Check for updates

Simple conversion of trisodium phosphide, Na₃P, into silyl- and cyanophosphides and the structure of a terminal silver phosphide†

Grégoire Le Corre 🆔 and Hansjörg Grützmacher 🆔 *

A reaction of trisodium phosphide (Na₃P) with chlorosilanes allows for simple derivatization into silyl- and cyano-substituted phosphanide species which were compared with each other. The recently discovered cyano(triphenylsilyl)phosphanide shows unique coordination properties compared to bis(silyl)phosphides.

Silylated phosphanes and phosphides are useful building blocks in phosphorus chemistry[1] and are soluble in organic solvents and suited to replace PH_3 or $M[PH_2]$ which are mostly insoluble and difficult to handle.[2] Particularly, tris(trimethylsilyl)phosphane $P(TMS)_3$[3] **1** (TMS = $SiMe_3$) and the alkali metal salts $M[P(TMS)_2]$ M[**2**] (M = Li, Na, K) are highly popular[4] but their preparation requires a sodium-potassium alloy[5] or phosphine gas which are hazardous materials.[6] Tris(triphenylsilyl)phosphane **3**[7] and the phosphides $M[P(SiPh_3)_2]$ M[**4**][8] were prepared *via* silylation of a metal phosphide produced from elemental phosphorus and a Na/K alloy but their chemistry remains unexplored (Scheme 1).[9]

In 2018, Cummins *et al.* reported the tetrabutylammonium salt of bis(trichlorosilyl)phosphide $Bu_4N[P(SiCl_3)_2]$ ($Bu_4N[$**5**$]$) which was prepared by reduction of a phosphate derivative.[10] This synthesis of a P^{3-} silyl derivative directly from a P(v) precursor is ground-breaking, although the use of ten equivalents of trichlorosilane (Cl_3SiH) per phosphorus atom is required. Therefore, a classical protocol which employs elemental phosphorus and a reducing agent, $12 M + P_4 \rightarrow 4 M_3P$, followed by a silylation reaction $M_3P + 3 R_3SiX \rightarrow P(SiR_3)_3 + 3 MX$ is still a competitive process.[11]

The phosphide $[P(SiCl_3)_2]^-$ can be used as a nucleophile but rather harsh reaction conditions are required. This indicates low nucleophilicity due to efficient depletion of the electron density from the P atom into the adjacent Si–Cl bonds *via* $p(P) \rightarrow \sigma^*(SiCl)$ negative-hyperconjugation. Therefore $[$**5**$]^-$ is related to the bis(cyano)phosphide anion $[$**6**$]^-$, first isolated as a sodium salt by Schmidpeter *et al.* more than 40 years ago.[12] In this anion the electron density at P is delocalized into the

$\pi^*(C\equiv N)$ orbitals to such an extent that $[P(CN)_2]^-$ even behaves as an electrophile and nucleophilic attack occurs under the displacement of cyanide, $[P(CN)_2]^- + Nuc^- \rightarrow [P(CN)(Nuc)]^- + CN^-$.[13]

Recently, we have shown the synthesis of a mixed cyano(silyl)phosphanide from Na(OCP) which shows unique reactivity towards electrophiles.[14]

In this study, we set out to find a more convenient method for the preparation of phosphides by reactions of sodium phosphide and chlorosilanes in 1,2-dimethoxyethane (DME) as the solvent.

The sodium salt $Na[P(SiCl_3)_2]$ ($Na[$**5**$]$) was prepared by a one-pot procedure by reacting red phosphorus with sodium metal in dimethoxyethane (DME) in the presence of 10 mol% naphthalene as an electron transfer reagent to give Na_3P fol-
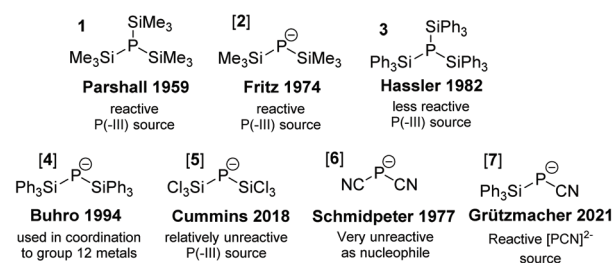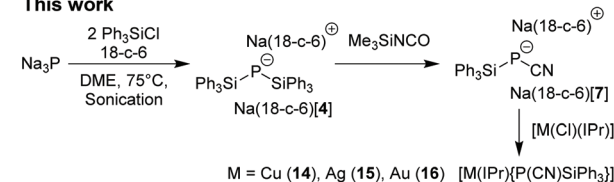
Scheme 1 Existing phosphide species (top); direct synthesis of bis(silyl)phosphide from sodium phosphide (bottom). IPr = 1,3-Bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene.

Department of Chemistry and Applied Biosciences ETH Zurich, Vladimir-Prelog-Weg 1, CH-8049 Zurich, Switzerland. E-mail: hgruetzmacher@ethz.ch

lowed by the addition of $SiCl_4$ at room temperature[15] (Scheme 2(a)).

This reaction is slow but in the presence of $^nBu_4NBr$ or Ph_4PBr and under sonication, the reaction time is shortened to 5 days and $[P(SiCl_3)_2]^-$ can be obtained as tetraphenylphosphonium salt $[\delta(^{31}P) = -171$ ppm$]$ in 53% yield (with respect to $SiCl_4$).

The structure of $Ph_4P[P(SiCl_3)_2]$, $Ph_4[5]$, was determined using single crystal X-ray diffraction (XRD). The resulting metric parameters are very similar to those of $Bu_4N[5]$ (see ESI Fig. S2†).[10]

With methylchlorosilanes $Me_{4-x}SiCl_x$ $(x = 1, 2, 3)$ as reagents, complex product mixtures are obtained and only with 3.3 equivalents of Me_3SiCl (TMSCl) a fair yield of $P(TMS)_3$ (52%) is achieved after distillation, consistent with previous work (Scheme 2(b)).[18] Notably, this reaction proceeds without the addition of phosphonium or ammonium salts.

The reaction with 2 equivalents of phenylchlorosilanes Ph_xSiCl_{4-x} $(x = 1, 2)$ in the presence of one equivalent of the phosphonium salt $^nBu_4PBr$ is more selective and after 16 h at 75 °C under sonication, the bis(silyl)phosphides $^nBu_4P[P(SiCl_2Ph)_2]$ [8] and $^nBu_4P[P(SiClPh_2)_2]$ [9] could be characterized by NMR spectroscopy (Scheme 2(c)).

Bis(triphenylsilyl)phosphide was prepared by sonication of Na_3P with Ph_3SiCl at 75 °C in DME in the absence of phosphonium salts, followed by precipitation with 18-crown-6 to afford $[Na(18-c-6)(dme)_{0.5}]^+[P(SiPh_3)_2]^-$ [4] in 60% yield (Scheme 2(d)). Note that the formation of tris(triphenylsilyl)phosphane 3[7] is not observed in the ^{31}P NMR spectrum of the reaction mixture even when the reaction was performed in dimethoxyethane at 115 °C in the presence of 10 mol% tetrabutylphosphonium bromide. This is in contrast to the reported synthesis of 3 from sodium–potassium phosphide and Ph_3SiCl in boiling DME.[7]

In the structure of $Na(18-crown-6)(DME)_{0.5}[4]$ (ESI Fig. S1†), no close cation–anion interaction is observed and in the separated ion pair the P–Si distance is 2.19 Å and the Si–P–Si angle is 105° (similar to the corresponding data of $[2]^-$).[16]

Although the isolation in the pure form was not possible for all derivatives, the ^{31}P chemical shifts and the $^1J_{PSi}$ coupling constants of the complete series of chloro organylsilyl phosphides $[P(SiPh_xCl_{3-x})_2]^-$ [5], [8], [9], and [4] $(x = 0, 1, 2,$ and 3, respectively) were obtained and allow a comparison with the data of $[P(SiMe_3)_2]^-$ [2], $[P(CN)_2]^-$ [6] and $[P(CN)SiPh_3]^-$ [7]. Clear trends are observed (Table 1): the higher the degree of chlorine substitution, the larger is $^1J_{PSi}$ and the more the ^{31}P NMR signal is shifted to higher frequencies (less negative $\delta(^{31}P)$). Chlorine substitution appears to lead to shortening of the P–Si distance and narrowing of the Si–P–Si angle, which is verified experimentally for $[4]^-$ and $[5]^-$ and coherent with the NMR data of $[8]^-$ and $[9]^-$. These effects are rationalized by the assumption that with increasing chlorine substitution negative hyperconjugation between the p-type lone-pair at phosphorus and the σ^*(Si–Cl)-orbitals increases, provoking a shortening of the phosphorus–silicon bond which in turn leads to an increase of the $^1J_{PSi}$ scalar coupling. Concomitantly, the electron density at the ^{31}P nucleus is depleted, leading to a high-frequency shift of the ^{31}P chemical shift. Both effects overcompensate the narrowing of the Si–P–Si angle which is expected to cause a low-frequency shift.[19]

Noteworthy is the structural and spectroscopic similarity between the anions $[P(SiCl_3)_2]^-$ $([5]^-$, entry 2) and $[P(CN)_2]^-$ $([6]^-$, entry 6) which suggests that the former is also a poor nucleophile. Indeed, $Ph_4P[5]$ does not react with $SiCl_4$ in excess or with CH_2Cl_2. On the other hand, the similarities between $[P(SiMe_3)_2]^{-16}$ $([2]^-)$ and $[P(SiPh_3)_2]^-$ $([4]^-)$ prompted us to investigate the reactivity of $[4]^-$ as a nucleophile in more detail.

As expected, the reaction of $[4]^-$ with dimethyl carbonate afforded $Na(OCP)$ $[\delta(^{31}P) = -394$ ppm$]$ comparable to the original synthesis of $Li(OCP)$ by Becker[20] using $Li[P(SiMe_3)_2]$ as a reagent. Furthermore, $[4]^-$ was reacted with pivaloyl or mesitoyl chloride to afford mixtures of E- and Z-isomers (about 3 : 1 and 1 : 1 ratio, respectively) of the phosphaalkenes 10 and 11 (Scheme 3(a)) in analogy to the E/Z mixtures when the TMS-substituted derivatives TMS-P = C(OTMS)R (R = Mes, tBu) were prepared from $P(TMS)_3$ 1 or $[P(TMS)_2]^-$ [2].[1d,21]

Only very few P-silyl phosphaalkenes TMS-P = C(OTMS)R (R = ferrocenyl or bicyclo[2.2.2]octanediyl) have been investigated
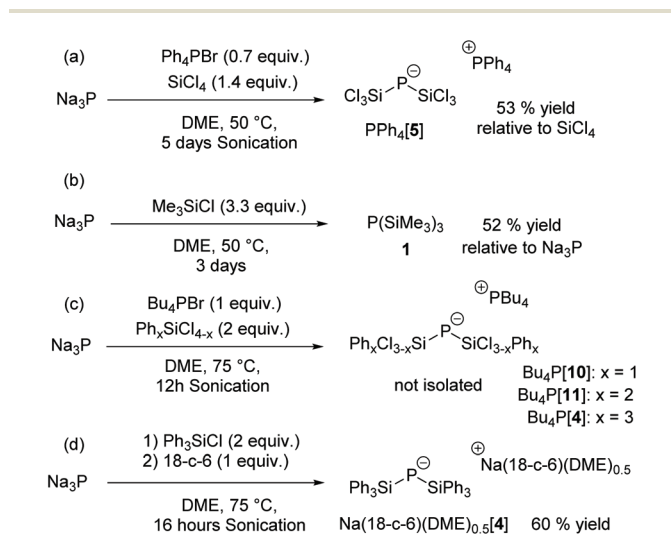

Scheme 2 Reactions of Na_3P with chlorosilanes. 18-c-6 = 18-crown-6.

Table 1 Structural and ^{31}P-NMR spectroscopic properties of silyl- and cyano-substituted phosphanides $[(R)(R')P]^-$

Anion	R	R'	δ (^{31}P) (ppm)	$^1J_{PSi}$ (Hz)	E-Si distance (ppm)	R–E–R angle(°)
$[2]^{-16}$	$SiMe_3$	$SiMe_3$	−298	35	2.20	105
$[5]^-$	$SiCl_3$	$SiCl_3$	−171	160	2.15	98
$[8]^-$	$SiPhCl_2$	$SiPhCl_2$	−228	130	—	—
$[9]^-$	$SiPh_2Cl$	$SiPh_2Cl$	−270	110	—	—
$[4]^-$	$SiPh_3$	$SiPh_3$	−310	80	2.19	105
$[6]^{-17}$	CN	CN	−195	—	—	94
$[7]^-$	$SiPh_3$	CN	−281	67	2.21	95
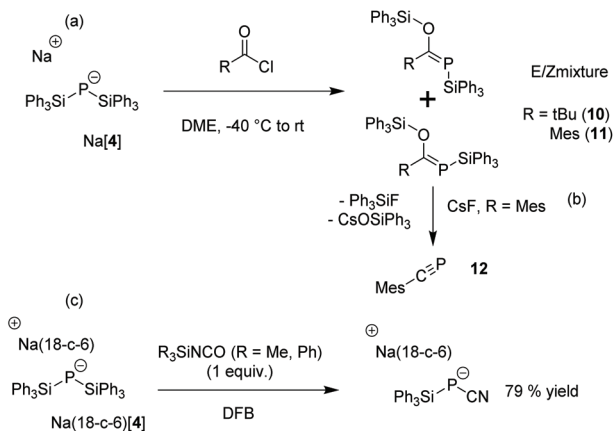
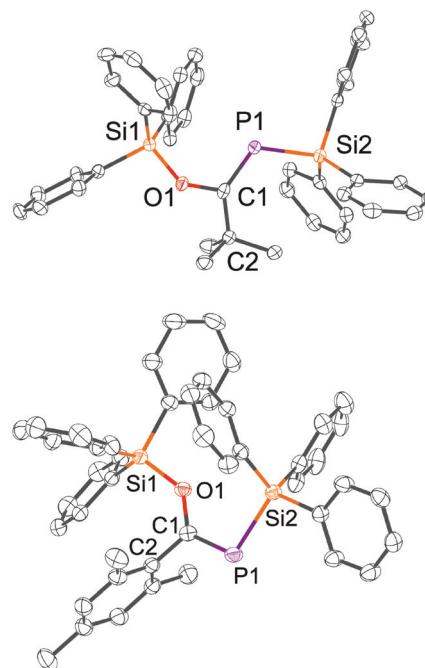**Scheme 3** Reactivity of Na[4]. Mes = Mesityl.

Fig. 1 Structure of *E*-10 (top) and *Z*-11 (bottom) in the crystal (hydrogens omitted for clarity). Selected bond distances [Å] and angles [°] for *E*-10: Si1–O1 1.6871(17); O1–C1 1.354(3); P1–C1 1.704(2); Si2–P1 2.2604(9); C1–C2 1.497(3); C2–C1–P1 117.33(17); O1–C1–P1 124.47(18); C1 P1 Si2 102.34(9) Si2–P1–C1–O1 6.1(2) P1–C1–O1–Si1 12.73(13); for *Z*-11: Si1–O1 1.6688(19); O1–C1 1.372(3); P1–C1 1.718(3); Si2–P1 2.2696(10); C1–C2 1.528(4); C2–C1–P1 137.92(19); O1–C1–P1 114.02(19); O1–C1–C2 108.1(2); C1–P1–Si2 113.82(9); Si2–P1–C1–O1 12.58(15) P1–C1–O1–Si1 37.6(3).

by X-ray diffraction (XRD). Compounds with R = Mes, ^{t}Bu are liquids at room temperature.[22] Single crystals of the *E*-isomer of 10 and the *Z*-isomer of 11 can be easily grown by slow evaporation of a concentrated solution in hexane and were subjected to XRD experiments.

In both structures (Fig. 1), the phosphorus–carbon bond is slightly longer (1.71 Å for *E*-10 and 1.70 Å for *Z*-11) than the average P=C bond length in previously reported phosphaalkenes (1.66 Å).[23] The phosphorus–silicon bonds (*E*-10: 2.27 Å; *Z*-11: 2.26 Å) are considerably elongated in comparison to [4]$^-$. Both compounds have an almost planar Si–P–C–O unit (Si–P–C–O dihedral angles: *Z*-11: 6.1°; *E*-10 13.6°). The atoms Si1, C2, and P1 around the C–O unit are arranged in an almost planar fashion in *Z*-11 (Si–O–C–P torsion angle φ = 6.2°), while in *E*-10 this angle is φ = 37°, likely because the triphenylsilyl group is both repelled by the bulky *tert*-butyl moiety and by the electron density at phosphorus.

It has been shown that TMS-P = C(OTMS)R can be used as precursors for the corresponding phosphaalkynes, R-C≡P, *via* thermal elimination of hexamethyldisiloxane[1d,24] or a reaction with AlCl$_3$ at lower temperatures.[21,25] Upon mixing 11 with one equivalent of cesium fluoride in order to initiate Ph$_3$SiF and Cs(OSiPh$_3$) elimination at room temperature in tetrahydrofuran (THF), the selective formation of phosphaalkyne 12 was observed by NMR [$\delta(^{31}P)$ = +1 ppm and $\delta(^{13}C)$ = 163.5 ppm ($^1J_{CP}$ = 45 Hz)] (Scheme 3(b), ESI Fig. S32 and S33†). 10 does not react using the same reaction conditions, presumably because the steric hindrance due to the *t*-butyl group prevents 10 from achieving a conformation suitable for Ph$_3$SiF and Cs(OSiPh$_3$) elimination. Heating alone or treatment with AlCl$_3$ did not lead to the formation of the corresponding phosphaalkynes R-C≡P (R = *t*Bu, Mes).

[4]$^-$ reacts with two equivalents of cyanogen bromide to generate bis(cyano)phosphide [6]$^-$. Since bromotriphenylsilane is generated as a byproduct in this reaction, we hypothesized that Ph$_3$SiCl could be used catalytically in a reaction between Na$_3$P and cyanogen bromide. While [6]$^-$ was not detected by ^{31}P NMR after the sonication of Na$_3$P for 16 h with two equiva-

lents of BrCN in DME at 50 °C, it is formed as the major product when 20 mol% Ph$_3$SiCl is added to the suspension. Na(18-crown-6)[6] was isolated in 43% yield from the reaction mixture. This provides a relatively efficient way to prepare Na$^+$[P(CN)$_2$]$^-$, Na$^+$[6]$^-$, as other syntheses require a tenfold excess of P$_4$[26] or the use of Ag salts or volatile HCN.[12c]

The reaction of [4]$^-$ with one equivalent of phenyl cyanate in DME gave a mixture of [6]$^-$ and cyano(triphenylsilyl)phosphide [7]$^-$ [$\delta(^{31}P)$ = −282 ppm]. When one equivalent of triphenylsilyl- or trimethylsilyl isocyanate is used as a milder cyanation agent, only [7]$^-$ was observed in the NMR spectrum, allowing us to isolate Na(18-crown-6)[7] in 79% yield.

We investigated whether a trimethylsilyl-substituted equivalent of [7]$^-$ would be accessible *via* the reaction of Na[2] with trimethylsilyl isocyanate in THF. The product of this reaction was identified as P(TMS)$_3$ 1 *via* ^{31}P- and ^{13}C-NMR. Moreover, the reaction of [4]$^-$ with Me$_3$Si-NCO in a DME/DFB mixture in the absence of 18-crown-6 afforded P(SiPh$_3$)$_2$(SiMe$_3$) 13[11] as the major product [$\delta(^{31}P)$ = −255 ppm] along with minor amounts of [7]$^-$.

From these two reactions, it can be concluded that both steric bulk on bis(silyl)phosphide and the complexation of sodium are essential in order to prevent salt metathesis with silyl isocyanates and favour the elimination of a disiloxane in the reaction of a bis(silyl)phosphide with a silyl isocyanate.
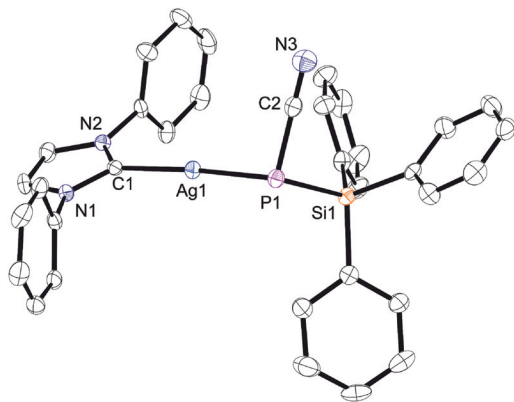
Fig. 2 Structure of **15** in the crystal (hydrogens and isopropyl groups omitted for clarity). Selected bond distances [Å] and angles [°]: P1–Ag1 2.3757(8) Ag1–C1 2.109(3); P1–C2 1.778(3); C2–N3 1.150(4); P1–Si1 2.2392(11); Ag1–P1–C2 101.27(10); Si1–P1–C2 83.59(10); Si1–P1–Ag1 107.30(4); Ag1–P1–C1 5.32(8).

While terminally bonded bis(silyl) phosphide complexes of d^{10} valence electron configured noble metals Cu^+ and Au^+ stabilised with N-heterocyclic carbenes are known, Ag^+ analogues remain elusive, as attempts to form such compounds typically result in the formation of Ag(I) phosphido clusters.[27] Therefore, the push–pull substituted Na(18-crown-6)[7] was reacted with a series of coinage metal complexes [M(Cl)(IPr)] (IPr = 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene; M = Cu, Ag, Au) which allowed us to isolate the homologous series of complexes [M(IPr){P(CN)(SiPh₃)}] **14** (M = Cu), **15** (M = Ag), and **16** (M = Au). These species have very similar conformations with a phosphorus atom in a pyramidal coordination sphere (the average sum of angles around phosphorus is 301°); see a plot of **15** in Fig. 2 as an example and the plots of **13** and **15** in Fig. S3 and S4,† respectively.

Compared to Na(18-c-6)[7], the P–C and P–Si bond distances in the coinage metal complexes are longer while the C–N bond distances are shorter (ESI Table S1†). This is expected because the dative P → M bond causes a depletion of electron density at P which in turn weakens the donation into the σ* (Si–Ph) bonds (negative hyperconjugation) and π*-orbitals of the CN group. The lower magnitude of $^1J_{P,C}$ and $^1J_{P,Si}$ couplings and the higher CN stretching frequencies in **14–16** reflect these changes (Table S1†). In [Au(IPr)X]-type complexes, the ^{13}C-NMR chemical shift of the carbenic carbon correlates with the σ-acidity of the [AuX] fragment.[28] In **16**, this carbon resonates at 195.8 ppm and at 188.6 ppm for [Au(IPr){P (SiMe₃)₂}].[27b] In **16**, there is a relatively short distance between the Au atom and the carbon of the CN group (Au–C2 = 3.25 Å; sum of the van der Waals radii of Au and C: 3.8 Å).[29] This secondary interaction is also found in **15** (Ag–C distance 3.23 Å; sum of van der Waals radii 3.8 Å) which may enhance the σ-acidity of the [M[7]] fragments thereby contributing to the overall stability. It also suggests that complexes of [7]⁻ in an η² or η³ binding mode may exist, as has been found in some complexes of related [X = C = P]⁻ anions.[30]

In conclusion, simple silylation of trisodium phosphide gives access to a variety of silyl-substituted phosphanides. Particularly, the salts of [P(SiCl₃)₂]⁻ and [P(SiPh₃)₂]⁻ could be easily prepared using one-pot procedures by first mixing sodium and red phosphorus to give Na₃P which was subsequently reacted with SiCl₄ or Ph₃SiCl. While [P(SiCl₃)₂]⁻ is a weak nucleophile (comparable to [P(CN)₂]⁻) which limits somewhat its use as a reagent, [P(SiPh₃)₂]⁻ is a versatile reagent which allows us to access a variety of organophosphorus compounds such as phosphaalkenes or the push–pull cyano(silyl)phosphide [P(CN)(SiPh₃)]⁻. The latter allowed us to access the first fully characterized example of a terminal Ag(I) phosphide, which highlights that this phosphide possesses unique properties. We hope to demonstrate by future work that especially [P(CN)(SiPh₃)]⁻ will allow the synthesis of new metal phosphides (for example via elimination of Ph₃SiCN) which are currently highly sought after catalytic materials.

Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

1 (a) M. D. Healy, P. E. Laibinis, P. D. Stupik and A. R. Barron, *J. Chem. Soc., Chem. Commun.*, 1989, 359–360; (b) R. Appel, D. Gudat, E. Niecke, M. Nieger, C. Porz and H. Westermann, *Z. Naturforsch., B: Chem. Sci.*, 1991, **46**, 865; (c) G. Becker, W. Schwarz, N. Seidler and M. Westerhausen, *Z. Anorg. Allg. Chem.*, 1992, **612**, 72–82; (d) G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch., B: Chem. Sci.*, 1981, **36**, 16–19.

2 G. Becker, G. Ditten, K. Hübler, U. Hübler, K. Merz, M. Niemeyer, N. Seidler, M. Westerhausen and Z. Zheng, *Organosilicon Chemistry Set: From Molecules to Materials*, 2005, pp. 161–186.

3 G. W. Parshall and R. V. Lindsey, *J. Am. Chem. Soc.*, 1959, **81**, 6273–6275.

4 (a) G. Fritz, H. Schäfer and W. Hölderich, *Z. Anorg. Allg. Chem.*, 1974, **407**, 266–286; (b) F. Uhlig and R. Hummeltenberg, *J. Organomet. Chem.*, 1993, **452**, C9–C10; (c) E. P. O. Fuchs, H. Heydt, M. Regitz, W. W. Schoeller and T. Busch, *Tetrahedron Lett.*, 1989, **30**, 5111–5114; (d) A. R. Barron, A. H. Cowley and S. W. Hall, *J. Chem. Soc., Chem. Commun.*, 1987, 980–981.

5 G. Becker and W. Hölderich, *Chem. Ber.*, 1975, **108**, 2484–2485.

6 Y. J. Shin, S. W. Jun and J. H. Park, *US Patent* 2017/226138, 2017.

7 K. Hassler, *Monatsh. Chem.*, 1982, **113**, 421–425.

8 M. A. Matchett, M. Y. Chiang and W. E. Buhro, *Inorg. Chem.*, 1994, **33**, 1109–1114.

9 D. C. Gary, B. A. Glassy and B. M. Cossairt, *Chem. Mater.*, 2014, **26**, 1734–1744.

10 M. B. Geeson and C. C. Cummins, *Science*, 2018, **359**, 1383.

11 (a) H. Diskowski and T. Hofmann, Phosphorus, in *Ullmann's Encyclopedia of Industrial Chemistry*, 2000; (b) W. Zulehner, B. Neuer and G. Rau, Silicon, in *Ullmann's Encyclopedia of Industrial Chemistry*, 2000.

12 (a) A. Schmidpeter and F. Zwaschka, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 704–705; (b) A. Schmidpeter, W. Gebler, F. Zwaschka and W. S. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 722–723; (c) P. Panne, *Ph.D. Thesis*, University of Köln, 2004; (d) J. F. Binder, S. C. Kosnik, P. B. J. St Onge and C. L. B. Macdonald, *Chem. – Eur. J.*, 2018, **24**, 14644–14648.

13 A. Schmidpeter and G. Burget, *Z. Naturforsch., B: Chem. Sci.*, 1985, **40**, 1306–1313.

14 G. Le Corre, J. J. Gamboa-Carballo, Z. Li and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2021, **60**(47), 24817–24822.

15 (a) M. C. J. M. Van Hooijdonk, G. Gerritsen and L. Brandsma, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2000, **162**, 39–49; (b) D. Stein, T. Ott and H. Grützmacher, *Z. Anorg. Allg. Chem.*, 2009, **635**, 682–686.

16 E. Hey, P. B. Hitchcock, M. F. Lappert and A. K. Rai, *J. Organomet. Chem.*, 1987, **325**, 1–12.

17 W. S. Sheldrick, J. Kroner, F. Zwaschka and A. Schmidpeter, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 934–935.

18 G. P. Weinberger, F. Sommer, A. Torvisco, R. C. Fischer and M. Flock, *Eur. J. Inorg. Chem.*, 2020, **2020**, 3778–3785.

19 J. H. Letcher and J. R. V. Wazer, *J. Chem. Phys.*, 1966, **44**, 815–829.

20 G. Becker, H. M. Hartmann and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1989, **577**, 9–22.

21 A. Mack, E. Pierron, T. Allspach, U. Bergsträßer and M. Regitz, *Synthesis*, 1998, 1305–1313.

22 (a) A. Grünhagen, U. Pieper, T. Kottke and H. W. Roesky, *Z. Anorg. Allg. Chem.*, 1994, **620**, 716–722; (b) F. Brodkorb, M. Brym, C. Jones and C. Schulten, *J. Organomet. Chem.*, 2006, **691**, 1025–1029.

23 P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 12770–12779.

24 (a) W. Rösch, U. Hees and M. Regitz, *Chem. Ber.*, 1987, **120**, 1645–1652; (b) W.-G. Veeck and M. Regitz, in *Comprehensive Organic Functional Group Transformations*, ed. A. R. Katritzky, O. Meth-Cohn and C. W. Rees, Elsevier Science, Oxford, 1995, pp. 1151–1160.

25 B. Breit and M. Regitz, *Chem. Ber.*, 1996, **129**, 489–494.

26 A. Schmidpeter, G. Burget, F. Zwaschka and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 1985, **527**, 17–32.

27 (a) B. Khalili Najafabadi and J. F. Corrigan, *J. Chem. Soc., Dalton Trans.*, 2015, 14235–14241; (b) B. Khalili Najafabadi and J. F. Corrigan, *Can. J. Chem.*, 2016, **94**, 593–598; (c) B. Khalili Najafabadi and J. F. Corrigan, *J. Chem. Soc., Chem. Commun.*, 2015, **51**, 665–667.

28 D. Marchione, M. A. Izquierdo, G. Bistoni, R. W. A. Havenith, A. Macchioni, D. Zuccaccia, F. Tarantelli and L. Belpassi, *Chem. – Eur. J.*, 2017, **23**, 2722–2728.

29 S. S. Batsanov, *Inorg. Mater.*, 2001, **37**, 871–885.

30 (a) F. A. Watt, L. Burkhardt, R. Schoch, S. Mitzinger, M. Bauer, F. Weigend, J. M. Goicoechea, F. Tambornino and S. Hohloch, *Angew. Chem., Int. Ed.*, 2021, **60**, 9534–9539; (b) L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, R. Suter, A. M. Tondreau and H. Grützmacher, *Chem. Sci.*, 2016, **7**, 2335–2341; (c) M. M. D. Roy, M. J. Ferguson, R. McDonald and E. Rivard, *J. Chem. Soc., Chem. Commun.*, 2018, **54**, 483–486; (d) A. Reinholdt, M. G. Jafari, C. Sandoval-Pauker, E. Ballestero-Martínez, M. R. Gau, M. Driess, B. Pinter and D. J. Mindiola, *Angew. Chem., Int. Ed.*, 2021, **60**, 17595–17600.