Abnormal N-Heterocyclic Carbenes

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Synthesis of an Imidazolium Phosphanide Zwitterion and Its Conversion into Anionic Imidazol-2-ylidene Derivatives**

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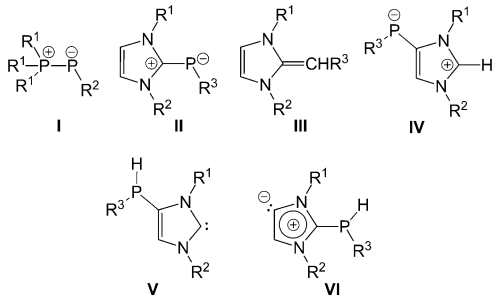
Dedicated to Professor Anthony J. Arduengo III

The development of isolable phosphorus species with low coordination numbers continues to play a central role in main group chemistry because of their inherently high reactivity, which presents unique synthetic challenges, and their potential application as molecular synthons. The first report on a zwitterionic compound having a low-coordinate phosphanide and a phosphonium center in a common bonding environment,[1] that is phosphoranylidene phosphanes (**I**),[2] appeared as early as 1961. Despite the clear relationship to Wittig ylides[3] and other mixed-valence compounds,[4] it took three decades before end-on metal complexes of **I** had been used as phosphinidene transfer reagents in phospha-Wittig reactions.[5] More recently, it was shown that imidazolium units,[6] derived from N-heterocyclic carbenes (NHCs),[7] can formally replace the phosphonium unit in **I** to create **II**, which has been considered as an NHC–phosphinidene adduct.[8] This formal substitution might also be regarded as the beginning of a new stabilization strategy that led to a series of interesting NHC adducts of P_2,[9] Si_2,[10] and B_2,[11] as well as other low-coordinate main group element species.[12] Interestingly, **II** represents the phosphorus analogue of the "deoxy-Breslow intermediate" (**III**),[13–15] which is a key structure in Umpolung reactions, for example, in C–C bond formation,[16] and, hence, might also be inspiring with respect to **II**. In light of the recently explored concept of "abnormal N-heterocyclic carbenes" (aNHCs),[17,18] the zwitterionic compound **IV** can be considered a highly interesting target, which also holds true for the tautomeric forms of **V** and **VI** (Scheme 1).



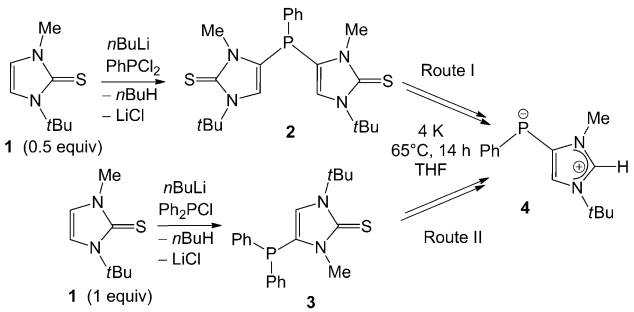
Scheme 1. Zwitterionic phosphorus species **I**–**IV** as well as tautomers **V** and **VI** (R^1,R^2,R^3 = organic substituent).

Recently, the first derivatives of **V** were reported[19] and these can also serve as bridging ligands for transition metals;[20] they had previously been demonstrated for the first time for η^5,η^1-NHCs ligands derived from annulated cyclopentadienido imidazolium salts.[21]

Herein, the syntheses of a novel zwitterionic species of type **IV**, its conversion into anionic imidazol-2-ylidenes, and ab initio studies on the stability and electronic structure of various isomers of **II**–**VI** are reported.

Following the new method for P-functionalization of the imidazole-2-thione backbone,[22] the imidazol-2-thion-4-yl-substituted phenyl phosphanes **2** and **3** were synthesized from **1** and treated with a fourfold excess of potassium (Scheme 2). Surprisingly, neither a free NHC derivative (by thione reduction) nor a normal phosphanide derivative (by reductive P,C bond cleavage) was obtained in either reaction (routes I and II), instead the novel zwitterionic compound **4** was formed.

In the case of the second route (**3**→**4**), a resonance at $\delta = -9.4$ ppm was detected in the $^{31}P\{H\}$ NMR spectrum of the reaction solution. This signal is assigned to $K[PPh_2]$,[23] but no



Scheme 2. Synthesis of zwitterionic imidazolium phosphanide **4**.

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further information on the reaction course(s) was obtained. Compound **4**, obtained by crystallization, showed a resonance at $\delta = -73.6$ ppm (t, $^3J_{P,H} = 5.4$ Hz) in the ^{31}P NMR spectrum as well as other diagnostic NMR spectroscopic resonances: C2 ($\delta = 140.8$ ppm), C4 ($\delta = 138.9$ ppm; d, $^1J_{P,C} = 61.4$ Hz), and C2-H ($\delta = 7.02$ ppm). The X-ray structure confirmed the molecular constitution of the zwitterion **4** (Figure 1), which contains both an imidazolium and a dicoordinate phosphanide center.

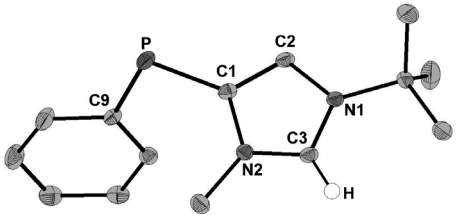
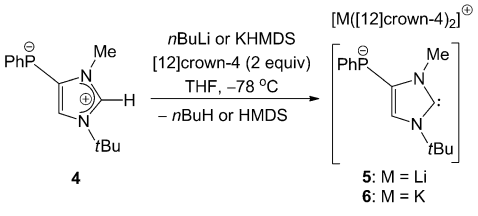


Figure 1. Molecular structure of compound **4** in the solid state. Hydrogen atoms (except C2-H) have been omitted for clarity (50% probability level). Selected atom distances [Å] and bond angles [°] for compound **4**: C1-N2 1.412(19), C2-N1 1.386(19), P-C1 1.8068(16), P-C9 1.8107(16), C1-C2 1.359(2), C3-N1 1.330(2), C3-N2 1.329(2); N2-C3-N1 108.92(14), N2-C1-C2 104.04(12), C9-P-C1 101.07(7).

The P–C bond lengths (P–C1 1.8068(16) Å and P–C^{Ph} 1.8107(16) Å) are similar to the P–C bond lengths of **II** (R^1, R^2 = Mes, R^3 = Ph; with 1.763 Å and 1.839 Å, respectively).[8b] The slight difference is likely to be attributable to the different rotational position of the phenyl substituents at the phosphorus atom (see discussion in the Supporting Information). Although the plane of the phenyl ring (containing the C9 atom) is perpendicular to the imidazolium ring in **4**, the *ipso* carbon atom of the phenyl ring in **II** (R^1, R^2 = Mes, R^3 = Ph) is coplanar to the imidazolium ring.[8b] The N1-C3-N2 bond angle of 108.92(14)° is in the typical range of the P-functionalized imidazolium salt reported earlier.[19c,d] The N2-C1-C2 bond angle of 104.04(12)° is larger than that reported for a crystalline aNHC (101.03(17)°).[18]

There is growing interest in the structural diversity of NHCs, in general, and anionic NHC derivatives,[12e,24] in particular. Therefore, **4** was deprotonated using *n*BuLi or potassium hexamethyldisilazide (KHMDS) in the presence of two equivalents of [12]crown-4 (Scheme 3); the obtained products **5** and **6** displayed signals at $\delta = -66.1$ ppm (t, $^3J_{P,H} =$ 5.4 Hz; **5**) and $\delta = -65.7$ ppm (t, $^3J_{P,H} = 5.1$ Hz; **6**) in the ^{31}P{^{1}H} NMR spectrum. The identification of signals at $\delta =$ 212.8 ppm ($^{3+4}J_{P,C} = 2.0$ Hz; **5**) and 212.5 (br s; **6**) in the ^{13}C{^{1}H} NMR spectrum is consistent with the presence of the



Scheme 3. Synthesis of P-anionic NHC derivatives **5** and **6**.

C2 nuclei of the anionic NHC derivatives **5** and **6**; signals at $\delta = 140.3$ ppm (d, $^1J_{P,C} = 66.5$ Hz; **5**) and $\delta = 140.4$ ppm (d, $^1J_{P,C} = 66.6$ Hz; **6**) were assigned to the C4 nuclei. It is evident from the solution ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra that the nature of the cation does not influence the chemical shift significantly of the carbene carbon or the phosphanido centers, thus indicating the existence of **5** and **6** in solution as separated ion pairs.[25]

The X-ray structure of the potassium salt (Figure 2) shows that **6** exists as a monomer in the solid state, with the potassium atom bound to the carbene carbon atom as well as

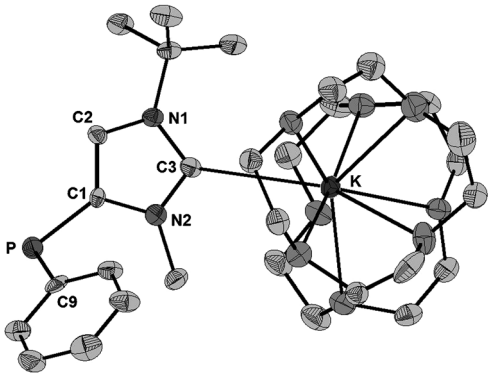
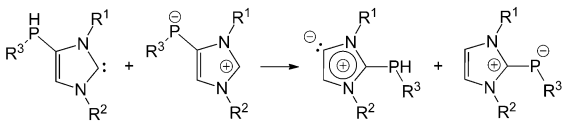


Figure 2. Molecular structure of compound **6** in the solid state. Hydrogen atoms have been omitted for clarity (50% probability level). Selected atom distances [Å] and bond angles [°] for compound **6**: C1-N2 1.431(8), C2-N1 1.389(8), P-C1 1.823(6), P-C9 1.800(6), C1-C2 1.369(8), C3-N1 1.385(8), C3-N2 1.354(8); N2-C3-N1 102.1(5), N2-C1-C2 103.4(5), C9-P-C1 103.3(3).

to two [12]crown-4 molecules. Despite being monomeric, the C3-K distance of 3.066(6) Å falls in the typical range of K-$C^{carbene}$ interactions found in the literature for polymeric potassium–imidazol-2-ylidene complexes.[26] The P–C1 bond of 1.823(6) Å is slightly longer than the P–C9 bond (1.800(6) Å), which is different from the situation in **4**. The most apparent change in the geometry of the imidazole ring was seen from the N1-C3-N2 bond angle of 102.1(5)° versus 108.92(14)° (in **4**), thus confirming the formation of a imidazol-2-ylidene.[8b] The N1-C3-N2 bond angle of 102.1(5)° and the N2-C1-C2 bond angle of 103.4(5)° are larger than was reported for an anionic N-heterocyclic dicarbene (NHDC; 100.5(2)° and 99.8(2)°, respectively).[12f]

Computations (for details see the Supporting Information) reveal that several close-lying rotational minima exist for **4** and the rotational barriers are small. The same holds true for other ylidic compounds, such as **II**, the deoxy-Breslow intermediate **III**,[27,28] and methylene-phosphorane $H_3P{=}CH_2$.[29] Further calculations (at different levels of theory, see the Supporting Information) on the isomeric structures revealed that **II** is the most stable structure for the parent system (R^1, R^2, R^3 = H), while **V** and **IV** are less stable by 16.6 and 18.6 kcal mol^{-1}, respectively, and **VI** is even more destabilized (34.8 kcal mol^{-1} less stable than **II**; Scheme 4).

The isodesmic reaction is nearly thermoneutral for the parent system (R^1, R^2, R^3 = H), thus indicating that the energy difference between structures of types and **II** and **IV** is equal



Scheme 4. Isodesmic reaction to compare the stability of inversely polarized ylides with the corresponding NHCs.

to the energy difference between the isomeric NHC and the aNHC derivative. These findings also indicate that the strength of the P–C bond is similar in the two inversely polarized ylidic compounds **II** and **IV**. With $R^1 = Me$, $R^2 = t$Bu, $R^3 = Ph$, the stability ordering of **IV** and **V** is reversed, and **IV** is more stable than **V** by 0.9 kcal mol^{-1}. In agreement with this stability ordering, no structure of type **V** was detected in the reaction mixture. Also, as a consequence of the apparently easy H shift,[30] compound **4** can easily react in its tautomeric form **V**, which might result in an interesting and complex reactivity. Substituents on the phenyl group with a +M effect stabilize **V** (see Table S2 in the Supporting Information). With the more bulky substituents on the nitrogen atom, the molecules at the right hand side of the isodesmic reaction are destabilized (see Figure S1 in the Supporting Information), most likely because of the effect of the steric encumbrance between the neighboring substituents.[31] To investigate the extent of the delocalization within the imidazolium ring the NICS(1),[32] Bird,[33] and BDSHRT[34] aromaticity measures were compared for **II**, **IV**, **V**, and **VI**. This study showed that the inversely polarized ylidic (zwitterionic, charge separated) compounds **II** and **IV** exhibit similar aromaticity, which is somewhat reduced with respect to the carbenes **V** and **VI** (Table 1).[15]

Table 1: Aromaticity of the investigated compounds (R^1, $R^2 = Me$, $R^3 = H$).

	II	IV	V	VI
NICS(1)	−6.7	−4.3[a]	−5.7	−8.3
Bird Index	59	52	67	74
BDSHRT	46	43	48	45

[a] Data from Ref. [28].

Accordingly, zwitterionic **4** (analogous to the type **II** isomeric structures) belongs to the inversely polarized zwitterionic P=C compounds, despite the fact that its bonding structure cannot be described by conventional single and double bonds. Its ylidic nature is reflected by the 9.6 Debye dipole moment and an extremely low ionization energy (IE): the adiabatic IE (the electron being removed from a lone pair type orbital on the phosphorus atom—see the Supporting Information) has been calculated to amount to 5.1 eV for **4**,[35] which is even lower by 0.3 eV than the IE of its "classical" isomer **II** ($R^1 = Me$, $R^2 = t$Bu, $R^3 = PPh$) and 1.2 eV lower than $(H_3C)_3P{=}CH_2$.

A facile synthetic approach has enabled access to the first example of a novel zwitterionic species that can formally be described as an adduct of an abnormal NHC and a phosphinidene. This was converted into corresponding first anionic P-functional imidazol-2-ylidenes, which might also be regarded as a phosphinidene adduct of an anionic N-heterocyclic dicarbene (NHDC). This will hopefully enable future systematic studies on P derivatization, in particular, as well as a wealth of coordination chemistry and adduct formation, in general.

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