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N-Heterocyclic Carbenes

Stabilization of Unsymmetrically Annelated Imidazol-2-ylidenes with Respect to Their Higher Group 14 Homologues by n-/π-HOMO Inversion**

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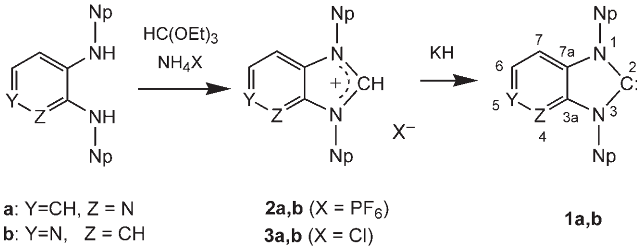
N-heterocyclic carbenes (NHCs)[1] are attracting much current attention not only as versatile ligands in transition-metal coordination chemistry and catalysis,[2] but also as nucleophiles in main-group-element chemistry,[3] organocatalysis, and organic synthesis.[4] The high stability of imidazol-2-ylidenes has also stimulated research in the higher Group 14 homologues.[5] To modify the ligand properties, various carbo- and heterocyclic annelated imidazole-2-ylidenes[6–10] have been studied, as have related N-heterocyclic silylenes,[11] germylenes,[12] and stannylenes.[13] Annelation significantly influences the stability[7] and the σ-donor/π-acceptor ligand properties[10] of carbenes and may be a tool for tuning their electronic properties. For the heavier homologues, the influence of annelation is different. Benzo- and naphthoannelation is stabilizing.[14] However, within a series of pyrido[*b*]-annelated N-heterocyclic silylenes, germylenes, and stannylenes, the kinetic stability strongly decreases in the order Sn > Ge > Si, and related pyrido[*c*]-annelated species were not accessible under the same conditions despite comparable thermodynamic stability.[11b] We have now investigated homologous pyridoannelated NHCs **1a**,**b** and found that they do not follow the above trend but are kinetically stable. This resembles the stability of the unsymmetric triazol-2-ylidene reported by Enders et al.[15] or pyrido[*a*]-annelated NHCs.[9] To understand the differences between the carbenes and their higher homologues, the experimental work was combined with a theoretical study.

Two synthetic routes to annelated NHCs are known: the reduction of thione precursors[6a,b,8] and the deprotonation of annelated imidazolium salts.[6a,b,7–10] The second strategy—cyclocondensation of diaminopyridines with triethyl orthoformate in the presence of NH$_4$X (X = PF$_6$ or Cl) to pyridoimidazolium salts **2a**,**b** or **3a**,**b** and deprotonation with potassium hydride in THF (Scheme 1)—is very efficient and furnishes both **1a** and **1b** in high yield (88 and 84 %). For purification the carbenes can be distilled in high vacuum.[16]



Scheme 1. Syntheses of **1**–**3**; Np = neopentyl.

The structure elucidation of **1**–**3** is based on NMR and high-resolution mass spectrometric (HRMS) data. The resonances of the divalent carbon (C$^{\mathrm{II}}$) atoms of **1a** and **1b** (δ = 235.2, 235.8 ppm) appear downfield from the C$^{\mathrm{II}}$ signal of dineopentylbenzimidazol-2-ylidene (δ = 231–232 ppm)[6a,b,8a] but upfield from that of dineopentylnaphtho[*b*]imidazol-2-ylidene (δ = 239 ppm).[8a] To elucidate the reason for the different properties and stabilities of **1a**,**b** and their heavier Group 14 homologues, the electronic structure was investigated by photoelectron (PE) spectra[17] of **1a** and **1b** (Figure 1) and comparison with calculated orbital ionization energies of pyrido[*b*]- and pyrido[*c*]-annelated *N*,*N'*-di-*tert*-butyl model compounds (the N-heterocyclic carbenes **4a**,**b**, silylenes **5a**,**b**, and germylenes **6a**,**b**). For a more general view, the analogous benzoannelated NHC **1c** and the model compounds **4c**–**6c** were included into this study. The structures were optimized at the B3LYP/cc-pVTZ level of theory, and the stationary points were characterized by second-derivative calculations using the same models. To interpret the PE spectra, the recorded vertical ionization energies (IP$_v$) were compared with calculated ionization potentials obtained at the ROVGF/cc-pVDZ level of theory on the optimized geometry.[18] The experimentally determined vertical ionization energies of **1a**–**c** and the first five values of the calculated ionization energies of **4a**, **5a**, and **6a**, relevant for the PE spectra, are compiled in Table 1.

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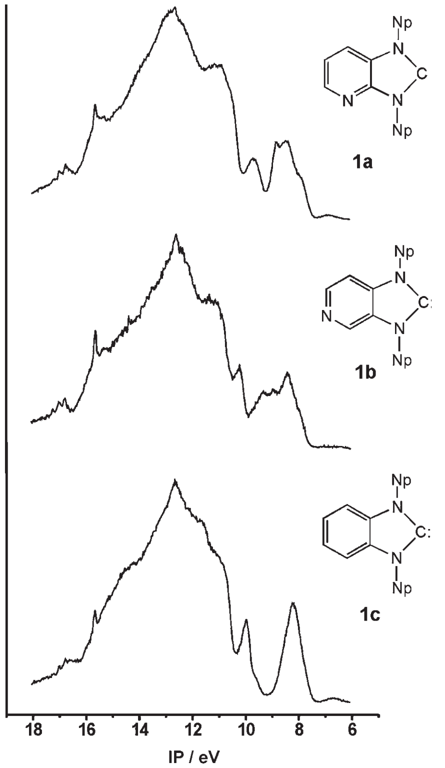


Figure 1. HeI-photoelectron spectra of **1a**, **1b**, and **1c**.

Table 1: Experimental ionization potentials (IP_v) of **1a–c** and calculated[a] ionization energies (in eV) of model compounds **4a–c**.

Assignment	**1a** (**4a**)	**1b** (**4b**)	**1c** (**4c**)
n_C	7.9 (7.72)	8.0 (7.83)	7.9–8.5 (7.57)
$\pi_{\text{an. ring}}+\pi_{\text{imidazole}}$	8.48 (8.20)	8.38 (8.22)	7.9–8.5 (7.82)
$\pi_{\text{an. ring}}-n_N$	8.79 (8.58)	8.9 (8.57)	7.9–8.5 (7.98)
n_N	9.65 (9.53)	9.3 (9.53)	–
$\pi_{\text{an.ring}}+n_N$	– (10.41)	10.13 (10.15)	9.89 (9.83)

[a] In parentheses, ROVGF/cc-pVDZ.

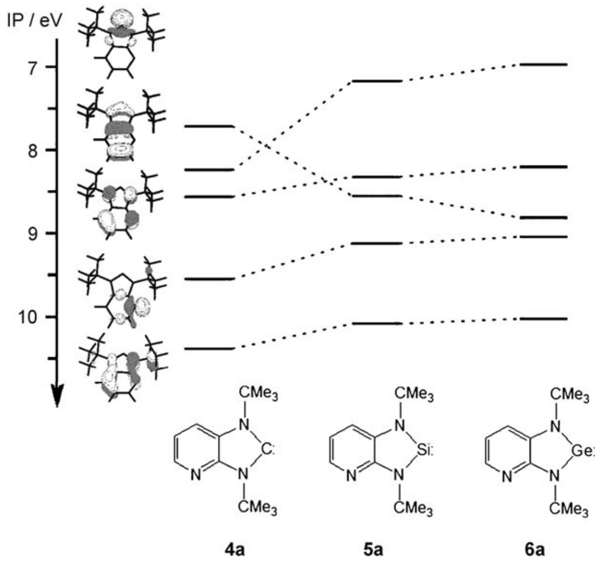
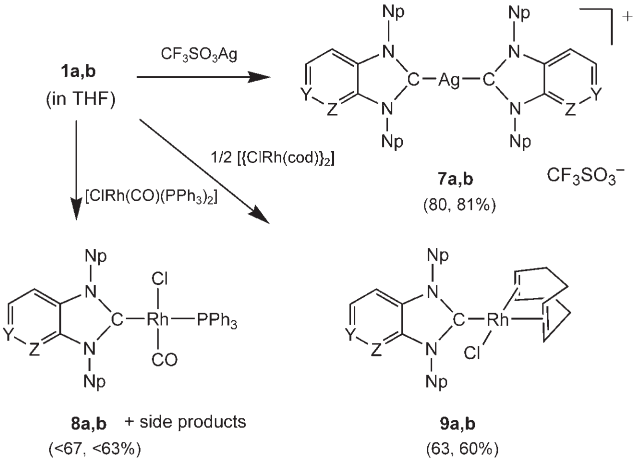


Figure 2. IP correlation scheme of model compounds **4a**, **5a**, and **6a**.

The band assignment and relationship of molecular orbitals (MOs) in annelated N-heterocyclic carbenes, silylenes, and germylenes are illustrated by the MO correlation Scheme for **4a**, **5a**, and **6a** (Figure 2). The MO correlation schemes for **4b**, **5b**, **6b** and **4c**, **5c**, **6c** are similar.[16] The HOMO−2 assignment of the lone pair of electrons at silicon was experimentally demonstrated by PE spectroscopic studies of *N,N'*-dineopentylpyrido[*b*]- and benzoannelated 1,3,2-diazasilol-2-ylidene and a dihydro derivative of the latter.[11b,19] The orbital correlations show for the highest occupied MOs an inverse order of n and π orbitals for the NHCs with respect to their higher homologues. In the latter, two π orbitals are higher in energy than the lone electron pair at the divalent atom. In non-annelated symmetric di-*tert*-butyl-imidazol-2-ylidene and its homologues, a similar n/π inversion (one π orbital above the n orbital in the silylene and germylene) was observed.[20] Thus, this HOMO inversion can be generalized and provides evidence that orbital-controlled reactions will be different for NHCs and their higher homologues. While non- and benzoannelated NHC homologues with symmetric π-charge density maintain their kinetic stability or are even stabilized by an increased weight of an *ortho*-quinone–diimine resonance structure,[14] strong unsymmetric π-charge distribution in the π HOMO of pyrido[*c*]-annelated silylenes,[11b] germylenes, and stannylenes dramatically enhances the reactivity and destabilizes these compounds compared to the respective benzoannelated species. Pyrido[*b*]-annelated N-heterocyclic silylenes, germylenes, or stannylenes with a nodal plane through the pyridine N atom are less destabilized and isolable at room temperature.[11b]

The orbital-correlation diagrams show furthermore that the ionization potentials for the lone electron pair of the novel pyridoannelated NHCs are much lower than those of the higher homologues. This property results in much higher basicity and nucleophilicity at the divalent carbon atom compared to Si^{II} and Ge^{II} and controls the reactions of the novel annelated carbenes. There are so far no hints of any effects by unsymmetric π-charge distribution or the lone pair of electrons at the nitrogen atom. As a first probe of the reactivity we studied reactions of **1a** and **1b** with transition-metal compounds as electrophiles. Late transition metals are known to coordinate to carbenes and pyridines as well as to catalyze reactions with π systems and thus may be suitable indicators for reaction control. Furthermore, novel NHC complexes are of potential interest as transition-metal catalysts, by the presence of a second donor group (here the free N-basic site at the pyridine ring) also as building blocks for inorganic–organic hybrid materials. Reactions with silver triflate, $[RhCl(CO)(PPh_3)_2]$, or $[\{RhCl(cod)\}_2]$ (cod = cyclooctadiene) in THF at room temperature (12–15 h) afforded the pyrido-NHC complexes **7a,b–9a,b** (Scheme 2) in good yields, each with coordination only at the carbene site. The structures are evident by multinuclear solution NMR data with typical one-bond $J_{\text{metal,C}}$ coupling constants, and by X-ray crystal structure analysis of **9a** and **9b**.[16] With $[RhCl(CO)(PPh_3)_2]$ small amounts of side products are observed in the



Scheme 2. Syntheses of **7**–**9**.

^{31}P NMR spectra, a rhodium–bis(phosphine) and the Wilkinson complex, thus indicating competing reactions.

The slightly distorted square-planar coordination at the Rh^{I} center by the two C=C groups of 1,5-cod, the chloride ligand, and the carbene ligand with its ring plane oriented almost perpendicular to the coordination plane (typical for [RhCl(NHC)(cod)] complexes) is maintained in **9a** (Figure 3) and **9b**. No intermolecular contacts between the Rh center and the pyridine nitrogen atom are observed.[16] The donor strengths of **1a** and **1b** are characterized by the hypsochromic shift of the CO bands of **8a** and **8b** ($\nu_{CO} = 1964.9$ and 1965 cm^{-1}, vs) compared to that of [ClRh(IMes)(PPh$_3$)(CO)] ($\nu = 1944$ cm^{-1}; IMes = dimesitylimidazol-2-ylidene).[21] This observation indicates a decrease compared to the donor strength of dimesitylimidazol-2-ylidene, which, since the effect of the different N substitution is opposite, may be attributed mainly to the electron-withdrawing effect of the pyridoannelation.

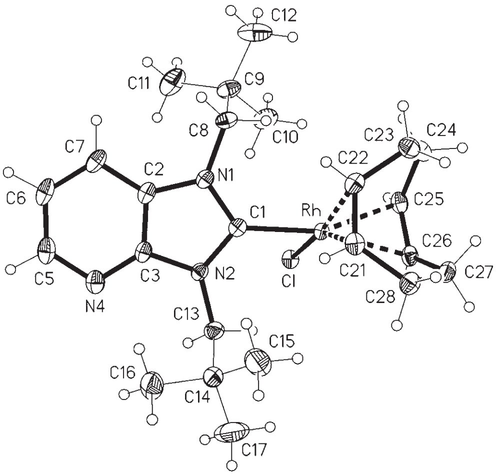


Figure 3. Molecular structure of **9a** (ellipsoids with 50% probability).[16]

In summary, novel pyrido[*b*]- and pyrido[*c*]-annelated *N*,*N'*-dineopentylimidazol-2-ylidenes were synthesized and show distinct properties and reactivity compared to heavier Group 14 homologues.[11b] Theoretical studies allow to explain these distinctions by the different nature of the HOMOs, a C^{II} lone pair of electrons for the NHCs providing high nucleophilicity, and a π state for the higher homologues, in which the symmetry of the π-electron distribution has a strong influence on the reactivity and kinetic stability. These findings lead us to conclude that unsymmetric NHCs are much less destabilized by low symmetry than heavier Group 14 homologues, and enables broad variations in ligand tuning of annelated imidazol-2-ylidenes, whereas the access to heavier Group 14 homologues will be limited to the more symmetric compounds.

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