A dicationic bis(NHC)-stabilised silyldiium complex, [bis(NHC)-SiPh₂]²⁺ (7²⁺) (bis(NHC) = [CH₂(NC₃H₂NDipp)₂], Dipp = 2,6-iPr₂C₆H₃), was synthesised for the first time. It reacts with sodium phosphaethynolate (NaOCP) as a source of monoanionic phosphorus to give the P-insertion product [bis(NHC)-PSiPh₂]⁺ (8⁺). The latter comprises a seven-membered heterocycle containing a Si–P moiety which can easily be desilylated when exposed to dichlorophosphanes as exemplified by the synthesis of the diphosphanide cations [bis(NHC)-PPCy]⁺ (9⁺) and [bis(NHC)-PPPh]⁺ (10⁺).

Since the first synthesis of a stable imidazol-2-ylidene in 1991,¹ N-heterocyclic carbenes (NHCs) have been employed for the stabilisation of various main group elements in unusual electronic states,² among them silicon and phosphorus.³ Commonly, the ligand is introduced in its deprotonated form, as “free” NHC, often followed by reduction reactions. However, in some cases, the use of a “free” NHC leads to side reactions, like for example the reduction of P³⁺ centres to P¹⁺, and is therefore not applicable.⁴,⁵ Other strategies have been developed to overcome this limit, such as aduct formation with silyl moieties and subsequent desilylation of the NHC. This approach has been used, inter alia, by Weigand et al. to access imidazoliym substituted phosphines by reacting the NHC-silyl adducts 1[OTf] and 2[OTf] with PCl₃ liberating Me₃SiCl (Fig. 1).⁵,⁶ The same group has also described the imidazoliym-functionalised diphosphorus cations 3⁺ and 6⁺, which are depicted in Fig. 1.⁷,⁸ A related synthetic approach to obtain carbone–phoshinidene transition metal complexes was used by Tamm and co-workers who introduced the IPr–PSiMe₃ adduct (IPr = 1,3-bis-(Dipp)imidazol-2-ylidene, Dipp = 2,6-iPr₂C₆H₃) as a silylated ligand precursor.⁹

In this case, the silicon moiety is also introduced as a leaving group and removed in the course of the synthetic route. Accordingly, the solvolysis of IPr–PSiMe₃ afforded IPr–PH, which had been prepared originally by transferring parent phosphinidene (:PH) from a silylene to IPr.¹⁰ The same species can also be obtained by reacting sodium phosphaethynolate (NaOCP) with the imidazolium salt [IPr–H][Cl].¹¹ Compared to other synthetic routes, the use of NaOCP as monoanionic phosphorus transfer reagent is advantageous by means of atom economy as only one equivalent of CO and the corresponding Na salt are generated in a salt metathesis reaction. By taking advantage of this approach some novel species were synthesised, among them the NHC–phosphinidene adducts IPr–PEPh₃ (E = Ge, Sn).¹²

Herein we report the synthesis of the novel bis(NHC)-silyldiium salt 7[OTf₂] (bis(NHC) = [CH₂(NC₃H₂NDipp)₂]) and its reactivity towards NaOCP which affords the cyclic bis(NHC)-PSiPh₂...
adduct $[\text{OTf}]$. The latter can be employed as a precursor for unprecedented seven-membered heterocycles by subsequent desilylation with dichlorophosphanes. This is illustrated by the reaction of $[\text{OTf}]$ with $\text{RPCl}_2$ ($R = \text{Cy}, \text{Ph}$), which gives rise to the phosphinidene–phosphanide cations $9^+$ and $10^+$.

The reaction of $\text{Ph}_2\text{Si}[\text{OTf}]_2$ with an equimolar amount of bis(NHC) in diethyl ether afforded the desired salt of the imidazolium moieties (Scheme 1), whose synthesis we have described previously from bis(NHC) and $\text{PhPCl}_2$. This desilylation complies with reported reactions of NHC-silyl adducts with halogenated phosphanes that have been used in the literature to access different carbene-stabilised phosphorus compounds, and, in this regard, the “SiPh$_2$” moiety in $[\text{OTf}]^+$ only serves as a leaving group.

Nevertheless expecting the silicon centre to be electrophilic and thus, to allow for unprecedented synthetic pathways, we probed the reactivity of the system towards the nucleophilic phosphaethynolate anion. While literature compound IPr–PSiMe$_3$ was synthesized using a different approach, IPr–PEPh$_3$ (E = Ge, Sn), IPr–PH$_2$ and an amino(phosphanylidene phosphorene)-stabilised germylene were obtained by using NaOCP as $P^-$ transfer reagent after CO loss at elevated temperatures. Interestingly, when mixing $7[\text{OTf}]_2$ with $\text{Na}(\text{dioxane})_2[\text{PCO}]$ (molar ratio 1:1) in $\text{CH}_2\text{Cl}_2$ at ambient temperature an immediate colour-change from ochre to red occurred, together with gas evolution (CO). Full conversion to $8[\text{OTf}]$ (Scheme 1) was evidenced by the rise of one singlet resonance ($\delta = -161.0$ ppm in the $^{31}\text{P}[\text{H}]$ NMR spectrum which is in the same range as for related carbene-stabilised phosphinidene adducts. Both $[\text{H}]$ and $^{13}\text{C}$ NMR spectra reflect the presence of two chemically inequivalent imidazolium moieties and confirm that decarbonylation has occurred in the course of the reaction. Compared to the starting material $7[\text{OTf}]_2$, the $^{29}\text{Si}$ NMR spectrum of $8[\text{OTf}]$ shows a low-field shifted doublet resonance at $\delta = -161.0$ ppm ($J_{\text{SiP}} = 85$ Hz). Unlike the above-mentioned literature reactions, the formation of $8[\text{OTf}]$ (including CO elimination) proceeds rapidly at ambient temperature and the product could be isolated in good yields (85%). No further reaction with excess NaOCP was observed, even upon addition of up to one more molar equivalent of NaOCP.

Finally, the connectivity of $8^+$ was confirmed by a single crystal X-ray structure determination and evidences this rare example of a seven-membered ring that contains a Si–P moiety (Fig. 3). The $\text{CH}_2\text{CN}$–P bond length (1.770(2) Å) compares well to those in similar NHC-phosphinidene adducts, whereas the P–$\text{Si}$ distance ($d(\text{P–Si}) = 2.1987(7)$ Å) in $8^+$ is slightly contracted compared to IPr–PSiMe$_3$. This could be explained by the cationic charge in $8^+$ which makes the Si centre more electrophilic or due to ring strain. In fact, the arrangement of the atoms in a seven-membered ring leads to a distortion of the ligand backbone with respect to $7^+$, as visualized by comparison of the tilt angle $\alpha$ between the two planes defined by the imidazoliumyl rings (compare Fig. 2 and 3). While $\alpha$ amounts to 31.4° for $7^+$, $\alpha$ adds up to 55.3° for $8^+$. Furthermore, the P-insertion leads to different bonding situations in the N–C–N moieties of the two imidazoliumyl-rings. The C–N bond lengths in the Si-bonded ring (average $d(\text{C–N}) = 1.35$ Å) are well comparable to those in $7^+$, whereas the C–N distances in the P-bonded ring are somewhat elongated (average $d(\text{C–N}) = 1.37$ Å). This possibly reflects contributions of the canonical structures $8b^+$ and $8c^+$ to the ground state (Fig. 4).
of $C_{\text{NHC-p}}$ ($\delta = 170.8$ ppm, $J_{CP} = 102.1$ Hz) and $C_{\text{NHC-Si}}$ ($\delta = 151.8$ ppm) also mirror these differences.

In order to investigate whether the reaction of 7$^{+}$ with NaOCP is a particular case, we synthesised the related non-cyclic NHC-silyl cation [IPr–SiPh$_3$]$_{1}^{+}$ from an equimolar mixture of Ph$_3$SiOTf and IPr in diethyl ether. The product precipitated from the reaction mixture in form of colourless microcrystals and was characterised by heteronuclear NMR spectroscopy and high-resolution mass spectrometry indicating that the Si atom is tetracoordinate in solution. Subsequently, mixing equimolar amounts of Ph$_3$SiOTf and IPr in THF led to formation of the rearrangement product [IPrSiPh$_3$]OTf and NaOCP in THF to form the cation [IPr–SiPh$_3$]$_{1}^{+}$ from an equimolar mixture of Ph$_3$SiOTf and IPr, as well. The observed 1$^{31P}$ chemical shift ($\delta = 398$ to 452 ppm) compared to $9^+$ what indicates that the double-bond character is not very pronounced.8,19,23 In the $1^{13C}$ NMR spectrum of $9[OTf]$ two doublet of doublet resonances with $\delta = 169.2$ ppm ($J_{CP} = 145.2$ Hz, $2J_{CP} = 10.6$ Hz) and 151.5 ppm ($J_{CP} = 76.2$ Hz, $2J_{CP} = 7.4$ Hz) assignable to the N$_x$C-carbon atoms evidence the presence of two chemically inequivalent imidazolium moieties. Furthermore, a doublet resonance at $\delta = 45.1$ ppm with a considerably smaller coupling constant ($J_{CP} = 22.5$ Hz) is observed for the cyclohexyl-carbon that is attached to one phosphorus atom.

An X-ray structure analysis confirmed the replacement of the SiPh$_2$ fragment by the respective PR moieties in the molecular structures of $9^+$ and $10^+$ (Fig. 5 and Fig. S23, ESI†). As observed for cation $8^+$, the arrangement in a seven-membered ring leads to distortion of the bis(NHC) backbone. The tilt angles $\alpha$ between the two planes defined by the imidazolium ring amounts to 57.1° for $9^+$ and 70.4° for $10^+$ and are hence even larger than $\alpha$ in the structure of $8^+$ (compare Fig. 3, 5 and Fig. S23, ESI†). The P–P distances of 2.1527(10) Å ($9^+$) and 2.1561(18) Å ($10^+$) are very close to the one reported for the related cation $6^+$ ($d(P–P) = 2.151(1)$ Å), but somewhat elongated in comparison to $4^+$ ($d(P–P) = 2.1067(10)$ Å) and $5^+$ ($d(P–P) = 2.096(2)$ Å) what may be due to the presence of phosphorus-bonded halogen atoms in the structures of $4^+$ and $5^+$. Furthermore, because of the chelating nature of the bis(NHC) ligand the torsion angles $\Phi$ defined by $C_{\text{NHC-P2}}$–$P_1$–$C_{\text{NHC-P1}}$
approach to synthesise novel cyclic compounds that assemble phosphanes represents a viable procedure for a modular to give the diphosphanide cations.

Compared to the P–P distances in cationic membered heterocyclic P–X compounds was demonstrated and 2.038(1) Å and 2.083(2) Å,8,19,23 the P–P bond lengths in towards sodium phosphaethynolate than observed for the related particular properties of this system induce a different reactivity corresponding (for clarity); selected experimental bond lengths (Å) and angles (°); P1–P2 2.1527(10), P1–P17 1.791(2), P2–C1 1.831(2), C17–P1–P2 105.42(9), C1–P1–P2 99.33(8).

In summary, we have presented the synthesis of the first bis[NHC]-stabilised silyldiium salt [P(OTf)2, and shown that the particular properties of this system induce a different reactivity towards sodium phosphineoxy than observed for the related NHC-silyl adduct [IPr-SiPMe2]2(OTf). The selective P-insertion reaction into one of the NHC–Si bonds in 7 afforded cation 8+, which was subsequently desilylated with RPCl3 (R = Cy, Ph) to give the diphenosilane cations 9+ and 10+. In this way, the utility of 8[OTf]2 as a precursor for unprecedented seven-membered heterocyclic P–X compounds was demonstrated and is subject of further research in our laboratories. This work was supported by the Einstein Foundation Berlin.

Conflicts of interest
There are no conflicts to declare.

Notes and references
† A comprehensive discussion on the bonding features of NHC-element adducts can be found in the literature.24

1 A. J. Arduengo, R. L. Harlow and M. Kline, J. Am. Chem. Soc., 1991, 113, 361–363.
2 (a) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, Chem. Rev., 2018, 118, 9678–9842; (b) G. Frenking and N. Holzmann, Science, 2012, 336, 1394–1395; (c) D. P. Curran, A. Solovyev, M. Maklouf Brahmi, L. Fensterbank, M. Malacria and E. Lacôte, Angew. Chem. Int. Ed., 2011, 50, 10294–10317; (d) H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radaelli and A. Vargs, Science, 2012, 336, 1420–1422; (e) Y. Xiong, S. Yao, G. Tan, S. Inoue and M. Diess, J. Am. Chem. Soc., 2013, 135, 5004–5007; (f) M. Y. Abraham, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer, P. V. R. Schleyer and G. H. Robinson, Chem. – Eur. J., 2010, 16, 432–435; (g) C. Jones, A. Sidiropoulos, N. Holzmann, G. Frenking and A. Stasch, Chem. Commun., 2012, 48, 9855–9857.
3 (a) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, J. Am. Chem. Soc., 2007, 129, 14180–14181; (b) Y. Wang, Y. Xie, M. Y. Abraham, R. J. Gilliard, P. Wei, H. F. Schaefer, P. V. R. Schleyer and G. H. Robinson, Organometallics, 2010, 29, 4778–4780; (c) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. V. R. Schleyer and G. H. Robinson, J. Am. Chem. Soc., 2008, 130, 14970–14971; (d) J. Arduengo Anthony III, H. V. R. Dias and J. C. Calabrese, Chem. Lett., 1997, 143–144; (e) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn and D. Stalke, Angew. Chem., Int. Ed., 2009, 48, 5683–5686; (f) Y. Xiong, S. Yao, S. Inoue, J. D. Epping and M. Diess, Angew. Chem., Int. Ed., 2013, 52, 7147–7150; (g) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, P. V. R. Schleyer and G. H. Robinson, Science, 2008, 321, 1069–1072.
4 B. D. Ellis, C. A. Dyker, A. Deeken and C. L. B. Macdonald, Chem. Commun., 2005, 1965.
5 S. J. Weigand, K. O. Feldmann and F. D. Hennen, J. Am. Chem. Soc., 2010, 132, 16321–16323.
6 F. D. Hennen, A. T. Dickschat, F. Hennersdorf, K.-O. Feldmann and J. J. Weigand, Inorg. Chem., 2015, 54, 6849–6861.
7 F. D. Hennen, E. M. Schnöckelborg, K. O. Feldmann, J. Grunenberg, R. Wolf and J. J. Weigand, Organometallics, 2013, 32, 6674–6680.
8 K. Schwedtman, M. H. Holthausen, C. H. Sala, F. Hennersdorf, R. Prohlich and J. J. Weigand, Chem. Commun., 2016, 52, 1409–1412.
9 A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones and M. Tamm, Angew. Chem., Int. Ed., 2014, 53, 13568–13572.
10 K. Hansen, T. Szilvási, B. Blom, E. Iiran and M. Diess, Chem. – Eur. J., 2014, 20, 1947–1956.
11 A. M. Tondreau, Z. Benko, J. R. Harmer and H. Grützmacher, Chem. Sci., 2014, 5, 1545–1554.
12 Z. Li, X. Chen, Y. Li, C. M. Su and H. Grützmacher, Chem. Commun., 2016, 52, 11343–11346.
13 T. Yakeuchi and T. Takayama, The Chemistry of Organic Silicon Compounds, John Wiley & Sons, Ltd., 1998, pp. 267–354.
14 A. J. Arduengo III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, Tetrahedron, 1999, 55, 14523–14534.
15 M. J. Woolford, T. C. Johnston, J. Lam, B. Bagh, A. Hermannsdorfer, M. Diess and D. W. Stephan, Dalton Trans., 2017, 46, 14149–14157.
16 N. Del Rio, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, D. Lutters, T. Müller and T. Kato, Angew. Chem., Int. Ed., 2016, 55, 4753–4758.
17 M. Balmer and C. von Hänisch, Z. Anorg. Allg. Chem., 2018, 29, 4778.
18 M. F. Silva Valverde, D. Stalke, E. Theuergarten, T. Bannenberg, M. Freytag, P. G. Jones and M. Tamm, Dalton Trans., 2015, 44, 9409–9408.
19 A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones and M. Tamm, Dalton Trans., 2017, 46, 15859–15864.
20 J. B. Waters, T. A. Everitt, W. K. Myers and J. M. Goicoechea, Chem. Sci., 2016, 7, 6981–6987.
21 (a) A. Beil, R. J. Gilliard and H. Grützmacher, Dalton Trans., 2016, 45, 2044–2052; (b) Y. Wang, H. P. Hickox, Y. Xie, P. Wei, D. Cui, M. R. Walter, H. F. Schaefer and G. H. Robinson, Chem. Commun., 2016, 52, 5746–5748.
22 (a) S. Bureck, K. Götz, M. Kaupp, M. Niegner, J. Weber, J. Schmedt auf der Günne and D. Gudat, J. Am. Chem. Soc., 2009, 131, 10763–10774; (b) S. Duangthai and G. A. Webb, Org. Magn. Reson., 1983, 21, 199–202; (c) A. H. Cowley and W. D. White, J. Am. Chem. Soc., 1969, 91, 1917–1921.
23 O. Back, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, Nat. Chem., 2010, 2, 369–373.
24 (a) G. Frenking, Angew. Chem., Int. Ed., 2014, 53, 6040–6046; (b) D. Himmel, I. Krossing and A. Schnepf, Angew. Chem., Int. Ed., 2014, 53, 370–374; (c) D. Himmel, I. Krossing and A. Schnepf, Angew. Chem., Int. Ed., 2014, 53, 6047–6048.