ARTICLE

Phosphinoborenium cations stabilized by *N*-heterocyclic carbenes: synthesis, structure, and reactivity

Kinga Kaniewska-Laskowska,[a]* Anna Ordyszewska,[a] Tomasz Wojnowski,[a] Hanna Halenka,[a] Marcin Czapla,[b] Jarosław Chojnacki,[a] and Rafał Grubba[a]*

Phosphinoborenium cations stabilized by *N*-heterocyclic carbenes (NHCs) were synthesized via the reaction of bromo(phosphino)boranes with NHCs. Their structures were investigated by heteronuclear magnetic resonance spectroscopy, X-ray diffraction, and density functional theory calculations. They possess a planar trigonal boron center directly bonded with the pyramidal phosphanyl group (PR_2) and can be treated as cationic phosphinoboranes. The reactivity of the selected NHC-phosphinoborenium cation was tested toward $AuCl \cdot SMe_2$ and Ph_2PCl. In both reactions, the titled compound acted as a phosphido group donor under heterolytic cleavage of the P–B bond. Control experiments with parent phosphinoborane emphasized differences between the reactivity of low-coordinate neutral and cationic species with P–B functionality.

Introduction

The rich and fascinating chemistry of boron cations provides many tools for chemical synthesis and catalysis. Within the realms of cationic boron species, borenium cations, $[R_2BL]^+$, have received the most attention.[1,2] Similarly to neutral triorganoboranes, R_3B, they possess trigonal planar geometry and a formally vacant *p*-orbital at the boron atom. However, in the case of borenium ions, one of the R groups is substituted by a neutral Lewis base (L), making them positively charged. Because of this internal electron deficiency, borenium ions are stronger Lewis acids and are more reactive than their neutral tricoordinate counterparts. As *N*-heterocyclic carbenes (NHCs) are widely used for the stabilization of low-valent main group compounds, it is not surprising that these ligands are used in the syntheses of borenium ions.[3] The application of NHCs enables better control of the electrophilic and steric properties of these reactive borocations, meaning that NHC-stabilized borenium cations have found applications in numerous stochiometric and catalytic transformations.[4,5,6] The first carbene stabilized borenium salt was obtained by Matsumoto and Gabbaï in the reaction of Mes_2BF with Me_3SiOTf and $[Ag(IMe)_2][Ag_2I_3]$ (IMe=1,3-dimethylimidazol-2-ylidene).[7] Regarding other aryl substituted borenium ions, polycyclic mono- and dicationic species were accessed starting from NHC–BH_3 adducts through sequential hydride abstraction and dehydrogenative ring closing C–H borylation.[8,9] An important group of NHC-borenium ions are those containing the 9-borabicyclo[3.3.1]nonane (9-BBN) moiety. These are usually obtained by hydride abstraction from an NHC adduct of 9-BBN, and have been utilized not only as dihydrogen activators but also as catalysts in the hydrogenation of imines, enamines, and unsaturated *N*-heterocycles in very mild conditions, and the selective catalytic *trans*-hydroboration of alkynes.[10,11,12,13] Borenium ions containing BH_2 fragments are also stabilized by NHCs; for example, the reaction of NHC–BH_3 adduct with $[Ph_3C]^+[B(C_6F_5)]^-$ gave access to highly reactive dicationic dimers $[NHC–BH_2]_2^{2+}$.[14] It is worth mentioning that transient NHC-borenium cations with a BH_2 moiety catalyze the hydroboration of alkenes with NHC-boranes.[15] Moreover, when the NHC–BH_3 adduct reacts with $AlCl_3$, dichloroborenium ions $[NHC–BCl_2]^+$ are formed.[14] Such species can also be easily obtained by chloride anion abstraction from the BCl_3 adduct of NHCs.[16] Furthermore, the BH_3 adduct of NHC acts as a precursor of the dihydroxoborenium ion $[NHC–B(OH)_2]^+$ in reaction with triflic acid.[17] Regarding other NHC-borenium ions bearing oxygen-donor ligands, those with the pinacol (Pin) moiety are worth mentioning. The combination of PinBH with bulky NHC (1,3-bis(tert-butyl)imidazol-2-ylidene) and GaR_3 (R= CH_2SiMe_3) gives an ion pair $[NHC–BPin]^+[GaR_3(\mu-H)-GaR_3]^-$, which exhibits catalytic activity in the hydroboration of aldehydes with PinBH.[18] Another interesting example of an NHC-borenium ion possessing the PinB fragment is the borylborenium cation $[NHC–B(BPin)Mes]^+$, which smoothly activates dihydrogen at −40°C, forming dihydroboronium cation $[NHC–BH_2(BPinMes)]^+$.[19] Furthermore, reactions of amino- and diamino-substituted halogenoboranes with NHCs give access to aminochloroborenium or diaminoborenium cations, respectively.[20,21] All NHC-borenium ions described above were stabilized by the most commonly used five-membered NHCs.

a. *Department of Inorganic Chemistry, Faculty of Chemistry and Advanced Materials Center, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland. E-mail: rafal.grubba@pg.edu.pl; kinga.kaniewska-laskowska@pg.edu.pl*
b. *Laboratory of Quantum Chemistry, Department of Theoretical Chemistry, Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland.*

However, it must be emphasized that six-membered saturated NHCs have also been utilized as σ-donor ligands for cationic boron fragments such as BBr_2^+, $B(OH)_2^+$, $PhBCl^+$ or $PhB(OH)^+$.[22,23,24]

Herein, we present synthesis and reactivity studies of the NHC-phosphinoborenium cation (Chart 1), containing a directly bonded tricoordinate boron center and tricoordinate phosphorus atom which retains a lone electron pair. These structural features promote both Lewis acidic and Lewis basic properties, which is unusual for borocations. In the case of known borenium cations having a B–P bond, PR_3 phosphine ligands have been utilized as neutral donors,[25,26,27,28] while there are no reports of borenium ions bearing the PR_2 phosphanyl moiety installed on the boron atom. Our group have explored the reactivity of low-coordinate main group compounds possessing B–P functionality; in particular phosphinoboranes $R_2BPR'_2$, diphosphinoboranes $RB(PR'_2)_2$, and triphosphinoboranes $P(PR'_2)_3$.[29–33] Recently we have turned our attention to cationic systems with B–P bonds, and have described the reactivity of *in-situ* generated phosphinoborinium cations which have strong tendency to dimerization, and exhibit high reactivity toward ketones, isocyanates, nitriles, and carbodiimides to form cycloaddition products.[34,35] As a next step in the exploration of ambiphilic cationic systems, we decided to synthesize phosphinoborenium cations stabilized by NHCs. These species can be treated as cationic phosphinoboranes, where one R substituent is replaced by an NHC ligand (Chart 1). Therefore, we additionally compare the reactivity of neutral phosphinoboranes with their cationic counterparts.
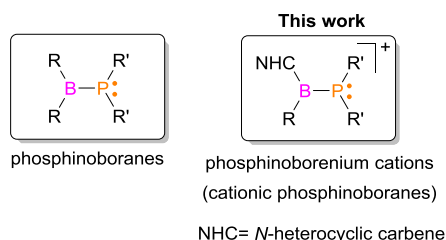

Chart 1. Structures of phosphinoboranes and phosphinoborenium cations.

Results and discussion

As substrates for the synthesis of NHC-phosphinoborenium cations, we selected bromo(phosphino)boranes **1–3** (Scheme 1). **1** and **3** were previously utilized by us in the synthesis of transient phosphinoborinium cations in reaction with the lithium salt of weakly coordinating anions.[34,35] Synthetic details, nuclear magnetic resonance spectroscopy (NMR), and X-structural data of **2** are placed in the Electronic Supplementary Information (ESI). We observed that bromide anion abstraction from R_2N–(Br)B–PR_2' led to the formation of unstable borocations $[R_2N$–B–$PR_2']^+$ with a di-coordinate boron center. Therefore, we decided to stabilize these cationic fragments with strong σ-donor ligands, such as NHC. The addition of a toluene or petroleum ether solution of NHC (**a** = 1,3-

diisopropylimidazol-2-ylidene; **b** = 1,3-dimethylimidazol-2-ylidene) to the petroleum ether solution of bromo(phosphino)borane (**1–3**) led to the precipitation of an NHC-borenium salt (**1a–3a**, **1b–3b**) (Scheme 1). The obtained products were isolated by filtration and evaporation of remaining volatiles as orange (NHC = **a**) or yellow (NHC = **b**) powders.
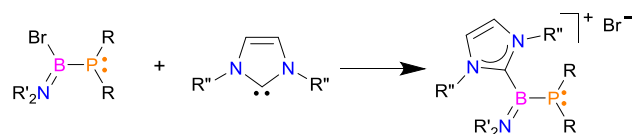
1 (PR_2= PtBu$_2$, R'= iPr) **a** (R"= iPr) **1a** (PR_2= PtBu$_2$, R'= iPr, R"= iPr)
2 (PR_2= PtBu$_2$, R'= Ph) **b** R"= Me) **1b** (PR_2= PtBu$_2$, R'= iPr, R"= Me)
3 (PR_2= tBuPhP, R'= Cy) **2a** (PR_2= PtBu$_2$, R'= Ph, R"= iPr)
2b (PR_2= PtBu$_2$, R'= Ph, R"= Me)
3a (PR_2= tBuPhP, R'= Cy, R"= iPr)
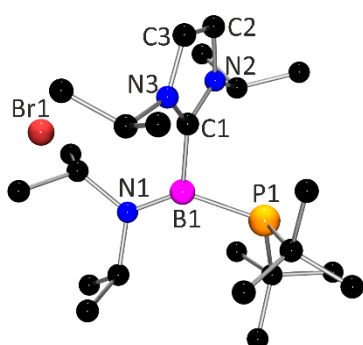**3b** (PR_2= tBuPhP, R'= Cy, R"= Me)

Scheme 1. Syntheses of phosphinoborenium cations.

Optimization of reaction conditions showed that an excess of NHC significantly increased yields of reactions. The optimum molar ratio of NHC:bromo(phosphinoborane) was found to be 2:1, which gave borenium salt yields from 67% to 90%. It is worth mentioning that the bromide anion can be easily exchanged for another counterion. The reaction of borenium salts with Li[WCA] ([WCA]⁻ = [Al(OC(CF$_3$)$_3$)$_4$]⁻) led to the precipitation of LiBr and replacement of Br⁻ with [WCA]⁻ (see ESI for details).

The ^{11}B NMR spectra of NHC-borenium cations display broad singlets in a narrow range from 39.2 ppm to 41.2, which is very similar to those observed for parent **1–3** (Table 1). ^{11}B NMR spectroscopic signatures indicate that the environment of the B atoms is tricoordinate. Compared with **1–3**, ^{31}P NMR chemical shifts of NHC-borenium cations are significantly downfield sifted, which can be explained by the inductive effect of the NHC ligand. What is more, the broadening of both ^{11}B and ^{31}P NMR signals confirms the presence of a B–P covalent bond. Inspection of ^{1}H and ^{31}C{^{1}H} NMR spectra of isolated **1a–3a** and **1b–3b** revealed signals attributable to the NHC ligand. Due to the direct connection of carbene carbon atoms with the boron center, the signals of these atoms were not detected in ^{13}C{^{1}H} NMR spectra. However, the ^{13}C NMR chemical shifts of these atoms have been determined based on ^{1}H–^{13}C HMBC spectral analysis, and they display values from 147.6 ppm to 151.8 ppm. Single crystals of representative the NHC-phosphinoborenium salt **1a** suitable for X-ray diffraction were obtained from CH$_2$Cl$_2$ solution layered with pentane at room temperature. The solid-state structure of **1a** is presented in Figure 1.

**Table 1.** ^{11}B and $^{31}P\{^1H\}$ NMR data of phosphinoborenium cations and their precursors.

No.	δ ^{11}B (ppm)	δ $^{31}P\{^1H\}$ (ppm)
1	38.6	−11.2
2	43.6	−14.7
3	39.0	−20.3
1a	40.2	24.2
1b	40.9	5.1
2a	40.7	47.1
2b	41.2	35.1
3a	41.0	−3.7
3b	39.8	−4.4

Figure 1. X-ray structure of **1a**. H-atoms and CH_2Cl_2 solvent molecule are omitted for clarity.

The single crystal X-ray diffraction analysis of **1a** salt confirmed bromide anion displacement and coordination of NHC ligand to the boron center. Additionally, the central B atom is bonded to amino and phosphanyl groups. As expected for a borenium ion, the geometry around the B atom is planar trigonal with a sum of angles equal to 359.21°. The electronic stabilization of the borenium cation by π-donation from the amino group manifests in a short B1–N1 distance (1.390(4) Å) and planar geometry of the iPr_2N1 unit (ΣN1 = 359.99°). Otherwise, the B1–P1 bond is relatively long (1.991(3) Å), and the phosphanyl group displays pyramidal geometry (ΣP1 = 331.95°). This observation suggests the presence of a lone pair of electrons on the phosphorus atom. The C1–B1 bond length of 1.604(4) Å has a similar value to those observed for NHC-stabilized aminoborenium cations (1.599(3) Å, 1.580(11) Å).[21] The dihedral angle between the plane of the NHC ligand and the plane on which the B1, C1, P1, and N1 atoms lie is 63.82°. The distance between the B1 atom and the bromide anion has a value of 8.961(3) Å, which excludes the presence of any significant bonding interactions.

To describe the electronic structure of NHC-phosphinoborenium cations, we performed density functional theory (DFT) calculations together with natural bond orbital (NBO) analysis. The calculations were done for the representative ion **1a⁺**. The frontier orbitals of **1a⁺** are presented in Figure 2. The lowest unoccupied molecular orbital (LUMO) is mainly localized on the B1 atom with some contribution from the NHC ligand and $NiPr_2$ group, whereas the

highest occupied molecular orbital (HOMO) is associated with a lone electron pair at the P1 atom. The natural population analysis (NPA) revealed the largest positive charge on the B1 atom (+0.70), which is in accord with the borenium character of **1a⁺**. The smaller positive charges are found on P1 (+0.51) and C1 (+0.16) atoms, whereas N1 of the amino group has the largest negative charge (−0.81). Thus, NPA analysis indicates that the bonds surrounding the central boron atom are polarized toward phosphorus, carbon, or nitrogen, respectively. Moreover, NBO analysis confirmed the presence of a double N1=B1 bond and single C1–B1 and P1–B1 bonds. Interestingly, according to second order perturbation analysis, additional donor-acceptor interactions between the lone electron pair of the P1 atom and antibonding σ*(N2–B1) and π*(N2–B1) orbitals were calculated to be 10.67 kcal/mol and 14.08 kcal/mol, respectively.
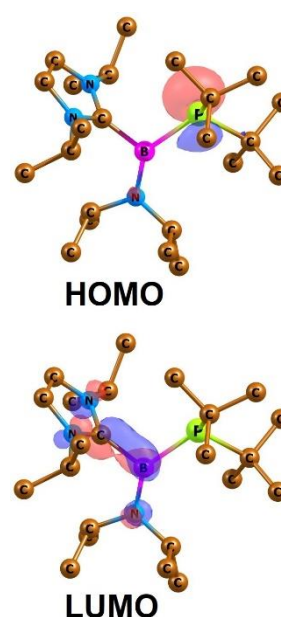
Figure 2. Optimized structure and frontier molecular orbitals of **1a⁺**.

For comparison, we performed analogous calculations for the parent phosphinoborane **1**. In contrast to **1a⁺**, NPA charges on phosphorus (+0.49) and boron (+0.53) atoms are comparable; thus the P–B bond is only very weakly polarized in the case of phosphinoborane **1**. Furthermore, regarding the electronic structure of **1**, there are no significant interactions between the phosphorus lone electron pair and the boron center. Instead, the lone electron pair of the Br atom interacts with the π*(N–B) orbital, where the value of respective delocalization energy is 27.25 kcal/mol.

The NHC-phosphinoborenium salts are thermally stable, and can be stored at room temperature under an argon atmosphere for months without any sign of decomposition. However, they are extremely moisture and oxygen sensitive. Within all isolated NHC-phosphinoborenium salts, the most stable product is **1a**, which bears bulky *t*Bu substituents at the phosphorus atom and the most voluminous NHC ligand. Therefore, we selected salt **1a** for further reactivity studies. The presence of the lone electron pair on the P-atom of NHC-phosphinoborenium cation **1a**

encouraged us to test its Lewis basic properties in the reaction with AuCl·SMe$_2$. For comparison, analogous reactions were performed for the parent phosphinoborane **1**. The addition of a dichloromethane solution of **1** to a suspension of AuCl·SMe$_2$ in dichloromethane yielded a neutral gold complex **1c** (Scheme 2). The ^{11}B NMR spectrum of **1c** displays a broad doublet at 34.1 ppm with $^1J_{PB}$ = 126.5 Hz. This signal is only slightly upfield shifted compared with parent **1**. Otherwise, ^{31}P{^{1}H} NMR resonance of **1c** at 32.3 ppm is strongly downfield shifted compared with **1**, suggesting coordination of a phosphorus atom to the metal center. X-ray diffraction analysis of crystalline **1c** confirmed this assumption (Figure 3). **1** coordinates to the gold cation via the P1 atom, with displacement of a SMe$_2$ molecule, where the Au1–P1 bond length is 2.264(2) Å.
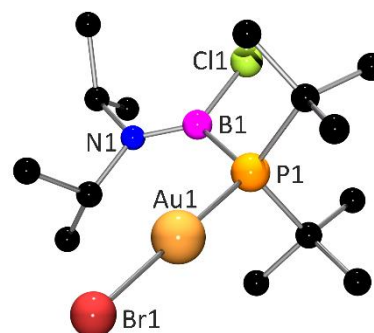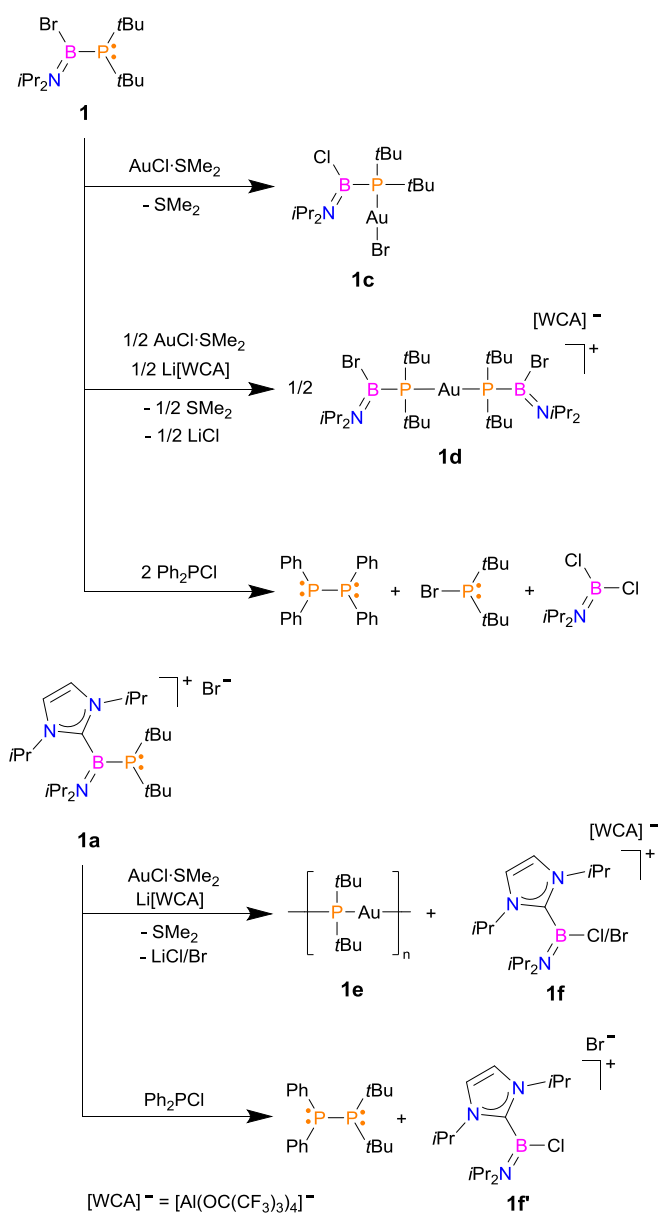

Figure 3. X-ray structure of **1c**. H-atoms are omitted for clarity.

Interestingly, there was an exchange of halide ligands between boron and gold atoms resulting in the formation of new B–Cl and Au–Br bonds. The geometry around the gold cation is nearly linear with a bond angle P1–Au1–Br1 of 178.77(7)°. The planar geometry of the B1 atom (ΣB1 = 360.17°) and relatively long B1-Au1 distance of 3.58(1) Å exclude any Z-type interactions. The P1–B1 bond distance of 1.978(11) Å is comparable to the one observed for a free ligand (1.958(2) Å).[33]

The reaction of **1** with AuCl·SMe$_2$ in the presence of Krossing's salt gave cationic complex **1d**, where the central gold cation is coordinated by two phosphinoborane molecules. The ^{11}B and ^{31}P{^{1}H} spectra of isolated crystalline **1d** show broad singlets at 32.9 ppm and 38.2, respectively. In contrast to **1c**, splitting of ^{11}B resonance is not observed. The presence of an [Al(OC(CF$_3$)$_3$)$_4$]$^-$ counterion was confirmed by employing ^{27}Al and ^{19}F NMR spectroscopy. The solid-state structure of **1d** is presented in Figure 4. The P1–Au1–P2 bond angle is slightly bent (171.55(6)°), and the boron trigonal planes of the two phosphinoborane ligands are almost perpendicular. Compared with neutral complex **1c**, the P–B bond distances are significantly longer with values of 2.3487(18) Å and 2.3455(18) Å. Moreover, in contrast to **1c**, the boron-bromide bonds are retained. Other structural features of PB ligands of **1d** are very similar to those observed in **1c**.

To the best of our knowledge, compounds **1c** and **1d** are the first examples of Au(I) complexes possessing phosphinoborane ligands with directly bonded P and B atoms. In the previously, reported Au(I) complexes with ambiphilic phosphinoborane ligands, organic fragments such as CH$_2$ or o-C$_6$H$_4$ were incorporated between P and B atoms.[36–43]

Next, we tested the reactivity of the NHC-phosphinoborenium cation **1a** toward AuCl·SMe$_2$ (Scheme 2). Inspection of the ^{31}P{^{1}H} spectrum of the reaction mixture showed several singlets at 102.8, 101.4, 100.7, 89.7, and 85.5 ppm. According to the literature, these spectroscopic data suggest the formation of a mixture of oligomeric Au(I) complexes with tBu$_2$P$^-$ phosphido ligands.[44] After the addition of Li[WCA] the number of signals decreased, and only one singlet at 91.7 ppm was observed in the ^{31}P{^{1}H} spectrum. Moreover, from this rection mixture crystals of NHC-borenium cation **1f–Cl/Br** were isolated. The ^{11}B NMR spectrum of these crystals displays two broad signals at 29.0 ppm and 25.3 ppm, attributable to chloro- and bromo- derivatives, respectively.

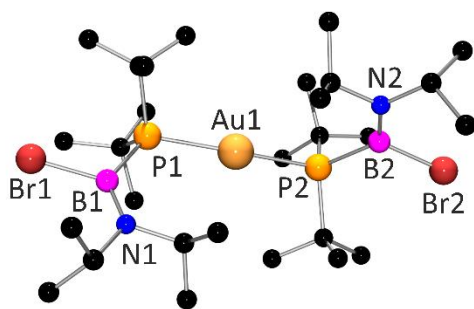**Scheme 2.** Comparison of the reactivity of **1** and **1a**.

Figure 4. X-ray structure of cation **1d**+. Counterion and H-atoms are omitted for clarity.

^{1}H and ^{13}C NMR spectra contained two sets of signals assigned to **1f–Cl** and **1f–Br** in a molar ratio of approximately 3:1 and additionally, they confirmed the presence of NiPr$_2$ and NHC moieties within the structures of these cations. Although the X-ray diffraction data of **1f–Cl/1f–Br** were of poor quality, it allowed us to establish atom connectivity and confirmed that **1f–Cl** and **1f–Br** crystalized as a solid-state solution. All these results together suggest that, in the aforementioned reaction, the P–B bond of the NHC-phosphinoborenium cation is heterotically cleaved and **1a** acts as a phosphido ligand source. We were curious to see if the NHC-phosphinoborenium cation would also be a phosphido group donor for the main group element compounds. For this reason, we performed the reaction of **1a** and its precursor **1** with Ph$_2$PCl (Scheme 2). Chlorophosphines are important substrates for the synthesis of organophosphorus compounds, including diphosphanes.

According to heteronuclear NMR spectroscopy, the control reaction of **1** with Ph$_2$PCl gave three main products: symmetrical diphosphane Ph$_2$PPPh$_2$,[45] tBu$_2$BBr, and iPr$_2$NBCl$_2$. Additionally, a significant amount of tBu$_2$PH and traces of unsymmetrical diphosphane tBu$_2$PPPh$_2$[45] and Ph$_2$PBr were present in the reaction mixture. Such product distribution may suggest a radical-mediated mechanism of this reaction. Otherwise, the reaction of cation **1a** yielded only two main products: unsymmetrical diphosphane tBu$_2$PPPh$_2$[45] and NHC-borenium salt **1f'**. In addition, based on ^{31}P{^{1}H} NMR spectroscopy, traces of tBu$_2$PPtBu$_2$,[45] Ph$_2$PPPh$_2$,[45] tBu$_2$PCl, tBu$_2$PCl, and unreacted Ph$_2$PCl were also identified in the reaction mixture. Similar to the reaction involving AuCl·SMe$_2$, **1a** reacted with Ph$_2$PCl via heterolytic cleavage of the P–B bond. This reaction can be classified as a metathesis reaction during which phosphido and chlorido anions are exchanged between boron and phosphorus centers.

Conclusions

We presented a simple access to NHC-phosphinoborenium cations utilizing bromo(phosphino)boranes. Regarding the chemistry of borenium cations, they possess unprecedented structures containing the PR$_2$ group directly bonded to the tricoordinate boron center. Because of these structural features, the title compounds can be viewed as cationic phosphinoboranes. The NHC-phosphinoborenium cations have a polar P–B bond, which undergoes heterolytic cleavage in

reactions with AuCl·SMe$_2$ and Ph$_2$PCl. The results of these reactions confirm that the title cations can be the source of a phosphido group both in reactions with transition metal complexes and compounds of main group elements.

Author Contributions

K.K-L.: funding acquisition, conceptualization, investigation, visualization, writing – original draft; A.O.: investigation, writing – original draft; T. W.: investigation, H. H.: investigation, M.C.: formal analysis; J.C.: investigation, formal analysis; R.G.: supervision, conceptualization, writing – original draft.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

Notes and references

1   P. Kolle and H. Nöth, *Chem. Rev.*, 1985, **85**, 399–418.
2   W. E. Piers, S. C. Bourke and K. D. Conroy, *Angew. Chemie - Int. Ed.*, 2005, **44**, 5016–5036.
3   V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, *Chem. Rev.*, 2018, **118**, 9678–9842.
4   T. S. De Vries, A. Prokofjevs and E. Vedejs, *Chem. Rev.*, 2012, **112**, 4246–4282.
5   P. Eisenberger and C. M. Crudden, *Dalt. Trans.*, 2017, **46**, 4874–4887.
6   X. Tan and H. Wang, *Chem. Soc. Rev.*, 2022, **51**, 2583–2600.
7   T. Matsumoto and F. P. Gabbai, *Organometallics*, 2009, **28**, 4252–4253.
8   J. M. Farrell and D. W. Stephan, *Angew. Chemie - Int. Ed.*, 2015, **54**, 5214–5217.
9   J. M. Farrell, D. Schmidt, V. Grande and F. Würthner, *Angew. Chemie - Int. Ed.*, 2017, **56**, 11846–11850.
10   J. M. Farrell, J. A. Hatnean and D. W. Stephan, *J. Am. Chem. Soc.*, 2012, **134**, 15728–15731.
11   J. M. Farrell, R. T. Posaratnanathan and D. W. Stephan, *Chem. Sci.*, 2015, **6**, 2010–2015.
12   J. S. McGough, S. M. Butler, I. A. Cade and M. J. Ingleson, *Chem. Sci.*, 2016, **7**, 3384–3389.
13   P. Eisenberger, B. P. Bestvater, E. C. Keske and C. M. Crudden, *Angew. Chemie - Int. Ed.*, 2015, **54**, 2467–2471.
14   A. Prokofjevs, J. W. Kampf, A. Solovyev, D. P. Curran and E.

Vedejs, *J. Am. Chem. Soc.*, 2013, **135**, 15686–15689.

15   A. Prokofjevs, A. Boussonnière, L. Li, H. Bonin, E. Lacôte, D. P. Curran and E. Vedejs, *J. Am. Chem. Soc.*, 2012, **134**, 12281–12288.

16   S. Muthaiah, D. C. H. Do, R. Ganguly and D. Vidović, *Organometallics*, 2013, **32**, 6718–6724.

17   A. Solovyev, S. J. Geib, E. Lacôte and D. P. Curran, *Organometallics*, 2012, **31**, 54–56.

18   L. J. Bole, M. Uzelac, A. Hernán-Gómez, A. R. Kennedy, C. T. O'Hara and E. Hevia, *Inorg. Chem.*, 2021, **60**, 13784–13796.

19   J. Zheng, Z. H. Li and H. Wang, *Chem. Sci.*, 2018, **9**, 1433–1438.

20   Y. Wang and G. H. Robinson, *Inorg. Chem.*, 2011, **50**, 12326–12327.

21   L. Weber, E. Dobbert, H. Stammler, B. Neumann, R. Boese and D. Bläser, *Chem. Ber.*, 1997, **130**, 705–710.

22   H. B. Mansaray, A. D. L. Rowe, N. Phillips, J. Niemeyer, M. Kelly, D. A. Addy, J. I. Bates and S. Aldridge, *Chem. Commun.*, 2011, **47**, 12295–12297.

23   G. Kundu, V. S. Ajithkumar, K. V. Raj, K. Vanka, S. Tothadi and S. S. Sen, *Chem. Commun.*, 2022, **58**, 3783–3786.

24   G. Kundu, K. Balayan, S. Tothadi and S. S. Sen, *Inorg. Chem.*, 2022, **61**, 12991–12997.

25   M. Devillard, R. Brousses, K. Miqueu, G. Bouhadir and D. Bourissou, *Angew. Chemie - Int. Ed.*, 2015, **54**, 5722–5726.

26   M. Devillard, S. Mallet-Ladeira, G. Bouhadir and D. Bourissou, *Chem. Commun.*, 2016, **52**, 8877–8880.

27   M. A. Dureen, A. Lough, T. M. Gilbert and D. W. Stephan, *Chem. Commun.*, 2008, **913**, 4303–4305.

28   M. Nazish, C. M. Legendre, Y. Ding, B. Schluschaß, B. Schwederski, R. Herbst-Irmer, P. Parvathy, P. Parameswaran, D. Stalke, W. Kaim and H. W. Roesky, *Inorg. Chem.*, 2023, **62**, 9343–9349.

29   N. Szynkiewicz, J. Chojnacki and R. Grubba, *Inorg. Chem.*, 2020, **59**, 6332–6337.

30   N. Szynkiewicz, A. Ordyszewska, J. Chojnacki and R. Grubba, *Inorg. Chem.*, 2021, **60**, 3794–3806.

31   N. Szynkiewicz, A. Ordyszewska, J. Chojnacki and R. Grubba, *RSC Adv.*, 2019, **9**, 27749–27753.

32   A. Ordyszewska, N. Szynkiewicz, J. Chojnacki and R. Grubba, *Inorg. Chem.*, 2022, **61**, 4361–4370.

33   A. Ordyszewska, N. Szynkiewicz, E. Perzanowski, J. Chojnacki, A. Wiśniewska and R. Grubba, *Dalt. Trans.*, 2019, **48**, 12482–12495.

34   K. Kaniewska-Laskowska, K. Klimsiak, N. Szynkiewicz, J. Chojnacki and R. Grubba, *Chem. Commun.*, 2022, **58**, 10068–10071.

35   K. Kaniewska-Laskowska, M. Czapla, J. Chojnacki and R. Grubba, *Dalt. Trans.*, 2023, **52**, 8311–8315.

36   D. H. A. Boom, A. W. Ehlers, M. Nieger, M. Devillard, G. Bouhadir, D. Bourissou and J. C. Slootweg, *ACS Omega*, 2018, **3**, 3945–3951.

37   M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron and D. Bourissou, *Angew. Chemie*, 2007, **119**, 8737–8740.

38   S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C. H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou,

Angew. Chemie - Int. Ed., 2008, **47**, 1481–1484.

39   J. W. Taylor, A. McSkimming, M. E. Moret and W. H. Harman, *Angew. Chemie - Int. Ed.*, 2017, **56**, 10413–10417.

40   A. Ueno, K. Watanabe, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2019, **55**, 4367–4370.

41   S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, *J. Am. Chem. Soc.*, 2006, **128**, 12056–12057.

42   M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, *J. Am. Chem. Soc.*, 2008, **130**, 16729–16738.

43   C. A. Theulier, Y. García-Rodeja, K. Miqueu, G. Bouhadir and D. Bourissou, *J. Am. Chem. Soc.*, 2023, **145**, 10800–10808.

44   D. M. Stefanescu, H. F. Yuen, D. S. Glueck, J. A. Golen, L. N. Zakharov, C. D. Incarvito and A. L. Rheingold, *Inorg. Chem.*, 2003, **42**, 8891–8901.

45   N. Szynkiewicz, Ł. Ponikiewski and R. Grubba, *Dalt. Trans.*, 2018, **47**, 16885–16894.