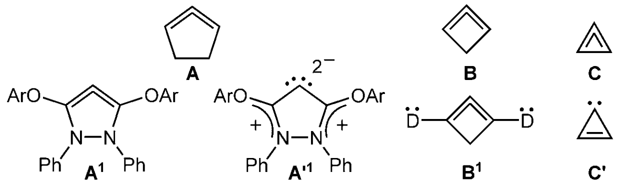
DOI: 10.1002/ange.200901117

Synthesis and Ligand Properties of a Persistent, All-Carbon Four-Membered-Ring Allene**

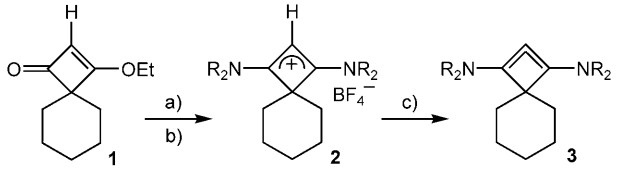
Mohand Melaimi, Pattiyil Parameswaran, Bruno Donnadieu, Gernot Frenking, and Guy Bertrand**

As early as the end of the nineteenth century, Adolf von Baeyer introduced the concept of ring strain,[1] and it is now well recognized that the strain energy increases with decreasing ring size from six to three atoms. This phenomenon is even more pronounced for cyclic allenes,[2] because of the rigidity and linearity of the CCC fragment.[3] Using isodesmic reactions, Johnson and co-workers estimated the strain energy of 1,2-cyclopentadiene (**A**) and 1,2-cyclobutadiene (**B**) at 55 kcal mol^{-1} and 90 kcal mol^{-1}, respectively;[4] the smallest allene-containing ring system, namely, cyclopropadiene (**C**) is much better described as the cyclopropenylidene **C′**.[5,6] Consequently, derivatives of types **A**[7] and **B**[8] have only been described as reactive intermediates.[9] However, we have recently prepared the dinitrogen-containing five-membered ring **A^1**,[10] which is stable at room temperature, both in solution and in the solid state. We have rationalized the surprising stability of **A^1** by the presence of the π-donating substituents, which induces severe disruption of the π system.[11,12] The central carbon atom is not sp-hybridized as in typical all-carbon allenes, but is likely approaching a configuration with two lone pairs of electrons as shown in **A′^{1}**. In other words, **A^1** can be regarded as a carbo(dicarbene), a carbon(0) center ligated by two singlet carbenes.[13]



Our rationalization for the stability of **A^1** has been challenged.[14] Christl and Engels argued that this compound was a deprotonated pyrazolium salt, which benefited from aromaticity. This prompted us to investigate if a push–push substitution pattern could allow the synthesis of a stable 1,2-cyclobutadiene of type **B^1**, an even smaller allene-containing ring system than **A^1**, and which cannot gain any stabilization other than from the two π-donor substituents.

3-Ethoxyspiro[3,5]non-2-en-1-one (**1**)[15] was alkylated with triethyloxonium tetrafluoroborate to afford the corresponding cationic four-membered carbocycle bearing two ethoxy groups, which upon addition of excess piperidine gives salt **2** (Scheme 1). This compound was isolated as air-stable light-yellow crystals in 72% yield and studied by X-ray diffraction[16] (Table 1, center). Addition at room temperature of lithium diisopropylamide (LDA) to a solution of **2** in THF leads to a complex mixture. However, when the same reaction is performed and maintained at −20 °C, allene **3** is cleanly produced. The ^{13}C NMR signals for the central and terminal carbon atoms of the allene moiety appear at $\delta = 151$ and 185 ppm, downfield shifted by $\delta = 58$ and 13 ppm, respectively, relative to those of the starting salt **2**; a similar trend was observed for cyclic allene **A^1** and its conjugate acid precursor ($\delta = 40$ and 35 ppm).



Scheme 1. Synthesis of cyclic allene **3** (R$_2$N = piperidino). a) Et$_3$OBF$_4$; b) piperidine; c) LDA, THF, −20 °C.

Allene **3** is stable for several hours at −20 °C, but readily decomposes above −5 °C to give a complex mixture of unidentified products. The low thermal stability of **3** precluded its isolation and single-crystal X-ray analysis, and we cannot exclude coordination to lithium. The optimized geometry of **3**, at the BP86/def-SVP level of theory (Table 1, left), reveals a very acute allene bond angle (85.0°) and coplanarity of the ring carbon atoms and two nitrogen centers (maximum deviation: 0.006 Å). The CC bonds of the allene fragment (1.42 Å) are significantly longer than standard allene bond lengths (1.31 Å),[17] and the CN bonds are short (1.36 Å). These features are unusual for typical allenes

---

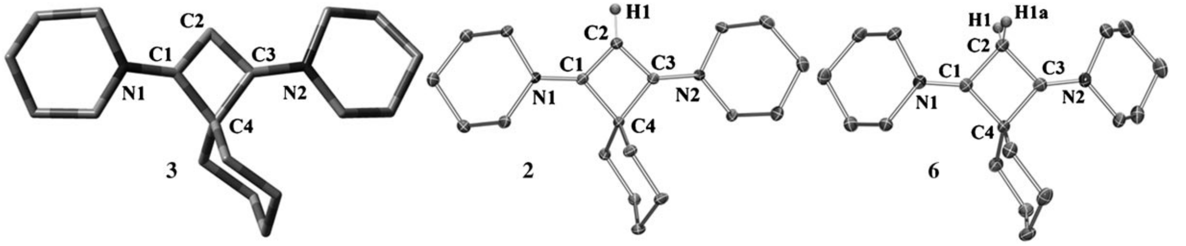
[*] Dr. P. Parameswaran, Prof. G. Frenking
Fachbereich Chemie, Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
Fax: (+49) 6421-282-5566
E-mail: frenking@chemie.uni-marburg.de
Homepage: http://www.uni-marburg.de/fb15/ag-frenking

Dr. M. Melaimi, B. Donnadieu, Prof. G. Bertrand
UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry, University of California
Riverside, CA 92521-0403 (USA)
Fax: (+1)951-827-2725
E-mail: guy.bertrand@ucr.edu
Homepage: http://research.chem.ucr.edu/groups/bertrand/guybertrandwebpage/

[**] Financial support from the NSF (CHE 0808825), Alexander von Humboldt Foundation (fellowship to P.P.), and the DFG is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901117.

Table 1: Calculated geometry of allene **3** and thermal ellipsoid diagrams (35% probability) of monocation **2** and dication **6** (hydrogen atoms are omitted). Selected bond lengths [Å] and angles [°].[a]



	C1C2	C2C3	C3C4	C4C1	N1C1	N2C3	C1C2C3	ΣCN1C	ΣCN2C	M_{dev}	*q*C2	PA
$\mathbf{3}_{calcd}$	1.421	1.425	1.561	1.545	1.358	1.359	85.0	360.0	359.95	0.006	−0.46	
$\mathbf{2}_{exp}$	1.395	1.397	1.558	1.542	1.313	1.314	91.3	359.94	359.90	0.018		
$\mathbf{2}_{calcd}$	1.410	1.414	1.572	1.557	1.329	1.330	92.0	360.0	360.0	0.003	−0.37	306.7
$\mathbf{6}_{exp}$	1.497	1.502	1.543	1.535	1.270	1.276	86.5	360.0	359.96	0.025		
$\mathbf{6}_{calcd}$	1.512	1.518	1.553	1.540	1.297	1.297	86.7	359.97	359.97	0.010	−0.57	152.3

[a] M_{dev}: maximum deviation (in Å) for N1C1C2C3C4N2; *q*C2: partial charge at C2; PA: proton affinity in kcal mol^{-1}.

but are very similar to those observed for $\mathbf{A^1}$ and are due to the polarization of the allenic π bonds towards the central carbon atom. The molecular orbitals (Figure 1) show that the HOMO and HOMO−1 have clearly the largest coefficients at the central carbon atom C2 and exhibit the typical shape of lone-pair molecular orbitals (MOs) with σ (HOMO) and π (HOMO−1) symmetry. Note that the order is reversed with respect to carbodiphosphoranes ($C(PR_3)_2$) and carbodicarbenes ($C(NHC)_2$; NHC = N-heterocyclic carbene).[13] This reversal can be explained by the stabilization of the π orbital (HOMO−1) through partial conjugation of the p(π) atomic orbital (AO) of C2 with the exocyclic C−N π orbitals. In contrast to the parent compound **B**, derivative **3** does not have diradical character; the triplet state in its equilibrium geometry is calculated to be 38.8 kcal mol^{-1} higher in energy than the singlet state.

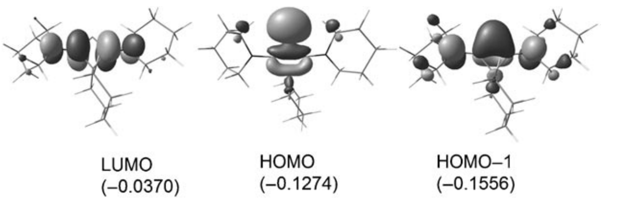
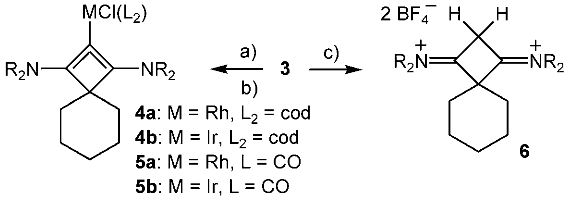


Figure 1. Important frontier molecular orbitals of four-membered-ring allene **3** at BP86/def2-TZVPP//BP86/def-SVP level of theory. Molecular orbital energies in a.u.



Scheme 2. Ligand behavior and double protonation of cyclic allene **3** (R_2N = piperidino). a) [{MCl(cod)}$_2$]; b) CO; c) $HBF_4 \cdot Et_2O$.

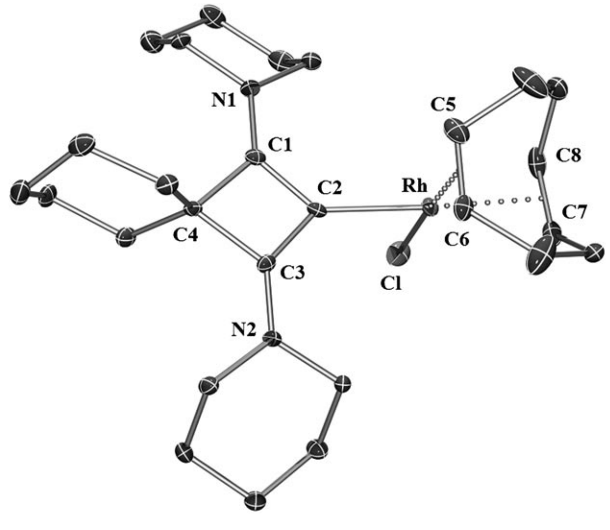


Figure 2. Thermal ellipsoid diagram (35% probability) of **4a** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh–C2 2.038(5), Rh–Cl 2.3803(15), Rh–C5 2.096(4), Rh–C6 2.104(3), Rh–C7 2.212(4), Rh–C8 2.191(5), C1–C2 1.404(6), C2–C3 1.406(6), C3–C4 1.566(5), C1–C4 1.557(5), N1–C1 1.325(5), N2–C3 1.324(5), C1-C2-C3 88.4(3), C2-C3-C4 96.7(3), C3-C4-C1 77.7(2), C4-C1-C2 97.2(3).

We then studied the ligand behavior of **3** (Scheme 2). When [{Rh(cod)Cl}$_2$] (cod = cycloocta-1,5-diene) was added to freshly generated allene **3** at −20 °C, the corresponding η^1 complex **4a** was isolated as thermally stable yellow crystals in 76% yield (Figure 2). As already observed for $\mathbf{A^1}$, upon coordination of **3**, the ^{13}C NMR chemical shift of the central carbon nucleus is shifted to higher field by about 15 ppm [136.6 ($^1J_{C-Rh}$ = 41 Hz)]. The average value of the carbonyl stretching frequencies in square-planar *cis*-[RhCl(CO)$_2$L] complexes is the classical method to assess the donor strength of ligands,[18] and therefore the *cis*-[RhCl(CO)$_2$(**3**)] complex **5a** was prepared by treatment of a solution of **4a** in THF with CO at room temperature. The observed value for the stretching frequency ($\tilde{\nu}_{av}$ = 2016 cm^{-1}) is significantly lower than those observed for analogous complexes bearing all types of cyclic and acyclic amino- and diaminocarbenes

(2020–2060 cm^{-1})[18] and in the range observed for acyclic and five-membered-ring bent allenes (2014 and 2018 cm^{-1}).[10,11] On the basis of the IR stretching frequencies of analogous iridium complexes,[19] the so-called abnormal carbenes (C4-bond NHCs)[20,21] are known as the strongest "carbene" donor ligands. Thus, the [IrCl(CO)$_2$(**3**)] complex **5b** was prepared by using the same reaction sequence as for **5a**, but with [{Ir(cod)Cl}$_2$] as a starting material. The observed average value for ν_{CO} (2002 cm^{-1}) is at the very lower end of the range observed for abnormal carbenes (1999–2020 cm^{-1}).

Therefore, it can be concluded that bent allene **3** is among the strongest donor ligands known so far, the best being the cyclic carbodiphosphorane recently reported by Baceiredo and co-workers ($\tilde{\nu}_{av} = 2001$ cm^{-1} for the Rh complex).[22]

Then, to provide evidence for the possibility of using two lone pairs at the central carbon atom, we investigated the double protonation of cyclic allene **3** (Scheme 2). Indeed, addition of tetrafluoroboric acid diethyl ether complex leads to desired dication **6**, which was isolated in 90% yield, as white crystals. As can be seen in Table 1, although the first protonation of **3** induces a shortening of the C1–C2 and C2–C3 bonds, the second protonation has the opposite effect; moreover, when the number of protons increases, the C–N bonds become shorter. The shortening of C1–C2, C2–C3, N1–C1, and N2–C3 bonds from **3** to **2** can be explained by the enhanced π donation from the nitrogen atoms into the p(π) AO of C2. This effect is correlated by the occupation of the p(π) AO of C2, which increases from 0.81 in **3** to 1.14 in **2**. The second protonation at C2 interrupts the π conjugation and yields essentially C1–C2 and C2–C3 single bonds, which consequently become much longer in **6** than in **2** and **3**. The calculated first and second proton affinities (PAs) of **3** are very high. The theoretically predicted values at the BP86/def2-TZVPP//BP86/def-SVP level are 306.7 and 152.3 kcal mol^{-1}, respectively. The latter value reveals the significant divalent carbon(0) character of the bent allene **3**. Another typical feature of divalent carbon(0) compounds[13] is the negative partial charge at the carbon(0) center, which is retained even in the dication because of the enhanced acceptor strength of the carbon atom after protonation. The natural bond orbital (NBO) charge at C2 is -0.46 e in **3**, -0.37 e in **2**, and -0.57 e in **6**.

These results clearly demonstrate that a single-donor substituent at each terminus is sufficient to make the CCC allene skeleton very flexible, and to give carbon(0) character to the central carbon atom. The relative stability of the very small carbocycle **3** clearly indicates that a wide variety of cyclic allenes can be isolated. Importantly, these compounds behave as strong electron-donating ligands for transition-metal centers, and consequently they should find applications in catalysis.

Received: February 27, 2009

Keywords: allenes · C ligands · reactive intermediates · strained molecules

---

[1] A. von Baeyer, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2269 – 2281.

[2] For reviews on cyclic allenes, see: a) M. Christl in *Modern Allene Chemistry* (Eds.: N. Krause, A. S. K. Hashmi), Wiley-VCH, Weinheim, **2004**, pp. 243 – 357; b) R. P. Johnson, *Chem. Rev.* **1989**, *89*, 1111 – 1124.

[3] *Modern Allene Chemistry* (Eds.: N. Krause, A. S. K. Hashmi), Wiley-VCH, Weinheim, **2004**.

[4] K. J. Daoust, S. M. Hernandez, K. M. Konrad, I. D. Mackie, J. Winstanley, R. P. Johnson, *J. Org. Chem.* **2006**, *71*, 5708 – 5714.

[5] a) M. Z. Kassaee, M. R. Nimlos, K. E. Downie, E. E. Waali, *Tetrahedron* **1985**, *41*, 1579 – 1586; b) C. A. Taatjes, S. J. Klippenstein, N. Hansen, J. A. Miller, T. A. Cool, J. Wang, M. E. Law, P. R. Westmoreland, *Phys. Chem. Chem. Phys.* **2005**, *7*, 806 – 813; c) R. A. Seburg, E. V. Patterson, J. F. Stanton, R. J. McMahon, *J. Am. Chem. Soc.* **1997**, *119*, 5847 – 5856.

[6] For isolated diamino substituted cyclopropenylidenes, see: a) V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722 – 724; b) V. Lavallo, Y. Ishida, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2006**, *118*, 6804 – 6807; *Angew. Chem. Int. Ed.* **2006**, *45*, 6652 – 6655; c) D. Holschumacher, C. G. Hrib, P. G. Jones, M. Tamm, *Chem. Commun.* **2007**, 3661 – 3663.

[7] a) H. Meier, P. Konig, *Nouv. J. Chim.* **1986**, *10*, 437 – 438; b) M. Zheng, K. J. DiRico, M. M. Kirchhoff, K. M. Phillips, L. M. Cuff, R. P. Johnson, *J. Am. Chem. Soc.* **1993**, *115*, 12167 – 12168.

[8] a) M. Balci, Y. Taskesenligil, *Adv. Strained Interesting Org. Mol.* **2000**, *8*, 43 – 81; b) F. Algi, R. Ozen, M. Balci, *Tetrahedron Lett.* **2002**, *43*, 3129 – 3131; c) R. O. Angus, M. W. Schmidt, R. P. Johnson, *J. Am. Chem. Soc.* **1985**, *107*, 532 – 537.

[9] The low-temperature NMR spectroscopic characterization of cyclic all-carbon allenes is limited to those containing more than seven carbon atoms; the only exception is 1,2,4,6-cycloheptatetraene, incarcerated in a molecular container: R. Warmuth, M. A. Marvel, *Angew. Chem.* **2000**, *112*, 1168 – 1171; *Angew. Chem. Int. Ed.* **2000**, *39*, 1117 – 1119.

[10] V. Lavallo, C. A. Dyker, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2008**, *120*, 5491 – 5494; *Angew. Chem. Int. Ed.* **2008**, *47*, 5411 – 5414.

[11] A stable acyclic bent allene has also been prepared: C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2008**, *120*, 3250 – 3253; *Angew. Chem. Int. Ed.* **2008**, *47*, 3206 – 3209.

[12] See also: a) O. Kaufhold, F. E. Hahn, *Angew. Chem.* **2008**, *120*, 4122 – 4126; *Angew. Chem. Int. Ed.* **2008**, *47*, 4057 – 4061; b) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 3254 – 3258; *Angew. Chem. Int. Ed.* **2008**, *47*, 3210 – 3214.

[13] a) R. Tonner, G. Frenking, *Angew. Chem.* **2007**, *119*, 8850 – 8853; *Angew. Chem. Int. Ed.* **2007**, *46*, 8695 – 8698; b) R. Tonner, G . Frenking, *Chem. Eur. J.* **2008**, *14*, 3260 – 3272; c) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273 – 3289; d) R. Tonner, G. Heydenrych, G. Frenking, *ChemPhysChem* **2008**, *9*, 1474 – 1480.

[14] a) M. Christl, B. Engels, *Angew. Chem.* **2009**, *121*, 1566 – 1567; *Angew. Chem. Int. Ed.* **2009**, *48*, 1538 – 1539; b) V. Lavallo, C. A. Dyker, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 1568 – 1570; *Angew. Chem. Int. Ed.* **2009**, *48*, 1540 – 1542.

[15] J. S. Brand, B. C. de Candole, J. A. Brown, *Org. Lett.* **2003**, *5*, 2343 – 2346.

[16] CCDC 721670 (**2**), 721671 (**4a**), 721672 (**4b**), and 721673 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1 – S19.

[18] a) A. Fürstner, M. Alcarazo, H. Krause, C. W. Lehmann, *J. Am. Chem. Soc.* **2007**, *129*, 12676 – 12677; b) W. A. Herrmann, J.

Schutz, G. D. Frey, E. Herdtweck, *Organometallics* **2006**, *25*, 2437 – 2448.

[19] a) A. R. Chianese, X. W. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663 – 1667; b) A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461 – 2468; c) G. D. Frey, C. F. Rentzsch, D. von Preysing, T. Scherg, M. Muhlhofer, E. Herdtweck, W. A. Herrmann, *J. Organomet. Chem.* **2006**, *691*, 5725 – 5738.

[20] For reviews on abnormal carbenes, see: a) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596 – 609; b) M. Albrecht, *Chem. Commun.* **2008**, 3601 – 3610.

[21] Note that pyrazolin-4-ylidene ligands, reported as remote NHCs, can be considered as five-membered-ring allenes: a) Y. Han, H. V. Huynh, *Chem. Commun.* **2007**, 1089 – 1091; b) Y. Han, H. V. Huynh, G. K. Tan, *Organometallics* **2007**, *26*, 6581 – 6585.

[22] a) S. Marrot, T. Kato, H. Gornitzka, A. Baceiredo, *Angew. Chem.* **2006**, *118*, 2660 – 2663; *Angew. Chem. Int. Ed.* **2006**, *45*, 2598 – 2601; b) S. Marrot, T. Kato, F. P. Cossio, H. Gornitzka, A. Baceiredo, *Angew. Chem.* **2006**, *118*, 7607 – 7610; *Angew. Chem. Int. Ed.* **2006**, *45*, 7447 – 7450.