

A stable chiral diaminocyclopropenyliidene†

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The chiral carbene bis[bis(*R*-1-phenylethyl)amino]cyclopropenyliidene **2** and its dicarbene–silver complex [Ag(**2**)₂]BF₄ (**3**) have been isolated in good yields from the reactions of bis[bis(*R*-1-phenylethyl)amino]cyclopropenylium tetrafluoroborate (**1**)BF₄ with potassium bis(trimethylsilyl)amide or with Ag₂O, respectively; the molecular structures of (**1**)ClO₄, **2** and **3** have been determined by X-ray diffraction analyses.

Nucleophilic carbenes of the imidazolin-2-ylidene type and related heterocyclic carbenes¹ are nowadays ubiquitous and indispensable to the development of research areas such as homogeneous transition metal catalysis and organocatalysis.^{2,3} The latest member of the family of stable “bottle-able” carbenes⁴ is bis(diisopropylamino)cyclopropenyliidene, (*i*Pr₂NC)₂C:, which was recently reported by Bertrand and co-workers,⁵ although cyclopropenyliidene complexes with transition metals and main group elements have been known for many years.^{6,7} Previous attempts to isolate these carbenes in the free state have failed,⁸ and the demonstration of their inherent stability will certainly stimulate interest in cyclopropenyliidene chemistry and establish diaminocyclopropenyliidene, (R₂NC)₂C:, as viable alternatives to the intensively studied imidazolin-2-ylidenes.^{2,3} It should be noted that these two carbene types represent constitutional isomers with the molecular formula C₃N₂R₄ (Fig. 1) and that the direct substitution of the carbene carbon atom by nitrogen atoms in imidazolin-2-ylidenes has now been replaced by a remote heteroatom stabilization of the cyclopropenyliidene ring by two secondary amine moieties.⁹ These amines can easily be varied, thus allowing tuning of the electronic and steric properties of the resulting carbene or the introduction of chirality by use of appropriate secondary amines. These chiral cyclopropenyliidene should have a similar potential as stereo ligands in asymmetric

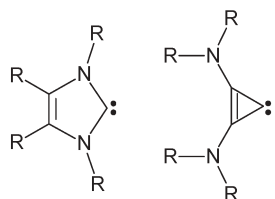


Fig. 1 Constitutional C₃N₂R₄ isomers: imidazolin-2-ylidenes (left) and diaminocyclopropenyliidene (right).

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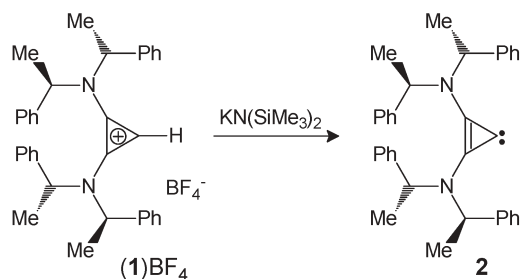
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catalysis as their *N*-heterocyclic congeners,^{2*h-j*} and with bis[bis(*R*-1-phenylethyl)amino]cyclopropenyliidene **2**, the first example is presented herein.

Treatment of a solution of tetrachlorocyclopropene in CH₂Cl₂ with bis(*R*-1-phenylethyl)amine followed by addition of HBF₄ leads to the formation of a chlorocyclopropenylium salt, which can be converted into (**1**)BF₄ by reaction with PPh₃ and subsequent hydrolytic cleavage of the dicationic phosphoniocyclopropenylium intermediate.^{8,10} At room temperature, the ¹H NMR spectrum exhibits two quartets for the methine protons and two doublets for the methyl groups together with two sets of resonances for the phenyl groups, indicating that the 1-phenylethyl substituents at each amine moiety are magnetically inequivalent due to hindered rotation around the N–C(ring) axes. Consequently, two sets of resonances are also observed in the ¹³C NMR spectra for the 1-phenylethyl groups together with two resonances for the ring carbon atoms at about 103 (CH) and 136 ppm (CN).

Potassium bis(trimethylsilyl)amide was used for the deprotonation of the cyclopropenylium salt (**1**)BF₄ in diethyl ether, and after stirring the reaction mixture for 3 h, the free cyclopropenyliidene **2** was isolated in 60% yield as an amber-colored crystalline solid after evaporation of the solvent and extraction with hexane (Scheme 1). The presence of the free carbene was unequivocally confirmed by ¹³C NMR spectroscopy revealing characteristic signals at 160.8 ppm (CN) and at 188.2 ppm for the carbene carbon atom, which agrees with the values reported for (*i*Pr₂NC)₂C: (159, 185 ppm).⁵ At room temperature, dynamic ¹H and ¹³C NMR behaviour is observed, and only one set of broad resonances is monitored for the 1-phenylethyl substituents, indicating that the rotation around the N–C(ring) axes is much faster in **2** than in the cation **1**. A variable-temperature ¹H NMR study showed separate signals for the two different PhCHCH₃ environments below an approximate coalescence temperature of *T*_c = –15.4 °C, and line-shape analysis allows an estimate of the barrier of rotation around the C–N bonds as about 52 kJ mol^{–1}.¹¹

To compare the structural characteristics of the carbene and of its cationic precursor, the molecular structures of **2** and of the



Scheme 1

perchlorate (**1**)ClO₄ have been established by means of X-ray diffraction analyses (Fig. 2).[‡] In both structures, the presence of effective N–C π -interaction is clearly evident from the observation of almost perfectly coplanar orientations of the amino groups towards the three-membered rings. As expected from their different dynamic NMR behaviour, this interaction is less pronounced in **2** than in cationic **1**, and the N–C(ring) bond distances [**2**: 1.342(3), 1.346(3) Å; **1**: 1.305(2), 1.313(2) Å] together with the C–C1(carbene) distances [**2**: 1.404(4), 1.400(4) Å; **1**: 1.369(3), 1.355(3) Å] are longer, whereas the formal C2–C3 double bond is significantly shorter [**2**: 1.357(3); **1**: 1.421(2) Å]. The smaller N–C bond order in **2** is also confirmed by IR spectroscopy with a N–C stretching frequency at 1431 cm⁻¹ (**2**), which is shifted by –125 cm⁻¹ compared to the absorption monitored at 1556 cm⁻¹ for (**1**)BF₄ and (**1**)ClO₄. All structural parameters are in good agreement with those reported previously for (*i*Pr₂NC)₂C: and its cyclopropenylidene precursor,⁵ and the decreasing N–C π -interaction in both cyclopropenylidene systems is compatible with the trend observed by structural comparison of imidazolium salts with the corresponding free imidazolin-2-ylidenes.^{4c,12}

Although it has now been established that diaminocyclopropenylidenes are stable in the free state, their isolation for further application, for instance as ancillary ligands in homogeneous

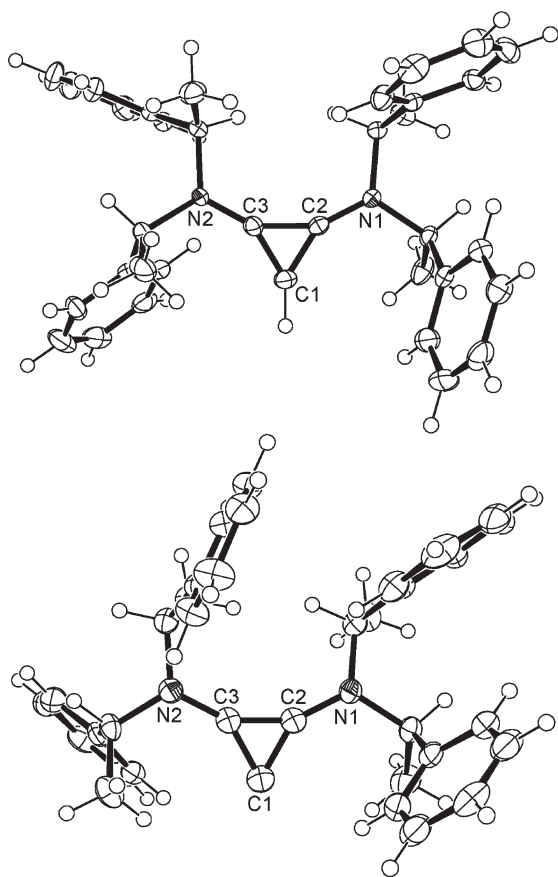


Fig. 2 ORTEP diagrams of the cation in (**1**)ClO₄ (top) and of **2** (bottom) with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°) of **1/2**: C1–C2 1.369(3)/1.404(4), C1–C3 1.355(3)/1.400(4), C2–C3 1.421(2)/1.357(3), C2–N1 1.305(2)/1.342(3), C3–N2 1.313(2)/1.346(3); C2–C1–C3 62.90(14)/57.89(18); C1–C2–C3 58.07(13)/60.90(19), C1–C3–C2 59.04(13)/61.21(18).

catalysis, might be disadvantageous because of their high reactivity. In contrast, silver(I) complexes can be used as convenient and robust carbene transfer reagents or serve as catalysts in their own right,¹³ and therefore, we aimed towards the synthesis of a cyclopropenylidene Ag(I) complex. Deprotonation of (**1**)BF₄ with Ag₂O in CH₂Cl₂ readily affords the homoleptic dicarbene complex [Ag(**2**)₂][BF₄] (**3**) as a colourless crystalline solid in good yield (67%).¹⁴ The ¹³C NMR resonance of the former carbene centers is shifted upfield from 188.2 ppm for **2** to 146.2 ppm for **3**, and the presence of two NMR active silver nuclei with spin 1/2 leads to the observation of two doublets with ¹J(¹³C–¹⁰⁷Ag) = 187 Hz and ¹J(¹³C–¹⁰⁹Ag) = 211 Hz, respectively, indicating that the cationic complex is inherently stable and does not experience rapid ligand exchange on the NMR time scale. The presence of a linear dicarbene–silver structural motif is also confirmed by X-ray diffraction analysis, and the molecular structure of one of the two crystallographically independent cations in **3** is shown in Fig. 3. The C–Ag–C angles are almost linear [molecule 1: 172.1(2)°; molecule 2: 175.3(2)°], and the planes of the two three-membered rings in each cation are twisted by 62.6° (molecule 1) and 37.3° (molecule 2) from coplanarity. The Ag–C bond lengths in both cations are equidistant within experimental error. The mean distance of 2.066 Å falls in the range of values reported for related complexes,¹³ e.g. Ag–C 2.067(4) and 2.078(4) Å in [Ag(IMes)₂][CF₃SO₃]¹⁵ and Ag–C 2.082(2) Å in [Ag₃(TIME^{Me})₂](PF₆)₃.¹⁶ Evaluation of the structural features of the diaminocyclopropenylidene moieties in **3** reveals an intermediate position between the structures of (**1**)ClO₄ and **2**. Accordingly, silver coordination of the carbene **2** leads to shorter N–C(ring) distances together with a significant elongation of the C–C bonds flanked by the nitrogen atoms.

The isolation of the first chiral cyclopropenylidene **2** paves the way for the use of these novel carbenes in asymmetric homogeneous catalysis. However, our initial studies on the benzoin condensation of benzaldehyde employing (**1**)BF₄ in combination with KO^tBu as the catalyst precursor did not reveal high chiral induction, and enantioselectivities of only up to 18% ee could be

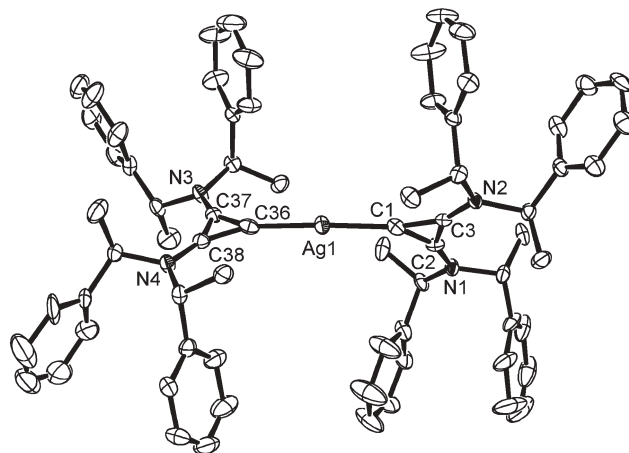


Fig. 3 ORTEP diagram of one of the two independent cations in **3**·0.5 CH₂Cl₂ with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°): Ag1–C1 2.059(6), Ag1–C36 2.063(6), Ag2–C71 2.070(6), Ag2–C106 2.071(6); C1–Ag1–C36 172.1(2), C71–Ag2–C106 175.3(2).

observed, which is presumably a consequence of rapid internal rotation of the chiral substituents (*vide supra*).^{2h-j,17} Therefore, diaminocyclopropenylenes with restricted flexibility and better definition of their active chiral space are currently being developed in our laboratory.

Notes and references

† *Crystal data*: (1) ClO_4 ; $\text{C}_{35}\text{H}_{37}\text{ClN}_2\text{O}_4$, $M = 585.12$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 8.9690(5)$, $b = 16.1071(9)$, $c = 21.0597(11)$ Å, $U = 3042.4(3)$ Å³, $T = 133$ K, $Z = 4$, $D_c = 1.277$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.167$ mm⁻¹, 47667 reflections measured, 8907 unique ($R_{\text{int}} = 0.0862$) which were used in all calculations. The final $wR(F^2)$ was 0.0981 (all data) with conventional $R1 = 0.0437$. CCDC 645869. (2) $\text{C}_{35}\text{H}_{36}\text{N}_2$, $M = 484.66$, monoclinic, space group $P2_1$ (no. 4), $a = 8.6057(9)$, $b = 15.5239(16)$, $c = 10.5267(11)$ Å, $\beta = 95.728(2)^\circ$, $U = 1399.3(3)$ Å³, $T = 133$ K, $Z = 2$, $D_c = 1.150$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.066$ mm⁻¹, 12453 reflections measured, 2970 unique ($R_{\text{int}} = 0.0814$) which were used in all calculations. The final $wR(F^2)$ was 0.0790 (all data) with conventional $R1 = 0.0428$. CCDC 645870. (3) $\text{C}_{70.5}\text{H}_{73}\text{AgBClF}_4\text{N}_4$, $M = 1206.46$, monoclinic, space group $P2_1$ (no. 4), $a = 13.464(1)$, $b = 32.293(2)$, $c = 14.143(1)$ Å, $\beta = 90.649(2)^\circ$, $U = 6148.6(8)$ Å³, $T = 133$ K, $Z = 4$, $D_c = 1.303$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.428$ mm⁻¹, 98358 reflections measured, 25122 unique ($R_{\text{int}} = 0.1127$) which were used in all calculations. The final $wR(F^2)$ was 0.1217 (all data) with conventional $R1 = 0.0560$. CCDC 645871. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706708a

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