Bent Allenes

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Synthesis of an Extremely Bent Acyclic Allene (A “Carbodicarbene”): A Strong Donor Ligand**

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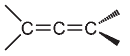
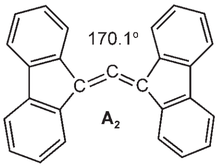
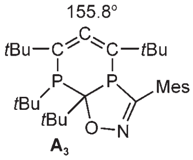
Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

In line with hybridization theory, allenes **A$_1$** have a linear C=C=C skeleton with orthogonal pairs of substituents.[1] The allene framework is so rigid that even minor deviations from linearity are of note. In a report from 1995, entitled “A remarkably bent allene. X-ray crystal structure and ab initio calculations”, Weber et al.[2] described compound **A$_2$**, which is still today the most severely bent acyclic allene known, with a C=C=C bond angle of 170.1°. They demonstrated that the nonlinearity was due to packing effects in the crystal. To induce greater bending in an allene it is necessary to constrain the C=C=C π system into a ring, but this eventually leads to very unstable compounds.[3–5] So far, the diphosphorus-containing six-membered ring **A$_3$** is the most severely bent allene that has been isolated and characterized by crystallography; it has a C=C=C angle of 155.8°.[6]

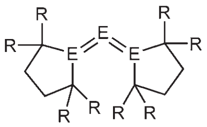

A$_1$



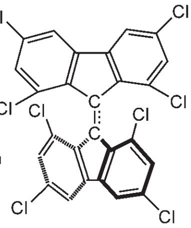
A$_2$



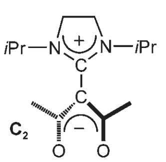
A$_3$



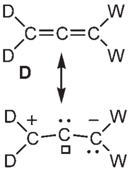
B$_1$: E = Si (136.5°)
B$_2$: E = Ge (122.6°)
R = SiMe$_3$



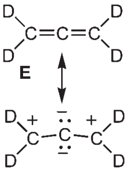
C$_1$



C$_2$



D **D'**



E **E'**

In marked contrast with all-carbon allene fragments (C=C=C), crystallographic[7] and computational studies[8] of allenes that are based on heavier Group 14 elements (E=E=E where E = Si, Ge; **B$_1$** and **B$_2$**, respectively) demonstrate that they are highly flexibile, and exhibit a bent structure (136.5° and 122.6°, respectively). The striking differences between the geometry between acyclic all-carbon allenes **A$_1$** and their heavier element congeners **B$_1$** and **B$_2$** is mainly due to the “first long-row anomaly”, as described by Grützmacher.[9] The first long-row elements tend to form hybrids from s and p orbitals that lead to the familiar linear, trigonal, and tetragonal bonding geometries of the carbon compounds. Second long-row elements largely avoid hybridization.[10a] Among the consequences is that second and higher row elements are generally reluctant to form multiple bonds, and therefore heavier element–heavier element π bonds are weak.[10]

From this analysis, we reasoned that weakening the π bonds of all-carbon allenes **A$_1$** should make them more flexible, and ultimately lead to a bending of the otherwise rigid and linear C=C=C skeleton.

It has been demonstrated that the carbon–carbon π bond of alkenes can be weakened by inducing either a diradical or zwitterionic character, as evidenced in each case by the twisting from planarity and lengthening of the C=C bond. The former option can be effected by steric congestion, as in the symmetrical compound **C$_1$** (twist angle = 66°; $d_{\mathrm{C=C}} = 1.39$ Å),[11] whereas the latter is a result of π-bond polarization, as in **C$_2$** (twist angle = 86°; $d_{\mathrm{C=C}} = 1.47$ Å).[12] The steric approach cannot be extended to allenes because the termini are too remote for significant interactions. Therefore, the only possible way to weaken the π bonds of allenes is by polarization, which can be accomplished by either a push–pull or a push–push substitution pattern. Push–pull allenes **D** have a carbene character as in **D′** (□ = empty orbital), and they are prone to dimerization.[13] Consequently, the best choice for preparing bent allenes is a push–push substitution pattern as in **E**,[14] which should promote the dicarbanionic resonance form **E′**.

Herein we report the isolation of an acyclic allene featuring a C=C=C bond angle of 134.8°. Importantly, we show that bent allenes should not be considered as laboratory curiosities, but instead a novel class of strong η^1-donor ligands for transition-metal centers.

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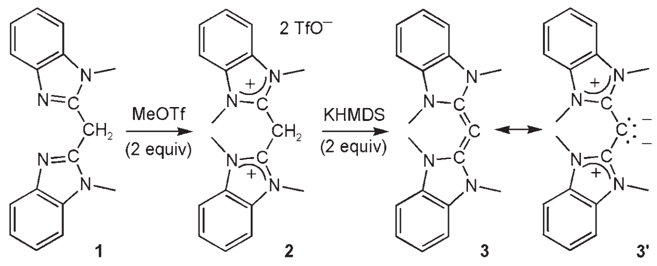
Among the possible synthetic routes to afford bent allenes, deprotonation of the conjugate acid was chosen. A major advantage of deprotonation is its swiftness, even at low temperatures, which enables species that are only moderately stable to be characterized. To maximize the pushing effects, and in the hope of obtaining a crystalline material, we chose allene **3** as the target molecule (Scheme 1). Indeed, we have already shown that the inclusion of an amino group onto a ring favors conjugation of the lone pair of electrons with the adjacent C=C π bond;[15] moreover, the benzannulation should promote crystallinity. Allene **3** was synthesized in two steps from the readily prepared bis(*N*-methylbenzimidazol-2-yl)methane (**1**).[16] Bisalkylation of **1** with excess methyl trifluoromethanesulfonate in acetonitrile gave the dicationic salt **2** in 50 % yield after isolation. Subsequent bis-deprotonation with potassium hexamethyldisilazane afforded allene **3**, which was isolated as a yellow crystalline material in 32 % yield. Although extremely water sensitive, **3** is indefinitely stable at room temperature both in solution and in the solid state (m.p. 150–152 °C). As a result of the poor solubility of **3** at room temperature, ^{13}C NMR characterization was performed at 50 °C in [D$_6$]benzene. The relative position of the signals for the central and terminal allenic carbon atoms of **3** ($\delta = 110.2$ and 144.8 ppm, respectively) are the reverse of that observed for nonpolarized allenes ($\delta = 185$–215 and 60–130 ppm, respectively),[13b] but similar to that reported for tetrakis(dimethylamino)allene ($\delta = 136$ and 162 ppm, respectively).[14a] This difference is indicative of the strong polarization of the π system, but not indicative of a bent structure (see below). Single-crystal X-ray analysis[17] reveals that the four amino groups do in fact have a dramatic effect on the geometry of allene **3** (Figure 1). Although the bond lengths are only slightly longer (C1=C2 = 1.343 Å) than the standard C=C bond length for an allene (1.31 Å),[18] the two N-C1-N planes are not perpendicular but are instead twisted by 69°. Most strikingly, the allene framework is severely bent with a C2=C1=C2′ angle of 134.8°. Clearly the allene π system has been severely perturbed, and the central carbon atom is not sp hybridized as in typical all-carbon allenes, but is more likely approaching a configuration with two lone pairs of electrons as in **3′**.[19]



Scheme 1. Synthesis of bent allene **3**. Tf = trifluoromethanesulfonyl, HMDS = hexamethyldisilazane.

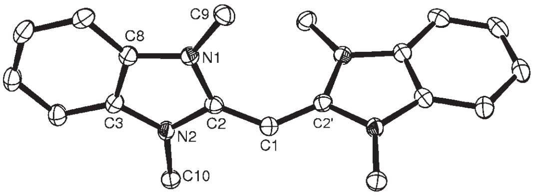
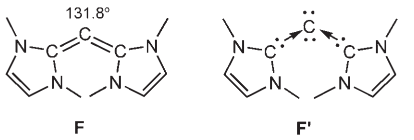


Figure 1. Molecular structure of **3** in the solid state (hydrogen atoms are omitted for clarity and ellipsoids are drawn at 50 % probability). Selected bond lengths [Å] and angles [°]: C1-C2 1.343(2), C2-N2 1.400(2), C2-N1 1.407(2), C2-C1-C2′ 134.8(2); C1-C2-N1 129.7(1), C1-C2-N2 125.8(1), N1-C2-N2 104.1(1), C2-N1-C9 124.3(1), C8-N1-C9 124.5(1); C8-N1-C2 110.6(1), C2-N2-C10 123.7(1), C2-N2-C3 111.1(1), C3-N2-C10 125.1(1).



Tonner and Frenking have validated these conclusions in their computational study[20] of compound **F**. The predicted equilibrium geometry (C=C=C bond angle 131.8° and C=C bond length of 1.358 Å) is very close to that which we observed experimentally for **3**. Importantly, they predicted that although the C=C bond length in the tetrakis(dimethylamino)allene (1.330 Å) is similar to those found in **3** and **F**, the former is perfectly linear. This contrast leads us to conclude that small variations in the nature of the donor substituents have a strong effect on the bonding. Interestingly, they described **F** as the "carbodicarbene" **F′**, which is a strongly basic compound featuring "a divalent carbon(0)[20–22] with two NHC ligands" (NHC = *N*-heterocyclic carbenes). Tonner and Frenking concluded that because the C(NHC)$_2$ can be electronically modified in many ways through variation of the NHC skeleton, they are therefore promising ligands for transition-metal complexes. Indeed, our preliminary results show that bent allene **3** readily binds metals.

"Regular allenes" react with transition-metal fragments to give η^2 complexes involving one of the C=C π bonds.[23] In contrast, because of the peculiar electronic structure of bent allenes, an η^1 coordination mode involving the central carbon atom was expected for **3**. Indeed, addition of **3** to half an equivalent of $[\{RhCl(CO)_2\}_2]$ afforded $[RhCl(CO)_2(\mathbf{3})]$ in 56 % yield (Figure 2). The carbonyl stretching frequencies of *cis*-$[RhCl(CO)_2(L)]$ complexes are recognized as an excellent measure of the electronic properties of the ligand (L).[24] The average value of the carbonyl stretching frequencies for the $[RhCl(CO)_2(\mathbf{3})]$ complex ($\tilde{\nu} = 2014$ cm^{-1}) is significantly lower[19] than those observed for analogous complexes featuring a five-membered NHC ($\tilde{\nu} = 2058$–2036 cm^{-1}), or even the strongly basic bis(diisopropylamino)carbene ($\tilde{\nu} = 2020$ cm^{-1}).[24] Clearly, bent allene **3**, with two formal lone pairs of electrons located on the carbon atom, is an even stronger σ donor and weaker π acceptor than stable singlet carbenes,[25] which have only one lone pair of electrons and a partially filled p orbital.

Usually, the bonding in compounds of the first long-row elements serves as a model for developing and understanding

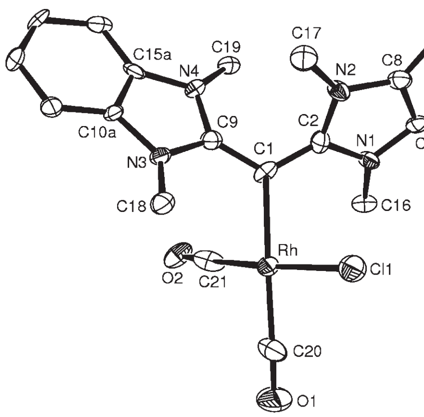


Figure 2. Molecular structure of $[RhCl(CO)_2(\mathbf{3})]$ in the solid state (hydrogen atoms are omitted for clarity; ellipsoids are drawn at 50% probability). Selected bond lengths [Å] and angles [°]: C1-C2 1.398(10), C1-Rh 2.089(7), C2-N1 1.419 (9), C2-N2 1.351(9); C2-C1-C9 121.2(7), C9-C1-Rh 121.3(5), C2-C1-Rh 117.4(5), C1-C2-N2 126.3(7), C1-C2-N1 127.9(7), N1-C2-N2 105.5(6).

the chemistry of their heavier congeners. The results reported herein demonstrate that, in the same way, the bonding in heavier main group elements can be a source of inspiration for new bonding situations in classical organic molecules. By analogy with the recent developments in carbene chemistry,[26] it is safe to say that bent allenes are not only laboratory curiosities, but should find applications as strong donor ligands for transtion metals. Similarly, cyclic carbenes are recognized as better ligands than their acyclic analogues, and the flexibility of push–push allenes should allow for the synthesis of small ring allenes; this topic is currently under active investigation by our research group.

Experimental Section

2: MeOTf (4.0 mL, 35.3 mmol) was added dropwise to a stirred mixture of **1** (3.0 g, 10.9 mmol) in acetonitrile (30 mL). After stirring the mixture for 1.5 hours at room temperature, diethyl ether (60 mL) was slowly added to the stirred mixture to afford a golden crystalline precipitate. Subsequent filtration, washing with diethyl ether (2 × 25 mL), and drying under vacuum afforded 6.05 g of **2**. The crude solid was dissolved in hot acetonitrile (40 mL) before dichloromethane (60 mL) was added and the mixture allowed to stand overnight. Filtration, washing with dichloromethane (5 × 12 mL), and drying afforded **2** as a white solid; 50% yield (3.30 g, 5.46 mmol); m.p. 246–250 °C; ^{1}H NMR (CD_3CN): $\delta = 3.97$ (s, 12H), 5.44 (s, 2H), 7.85 ppm (AA′BB′, 8H); ^{13}C NMR (CD_3CN): $\delta = 22.9$ (CH_2), 34.2 (NCH_3), 114.8 (CH arom.), 129.1 (CH arom.), 133.5 (C arom.), 144.7 ppm (NCN).

3: A solution of KHMDS (0.73 g, 3.66 mmol) in benzene (12 mL) was added dropwise to a suspension of **2** (1.0 g, 1.65 mmol) in benzene (4 mL) at room temperature. After stirring the mixture for 35 min, the mixture was heated to reflux and filtered. After the filtrate had cooled to room temperature for 30 min, the yellow crystalline precipitate of **3** was collected by filtration, washed with diethyl ether (3 × 15 mL), and dried under vacuum (0.087 g). The benzene filtrate was added to the original precipitate and again heated to reflux and filtered. Volatiles were removed under vacuum and the residue was washed with diethyl ether (3 × 15 mL) and dried. The resulting solid was then recrystallized from THF (2 mL) at reflux, and dried under vacuum to afford **3** (0.073 g) as yellow crystals suitable for X-ray analysis; 32% yield (0.160 g, 0.526 mmol); m.p. 150–152 °C (decomp.); ^{1}H NMR (C_6D_6): $\delta = 2.89$ (s, 12H), 6.47 (m, 4H), 6.93 ppm (m, 4H); ^{13}C NMR (C_6D_6, 50 °C): $\delta = 29.7$ (NCH_3), 105.2 (CH arom.), 110.2 (CCC), 135.9 (C arom.), 144.8 ppm (NCN); IR (KBr) $\tilde{\nu} = 1717\ cm^{-1}$.

[$RhCl(CO)_2(\mathbf{3})$]: A suspension of **3** (0.060 g, 0.197 mmol) in benzene (3 mL) was added dropwise to a solution of $[Rh(CO)_2Cl]_2$ (0.038 g, 0.098 mmol) in benzene (4 mL), which immediately gave a red mixture. The resulting orange precipitate was isolated by filtration; 56% yield (0.055 g, 0.110 mmol); m.p. 205–210 °C (decomp.); ^{1}H NMR ($CDCl_3$): $\delta = 3.62$ (s, 12H), 7.07 (m, 8H), 7.18 ppm (m, 8H); ^{13}C NMR ($CDCl_3$): $\delta = 33.2$ (NCH_3), 64.1 (d, $^1J_{CRh} = 27.1$ Hz, CRh), 108.3 (CH arom.), 122.4 (CH arom.), 133.5 (C arom.), 159.0 (NCN), 185.5 (d, $^1J_{CRh} = 56.8$ Hz, RhCO), 185.3 ppm (d, $^1J_{CRh} = 78.4$ Hz, RhCO); IR (CH_2Cl_2): $\tilde{\nu} = 2052$, $1976\ cm^{-1}$. Single crystals suitable for X-ray analysis were grown from a 1:1 benzene/tetrahydrofuran solution.

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Keywords: allenes · carbenes · donor–acceptor systems · structure elucidation

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