

## 1,3-Bis(*N,N*-dialkylamino)imidazolin-2-ylidenes: Synthesis and Reactivity of a New Family of Stable *N*-Heterocyclic Carbenes

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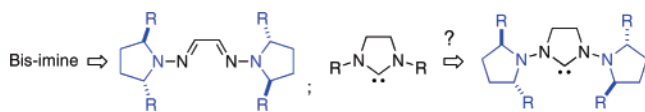
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Since the discovery of a stable, crystalline *N*-heterocyclic carbene by Arduengo and co-workers,<sup>1</sup> the chemistry of these compounds has been studied intensively,<sup>2</sup> a good part of the interest being a consequence of their excellent properties as transition metal ligands.<sup>3</sup> Their well-established resistance toward dissociation is of particular importance in the field of asymmetric catalysis, but despite the intensive research in this area, only a few efficient enantioselective catalysts based on chiral carbene ligands are known;<sup>4</sup> therefore, novel strategies for the introduction of chirality into these systems are required.

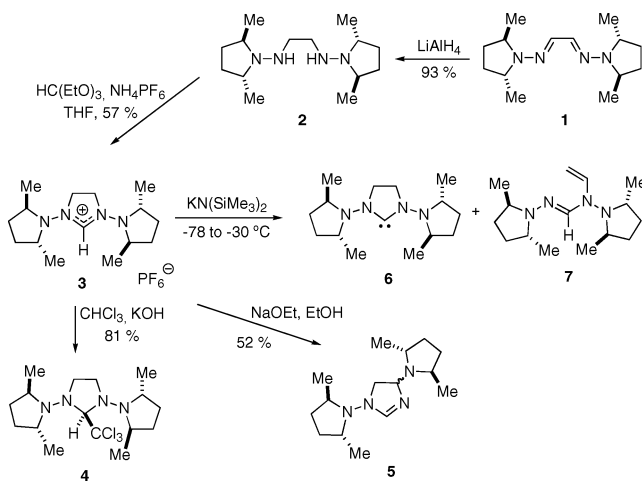
Much work has focused on the study of structure–reactivity relationships in diaminocarbenes. Thus, useful information has been collected about the influence of several structural factors, including the steric bulkiness around the carbene carbon,<sup>5</sup> the presence of electron-withdrawing groups in the imidazole backbone<sup>6</sup> or in *N*-aryl substituents,<sup>7</sup> and the presence or absence of unsaturation at the C4–C5 bond in the imidazole/dihydroimidazole series.<sup>8</sup> Other reported families of stable carbenes include those containing six-membered rings,<sup>9</sup> acyclic systems,<sup>10</sup> and different heterocyclic derivatives such as 1,3,4-triazol-2-ylidenes<sup>11</sup> and benzimidazol-2-ylidenes.<sup>12</sup> Surprisingly, there is no information about the effect of *N*-alkoxy or *N*-amino groups on the diaminocarbene system. We wish to report herein the synthesis and reactivity of 1,3-bis(*N,N*-dialkylamino)imidazolin-2-ylidenes as a new class of stable heterocyclic carbenes and the first metal complexes derived therefrom.

We have recently reported the use of bis-hydrazones as a novel ligand class for the copper-catalyzed enantioselective Diels–Alder reaction.<sup>13</sup> The introduction of *C*<sub>2</sub>-symmetric chiral amines, making *N*–*N* bond rotations inconsequential, proved to be the key design element. In connection with that work, we decided to explore the introduction of a related structural motif and strategy in the field of stable diaminocarbenes.



Accordingly, glyoxal bis-hydrazone **1** was transformed into the desired dihydroimidazolium salt **3** by reduction ( $\text{LiAlH}_4$ ) to bis-hydrazine **2** and condensation with  $\text{HC}(\text{OEt})_3$  in the presence of  $\text{NH}_4\text{PF}_6$  (Scheme 1). The structure of **3**, an unprecedented class of dihydroimidazolium salt, was confirmed by X-ray diffraction analysis (see Supporting Information). Structural parameters such as the pyramidalization percentages of the pyrrolidine *N* atoms (71 and 77%), the  $\text{CNNC}(2)$  torsional angles (84.6°, 41.2°, 36.4°, and

Scheme 1



87.5°) and the *N*–*N* bond distances (140.0 and 140.2 pm) do not point toward a significant conjugation with the amidinium system.<sup>14</sup>

Several experiments were performed to explore the reactivity of **3**. Like its mesityl analogue,<sup>15</sup> **3** reacts with chloroform in the presence of  $\text{KOH}$  to afford the  $\text{CH}$  insertion product **4** in 81% yield. In contrast, heating with  $\text{NaOEt}$  in  $\text{EtOH}$  did not afford the expected  $\text{OH}$  insertion product, but instead gave dialkylamino 1,2-migration product **5** as a 9:1 mixture of diastereoisomers in 52% yield. Deprotonation of **3** was achieved with  $\text{KN}(\text{SiMe}_3)_2$  in  $\text{THF}$  at low temperature ( $-78 \rightarrow -30^\circ\text{C}$ ); removal of the solvent and extraction with  $\text{C}_6\text{D}_6$  afforded the expected free carbene **6** in solution, identified mainly by its characteristic  $^{13}\text{C}$  NMR  $\text{C}(2)$  resonance at  $\delta$  234.9 ppm. Interestingly, this peak persisted unchanged after several days at room temperature, thereby confirming the stability of the free carbene in solution. A minor amount ( $\sim 30\%$ ) of open-chain enamine **7** was also detected in the reaction. This air-sensitive compound was formed as the major product when the reaction mixture was warmed to room temperature in  $\text{THF}$ . For a preliminary evaluation of the properties of **6** as a ligand, **3** was treated with  $[\text{Rh}(\text{COD})\text{Cl}]_2/\text{KN}(\text{SiMe}_3)_2$  according to Herrmann's methodology<sup>16</sup> (Scheme 2). In this way, the expected  $\text{Rh}(\text{I})$  complex **8** was obtained in 55% yield after column chromatography. The  $^{13}\text{C}$  NMR spectrum of **8** shows the characteristic  $\text{C}(2)$  doublet at 217.1 ppm ( $J_{\text{Rh,C}} = 47.3$  Hz), and its X-ray diffraction analysis (Figure 1) confirmed a square-planar geometry [ $\text{C}(2)$ – $\text{Rh}$ – $\text{Cl}$  angle of  $90.8^\circ$ ], with a  $\text{C}(2)$ – $\text{Rh}$  distance of 200.7 pm and a  $\text{N}$ – $\text{C}$ – $\text{N}$  angle of  $106.1^\circ$ . To acquire additional information about the properties of **6** as a ligand, complex **9** was synthesized by reacting **8** with  $\text{CO}$ , and its  $\nu(\text{CO})$  stretching frequencies (2071 and  $1990\text{ cm}^{-1}$ ) were compared

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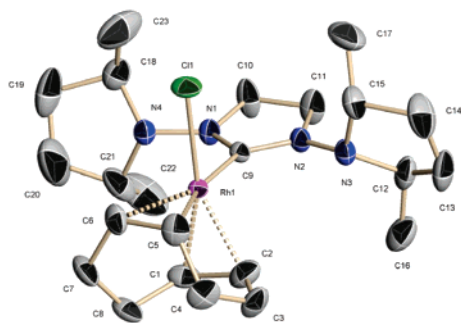
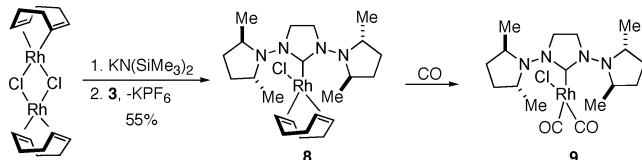
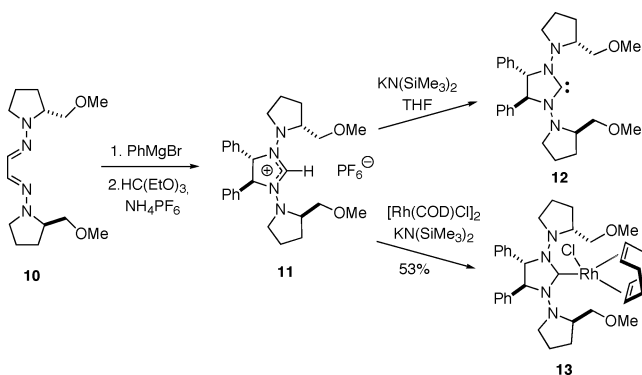


Figure 1. ORTEP drawing of **8**. Hydrogen atoms are omitted for clarity.

#### Scheme 2



#### Scheme 3. Alternative Strategy for Proline Derivatives



with previously reported data, indicating that the donor capacity of **6** is higher than for any other imidazolin-2-ylidenes,<sup>17</sup> approaching that of the best known donors.<sup>17,18</sup> This fact suggests a slight conjugative  $n \rightarrow \pi$  interaction by the exocyclic dialkylamino groups in solution.

A related strategy for the introduction of a chiral backbone into the target structures was also investigated using proline derivatives. Thus, addition of  $\text{PhMgCl}$  to glyoxal RAMP bis-hydrazone **10** afforded an air-sensitive bis-hydrazone, **11** which was directly reacted with  $\text{HC(OEt)}_3$  and  $\text{NH}_4\text{PF}_6$  to afford azolium salt **11** (Scheme 3). Assuming that the ring-opening side reaction (**3**  $\rightarrow$  **7**) proceeds via deprotonation at C(4) or C(5),<sup>24</sup> the presence of Ph groups at these positions in **11** should interfere with this process. In fact, treatment of **11** with  $\text{KN}(\text{SiMe}_3)_2$  afforded pure carbene **12**, characterized by its clean  $^{13}\text{C}$  NMR spectrum with the C(2) signal at  $\delta$  228.6 ppm.  $^1\text{H}$  and  $^{13}\text{C}$  NMR monitoring confirmed the stability of **12**, as no changes were observed after a week at room temperature. On the other hand, reaction of **11** with  $[\text{RhCl}(\text{COD})]_2/\text{KN}(\text{SiMe}_3)_2$  as above furnished complex **13** in 53% yield. The crystal structure of this compound (Figure 2) reveals close similarities [ $\text{C}(2)\text{--Rh--Cl} = 89.8^\circ$ ,  $\text{C}(2)\text{--Rh} = 203.1$  pm,  $\text{N--C--N} = 106.4^\circ$ ] with that of **8**.

We conclude that the introduction of exocyclic *N,N*-dialkylamino groups maintains many of the properties of imidazolin-2-ylidenes and even gives rise to a slightly improved  $\sigma$ -donor capacity. Consequently, the high structural variability of chiral dialkylamino groups offers promising possibilities for the introduction of tunable chiral environments into carbene-based metal catalysts.

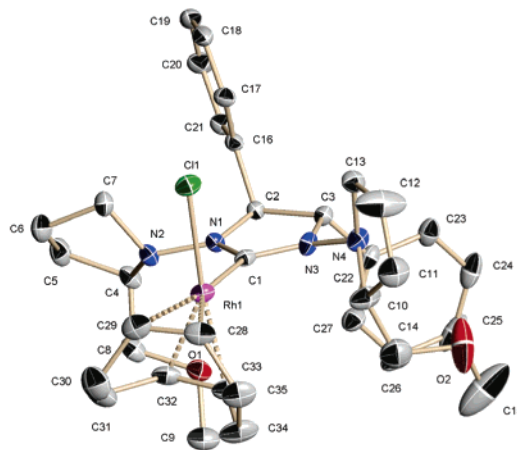


Figure 2. ORTEP drawing of **13**. Hydrogen atoms are omitted for clarity.

**Acknowledgment.** We thank the Ministerio de Educación y Ciencia (grant BQU2001-2376 and predoctoral fellowship to M.A.) and the European Commission (HPRN-CT-2001-00172 and HPMT-CT-2001-00248) for financial support.

**Supporting Information Available:** Crystallographic data for **3**, **8**, and **13** (CIF); experimental procedures and spectra for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0471119