Bent Allenes

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Synthesis and Ligand Properties of Stable Five-Membered-Ring Allenes Containing Only Second-Row Elements**

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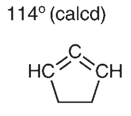
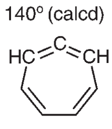
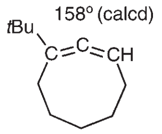
Allenes are compounds with two contiguous carbon–carbon double bonds. They consequently feature a linear CCC skeleton with orthogonal pairs of substituents.[1] Because of their rigidity, allene frameworks can only be accommodated into a ring with difficulty, and calculations predict that the ring strain increases considerably with each successive removal of a carbon atom from the backbone of cyclic allenes [from 1,2-cyclooctadiene (12 kcal mol^{-1}) to 1,2-cyclobutadiene (90 kcal mol^{-1})].[2] Even the low-temperature NMR spectroscopic characterization of all-carbon cyclic allenes is limited to those containing more than seven carbon atoms;[3] the only exception is the 1,2,4,6-cycloheptatetraene $\mathbf{A_2}$, which was incarcerated in a molecular container by Warmuth and Marvel.[4] The kinetically protected 1,2-cyclooctadiene $\mathbf{A_3}$ (calculated C-C-C angle: 158°),[5] the trisilicon-[6] and diphosphorus-containing[7] hexacycles $\mathbf{A_4}$–$\mathbf{A_6}$ (crystallographically observed C-C-C angles: 166, 161, and 156°, respectively; Mes = mesityl), and the recently isolated five-membered halfnium-containing allenoid $\mathbf{A_7}$ (C-C-C angle: 156°)[8] are the most bent cyclic allenes isolated to date. Because of the presence of the heavier elements, the allene fragments in $\mathbf{A_4}$–$\mathbf{A_7}$ are not significantly more distorted than in the eight-membered ring $\mathbf{A_3}$. More-strained cyclic allenes, such as 1,2-cyclopentadiene ($\mathbf{A_1}$; calculated C-C-C angle: 114°), are only known as reaction intermediates, in line with calculations that predict that they have a strong diradical character.[2]



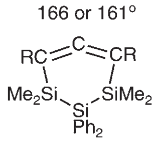
$\mathbf{A_1}$



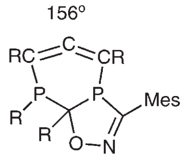
$\mathbf{A_2}$



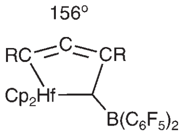
$\mathbf{A_3}$



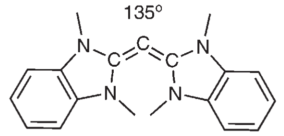
$\mathbf{A_{4,5}}$
(R=Ph,SiMe$_3$)



$\mathbf{A_6}$
(R=*t*Bu)



$\mathbf{A_7}$
(R=SiMe$_3$)



$\mathbf{A_8}$

We showed recently[9] that a push–push substitution pattern[10] can induce a severe deviation from the classical geometry of acyclic allenes. Indeed, a single-crystal X-ray diffraction study revealed that allene $\mathbf{A_8}$ has a C-C-C bond angle of 134.8°, with the two NCN planes not perpendicular to one another but twisted by 69°. Moreover, theoretical studies by Tonner and Frenking[11] on tetraaminoallenes predict that these push–push-substituted allenes, which they described as "carbodicarbenes" (compounds featuring a divalent carbon(0) center[12–13] with two N-heterocyclic carbene (NHC) ligands), are highly flexible.

On the basis of these results, it seemed likely that a push–push substitution pattern could enable the synthesis of allenes confined within relatively small ring systems. Herein we report the synthesis and X-ray crystallographic characterization of the first lithium-salt adduct and salt-free derivative of five-membered ring allenes consisting only of second-row elements. A preliminary account of the ligand properties of these species is also given on the basis of infrared analysis of a rhodium(I) dicarbonyl chloride complex.

The readily available, thermally and air-stable 3,5-diaminopyrazolium salt **2a**[14] was a logical precursor to a five-membered ring allene with four π-donor amino groups (Scheme 1). When **2a** was treated with *n*-butyllithium at −78 °C, ^{1}H NMR spectroscopy of the reaction mixture revealed clean deprotonation, as shown by the disappearance of the signal at $\delta = 5.4$ ppm due to the hydrogen atom on the pyrazolium ring. The ^{13}C NMR spectrum showed two distinct resonances at $\delta = 114$ and 176 ppm, which are in the range of those observed for the central and terminal CCC carbon atoms of the acyclic bent allene $\mathbf{A_8}$ ($\delta = 110.2$ and 144.8 ppm, respectively). An X-ray diffraction study[15] of the compound obtained from the deprotonation of **2a** revealed that it was not the desired cyclic allene, but its lithium tetrafluoroborate adduct **3a** (orange crystals, 26 % yield; Figure 1). It is known that some highly basic compounds, such as bis(diisopropylamino)cyclopropenylidene[16] and phosphorus ylides,[17] are formed as the lithium salt adduct whenever a lithium base is used. If the salt-free compound is desired, then alternative sodium or potassium bases must be used. A number of such

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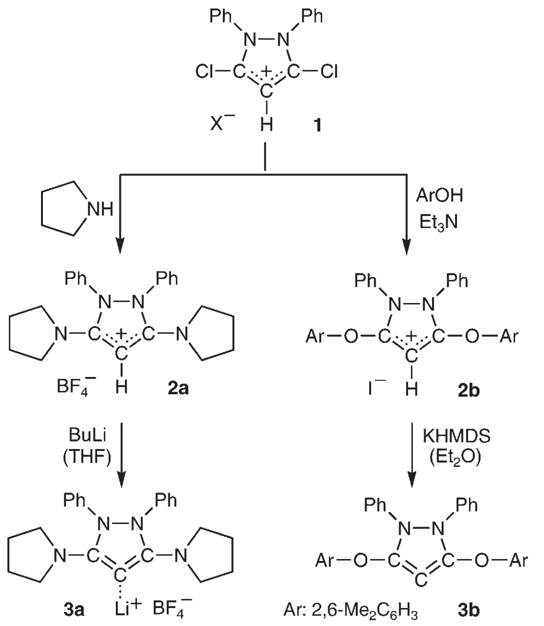


Scheme 1. Synthesis of the allene–lithium adduct **3a** and the salt-free allene **3b**.

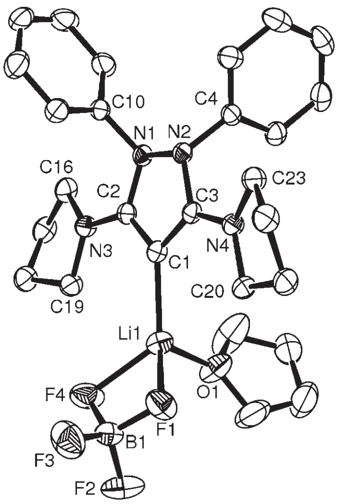


Figure 1. Solid-state structure of one of the enantiomers of **3a**·thf (hydrogen atoms and a noncoordinated THF molecule are omitted for clarity; ellipsoids are drawn at 50% probability). Selected bond lengths [Å] and angles [°]: C1–C2 1.403(2), C1–C3 1.398(2), C2–N1 1.411(2), N1–N2 1.444(2), C3–N2 1.408(2), C2–N3 1.349(2), C1–Li 2.106(3), C3–N4 1.353(2); C2-C1-C3 100.8(1), C2-C1-Li 129.5(1), C3-C1-Li 129.2(2), C1-C3-N4 128.3(2), C1-C3-N2 114.7(1), N2-C3-N4 117.0 (1), C2-N1-N2 104.2(1), C2-N1-C10 122.0(1), N2-N1-C10 109.6(1), N1-N2-C4 111.9(1), N1-N2-C3 104.9(1), C4-N2-C3 121.0(1), C1-C2-N3 127.3(2), C1-C2-N1 114.8(1), N1-C2-N3 117.9(1), C2-N3-C16 125.5(1), C2-N3-C19 120.2(1), C19-N3-C16 111.6(1), C3-N4-C23 123.7(1), C3-N4-C20 120.7(1), C20-N4-C23 111.6(1).

bases (NaHMDS (HMDS = hexamethyldisilazide), $NaNH_2$, KHMDS, KH, KO*t*Bu, KN*i*Pr_2) were screened for the deprotonation of **2a**; however, no clean deprotonation was observed.

In the hope of favoring the formation of a free five-membered-ring allene, we modified the pyrazolium scaffold to make the central carbon atom less basic. We chose to replace the exocyclic amino groups of **2a** by weaker-π-donor and more-electronegative aryloxy groups. Thus, the treatment of **1** (X = I) with excess 2,6-dimethylphenol and triethylamine in chloroform afforded the new pyrazolium salt **2b** in 45% yield. The reaction of **2b** with KHMDS was then monitored by NMR spectroscopy, which indicated clean and quantitative deprotonation and the formation of a new species, **3b**. Single-crystal X-ray diffraction demonstrated that **3b** is a salt-free cyclic allene with an extremely small C-C-C angle of 97.5° (Figure 2),[15] almost 20° smaller than that predicted for the all-carbon analogue $\mathbf{A_1}$! Furthermore, in contrast with the perpendicular arrangement of the substituents in classical allenes, the 69° twist angle observed for the acyclic push–push-substituted allene $\mathbf{A_8}$, and even the *trans* arrangement of the exocyclic allene substituents calculated for $\mathbf{A_1}$, the two nitrogen and two oxygen centers of **3b** are coplanar with the C2–C1–C3 fragment (maximum deviation: 0.0478 Å). Finally, the C–C bond distances (C1–C2: 1.370 Å; C1–C3: 1.386 Å) are significantly longer than the standard allene bond length (1.31 Å).[18] These peculiar features of **3b** are all due to the polarization of the allenic π bonds towards the central carbon atom C1. Clearly, the oxygen centers act as π donors, as they are sp^2 hybridized (C-O-C: 120.0 and 117.1°), they have rather short bonds to the allenic linkage (O1–C2: 1.358 Å; O2–C3 = 1.347 Å), and they are arranged to enable lone-pair conjugation with the allene π system (C-O-C-C torsional angles: 2.65 and 6.29°). Surprisingly, although π donation from the nitrogen atoms is evidenced

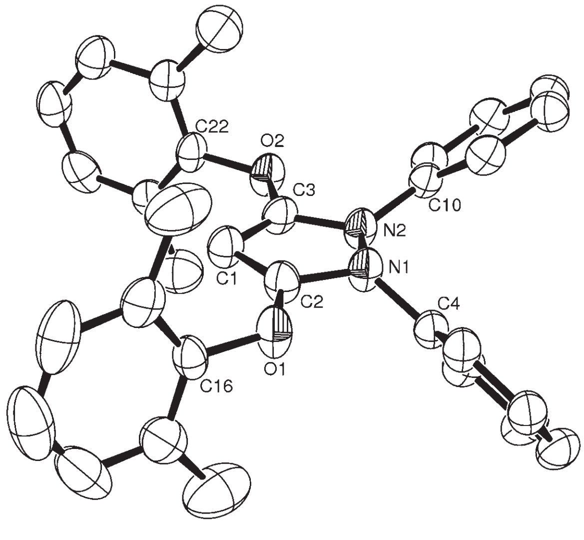


Figure 2. Molecular structure of **3b** in the solid state (hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50% probability). Selected bond lengths [Å] and angles [°]: C1–C2 1.370(4), C1–C3 1.386(3), O1–C2 1.358(3), O2–C3 1.347(3), N1–C2 1.388(3), N2–C3 1.385(3), N1–N2 1.401(3); C2-C1-C3 97.5(2), C1-C2-N1 117.5(2), N2-C3-C1 116.9(2), C2-N1-N2 103.8(2), C3-N2-N1 104.1(2), C2-O1-C16 120.0(2), C3-O2-C22 117.1(2), C2-N1-C4 125.0(2), N2-N1-C4 118.3(2), C3-N2-C10 128.7(2), N1-N2-C10 118.2(2).

by the short C–N bond lengths (C2–N1: 1.388 Å; C3–N2: 1.385 Å), **3b** exists in the solid state as a racemic mixture as a result of the pyramidalization of the nitrogen atoms with a *trans* arrangement of the Ph groups (sum of the angles at N1: 347.1°, N2: 351.0°).[19]

The ligand properties of the cyclic allene **3b** were assessed by infrared analysis of the corresponding rhodium(I) dicarbonyl chloride complex **4** (Figure 3), which was prepared readily by the addition of [{Rh(CO)$_2$Cl}$_2$] (0.5 equiv) to **3b**. Interestingly, the average ν_{CO} values for complex **4** (2018 cm^{-1}) are very similar to those observed for the corresponding complex with the acyclic bent allene **A$_8$** (2014 cm^{-1}). All bent allenes appear to be stronger donor ligands than phosphines, five-membered NHCs (2036–2060 cm^{-1}), and even strongly basic bis(diisopropylamino)-carbene (2020 cm^{-1}).[20]

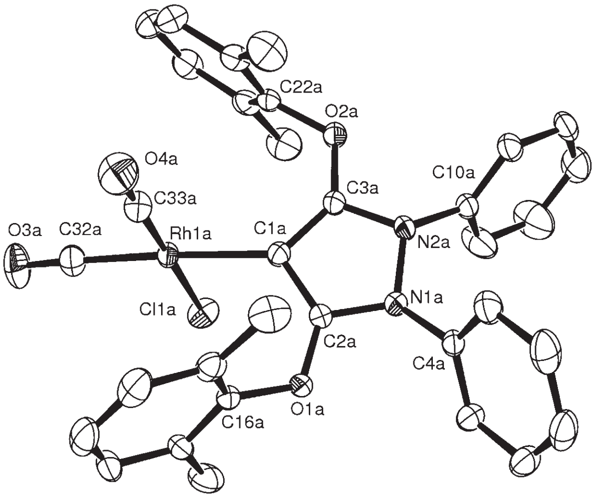
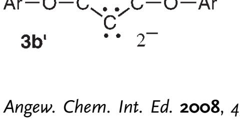


Figure 3. Molecular structure of **4** in the solid state (hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50% probability). Selected bond lengths [Å] and angles [°]: C1a–C3a 1.384(3), C3a–N2a 1.374(3), N2a–N1a 1.398(2), N1a–C2a 1.361(3), C2a–C1a 1.400(2), C1a–Rh1a 2.096(2); C3a-C1a-C2a 100.6(2), C3a-C1a-Rh1a 132.6(1), C2a-C1a-Rh1a 125.9(2), C1a-Rh1a-C33a 91.1(1), C33a-Rh1a-C32a 92.6(1), C32a-Rh1a-Cl1a 87.5(1), C1a-Rh1a-Cl1a 88.8(1).

The results reported herein demonstrate that extremely bent allenes can be prepared by using a push–push substitution pattern and confining the CCC skeleton to a five-membered ring. The remarkable stability of allene **3b**, which is stable for weeks at room temperature (the crystals decompose at 95 °C) suggests that a variety of cyclic push–push-substituted allenes could be isolated. Moreover, the facile electronic and steric tuning of these systems should give rise to a diverse family of new ligands for transition metals. Of special interest is the resonance structure **3b′**, which shows that bent allenes are potentially four-electron donors. We are currently investigating this possibility.



3b'

Experimental Section

All experiments were carried out under dry argon by using standard Schlenk or dry-box techniques. Solvents were dried by standard methods and distilled under argon.

Synthesis of **3a**: *n*BuLi (2.5 M, 0.9 mL, 2.24 mmol) was added to a suspension of **2a**[14] (1.0 g, 2.24 mmol) in THF (50 mL) at −78°. The mixture was stirred for 15 min at this temperature and then removed from the cold bath. When the temperature of the reaction mixture had reached room temperature, the solvent was concentrated to 50% of the original volume, and diethyl ether (20 mL) was added. The solution was maintained at −20 °C overnight, and then orange crystals of **3a** (0.308 g, 26.2%) suitable for X-ray diffraction were collected. M.p.: 130–132 °C (decomp.); ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 1.26–1.30 (br m, 8H), 1.43–1.48 (br m, 4H), 3.28–3.33(br m, 8H), 3.60–3.65 (br m, 4H), 6.95–7.05 ppm (br m, 10H); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 26.0 (CH$_2$), 26.1 (CH$_2$), 51.2 (NCH$_2$), 68.3 (OCH$_2$), 114.4 (C*C*C), 127.9 (CH^{Ar}), 128.2 (CH^{Ar}), 129.3 (CH^{Ar}), 144.7 (NC^{Ar}),176.3 ppm (NCN).

Synthesis of **2b**: Triethylamine (7.5 mL, 54 mmol) was added in a steady stream with a syringe to a stirred mixture of **1** (5.0 g, 12 mmol) and 2,6-dimethylphenol (4.1 g, 34 mmol) in chloroform (50 mL). The resulting mixture was stirred overnight, then diethyl ether (250 mL) was added to precipitate the product and ammonium salts. The precipitated material was filtered, washed with diethyl ether (40 mL), and then washed with water (150 mL) with vigorous stirring for 20 min. The solid material was then filtered, washed with water (2 × 80 mL) then diethyl ether (4 × 60 mL), recrystallized from methanol, and dried under vacuum to give **2b** (3.2 g, 45%) as a colorless solid. M.p.: 306–307 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.32 (s, 12H), 4.75 (s, 1H), 7.05–7.07 (m, 6H), 7.45–7.48 (m, 6H), 8.06–8.10 ppm (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 17.2 (CH$_3$), 75.5 (CH), 127.7 (CH^{Ar}), 129.5 (NCO), 129.8 (CH^{Ar}), 129.9 (CH^{Ar}), 130.1 (*C*CH$_3$), 130.2 (CH^{Ar}), 131.9 (CH^{Ar}), 150.2 (NC^{Ar}), 157.8 ppm (OC^{Ar}).

Synthesis of **3b**: Diethyl ether (3 mL) was added to a stirred mixture of **2b** (0.639 g, 1.09 mmol) and KHMDS (0.217 g, 1.09 mmol) at −78 °C. The cold bath was then removed, and the mixture was stirred for a further 50 min and then filtered. The solid collected was washed with diethyl ether (2 × 3 mL). Volatiles were removed from the solid under vacuum, hexanes (6 mL) were added, and the mixture was stirred vigorously for 15 min. The mixture was then cooled to −78 °C, and the hexanes were removed by filtration at this temperature. This process was repeated, and the product was dried under vacuum to give **3b** (0.236 g, 47%) as a pale-yellow solid. Single crystals suitable for X-ray diffraction were grown from a solution in hexanes at −20 °C. M.p.: 95 °C (decomp. begins); ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 2.18 (s, 12H), 6.76–6.79 (m, 8H), 6.91–6.96 (m, 4H), 7.34–7.38 ppm (m, 4H); ^{13}C NMR (75 MHz, C$_6$D$_6$,): δ = 17.2 (CH$_3$), 115.5 (C*C*C), 125.0 (CH^{Ar}), 125.9 (CH^{Ar}), 127.5 (CH^{Ar}), 129.3 (CH^{Ar}), 129.7 (CH^{Ar}), 130.8 (*C*CH$_3$), 137.4 (NC^{Ar}), 152.9 (OC^{Ar}), 174.8 ppm (NCO).

Synthesis of **4**: Benzene (2 mL) was added to a mixture of **3b** (0.111 g, 0.24 mmol) and [{Rh(CO)$_2$Cl}$_2$] (0.046 g, 0.12 mmol) in a Schlenk flask. The reaction mixture was stirred for 30 min, then concentrated to dryness. The resulting solid was washed with hexanes (2 × 3 mL) and dried under vacuum to afford **4** (0.150 g, 97%). Yellow crystals suitable for X-ray diffraction were grown by the slow evaporation in air of a solution in acetone. M.p.: 234–236 °C (decomp.); IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2059, 1978 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.20 (br s, 12H), 7.03–7.06 (br m, 6H), 7.34–7.42 ppm (br m, 10H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 17.3 (CH$_3$), 96.3 (d, $^1J_{C,Rh}$ = 34.6 Hz, CRh), 126.3 (CH^{Ar}), 126.4 (CH^{Ar}), 129.3 (br, CH^{Ar}), 129.5 (CH^{Ar}), 129.8 (CH^{Ar}), 130.3 (br, *C*CH$_3$), 133.9 (NCO), 150.9 (NC^{Ar}), 166.8 (OC^{Ar}), 183.7 (d, $^1J_{C,Rh}$ = 76.9 Hz, RhCO), 185.3 ppm (d, $^1J_{C,Rh}$ = 56.6 Hz, RhCO).

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