

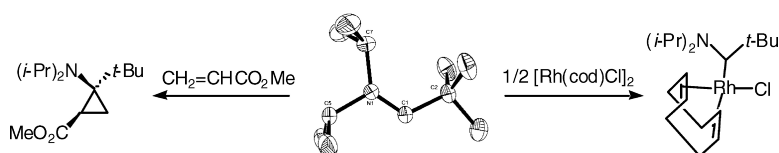
Communication

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## Synthesis, Reactivity, and Ligand Properties of a Stable Alkyl Carbene

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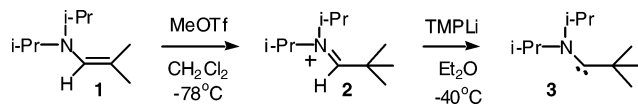
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In the last 15 years persistent triplet diaryl carbenes have been prepared,<sup>1</sup> and two very different types of singlet carbenes have been isolated.<sup>2,3</sup> The so-called push–pull carbenes such as phosphino silyl carbenes react readily with electron-poor alkenes to afford cyclopropanes<sup>4</sup> but are reluctant to bind metals.<sup>5,6</sup> In contrast, push–push carbenes such as diamino carbenes, and especially N-heterocyclic carbenes (NHCs), are excellent ligands for transition metals,<sup>2</sup> but no cyclopropanation reactions have yet been reported.<sup>7</sup> The peculiar reactivity of diamino carbenes is due to their high nucleophilicity (they are strong  $\sigma$ -donors) and low electrophilicity (they are weak  $\pi$ -acceptors).

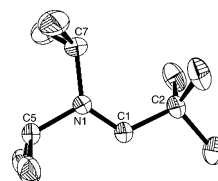
Direct observation of singlet alkyl carbenes usually requires matrix isolation conditions<sup>8a,b</sup> or nanosecond time-resolved laser flash photolysis techniques,<sup>8b,c</sup> the exception being the (*tert*-butyl)-[bis(diisopropylamino)phosphino]carbene, which has a lifetime of about three minutes at  $-10$  °C.<sup>3c</sup> Here we report the synthesis, X-ray crystal structure, cyclopropanation reaction, and ligand properties of the first isolable alkyl amino carbene. Calculations corroborate the experimental observations and suggest that this carbene is both more nucleophilic and electrophilic than diamino carbenes.

The fact that 1,2-H migration readily occurs for singlet carbenes<sup>9</sup> implies that only *tertiary*-alkyl amino carbenes could be stable. Moreover, we have previously shown that deprotonation of *N*-methyl iminium salts does not occur at the iminium carbon to give the desired carbenes but at the  $\text{CH}_3\text{-N}$ , affording transient azomethine ylides.<sup>10</sup> All our attempts to alkylate *i*-PrN=C(H)(*t*-Bu) with a secondary alkyl group and to transform *i*-Pr<sub>2</sub>NCH<sub>2</sub>(*t*-Bu) into the corresponding aldiminium salt failed. However, despite potential steric constraints, we found that the desired carbene precursor **2** was accessible by methylation of the readily available enamine **1**. The reaction was complete in less than 2 h at room temperature, and **2** was isolated as colorless crystals in 95% yield.<sup>11</sup> Deprotonation of **2** with the lithium salt of 2,2,6,6-tetramethylpiperidine occurred cleanly at  $-40$  °C in ether. After workup and recrystallization at  $-20$  °C from hexanes, carbene **3** was isolated as light yellow crystals (35% yield, mp < 20 °C) (Scheme 1).<sup>11</sup>

### Scheme 1

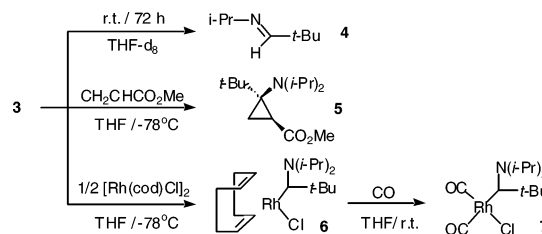


The main feature of the NMR spectra of **3** is the very low field values of the <sup>13</sup>C chemical shift of the carbene carbon ( $\delta$  326 ppm); for comparison the bis(diisopropylamino)carbene (BDAC) shows a signal at 255 ppm.<sup>12</sup> As expected, the single-crystal X-ray diffraction study of **3**<sup>13</sup> (Figure 1) shows the nitrogen atom to be in a perfectly planar environment (sum of bond angles = 360.0°),



**Figure 1.** Thermal ellipsoid diagram (50% probability) of **3** (H atoms omitted). Selected bond distances (Å) and angles (deg): N1–C1 1.2976(17), C1–C2 1.5392(18), N1–C1–C2 120.50(12), C1–N1–C5 116.36(11), C1–N1–C7 130.13(11), C5–N1–C7 113.51(10).

### Scheme 2



a very short (1.297 Å) N–C bond length, and a rather acute (120.5°) carbene bond angle (BDAC: 1.363 Å, 121.0°).

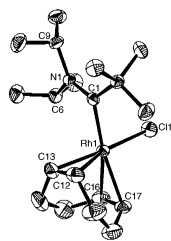
At room temperature, carbene **3** can be stored indefinitely in the solid state, but in solution it transforms quantitatively into the corresponding (*E*)-imine **4** and propene within 3 days (Scheme 2). This intramolecular fragmentation (no trace of iminium salt **2** was observed) gives the first indication of the high basicity of the carbene center.

Carbene **3** reacts instantaneously at  $-40$  °C with methyl acrylate and, according to NMR spectroscopy, cyclopropane **5** was obtained as a single diastereomer, which was isolated in 85% yield. The total syn selectivity, with respect to the amino group, was demonstrated by a single-crystal X-ray diffraction study.<sup>13</sup> The same total syn selectivity, which cannot be due to steric factors, has previously been observed for phosphino silyl carbenes and was rationalized on the basis of favorable “secondary orbital interactions” LUMO<sub>carbene</sub>–HOMO<sub>alkene</sub>.<sup>4c</sup> Due to donation of the nitrogen (or phosphorus) lone pair, the LUMO<sub>carbene</sub> has some  $\pi^*$  character and therefore has significant bonding overlap between the nitrogen center and the ester group of the alkene. The formation of **5** indicates that carbene **3** retains some electrophilic character.<sup>14</sup> Interestingly, the only other known cyclopropanation reaction involving an amino carbene was observed by Jones et al. for the transient 3,5,7-trimethyl-1-azatricyclo-[3.3.1.13,7]decan-2-ylidene for which the nitrogen lone pair cannot interact with the carbene vacant orbital.<sup>15</sup>

Rh(cod)Cl and Rh(CO)<sub>2</sub>Cl complexes of several cyclic- and acyclic diamino carbenes are known.<sup>3a,b,16</sup> Therefore, to evaluate the ligand properties of **3**, we have prepared the corresponding carbene complexes **6** and **7**. Complex **6** was isolated as highly thermally stable single crystals (mp 158–160 °C). The <sup>13</sup>C NMR

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**Figure 2.** Thermal ellipsoid diagram (50% probability) of **6** (H atoms are omitted). Selected bond distances (Å) and angles (deg): N1–C1 1.317(3), C1–Rh1 2.039(2), Rh1–C12 2.109(2), Rh1–C13 2.119(2), Rh1–C16 2.208(2), Rh1–C17 2.237(2), N1–C1–C2 121.14(18), N1–C1–Rh1 120.78(15), C2–C1–Rh1 118.00(14).

signal for the carbene center (279.5 ppm, d,  $^1J_{\text{CRh}} = 40$  Hz) is the most deshielded and the C–N bond (1.317 Å) the shortest of related known complexes; however, the  $\text{C}_{\text{carbene}}\text{–Rh}$  bond length (2.039 Å) is in the typical range (Figure 2). Complex **7** was readily obtained by treatment of a thf solution of **6** with CO at room temperature. The substitution of the cod ligand by the stronger acceptor CO ligands shows the strong donor capability of carbene **3**.<sup>16b</sup> The carbonyl stretching frequencies of complex **7** (2070 and 1989  $\text{cm}^{-1}$ ) fall between those observed for the analogous complexes featuring the BDAC (2057 and 1984  $\text{cm}^{-1}$ ), the most basic known carbene ligand, and the saturated NHCs (2081 and 1996  $\text{cm}^{-1}$ ).<sup>16</sup> A very basic carbene ligand is predicted to result in a relatively low wavenumber of the CO-stretching frequencies induced by a strong donation of the carbene to the metal and little  $\pi$ -back-donation from the metal center to the ligand.<sup>16b</sup> Following this hypothesis, one could conclude that the donor and acceptor properties of carbene **3** are comparable to those of cyclic- and acyclic diamino carbenes; however, this is not consistent with their differences in reactivity and especially with the observation of the cyclopropanation reaction leading to **4**.

According to calculations performed at the (U)B3LYP/6-31g\* level, the singlet–triplet gap (26.7 kcal/mol) and the HOMO (–4.3 eV) for **3** are much smaller and higher in energy, respectively, than for NHCs (79.6 kcal/mol and –5.4 eV) and acyclic diamino carbenes (58 kcal/mol and –5.2 eV).<sup>17</sup>

From these results as a whole, it can be concluded that alkyl amino carbenes can be isolated, they are more nucleophilic but also more electrophilic than diamino carbenes. We are currently investigating the catalytic properties of various metal complexes of **3**. Moreover, the presence of a tertiary alkyl group linked directly to the carbene carbon should allow for the synthesis of optically active carbene complexes featuring the chiral center in a position  $\beta$  to the metal, which might result in a high degree of chiral induction.

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**Supporting Information Available:** Full experimental details, spectroscopic data; X-ray crystallographic data for **3**, **5**, and **6** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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