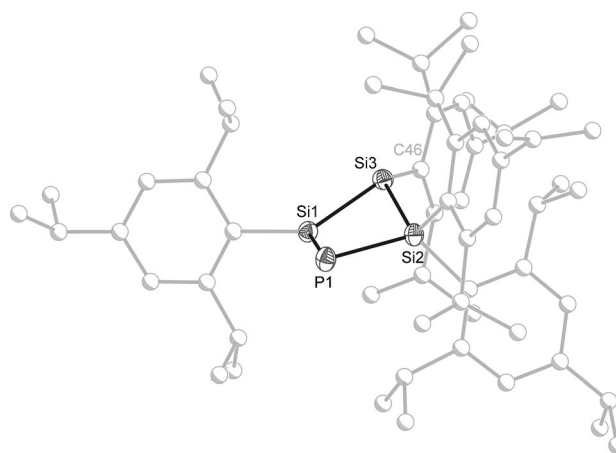
UV irradiation of a solution of  $[\text{K}(2,2,2\text{-crypt})]\text{1}$  is accompanied by a notable color change (from orange to blue–green) and quantitatively affords a new compound with a singlet resonance in the  $^{31}\text{P}$  NMR spectrum. For preparative purposes, the same product (albeit with a different counter-cation) can be isolated by photolyzing a mixture of  $[\text{K}(18\text{-crown-6})][\text{PCO}]$  and  $c\text{Si}_3(\text{Tip})_4$  in toluene, affording a compound with a  $^{31}\text{P}$  NMR resonance at  $-93.9$  ppm. This corresponds to the lowest field resonance observed from the crude reaction between  $\text{PCO}^-$  and  $c\text{Si}_3(\text{Tip})_4$  in non-polar solvents. Notably, the characteristic  $^{13}\text{C}$  NMR signal of the carbonyl moiety in **1** at  $222.7$  ppm disappears, suggesting decarbonylation of **1** on irradiation. This is further corroborated by electrospray mass-spectrometric measurements, which reveal the molecular ion as  $[\text{PSi}_3(\text{Tip})_4]^-$  (observed at  $928.11$  Da). The  $^1\text{H}$  NMR spectrum confirmed the presence of one molecule of 18-crown-6 in the product, which was thus

tentatively identified as [K(18-crown-6)]**2** (Scheme 2). The net reaction between  $\text{PCO}^-$  and  $c\text{Si}_3(\text{Tip})_4$  under photolytic conditions may be considered as a direct incorporation of a phosphide into an unsaturated ring system. As already mentioned (see above), the use of the 2-phosphaethynolate anion as a phosphide anion transfer agent has previously been reported by Grützmacher and co-workers to yield an N-heterocyclic carbene-stabilized phosphinidene.<sup>[11]</sup>

It is worth noting that the  $^{31}\text{P}$  NMR chemical shift of [K(18-crown-6)]**2** is strongly dependent on the nature of the solvent: while it appears at  $-56.6$  ppm in  $[\text{D}_8]\text{THF}$ , it is observed at  $-93.9$  ppm in  $[\text{D}_8]\text{toluene}$ . This effect may arise from solvent coordination to **2** or the separation of ion pairs in solution. There is a large upfield shift observed for the  $^{29}\text{Si}$  NMR resonance arising from the  $\beta$ -silicon (with respect to the phosphide center) of the formal silicon–silicon double bond, which was observed at  $-39.9$  ppm ( $^2J_{\text{Si-P}} = 35.4$  Hz) (consistent with significant delocalization of negative charge onto this atom, as represented in the second resonance form in Scheme 2). While the resonance of the saturated silicon atom was recorded at  $-14.9$  ppm ( $^1J_{\text{Si-P}} = 72.5$  Hz), the resonance for the remaining unsaturated silicon center is found far downfield at  $193.1$  ppm ( $^1J_{\text{Si-P}} = 138.2$  Hz). Strongly polarized  $\text{Si}=\text{Si}$  bonds with their characteristically wide dispersion of  $^{29}\text{Si}$  NMR shifts have been subject to detailed experimental and computational studies.<sup>[24,25]</sup>

The UV/Vis absorption spectrum of [K(18-crown-6)]**2** in THF reveals its longest wavelength absorption at significantly lower energy than in case of **1** (**1**:  $\lambda_{\text{max}} = 490$  nm; **2**:  $\lambda_{\text{max}} = 594$  nm) consistent with the blue–green color of the product. TDDFT calculations on the optimized structure of the contact ion pair [K(18-crown-6)]**2**<sub>calc</sub> ( $\omega\text{B97XD}/6\text{-311g(d,p)}$ ; with polarized continuum solvent model for THF)<sup>[23]</sup> quantitatively reproduce the trend although the signals are considerably blue-shifted (**1**<sub>calc</sub>:  $\lambda_{\text{max}} = 437$ ; [K(18-crown-6)]**2**<sub>calc</sub>:  $\lambda_{\text{max}} = 514$  nm). As expected the longest wavelength transition in [K(18-crown-6)]**2**<sub>calc</sub> is largely dominated by the HOMO–LUMO transition (94%), which corresponds to the  $\pi$  and  $\pi^*$  orbitals of the  $\text{Si}=\text{Si}-\text{P}$  moiety. The calculated chemical shifts of optimized **2**<sub>calc</sub> reasonably agree with experimental values, and are independent of the existence (or absence) of a contact ion pair (see the Supporting Information).

Dark-green crystals of **2** were grown from toluene (as [K(18-crown-6)]**2** $\cdot 0.5\text{C}_7\text{H}_8$ ) and characterized by single-crystal X-ray diffraction (Figure 2). The anionic moiety consists of a slightly folded  $\text{PSi}_3$  four-membered ring (folding angle between  $\text{P}-\text{Si}1-\text{Si}2/\text{Si}1-\text{Si}2-\text{Si}3$   $24.056(24)^\circ$ ). The structure is consistent with a significant allylic character across the unsaturated atoms in the ring (resonance forms in Scheme 2), which is manifested in the interatomic bond distances. Consequently,  $\text{P}1-\text{Si}1$  is notably ( $0.11$  Å) shorter than  $\text{P}1-\text{Si}2$  ( $2.156(1)$  and  $2.263(1)$  Å, respectively), as expected for a phospho-allylic system. The  $\text{Si}1-\text{Si}3$  distance of  $2.212(1)$  Å is longer than the typical  $\text{Si}-\text{Si}$  double bond, but very similar to that of a related cyclo-tetrasilene anion reported by Sekiguchi and co-workers.<sup>[26]</sup> The delocalization of the negative charge over  $\text{P}1$ ,  $\text{Si}1$ , and  $\text{Si}3$  is also apparent in the upfield  $^{29}\text{Si}$  chemical shift and the pyramidalization of the  $\text{Si}3$  center ( $\Sigma_{\text{angles}} = 332.64^\circ$ ). It is located  $0.610(1)$  Å above the



**Figure 2.** Molecular structure of the anionic moiety in [K(18-crown-6)]**2** $\cdot 0.5\text{C}_7\text{H}_8$  (ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity; atoms of Tip groups are pictured as spheres of arbitrary radius). Selected interatomic distances [Å] and angles [°]:  $\text{P}1-\text{Si}1$   $2.156(1)$ ,  $\text{P}1-\text{Si}2$   $2.263(1)$ ,  $\text{Si}1-\text{Si}3$   $2.212(1)$ ,  $\text{Si}2-\text{Si}3$   $2.364(1)$ ;  $\text{Si}1-\text{P}1-\text{Si}2$   $80.785(16)$ ,  $\text{P}1-\text{Si}1-\text{Si}3$   $101.669(18)$ ,  $\text{P}1-\text{Si}2-\text{Si}3$   $94.108(16)$ ,  $\text{Si}1-\text{Si}3-\text{Si}2$   $77.427(15)$ ,  $\text{Si}1-\text{Si}3-\text{C}46$   $128.46(4)$ ,  $\text{Si}1-\text{Si}3-\text{C}46$   $126.75(4)$ .

plane defined by  $\text{Si}1$ ,  $\text{Si}2$ , and the *ipso*-carbon atom of the Tip substituent to which it is bonded.

In conclusion, we report the incorporation of a phosphide into an unsaturated silicon scaffold. The reaction of the highly versatile cyclo-trisilene  $c\text{Si}_3(\text{Tip})_4$  with potassium phosphoethynolate under photolytic conditions and loss of carbon monoxide results in a formal ring expansion to yield an anionic heavier cyclobutene analogue. The intermediate prior to decarbonylation was isolated and already displays a completely cleaved phosphorus–carbon bond, the extreme case of  $\text{P}-\text{C}$  bond activation. The reactivity of both compounds in particular regarding the nucleophilic phosphide functionality and the formal  $\text{Si}=\text{Si}$  moiety is currently being investigated in our laboratories.

Received: October 9, 2014

Published online: November 21, 2014

**Keywords:** 2-phosphaethynolate · main-group chemistry · multiple bonds · silenes · silicon

- [1] See, for example: a) R. J. Hamers, U. K. Köhler, J. E. Demuth, *Ultramicroscopy* **1989**, *31*, 10–19; b) M. T. Swihart, S. L. Girshick, *J. Phys. Chem. B* **1999**, *103*, 64–76; c) M. T. Swihart, S. L. Girshick, *Chem. Phys. Lett.* **1999**, *307*, 527–532; d) N. Ning, H. Vach, *J. Phys. Chem. A* **2010**, *114*, 3297–3305; e) W. O. Filtvedt, A. Holt, P. A. Ramachandran, M. C. Melaaen, *Sol. Energy Mater. Sol. Cells* **2012**, *107*, 188–200.
- [2] T. Iwamoto, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **1999**, *121*, 886–887.
- [3] M. Ichinohe, T. Matsuno, A. Sekiguchi, *Angew. Chem. Int. Ed.* **1999**, *38*, 2194–2196; *Angew. Chem.* **1999**, *111*, 2331–2333.
- [4] a) K. Leszczyńska, K. Abersfelder, A. Mix, B. Neumann, H.-G. Stämmler, M. J. Cowley, P. Jutzi, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2012**, *51*, 6785–6788; *Angew. Chem.* **2012**, *124*, 6891–6895; b) M. J. Cowley, V. Huch, H. S. Rzepa, D. Scheschkewitz, *Nat. Chem.* **2013**, *5*, 876–879.

- [5] S. M. Sze, K. K. Ng, *Physics of Semiconductor Devices*, 3rd ed., Wiley, Hoboken, 2007.
- [6] a) G. Fritz, P. Scheer, *Chem. Rev.* **2000**, *100*, 3341–3401; b) C. von Hänisch, *Z. Anorg. Allg. Chem.* **2008**, *634*, 23–29.
- [7] Selected references: a) C. N. Smit, F. Bickelhaupt, *Organometallics* **1987**, *6*, 1156; b) M. Driess, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1022–1024; *Angew. Chem.* **1991**, *103*, 979–981; c) M. Driess, S. Rell, H. Pritzkow, R. Janoschek, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1326–1329; *Angew. Chem.* **1997**, *109*, 1384–1387; d) M. Driess, S. Block, M. Brym, M. T. Gamer, *Angew. Chem. Int. Ed.* **2006**, *45*, 2293–2296; *Angew. Chem.* **2006**, *118*, 2351–2354; e) V. Y. Lee, M. Kawai, A. Sekiguchi, H. Ranaivonjatovo, J. Escudíé, *Organometallics* **2009**, *28*, 4262–4265; f) K. Hansen, T. Szilvási, B. Blom, E. Irran, M. Driess, *Chem. Eur. J.* **2014**, *20*, 1947–1956; g) P. Willmes, M. J. Cowley, M. Hartmann, M. Zimmer, V. Huch, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2014**, *53*, 2216–2220; *Angew. Chem.* **2014**, *126*, 2248–2252.
- [8] M. Hartmann, A. Haji-Abdi, K. Abersfelder, P. R. Haycock, A. J. P. White, D. Scheschkewitz, *Dalton Trans.* **2010**, *39*, 9288–9295.
- [9] Y. Ohmori, M. Ichinohe, A. Sekiguchi, M. J. Cowley, V. Huch, D. Scheschkewitz, *Organometallics* **2013**, *32*, 1591–1594.
- [10] a) M. J. Cowley, Y. Ohmori, V. Huch, M. Ichinohe, A. Sekiguchi, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2013**, *52*, 13247–13250; *Angew. Chem.* **2013**, *125*, 13489–13492; b) M. J. Cowley, V. Huch, D. Scheschkewitz, *Chem. Eur. J.* **2014**, *20*, 9221–9224.
- [11] A. M. Tondreau, Z. Benkó, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, *5*, 1545–1554.
- [12] G. Becker, W. Schwarz, N. Seidler, M. Westerhausen, *Z. Anorg. Allg. Chem.* **1992**, *612*, 72–82.
- [13] F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2011**, *50*, 8420–8423; *Angew. Chem.* **2011**, *123*, 8570–8574.
- [14] D. Heift, Z. Benkó, H. Grützmacher, *Dalton Trans.* **2014**, *43*, 831–840.
- [15] A. R. Jupp, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2013**, *52*, 10064–10067; *Angew. Chem.* **2013**, *125*, 10248–10251.
- [16] X. Chen, S. Alidori, F. F. Puschmann, G. Santiso-Quinones, Z. Benkó, Z. Li, G. Becker, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2014**, *53*, 1641–1645; *Angew. Chem.* **2014**, *126*, 1667–1671.
- [17] D. Heift, Z. Benkó, H. Grützmacher, *Angew. Chem. Int. Ed.* **2014**, *53*, 6757–6761; *Angew. Chem.* **2014**, *126*, 6875–6879.
- [18] Full experimental details, including crystallographic data, are provided in the Supporting Information. CCDC 1027426 ([K(2,2,2-crypt)]**1**·2C<sub>6</sub>H<sub>6</sub>) and 1027427 ([K(18-crown-6)]**2**·0.5C<sub>7</sub>H<sub>8</sub>) contain the supplementary crystallographic data for this paper. These can be obtained free of charge from the CCDC via [www.ccdc.cam.ac.uk/Community/Requeststructure/Pages/DataRequest.aspx](http://www.ccdc.cam.ac.uk/Community/Requeststructure/Pages/DataRequest.aspx).
- [19] Review: M. D. Levin, P. Kaszynski, J. Michl, *Chem. Rev.* **2000**, *100*, 169–234.
- [20] T. Iwamoto, D. Tsushima, E. Kwon, S. Ishida, H. Isobe, *Angew. Chem. Int. Ed.* **2012**, *51*, 2340–2344; *Angew. Chem.* **2012**, *124*, 2390–2394.
- [21] A. Rammo, I. Bejan, A. Meltzer, K. Radacki, H. Braunschweig, D. Scheschkewitz, *Aust. J. Chem.* **2013**, *66*, 1311–1314.
- [22] a) B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838; b) P. Pykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186–197.
- [23] Calculations were carried out with the Gaussian09 program package: Gaussian09 (Revision D.01), M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, **2013**. For the full reference, see the Supporting Information.
- [24] See, for example: a) M. Ichinohe, Y. Arai, A. Sekiguchi, N. Takagi, S. Nagase, *Organometallics* **2001**, *20*, 4141–4143; b) K. Abersfelder, D. Scheschkewitz, *J. Am. Chem. Soc.* **2008**, *130*, 4114–4121.
- [25] D. Auer, C. Strohmman, A. V. Arbuznikov, M. Kaupp, *Organometallics* **2003**, *22*, 2442–2449.
- [26] T. Matsuno, M. Ichinohe, A. Sekiguchi, *Angew. Chem. Int. Ed.* **2002**, *41*, 1575–1577; *Angew. Chem.* **2002**, *114*, 1645–1647.