Cationic 5-phosphonio-substituted N-heterocyclic carbenes†

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2-Phosphanyl-substituted imidazolium salts 2-PR₃(4,5-CI-Im)[OTf] (9a,b[OTf]) (4,5-CI-Im = 4,5-dichloro-1,3-bis(2,6-di-isopropylphenyl)-imidazolium) (a: R = Cy, b: R = Ph) are prepared from the reaction of R₂PCI (R = Cy, Ph) with NHC 8 (4,5-dichloro-1,3-bis(2,6-di-isopropylphenyl)-imidazolin-2-yldene) in the presence of Me₃SiOTf. 5-Phosphanylo-substituted imidazolium salts 5-PR₃(2,4-CI-Im)[OTf] (10a,b[OTf]) are obtained in quantitative yield when a slight excess of the NHC 8 is used. 5-Phosphonio-substituted imidazolium salts 5-PR₃Me(2,4-CI-Im)[OTf]₂ (14a,b[OTf]₂) and 5-PR₃F(2,4-CI-Im)[OTf]₂ (16a,b[OTf]₂) result from methylation reaction or oxidation of 10a,b[OTf] with XeF₂ and subsequent fluoride abstraction. According to our quantum chemical studies the C11 atom at the 2-position at the imidazolium ring of dication 14b²⁺ carries a slightly positive charge and is therefore accessible for nucleophilic attack. Accordingly, the reaction of 14a,b[OTf]₂ and 16a,b[OTf]₂ with R₃P (R = Cy, Ph) affords cationic 5-phosphonio-substituted NHCs 5-PR₃Me(4-CI-NHC)[OTf] (17a,b[OTf]) and 5-PR₃F(4-CI-NHC)[OTf] (18a,b[OTf]) via a S_n2(Cl)-type reaction. A series of transition metal complexes such as [AuCl(5-PPh₂Me(4-CI-NHC))[OTf]] [19[OTf]], [CuBr(5-PPh₂Me(4-CI-NHC))[OTf]] [20[OTf]], [AuCl(5-PPh₂F(4-CI-NHC))[OTf]] [21[OTf]] and [RhCl(cod)(5-PPh₂Me(4-CI-NHC))[OTf]] [23[OTf]] are prepared to prove the coordination abilities of carbenes 17b[OTf] and 18b[OTf]. The isolation of a rare example of a tricationic bis-carbene silver complex [Ag(5-Ppy₂Me(4-CI-NHC))[OTf]] [22[OTf]] is achieved by reducting 14b[OTf] with CysP and subsequent deprotonation reaction with LDA affords the cationic NHO (N-heterocyclic olefin) 35⁺ of which the gold complex 36⁺ is readily accessible via the reaction with AuCl(tht).

Introduction

The application of N-heterocyclic carbenes (NHCs) in phosphorus chemistry has led to some remarkable discoveries in recent years and is a growing field with considerable impact. The most general feature of NHCs is their tendency to react at the 2-position with electrophilic PIII compounds, leading to the corresponding 2-phosphanyl-substituted imidazolium salts or to donor–acceptor complexes of the NHC and the respective P-centered moiety. In contrast, only a few examples are known where the 4/5-position of NHCs can be selectively addressed to yield 4/5-phosphanyl-substituted NHCs or imidazolium salts. Reactions are reported involving inter alia phosphaalkenes¹ and chlorophosphines. In 2009 Gates and co-workers observed the unusual reaction of 1,3-di(mesityl)imidazolin-2-yldiene 1 with phosphaalkene Mes₃CPh₂ to afford the first example of a neutral 4-phosphanyl-substituted NHC 2 (Scheme 1, top). Shortly afterwards, Bertrand and co-workers observed the rearrangement reaction of 2-phosphanyl-substituted imidazolium salt 3[Cl] to the 4-substituted derivative 4 when treated with a base [e.g. KHMX; Scheme 1, middle]. The neutral 4-phosphanyl-substituted NHCs 2 and 4 were used as ligands in transition metal chemistry to generate mono metallic, homo- and hetero-bimetallic complexes. In 2013 our group reported on the reaction of P-centered imidazolium salt 5[OTf] with NHC 6 leading to the cationic phosphorane derivative 7[OTf] where the second imidazolium-substituent is bonded via the 4-position to the P atom (Scheme 1, bottom). The proposed mechanism

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includes the formation of an abnormal carbene\(^8\) followed by an intermolecular rearrangement, which we believe is related to Bertrand’s mechanism for the formation of 4.\(^4\)

Only very few examples of 4-, 4,5-bisphosphoryl\(^9\) and 4,5-bis-phosphanyl\(^10\) substituted imidazolium salts and 4-phosphanylo-substituted NHC\(^11\) are reported in the literature so far. The aforementioned compounds exhibit either one or two Lewis basic functionalities. However, so far there is no example of a cationic NHC featuring a phosphonium functionality at the 4/5-position, which should have a significant influence on the reactivity of the carbene.

### Results and discussion

The reaction of chlorophosphanes R\(_2\)PCl (R = Cy, Ph) with Me\(_3\)SiOTf and NHC\(^8\)\(^12\) in a precise 1:1:1 reaction gives the corresponding 2-phosphanyl-substituted imidazolium salts 9a, b[OTf] in excellent yield [9a[OTf]: 91%; 9b[OTf]: 99%; Scheme 2]. The \(^{31}\)P NMR spectra of the purified, colorless solids show a singlet resonance in each case (9a\(^+\): \(\delta(P) = 12.7\) ppm; 9b\(^+\): \(\delta(P) = -5.1\) ppm), which is significantly upfield shifted compared to the respective chlorophosphanes (Cy\(_2\)PCl: \(\delta(P) = 127.1\) ppm; Ph\(_2\)PCl: \(\delta(P) = 81.9\) ppm)\(^13\) due to the presence of the imidazolium substituents. Suitable single crystals for X-ray analysis are obtained by slow diffusion of \(n\)-hexane into a saturated CH\(_2\)Cl\(_2\) solution of 9b[OTf] [Fig. 1]. The P–C bond lengths (P–C1 1.8437(9) Å, P–C28 1.8205(10) Å, P–C34 1.8249(10) Å) are in the expected range of a P–C single bond (1.83 Å) involving a tri-coordinate phosphorus atom.\(^14\)

Increasing the amount of NHC 8 to 1.2 equivalents in the reaction leads to the quantitative formation of 5-phosphanyl-substituted imidazolium salts 10a,b[OTf] (10a[OTf]: 92%; 10b[OTf]: 97%); conversion of 9a,b[OTf] to 10a,b[OTf], (iii) 0.3 eq. 8, o-C\(_6\)H\(_4\)F\(_2\), r.t. 30 h, quantitative.

![Scheme 1](image1)

**Scheme 1** Preparation of 2, 4, and 7[OTf] (Mes = 1,3,5-trimethylphenyl, Dipp = 2,6-diisopropylphenyl, Ph = phenyl, HMDS = bis(trimethylsilyl) amide); for all examples, only one representative Lewis structure is depicted.

![Scheme 2](image2)

**Scheme 2** Preparation of 9a,b[OTf], (i): C\(_6\)H\(_5\)F, r.t., 6 h, 9a[OTf] 91%; 9b [OTf] 99%; preparation of 10a,b[OTf]; (ii): o-C\(_6\)H\(_4\)F\(_2\), r.t. 14 h, 10a[OTf] 92%; 10b[OTf] 97%; conversion of 9a,b[OTf] to 10a,b[OTf], (iii) 0.3 eq. 8, o-C\(_6\)H\(_4\)F\(_2\), r.t. 30 h, quantitative.

![Fig. 1](image3)

**Fig. 1** Molecular structures of cations 9b\(^+\) and 10b\(^+\) of the respective triflate salts; hydrogen atoms, solvate molecules and anions are omitted for clarity and thermal ellipsoids are displayed at 50% probability; selected bond lengths (Å) and angles (°) for 9b\(^+\): P–C1 1.8437(9), P–C28 1.8205(10), P–C34 1.8249(10); C1–P–C28 107.15(4), C1–P–C34 100.59(4), C28–P–C34 101.71(4); and 10b\(^+\): P–C2 1.831(4), P–C28 1.827(4), P–C34 1.830(4); C2–P–C28 100.22(16), C2–P–C34 103.41(16), C28–P–C34 103.52(17).
spectra of \(10a, b[\text{OTf}]\) show the expected additional sets of resonances for the isopropyl-groups of the Dipp-substituents due to a lower symmetry compared to \(9a, b[\text{OTf}]\) (see Fig. S2.1†). Compounds \(9a, b[\text{OTf}]\) are cleanly converted to the 5-substituted derivatives \(10a, b[\text{OTf}]\) within 30 h when adding 0.3 equivalents of NHC 8 to the dissolved material in \(\text{C}_6\text{H}_4\text{F}_2\).

The time dependent \(^{31}\text{P}\) NMR spectra also confirm our suggestion that \(9a, b\) is first formed and slowly converted into \(10a, b\) during the reaction (Fig. 2). After 2 h, significant amounts of \(9b\) are consumed along with the formation of the structural isomer \(10b\) (\(9b\): \(\delta(P) = -5.1 \text{ ppm and } 10b\): \(\delta(P) = -28.9 \text{ ppm})]. The presence of two doublet resonances at \(\delta(P) = -7.5 \text{ ppm and } 30.7 \text{ ppm}\), (marked with a red and blue dot) with low intensity and a coupling constant of \(J_{PP} = 7 \text{ Hz}\) indicates the formation of intermediately formed cation \(12b^+\) (Fig. 2). We thus propose for the rearrangement reaction for the first step a chlorenium ion abstraction from cation \(9b\) by NHC 8 to give chloroimidazolium salt \(8\text{Cl}^+\) and mesoionic NHC \(11b\) (Scheme 3). The latter reacts with \(9b\) via phosphanyl-abstraction to NHC 8 and cation \(12b^+\) whose formation is observed in the time dependent \(^{31}\text{P}\) NMR spectra (Fig. 2). NHC 8 abstracts a PR₂-moietry from cation \(12b^+\) to liberate cation \(9b\) and intermediately formed NHC \(13b\). The catalytic cycle is closed by the chlorenium ion abstraction from \(8\text{Cl}^+\) by \(13b\) to yield 5-phosphanyl-substituted imidazolium cation \(10b\) and catalyst NHC 8. This catalytic cycle also explains the formation of cation \(10a^+\) and is related to a mechanism we proposed recently elsewhere.⁵

The reaction of \(10a, b[\text{OTf}]\) with methyltriflate (MeOTf) in \(\text{CH}_2\text{Cl}_2\) leads to the quantitative formation of the corresponding 5-phosphonium ions \(14a, b^{2+}\) as triflate salts (isolated yield \(14a[\text{OTf}]_2: 68%; 14b[\text{OTf}]_2: 79%;\) Scheme 4). This is indicated by a pronounced downfield shifted quartet resonance (\(14a^{2+}\): \(\delta(P) = 38.8 \text{ ppm, } J_{PP} = 12 \text{ Hz; } 14b^{2+}\): \(\delta(P) = 16.9 \text{ ppm, } J_{PP} = 14 \text{ Hz}\) in the respective \(^{31}\text{P}\) NMR spectrum. Single crystals of \(14b^+\) suitable for X-ray crystallography are obtained by slow diffusion of \(n\)-hexane into a saturated \(\text{CH}_2\text{Cl}_2\) solution of \(14b[\text{OTf}]_2\) (Fig. 3). The molecular structure of cation \(14b^{2+}\) shows the expected tetra-coordinate bonding environment at the P atom and slightly shortened P–C bond distances (P–C2 1.810(2) Å, P–C38 1.782(2) Å, P–C34 1.787(2) Å, P–C30 1.790(2) Å) compared to cation \(10b^+\). Selected geometrical parameters are given in Table 1.

One of the oxygen atoms of one triflate anion shows a close contact to the Cl1 atom that is well within the sum of the van der Waals radii (O4–Cl1 2.813(2) Å; \(r_{A(O)} + r_{A(Cl)} = 3.21\) Å).¹⁹ Also the almost linear C1–Cl1–O4 angle of 170.879(6)° is indicative for a strongly directional rather than purely electrostatic interaction, namely a halogen bonding.²⁰

Fig. 2 Time-dependent \(^{31}\text{P}\) NMR spectra for the reaction of \(9b[\text{OTf}]\) with 0.3 eq. of NHC 8 (α-C₆H₄F₂, C₆D₆-capillary, 300 K). The intermediately formed cation \(12b^+\) is indicated by red and blue dots, not identified intermediates by asterisks.

Scheme 3 Proposed mechanism for the formation of cations \(10b^+\): anions are omitted for clarity.

Scheme 4 Preparation of: \(14a, b[\text{OTf}]_2\), (i): + MeOTf, C₆H₄F, r.t., 6 h, \(14a[\text{OTf}]_2: 68%; 14b[\text{OTf}]_2: 79%;\) \(15a, b[\text{OTf}]\), (ii): + XeF₂, CH₂Cl₂, r.t. 2 h, –Xe, \(15a[\text{OTf}]: 81%; 15b[\text{OTf}]: 89%; 16a, b[\text{OTf}]_2\), (iii): + Me₃SiOTf, α-C₆H₄F₂, r.t. 5 h, –Me₃Si, \(16a[\text{OTf}]_2: 72%; 16b[\text{OTf}]_2: 71%\).
This effect might be attributed to a slightly increased electrophilic character of the Cl1 atom caused by the high group electronegativity of dication 14b2+ (vide infra).20–22

The quantitative oxidation of 10a,b[OTf] via the slow addition of a solution of XeF2 in CH2Cl2 affords the difluorophosphoranes 15a,b[OTf] (isolated yield >80%; Scheme 4). Analytically pure compounds are obtained via precipitation with n-hexane. For both compounds the 31P NMR spectra show the expected triplet resonance with a typical JPF coupling due to the presence of two chemically equivalent fluorine atoms (15a+: δ(P) = −28.6 ppm, JPF = 722 Hz; 15b+: δ(P) = −64.9 ppm, JPF = 715 Hz). Single crystals suitable for structure investigation are obtained by slow diffusion of n-hexane into a saturated CH2Cl2 solution of 15b[OTf]. Cation 15b+ shows a trigonal bipyramidal bonding environment at the P atom with the F atoms being in the axial positions displaying an almost linear P–F–P angle of 172.91(10)° and typical P–F bond lengths (P–F1 1.6523(19) Å, P–F2 1.6582(19) Å; Fig. 3).

In contrast to a related difluorophosphorane,23 which requires a very strong fluoride abstracting reagent such as Et3Si[B(C6F5)4]2(C7H8), the reaction of 15a,b[OTf] with Me3SiOTf in CH2Cl2 quantitatively gives the fluorophosphonium salts 16a,b[OTf]. Analytically pure compounds are obtained after the addition of n-hexane (isolated yield >70%). The 31P NMR spectra of the isolated compounds display a pronounced downfield shifted doublet resonance (16a2+: δ(P) = 109.6 ppm, JPF = 988 Hz; 16b2+: δ(P) = 70.5 ppm, JPF = 995 Hz), coinciding with the electron deficiency at the P atom as observed for similar Lewis acidic fluorophosphonium derivatives.23,24 Accordingly, the much larger JPF coupling constant in 16a,b2+ compared to 15a,b+ results from a decreased electron density at the P atom.25 The formation of dication 16b2+ was also confirmed by X-ray crystallography (Fig. 3). The P–F bond (1.5612(19) Å) is substantially shortened compared to the P–F bond lengths in 15b+ (P–C28 1.808(3) Å, P–C34 1.804(3) Å). Similarly, the P–C2 bond length in 16b2+ (P–C2 1.782(3) Å) is significantly shortened compared to that in 15b+ (P–C2 1.826(3) Å). Selected geometrical parameters are given in Table 2.

In order to shed light on the reactivity of dications 14a,b2+ and 16a,b2+ we analyzed the Merz–Kollman (M–K) and the Mulliken (Mull) charge distribution of 14b2+ which are shown in Fig. 4 (left). Moreover, the Molecular Electrostatic Potential (MEP) distribution of 14b2+ was calculated and plotted onto the van der Waals surface were regions of high charge are blue and regions with lower charge red (Fig. 4, right). For this study the geometries and energies were calculated applying the density functional theory (DFT) model BP8626 with the latest correction of dispersion (D3),27 together with the def2-TZVP basis set.28,29 Both methods confirm a significant positive charge of the Cl atoms (Cl1: +0.41e (M–K), +0.12e (Mull); Cl2:

![Fig. 3 Molecular structures of 14b2+, 15b+, and 16b2+ of the respective triflate salts; hydrogen atoms, solvent molecules and anions are omitted for clarity and thermal ellipsoids are displayed at 50% probability. Selected geometrical parameters are given in Tables 1 and 2.](Image)

![Fig. 4 Two orientations of cation 14b2+ calculated at BP86-D3/def2-TZVP level of theory; Merz–Kollman (M–K) and the Mulliken (Mull, italics) charge distribution (left); Molecular Electrostatic Potential (MEP) distribution plotted onto the van der Waals surface (right).](Image)
+0.30 e (M–K), +0.01 e (Mull)) which are bonded to the imidazole ring, whereas the Cl1 atom, bonded to the 2-position, is more positive. The MEP surface illustrates that the imidazole ring has the highest charge, however, it is not accessible for a nucleophilic attack due to steric effects. In sharp contrast, the Cl1 atom is very exposed and presents a σ-hole – a well-defined positively charged region on the extension of the C1– Cl1 bond. 16,32 Therefore, the most reactive site towards voluminous nucleophiles in dication 14b+ is indeed the Cl1 atom bonded at the 2-position.

As for dications 14a,b+ and 16a,b+ we aimed at the synthesis of the corresponding cationic 5-phosphonio-substituted NHCs and proceeded to react dications 14a,b+ and 16a,b+ with Cy3P or PPh3, respectively (Scheme 5). The reaction of 14a,b[OTf]2 with Cy3P in C6H5F gives quantitatively Cy3PCl[OTf] of which the cation Cy3PC1+ was unambiguously identified by its 31P NMR chemical shift of δ(P) = 104.2 ppm (ref. 31) in the reaction mixture. The 31P NMR spectra of the reaction mixtures also show a second resonance which can be assigned to the cationic NHCs 17a,b+. The isolation of 17a[OTf] was hampered due to a similar solubility of 17a[OTf] and Cy3PCl[OTf]. Analytically pure 17b[OTf] was isolated as colorless powder in good yield (75%) via precipitation and washing with benzene. For cation 17b+ a slightly high field shifted singlet resonance in the 31P NMR spectrum (δ(P) = 10.6 ppm) compared to 14b+ (δ(P) = 16.9 ppm) is observed. The 13C NMR spectrum displays a resonance at δ(C) = 230.2 ppm confirming the formation of an NHC. 16,32 This signal, which is downfield shifted compared to NHC 8 (δ(C) = 219.4 ppm, in C6D6)12 splits into a doublet due to the coupling to the P atom in 5-position (JCP = 6 Hz). As compound 17b[OTf] can be handled in solvents such as CH2Cl2 and CH3CN without decomposition the scope of application is significantly broadened. Single crystals suitable for X-ray crystallography are obtained by slow diffusion of n-hexane into a saturated C6H5F solution of 17b[OTf] (Fig. 5). Major differences in this cation compared to dication 14b+ are the elongation of the C1–N1/N2 bond lengths (17b+: C1–N1 1.375(3) Å, C1–N2 1.362(3) Å vs. 14b+: C1–N1 1.335(2) Å, C1–N2 1.337(2) Å) and the reduced bond angle N1–C1–N2 (17b+: 102.40(16)° vs. 14b+: N1–C1–N2 110.42(14)°). These effects are explained by a diminished π-delocalization 16,32 in the N1–C1–N2 moiety and an increased p-orbital character of the C1–N1/N2 bonds. As a result of the diminished π-delocalization within the imidazole ring the P–C2 bond length in 17b+ (1.779(2) Å) is significantly shortened compared to that in 14b+ (P–C2 1.810(2) Å). Selected geometrical parameters are summarized in Table 1.

Similarly, the reaction of 16a,b[OTf]2 with Ph3P leads to the quantitative formation of chlorophosphonium salt Ph3PCl[OTf] (δ(P) = 65.5 ppm)31 and NHCs 18a,b[OTf]. The isolation of NHC 18a[OTf] was hampered due to similar solubility of 18a[OTf] and PPh3Cl[OTf]. 18b[OTf] shows a slightly downfield shifted doublet resonance at δ(P) = 76.8 ppm (JFW = 996 Hz) in the 31P NMR spectrum compared to the starting material 15[OTf]2+ (δ(P) = 70.5 ppm). The confirmation of the carbene was given by the 13C{1H} NMR spectrum showing a resonance at δ(C) = 230.8 ppm (ref. 31) which splits into a pseudo triplet (JCP = 5 Hz, JCP = 5 Hz) due to the coupling to the phosphorus atom and the fluorine atom, respectively. Mechanistically, the formation of NHCs 17a,b+ and 18a,b+ proceeds via a Sn2(Cl) type reaction33 which is initiated by the nucleophilic attack of R3P (R = Ph, Cy) on the σ-hole of the Cl1 atom bonded to the C2-position. This suggestion is supported by a detailed computational study considering a Sn2(Cl) type reaction. The calculations were performed using the high level ab initio method RI-MP234 with the def2-TZVP 28 basis set to obtain reliable reaction barriers (Fig. 6, left). 29 In initial calculations a minimalistic model was used considering PH3 as nucleophile which reacts with 14b+ where the Dipp-substituents are replaced by H atoms. The reaction is initiated by the formation of a hypercoordinate complex I in which a P⋯Cl halogen bond 20 with a comparatively short bond distance of 3.151 Å is observed. This intermediate was found to be 9.2 kcal mol−1 lower in energy than the corresponding starting materials and is well organized for the subsequent Sn2(Cl) type reaction 33 as it presents an ideal directionality for the

![Scheme 5 Preparation of 17b[OTf] (R1 = Me): + Cy3P, C6H5F, r.t., 2 h, – Cy3PCl[OTf], 75%; preparation of 18b[OTf] (R1 = Me): + Ph3P, C6H5F, r.t., 2 h, – Ph3PCl[OTf], 55%. Proposed transition state of a Sn2(Cl) type reaction (grey).](Image 1)
nucleophilic attack. The transition state $\text{TS}$ is only 9.4 kcal mol$^{-1}$ higher in energy than the intermediate $\text{I}$, thus confirming that the formation of the carbene is energetically feasible. The resulting adduct $\text{P}$ is 6 kcal mol$^{-1}$ lower in energy than the intermediate $\text{I}$ and in total 15.2 kcal mol$^{-1}$ more stable than the starting materials. These findings were then transferred to the complete model with dicationic $14\text{b}^{2+}$ and $\text{PPh}_3$ as nucleophile using the density functional theory methods BP86-D3/def2-TZVP$^{26, 29}$ (Fig. 6, right). The hypercoordinate complex $\text{I}'$ with a $\text{P} \cdots \text{Cl}$ bond distance of 2.702 Å and the product $\text{P}'$ were computed. The obtained energy difference between $\text{I}'$ and $\text{P}'$ with a value of $-9$ kcal mol$^{-1}$ is in good agreement with the high level $ab$ initio MP2/def2-TZVP calculation of the minimalistic model.

As NHCs are extensively used in coordination chemistry of transition metals, the formation of a series of complexes was investigated. The isolation of transition metal complexes $19$ [OTf], $20$ [OTf], $21$ [OTf] and $23$ [OTf] succeeds via the $in$ $situ$ reaction of compounds $14\text{b}[\text{OTf}]_2$ or $16\text{b}[\text{OTf}]_2$ with $\text{R}_3\text{P}$ ($\text{R} = \text{Cy}$, for $19$ [OTf], $20$ [OTf], and $23$ [OTf]; $\text{R} = \text{Ph}$, for $21$ [OTf]) in the presence of one equivalent of the corresponding transition metal salts at ambient temperature (Scheme 6; AuCl(tht) for $19$ [OTf] and $21$ [OTf], CuBr(tht) for $20$ [OTf], $[\text{RhCl(cod)}]_2$ for $23$ [OTf]) in THF. The formation of the complexes is indicated by the $^{13}\text{C} (^1\text{H})$ NMR spectra of the respective compounds showing resonances at $\delta(\text{C}) = 183.0$ ppm for $19$ [OTf], $\delta(\text{C}) = 186.5$ ppm for $21$ [OTf], $\delta(\text{C}) = 189.51$ ppm for $20$ [OTf] and $\delta(\text{C}) = 206.03$ ppm for $23$ [OTf]$. The reaction of $14\text{b}[\text{OTf}]_2$ with Cy$_3$P and one eq. AgOTf in THF leads to the formation of $22$ [OTf]$^3$, which is a rare example of a tricationic bis-carbene silver complex. The investigation of the NMR spectra of isolated $22$ [OTf]$^3$, show only one set of resonances (e.g. $\delta(\text{C}) = 186.5$ ppm, $\delta(\text{P}) = 14.1$ ppm), indicating a symmetric arrangement of the two ligands around the Ag atom. Single crystals suitable for X-ray crystallography of the triflate salt of $22^{3+}$ are obtained by slow diffusion of Et$_2$O into a saturated CH$_3$CN solution (Fig. 7). The Ag atom is in an almost linear arrangement between the two

![Fig. 6 MP2/def2-TZVP reaction coordinate, energies and geometries of the $S_N2(\text{Cl})$ type reaction (left, A); DFT optimized geometries of the intermediate $\text{I}$ and products $\text{P}$ of the experimental system (right, B and C; distances are given in Å).](image)
Carbenes ([C1–Ag–C41 178.27(15)°]) but the NHC ligands are slightly twisted as illustrated by the torsion angle of N1–C1–C41–N3 34.380°. Molecular structures of the transition metal complexes 19⁺, 20⁺, 21⁺, 22³⁺ and 23⁺ are depicted in Fig. 7 and selected geometrical parameters are given in Tables 1 or 2. As expected, the average N1–C1–N2 bond angles of cationic NHC complexes (N1–C1–N2; range of 103.2(3)°–106.2(3)°) are wider than the corresponding bond angle in free cationic NHC 17b⁺ (N1–C1–N2 102.40(16)°).35 Accordingly, the N1–C1/N2–C1 bond lengths in complexes 19⁺, 20⁺, 21⁺, 22³⁺, 23⁺ (N1–C1/N2–C1: range of 1.346(3) Å–1.366(3) Å) are slightly shortened compared to those in 17b⁺ (av. N1–C1/N2–C1 1.369 Å), which

![Molecular structures of 19⁺, 20⁺, 21⁺, 22³⁺ and 23⁺](image)

Table 1. Selected geometrical parameters of crystallographically characterized cations 14b²⁺, 17b⁺, 19⁺, 20⁺, 22³⁺ and 23⁺

|          | 14b²⁺ | 17b⁺ | 19⁺ | 20⁺ | 22³⁺ | 23⁺ |
|----------|-------|------|-----|-----|------|-----|
| P–C2 in Å | 1.810(2) | 1.779(2) | 1.794(3) | 1.788(2) | 1.792 | 1.783(2) |
| P–C28 in Å | 1.782(2) | 1.785(5) | 1.780(3) | 1.783(2) | 1.787 | 1.795(2) |
| P–C40 in Å | 1.787(2) | 1.780(2) | 1.772(3) | 1.782(2) | 1.790 | 1.792(2) |
| C1–N1 in Å | 1.335(2) | 1.375(3) | 1.350(4) | 1.346(3) | 1.359 | 1.360(3) |
| C1–N2 in Å | 1.337(2) | 1.362(3) | 1.354(4) | 1.365(3) | 1.358 | 1.380(3) |
| C1–M° in Å | — | — | 1.981(3) (M = Au) | 1.884(2) (M = Cu) | 2.139 (M = Ag) | 2.039(2) (M = Rh) |
| N1–C1–N2 in (°) | 110.42(14) | 102.40(16) | 106.2(3) | 104.81(19) | 104.35 | 104.78(19) |
| C1–M–X° in (°) | — | — | 176.75(10) (X = Cl) | 174.88(7) (X = Br) | 178.27(5) (X = C) | 86.85(6) (X = Cl) |
| C1–O₃triflate in Å | — | — | 2.813(2) | — | — | — |

a M = transition metal. b X = halogen atom. Average bond lengths and angles are given.

Table 2. Selected geometrical parameters of crystallographically characterized cations 15b⁺, 16b²⁺ and 21⁺

|          | 15b⁺ | 16b²⁺ | 21⁺ |
|----------|------|-------|-----|
| P–C2 in Å | 1.826(3) | 1.782(3) | 1.774(3) |
| P–C28 in Å | 1.808(3) | 1.778(3) | 1.754(3) |
| P–C40 in Å | 1.804(3) | 1.769(3) | 1.748(3) |
| P–F1 in Å | 1.6523(19) | 1.561(2) | 1.5422(17) |
| P–F2 in Å | 1.6582(19) | — | — |
| C1–N1 in Å | 1.332(4) | 1.320(3) | 1.350(3) |
| C1–N2 in Å | 1.334(4) | 1.335(3) | 1.366(3) |
| C1–Au in Å | 109.5(2) | 110.0(2) | 105.2(2) |
| C1–Au–Cl in (°) | — | — | 177.7(4) |
is also in line with the coordination to transition metals. The C1–metal bond lengths in cationic complexes $19^+, 20^+, 21^+, 22^+$, and $23^+$ are comparable to those observed in other neutral NHC metal complexes.

In order to elucidate the donor/acceptor properties of cationic NHC $17b[\text{OTf}]$, we synthesized the cis-chlorodicarbonyl-rhodium complex $24[\text{OTf}]$ via the reaction of carbon monoxide with $23[\text{OTf}]$ (Scheme 6) and subsequently investigated the IR stretching frequencies for the carbonyl ligands of the formed carbonyl complex (see Fig. S2.10). The average CO stretching frequency ($\nu_{av}(\text{CO}) = 2040.3$ cm$^{-1}$, TEP = 2051 cm$^{-1}$) indicate a weak donor ability of cationic NHC $17b[\text{OTf}]$.

According to a recent work by Ganter and co-workers, the $\lambda_{JCH}$ coupling constant in imidazolium salts correlates with the $\sigma$-donor strength of the corresponding carbene. It was found that poor $\sigma$-donors reveal high coupling constants for the C–H bond, which can be explained by a higher s-orbital character of the corresponding C–H bond (compare [ImMes-H]$^+$: $1J_{CH} = 206$ Hz and [4,5-Cl-ImDipp-H]$^+$: $1J_{CH} = 229$ Hz). For imidazolium salt $17b[H]^+$ (17b protonated at C1), we observed a $1J_{CH}$ coupling constant of 233 Hz (see Fig. S2.2) rendering cationic NHC $17b^+$ a weak $\sigma$-donor. We thus conclude that our cationic NHCs are very electron deficient (weak $\sigma$-donor), which is promising for interesting follow up chemistry.

The ambiphilic nature of $18b^+$ is displayed by the reaction of $18b[\text{OTf}]$ with silver fluoride (AgF) in a 1 to 1 stoichiometry at ambient temperature in C$_6$H$_5$F yielding complex $25[\text{OTf}]$ (Scheme 7). The $31P$ NMR spectrum of $25[\text{OTf}]$ shows a triplet resonance at $\delta(P) = -65.3$ ppm ($1J_{PF} = 701$ Hz) indicating a clean formation of cation $25^+$ (see Fig. S2.3). Additionally, the $13C\{1H\}$ NMR spectrum shows two doublets at $\delta(C) = 184.3$ ppm ($1J_{CAg109} = 232$ Hz, $1J_{CAg107} = 200$ Hz; see Fig. S2.4), indicative for the coordination of carbene to the silver atom.

$25[\text{OTf}]$ is extremely sensitive and decomposes readily in solution which prevents its isolation. In 2010 Bertrand and co-workers reported on the activation of the primary phosphane PhPH$_2$ using NHC $26^+$ and isolated the insertion product of the oxidative addition $27$ in high yield (Scheme 8-I). Only recently, Radius and co-workers reported on the dehydrogenative coupling of primary and secondary phosphanes utilizing the more electron deficient NHC $28$ (Scheme 8-II). For the 1 to 2 reaction of $28$ with Ph$_3$PH an oxidative addition of the phosphane into the carbene moiety followed by a reductive elimination of the corresponding diphosphane and the 2,3-dihydro-1H-imidazole $29$ was assumed.

Similarly, the reaction of prim. and sec. phosphanes with the electron deficient cationic NHC $17b^+$ was performed. The reaction of two equivalents Ph$_3$PH with $17b^+$ in 1,2-dichloroethane (DCE) at ambient temperature affords the quantitative formation of diphosphane Ph$_4$P$_2$ after 12 h (Scheme 9, Scheme 8).

Scheme 8 Reaction of $26$ with $\text{H}_2\text{PPh}$ (I) and dehydrocoupling reactions of $\text{HPPh}_2$ or $\text{H}_2\text{PPh}$ with $28$ (II).

### Scheme 7 Reaction of $18b[\text{OTf}]$ with AgF: (i) C$_6$H$_5$F, r.t., 10 h.

### Scheme 9 P–P coupling reactions of $\text{R}_2\text{PH}$ ($\text{R} = \text{Ph, Cy, }^\text{Bu}$; top) and $\text{PhPH}_2$ (bottom) using $17b[\text{OTf}]$ as hydrogen acceptor: (i) +2 eq. $\text{Ph}_3\text{PH}$, DCE, r.t., 12 h; (ii) +2 eq. Cy$_2\text{PH}$, CH$_2$CN, r.t., 12 h; (iii) +2 eq. $^\text{Bu}_2\text{PH}$, CH$_2$CN, r.t., 10 h; (iv) +$\text{PhPH}_2$, r.t., 10 h; product distribution estimated by integration of the $31P$ NMR spectrum of the reaction mixture; (v) +Ph$_3$PH, r.t., 24 h, product distribution estimated by integration of the $31P$ NMR spectrum of the isolated solid.
When alkyl phosphines R₂PH (R = Cy, Bu) are reacted with 17b[OTf] in a 2 to 1 stoichiometry in CH₃CN at ambient temperature, a clean formation of the corresponding diphosphane R₄P₂ (R = Cy, iBu) is observed after 10 h reaction time. The reaction of 2 eq. Cy₂PH with 17b[OTf] in CH₃CN leads to the formation of a colorless precipitate. The ³¹P NMR spectrum of the isolated precipitate reveals a singlet resonance at δ(P) = 17.6 ppm illustrating a clean and quantitative formation of diphosphane Cy₄P₂ (see Fig. S2.6†). The ³¹P NMR spectrum for the reaction of 2 eq. iBu₂PH with 17b[OTf] shows a singlet at δ(P) = 13.5 ppm for 30 and a singlet resonance at δ(P) = −52.4 ppm which is attributed to iBu₄P₂. Small amounts of unreacted iBu₂PH give rise to a doublet resonance at δ(P) = −83.7 ppm due to a slight excess of the inserted phosphane in the reaction (see Fig. S2.7†). No conversion is observed when 2 eq. of the more sterically encumbered 'Bu₂PH is reacted with 17b[OTf], leading to the assumption that the dehydrogenative coupling reaction maybe limited by the steric demand but not necessarily by electronic effects of the corresponding substituents on the phosphane.

The equimolar reaction of cationic NHC 17b with primary phosphane PhPH₂ in 1,2-dichloroethane at ambient temperature led to the formation of cyclo-phosphines Ph₃P₃, Ph₂P₄, Ph₃P₅ and Ph₄P₆ (>90%) along with small amounts of unidentified side products and imidazolium dication 30. The proton decoupled ³¹P NMR spectrum of the reaction mixture revealed an approximate product distribution of the cyclo-phosphines of which Ph₂P₃ (ca. 84%) is found to be the main product (see Fig. S2.8†). Reacting the alkyl phosphane CyPH₂ with 17b[OTf] in a 1:1 stoichiometry in CH₃CN afforded the quantitative precipitation of Cy₅P₃ and Cy₆P₄ after 24 h. The ³¹P NMR spectrum of the isolated solid shows two singlet resonances which are assigned to Cy₅P₃ (δ(P) = −68.8 ppm, 65%) and Cy₆P₄ (δ(P) = 7.7 ppm, 35%; see Fig. S2.9†), illustrating that NHC 17b is also suitable for the dehydrocoupling of prim. phosphanes to cyclo-phosphines.

To support a possible reaction mechanism (Scheme 10), 5 eq. of Ph₂PH and 17b[OTf] were mixed together in DCE and the reaction mixture was investigated by means of ³¹P NMR spectroscopy (Fig. 8). We assume that the first step of this reaction involves the nucleophilic attack of cation 17b towards Ph₂PH to give the hyper-coordinate intermediate 31. Related phosphoranes were recently reported. This intermediate reacts with a second eq. of Ph₂PH to 31H⁺, accompanied by the formation of Ph₂PCl (δ(P) = 81.8 ppm). Cation 31H⁺ shows a doublet resonance due to proton coupling at δ(P) = 18.9 ppm (JHP = 477 Hz) and a singlet at δ(P) = 27.6 ppm for the tetra-coordinate phosphorus atom. Small amounts of cation 31 are present in the spectrum as indicated by the observation of a singlet of low intensity at δ(P) = 26.4 ppm. The corresponding doublet for the penta-coordinate P-atom coincides with that of 31H⁺. Intermediate 31H⁺ rearranges to 2,3-dihydro-1'H-imidazole 32 in accordance to the work by Bertrand, Röschenthaler and Radius. This cation readily reacts with the liberated Ph₂PCl to dication 33⁺ which is indicated by the observation of two doublets at δ(P) = −23.4 ppm and δ(P) = 34.6 (JPP = −227 Hz) and a singlet resonance at δ(P) = 33.3 ppm for the phosphonium moiety in the backbone. In the last step, cation 33⁺ liberates Ph₄P₂ accompanied by the formation of dication 30. The ³¹P NMR spectrum of the reaction mixture shows a singlet resonance at δ(P) = −16.3 ppm which can be attributed to Ph₅P₃ and a singlet at δ(P) = 12.1 ppm, corresponding to the byproduct which is formed during the reaction. To our surprise, in depth NMR spectroscopic studies reveal dication 30 as byproduct of this reaction and not the corresponding 2,3-dihydro-1'H-imidazole. It was reported that aryl substituents at the phosphane are beneficial for the NHC mediated or transition metal catalysed dehydrocoupling reaction, since electron rich alkyl phosphanes gave either no, or a non-selective conversion.

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Further reactivity studies of 17b[OTf] were directed towards the synthesis of a cationic N-heterocyclic olefin (NHO). Therefore we methyalted in a first step the in situ formed cation 17b⁺ obtained from 14b[OTf]₂ and Cy₃P with one equivalent of MeOTf to give dication 34⁺⁺ (Scheme 11). Dication 34⁺⁺ was isolated as triflate salt (isolated yield 91%) and investigated by means of multinuclear NMR spectroscopy and X-ray analysis (Fig. 9). The ³¹P NMR spectrum of dissolved 34[OTf]₂ in CD₂Cl₂ reveals a doublet resonance at δ(P) = 2.91 ppm (JₚH = 13.8 Hz) for the CH₃⁺-group which is bonded to the phosphorus atom whereas the CH₃⁺-group at the 2-position of the imidazolium ring gives a singlet resonance at δ(H) = 2.38 ppm. The ³¹P NMR spectrum shows a quartet resonance at δ(P) = 15.6 ppm which is slightly upfield shifted compared to 14b⁺⁺ (δ(P) = 16.9 ppm). Derivative 34[OTf]₂ is readily deprotonated in a subsequent step by lithium disopropylamide (LDA) in THF to give 35[OTf] as yellow powder in excellent yield (93%). The ³¹P NMR spectrum shows an upfield shifted quartet resonance at δ(P) = 9.6 ppm compared to dication 34⁺⁺ (δ(P) = 15.6 ppm).

The doublet resonance for the CH₃-group bound to the P atom is shifted to higher field (δ(H) = 1.83 ppm; JₚH = 13.6 Hz) compared to the corresponding CH₂-group in 35⁺⁺ (δ(H) = 2.91 ppm; JₚH = 13.8 Hz). The CH₂⁺-group at the 2-position of the imidazole ring gives rise to a doublet resonance at δ(H) = 2.54 ppm and a doublet of doublet resonance at δ(H) = 2.61 ppm due to the hindered rotation around the C₁–C₂ bond. Both signals exhibit a geminal coupling constant of JₚH = 3.7 Hz and the latter resonance shows an additional coupling to the P atom (JₚH = 1.6 Hz) which is explained by the spatial arrangement of this proton (see Fig. S2.11†). The C atom of the CH₂⁺-group resonates at δ(P) = 55.1 ppm which is in the typical range for an olefinic C atom. Single crystals suitable for X-ray crystallography are obtained by slow diffusion of Et₂O into a saturated solution of 35[OTf] in CH₃CN at −35 °C (Fig. 9). Compared to the molecular structure of 34⁺⁺ the major differences are the elongated C₁–N₁/N₂ bond distances (C₁–N₁ 1.404(3) Å, C₁–N₂ 1.399(3) Å in 35⁺⁺ and C₁–N₁ 1.347(5) Å, C₁–N₂ 1.332(5) Å in 34⁺⁺) and the reduced bond angle between N₁–C₁–N₂ (104.6(2)° in 35⁺⁺ and N₁–C₁–N₂ 109.141(9)° in 34⁺⁺) and are explained by a diminished degree of π-delocalization between the N₁–C₁–N₂ moiety and an increased p-orbital character of the C₁–N₁/N₂ bonds. The C₁–C₄ bond length of 1.334(4) Å is well within the range of a typical olefinic C=C double bond (1.34 Å). Cation 35⁺⁺ is regarded as cationic N-heterocyclic olefin (NHO) of which the main resonance structures (A, B) are depicted in Scheme 11, indicating the highly polarized nature of the exocyclic C=C double bond. As already discussed by others, NHOs are of great interests as strong two-electron donors due to their considerable nucleophilic character.⁴⁵,⁴⁶

Fig. 9 Molecular structures of 34⁺⁺, 35⁺⁺, and 36⁺⁺ of the respective triflate salts; hydrogen atoms, solvent molecules and anions are omitted for clarity and thermal ellipsoids are displayed at 50% probability; selected bond lengths (Å) and angles (°) for 34⁺⁺: C₁–C₄ 1.499(5), C₁–N₁ 1.347(5), C₁–N₂ 1.332(5); N₁–C₁–N₂ 109.141(9); 35⁺⁺: C₁–C₄ 1.334(4), C₁–N₁ 1.404(3), C₁–N₂ 1.339(3); N₁–C₁–N₂ 104.6(2); for 36⁺⁺: C₁–C₄ 1.453(4), C₁–N₁ 1.344(4), C₁–N₂ 1.356(4), C₂₈–Au 2.062(3), Au–Cl 2.3080(8); N₁–C₁–N₂ 107.5(5), C₁–C₄–Au 116.2(2), C₄–Au–Cl 174.90(9).
To proof the donor properties of cationic NO 35, the triflate salt was reacted with one equivalent AuCl(tht) in THF at ambient temperature to afford the NO gold complex 36[OTf] in good yield (71%, Scheme 12). The 31P NMR spectrum of 36[OTf] reveals a slightly downfield shifted resonance at δ(P) = 9.6 ppm compared to the free ligand 35 (δ(P) = 14.3 ppm). The 1H NMR spectrum of 36 shows a singlet resonance for the CH2-group at δ(H) = 2.36 ppm, thus the two protons of the CH2 moiety become magnetically equal upon coordination to the transition metal due to the free rotation around the C1–CH1 bond (see Fig. S2.11†). The coordination of the gold chloride fragment to the CH2-group causes a pronounced high field shift in the 13C NMR spectrum (δ(C) = 8.5 ppm) compared to cation 35 (δ(C) = 55.1 ppm). Single crystals suitable for X-ray crystallography are obtained by slow diffusion of Et2O into a saturated solution of 36[OTf] in CH3CN at −5 °C (Fig. 9). The molecular structure of cation 36 displays a tetra-coordinate bonding environment at the C4 atom with a C1–C4–Au bond angle of 116.2(2)° and an elongated C1–C4 bond length of 1.453(4) Å compared to that in 35 (C1–C4 1.399(3) Å). This elongation is a result of the reduced π-bond character of the C1–C4 bond caused by the coordination of the gold chloride fragment.

Conclusions

In this contribution, we present a facile and high yielding syntheses of 2-phosphanyl-[9a,b[OTf]] and 5-phosphanyl-[10a, b[OTf]] substituted imidazolium salts from the reaction of the corresponding chlorophosphines and NHC 8. Methylation or oxidation with XeF2 and subsequent fluoride abstraction of these salts affords 5-phosphonio substituted imidazolium salts 14a,b[OTf]3 and 16a,b[OTf]2 in good to very good yields. Quantum chemical calculations revealed the C1 atom (σ-hole) the most reactive position towards bulky nucleophiles. Chlorination abstraction is achieved by the addition of R3P (R = Ph, Cy) in a S2(2Cl) type reaction to yield the first cationic 5-phosphonio-substituted NHCs 17a,b+ and 18a,b+ as triflate salts.

These salts are a new class of electron deficient cationic NHCs which conveniently form transition metal complexes with corresponding metals salts [AuCl(tht) for 19[OTf]2, and [21[OTf]2, CuBr(tht) for 20[OTf]2, [RhCl(cod)]2 for 23[OTf]2] and AgOTf for 22[OTf]2. As shown for derivative 17b[OTf]2, the methylated derivatives can be handled also in solvents such as CH3Cl, and CH3CN without decomposition which significantly broadens the scope of application. 17b[OTf] is used in de-hydrocoupling reactions of prim. and sec. aryl and even alkyl phosphonates. The preparation of a highly nucleophilic N-heterocyclic olefin (NHO, 35[OTf]) proceeds via a two step synthesis involving the reaction of in situ formed 17b[OTf] with MeOTf and subsequent deprotonation with LDA. Cation 35 acts as a two-electron donor as confirmed by the isolation of the AuCl complex 36[OTf].

The isolation of the first NHC salts does impact the broad field of NHC chemistry since it allows the design of new charged systems (Chart 1). Thus, the opportunity of including a variety of different onio-substituents (phosphines, amines, pyridines etc.) allows for the introduction of additional cationic charges in 4/5-position. This should have a tremendous influence on the reactivity of the resulting carbenes which was already shown by a in situ formed pyridinio-substituted NHC derivative. The introduction of a stereogenic center is feasible by the variation of the substituents at the phosphonium center, the substituents of the N atoms in the heterocycle, as well as the choice of counter-ions which makes the resulting systems interesting candidates for stereoselective transition metal or organo catalysis.

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Chart 1 Possible variations for a new class of NHC systems.
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