A persistent *P*,*N*-heterocyclic carbene†

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Conjugate acids of cyclic (amino)(phosphino)carbenes (P-NHCs) have been prepared, and several different processes have been observed during their deprotonation, which include the formation of a metastable P-NHC, an azomethine ylide, and a bicyclic phosphirane.

Following the discovery of a distillable (phosphino)(silyl)carbene in 1988,[1] a variety of stable acyclic and cyclic carbenes have been prepared.[2] With the exception of bis(amino)cyclopropenylidenes,[3] all these carbenes feature at least one amino or phosphino group directly bonded to the electron-deficient center. Surprisingly, although cyclic diaminocarbenes (NHCs) **I**,[4] cyclic diphosphinocarbenes (PHCs) **II**,[5] and acyclic (amino)(phosphino)carbenes **III** have been isolated,[6] cyclic carbenes of type **IV** have eluded the synthetic skills of investigators (Fig. 1). Cyclic carbenes have found numerous applications as ligands for transition metal based catalysts,[7,8] as catalysts on their own rights,[9] and as initiators for polymerization.[10] In contrast, most acyclic carbenes are poor ligands or give fragile complexes with transition metals,[11] probably because of large carbene bond angles (120–153°).[12,13] The only notable exceptions are the (amino)(phosphino)carbenes **III**, which allow for different coordination modes.[14] Here we report our efforts towards the synthesis of cyclic (amino)-(phosphino)carbenes (P-NHCs), which should feature the advantages of cyclic carbene systems, and the different coordination modes already described for their acyclic analogues.

We have recently shown that conjugate acids of cyclic bis(amino)carbenes (NHC,H$^+$s), (amino)(thio)carbenes and (alkyl)(amino)carbenes can be readily prepared by the addition of a compound featuring two leaving groups to 1,3-diaza-allyl-, 1,3-azathio-allyl and 1-aza-allyl anions, respectively.[15] By analogy, phosphaformamidinates **1**,[16] prepared by deprotonation of the corresponding phosphaformamidines with butyllithium in diethyl ether, appeared to be potential starting materials for the desired P-NHC precursors. Indeed, when the lithium phosphaformamidinate **1a** was treated with an excess (4–6 eq.) of 1,3-dibromopropane in Et_2O, the P-substituted phosphaformamidine **2a** was obtained as a light yellow oil in 90% yield (Scheme 1). A THF solution of **2a** was then heated at 40 °C for 18 h, and after workup, the cyclic salt **3a** was isolated as a white powder in 85% yield. The down field ^{1}H (d, 8.3 ppm, J_{PH} = 6.9 Hz) and ^{13}C NMR signals (d, 178.4 ppm, J_{PC} = 2.9 Hz) confirmed the iminium structure of **3a**. All attempts to deprotonate **3a** with a variety of strong bases (LDA, LiTMP, *etc.*) led to the cyclic alkene **4a**, which was isolated in 75% yield. Interestingly monitoring the deprotonation reaction in THF at −60 °C, by multinuclear NMR spectroscopy, showed the disappearance of the starting material **3a**, and the clean formation of a new product, tentatively identified as the cyclic azomethine ylide **5a**,[17] instead of the desired P-NHC. Indeed, the ^{13}C NMR spectrum shows two CH signals at 89.7 (d, J_{PC} = 26.9 Hz) and 103.8 ppm (s), and no signal at low field as expected for a carbene. Note, that the formation of a transient azomethine ylide has already been postulated in the deprotonation of (amino)(aryl)carbenes.[18] Warming up the solution to room temperature afforded again the alkene **4a**, which probably results from the intermolecular deprotonation of the carbon at the β-position of N by the negatively charged azomethine ylide carbon.

These results suggest that the electropositivity of phosphorus decreased the acidity of the iminium proton of **3a**, and favored the deprotonation at the α′ position of nitrogen. Therefore, we first chose to protect this position by a methyl substituent. However, deprotonation of iminium **3b** yielded again the corresponding alkene **4b**.

It is well recognized that bulky substituents decrease the inversion barrier at phosphorus, but also at nitrogen.[19] Consequently, the lone pair of the nitrogen becomes parallel with the vacant orbital of the adjacent electron-deficient species, which allows for maximum donation. This should result in an increase acidity of the iminium proton and stability of the ensuing carbene. Therefore, we replaced the mesityl group of **3b** by a 2,6-diisopropylphenyl group (Dipp). In order to expedite the synthesis, lithium phosphaformamidinate **1c** was reacted with 1,3-dibromobutane in THF at 70 °C (Scheme 2).

However, two products were isolated from the reaction, the expected salt **3c** along with derivative **3c′** (40/60 ratio) in which the methyl group is in α-position of the phosphorus atom. Both compounds have been characterized by X-ray

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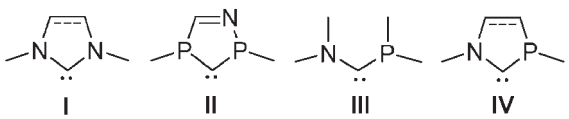
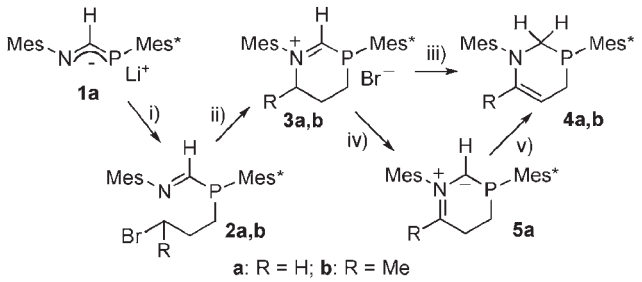
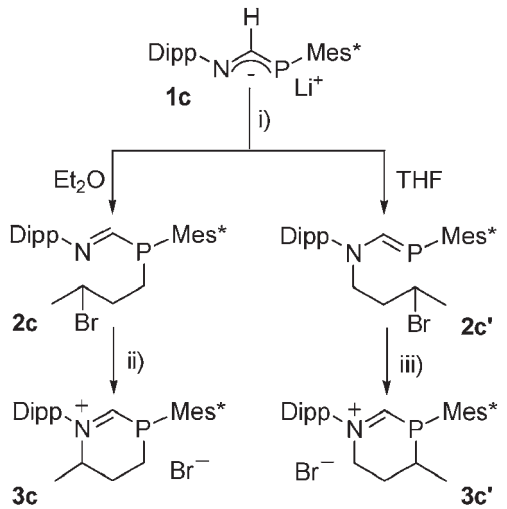


Fig. 1



Scheme 1 *Reagents and conditions*: (i) 1,3-dibromopropane, Et_2O, R.T., 14 h; (ii) for **2a**: THF, 40 °C, 18 h; for **2b**: THF, 70 °C, 6 h; (iii) LDA, THF, −78 °C, 1 h; (iv) LiHMDS, THF, −78 °C; (v) THF, R.T., 1 h.



Scheme 2 *Reagents and conditions*: (i) 1,3-dibromobutane, R.T., 14 h; (ii) THF, 50 °C, 48 h; (iii) THF, 70 °C, 72 h.

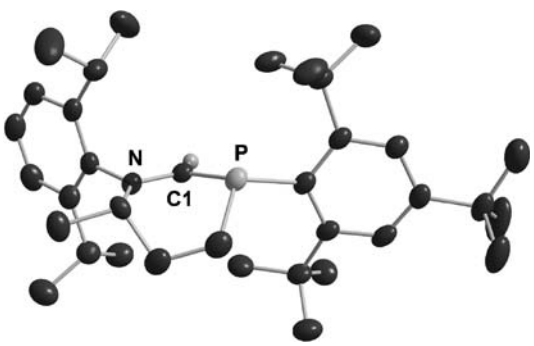
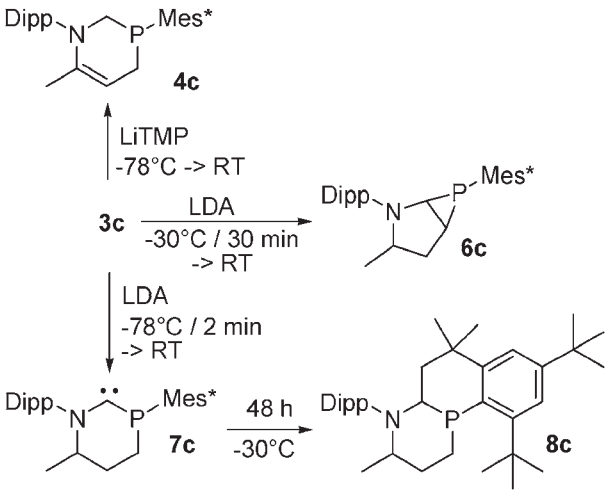


Fig. 2 Molecular structure of compound **3c** in the solid state (hydrogen atoms, except this for C1 are omitted for clarity; ellipsoids are drawn at 50% probability).

diffractions studies, and the molecular structure of **3c** is shown in Fig. 2. The C1–N bond distance [1.302(6) Å] is typical for an NC double bond, and the C1–P bond length [1.761(5) Å] is halfway between those expected for single and double bonds, and significantly longer than in PHC,H^+s (1.69–1.72 Å). Since the phosphorus center is much more pyramidalized (sum of angles: 330°) than in PHC,H^+s (348–354°), one can conclude that the nitrogen and phosphorus lone pairs strongly and poorly interacts, respectively, with the cationic carbon center. The non-selectivity leading to **3c**,**c′** can be avoided by using



Scheme 3

diethyl ether as the solvent for the coupling reaction of **1c** with 1,3-dibromobutane. Then, heating a THF solution of **2c** at 50 °C for 48 h afforded **3c** in 89% isolated yield.

We first used LiTMP in Et_2O at −78 °C to deprotonate salt **3c**. After the solution was warmed to room temperature, and after workup, the cyclic alkene **4c** was isolated as a yellow solid in 76% yield (Scheme 3). In marked contrast, when LDA was added to a THF solution of **3c** at −78 °C, the reaction mixture stirred at −30 °C for 30 min and then warmed to room temperature, bicyclic phosphirane **6c** was obtained in 84% yield, as a 70 : 30 mixture of diastereomers. The three-membered ring structure was apparent from the high field ^{31}P NMR signals (−151 and −175 ppm),[20] and unambiguously confirmed by a single-crystal X-ray diffraction study of the major isomer. Note that compared to **3c** and **3c′**, the phosphorous atom in **6c** is highly pyramidalized (sum of the angles ∼244°), but this is usual for phosphiranes.[20] The formation of **6c** implies that the deprotonation occurs at the CH_2-group in α′-position of the phosphorous atom of **3c**, and this surprisingly result has not yet been explained.

Monitoring the previous reaction by ^{31}P NMR spectroscopy, we observed a small signal at −32.8 ppm, which was replaced after a few hours at room temperature by a signal at −68.4 ppm. Therefore, we carried out the deprotonation reaction of **3c** with LDA under various experimental conditions. The best results were obtained, when the reaction mixture was kept for only 2 min at −78 °C, and rapidly warmed up to room temperature. In this case the ^{31}P NMR spectrum showed mainly the signal at −32.8 ppm (>90%). Importantly, in the ^{13}C NMR spectrum there was a doublet at very low field (314.5 ppm, J_{PC} = 122 Hz) in the range expected for the carbene carbon of the desired P-NHC **7c**, the acyclic (amino)(phosphino)carbenes **III** appearing between 320 and 348 ppm (J_{PC} = 22–101 Hz).[6]

Note that the carbene carbon chemical shift for **7c** is much further downfield shifted than those observed for both NHCs **I** (205–245 ppm)[2] and PHCs **II** (184 ppm),[5] but comparable with those for cyclic (alkyl)(amino)carbenes (304–320 ppm).[21] This implies that the phosphorus center plays the role of a spectator substituent, as observed in the acyclic version **III**. All attempts to obtain single crystals of carbene **7c** failed. After

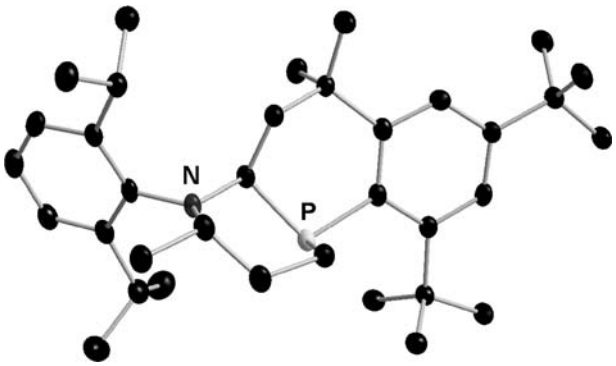


Fig. 3 Molecular structure of derivative **8c** in the solid state (hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50% probability).

two days at −30 °C, compound **8c** resulting from the carbene insertion into the CH bond of a *tert*-butyl group was obtained quantitatively, and characterized by an X-ray diffraction study (Fig. 3).

These results as a whole are very surprising. In contrast to the imidazolidinium salts (NHC,H^+s), the conjugate acids of P-NHCs can undergo deprotonation at the iminium carbon, but also in position α' of the nitrogen and phosphorus centers. The kinetic instability of the P-NHC **7c** contrasts with the high stability of NHCs **I**, PHCs **II**, and even acyclic (amino)-(phosphino)carbenes **III**, and this is not yet understood. In the hope of isolating cyclic (amino)(phosphino)carbenes, the synthesis of an unsaturated five-membered ring version is under active investigation.

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