Bent Allenes

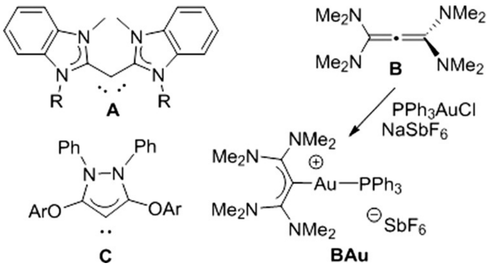
International Edition: DOI: 10.1002/anie.201600765
German Edition: DOI: 10.1002/ange.201600765

Synthesis of a Carbodicyclopropenylidene: A Carbodicarbene based Solely on Carbon

*Conor Pranckevicius, Liu Liu, Guy Bertrand, and Douglas W. Stephan**

***Abstract:** The first carbodicarbene stabilized by flanking cyclopropenylidenes is reported. Tetraphenylcarbodicyclopropenylidene (**2**) is accessed by deprotonation of the corresponding triafulvene cyclopropenium salt, and has been spectroscopically characterized in [D$_8$]THF solution at −60°C. Main-group and transition-metal complexes of **2** have been accessed, and have revealed the high sigma donating ability, and exclusive η^1 binding of this neutral all carbon ligand. Variable temperature NMR spectroscopy studies reveal varying degrees of free rotation in the flanking cyclopropenylidene groups of **2** in its coordination compounds.*

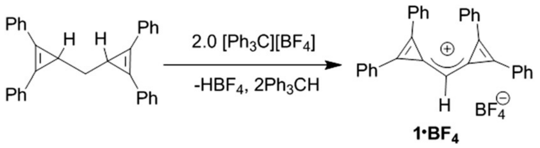
Carbodicarbenes (CDCs) are an emerging family of strongly electron-donating divalent carbon ligands that can be broadly defined as a carbon atom bound to two singlet carbenes to form complexes L→C←L.[1] The electronic nature of the central carbon atom is greatly influenced by the π-accepting nature of the flanking carbenes. Weakly π-accepting carbenes, such as unsaturated N-heterocyclic carbenes (NHCs), yield CDCs with strong σ and π basicity, and significantly bent L-C-L units (Scheme 1; **A**).[2] The incorporation of more strongly π-acidic carbenes, such as acyclic di-amino carbenes, and alkylamino carbenes results in a nearly linear allene like L-C-L configuration.[3] However, these "masked carbone" species have low bending energies, and can bind to transition metals via η^1 coordination through the central carbon atom (Scheme 1; **B**, **BAu**). Cyclic systems have also been used to enforce a bent ground state; a subclass of CDCs known as "cyclic bent allenes" (Scheme 1, **C**).[4] These species have recently been shown to be highly effective spectator ligands in transition-metal-catalyzed hydrogenation,[4d] hydroarylation,[4e] and hydroamination[4f] reactions. While representative CDCs of many of the major classes of singlet carbenes have been accessed, there have been no reports of such systems stabilized by cyclopropenylidenes.



Scheme 1. Representative members of the carbodicarbene ligand family. **A**: Acyclic bent allenes. **B**: Tetraaminoallenes. **C**: Cyclic bent allenes.

The isolation of free 1,2-diaminocyclopropenylidene was reported by Bertrand and co-workers in 2006.[5] The stability of this system is derived by the amino groups at the 1,2 positions, which stabilize carbenoid carbon via charge delocalization.[6] A related species is the singlet 1,2-diphenylcyclopropenylidene. While this carbene has been shown to behave as an effective spectator ligand in cross-coupling catalysts,[7] in free form it has only been observed in an Ar matrix isolation at 10 K.[8] Nevertheless, we rationalized that the CDC derived from this species should yield stable complexes, with an electronic structure similar to the "masked carbone" **B** (Scheme 1). Herein we report the first example of an all carbon-based CDC stabilized by flanking cyclopropenylidenes. The free carbodicyclopropenylidene is characterized in solution and has been captured by main-group fragments and transition-metal complexes.

The synthesis of 1,2-diphenyl-3-(1,2-diphenyltriafulvene-4-yl)cyclopropenium perchlorate **1·ClO$_4$** was reported in 1982 by Okamoto and co-workers in the course of their extensive studies on hydrocarbon salts.[9] By an analogous method, we have prepared the tetrafluoroborate derivative by the addition of two equivalents of trityl tetrafluoroborate to bis(1,2-diphenylcyclopropen-3-yl)methane (Scheme 2). As was observed in **1·ClO$_4$**, the transiently produced dicyclopropenium salt spontaneously loses a proton from the central carbon atom in CH_2Cl_2 solution to form **1·BF$_4$**, which was isolated in a 78% yield. The pale yellow salt is stable to air and moisture, and single crystals can be grown from slow diffusion of Et_2O into a CH_2Cl_2 solution (Figure 1). In the solid state, the three membered rings are canted 16.5(3)° with



1·BF$_4$

Scheme 2. Synthesis of the precursor salt **1·BF$_4$**.

---

[*] C. Pranckevicius, Prof. Dr. D. W. Stephan
Department of Chemistry
University of Toronto
Toronto, ON M5S 3H6 (Canada)
E-mail: dstephan@chem.utoronto.ca

L. Liu, Prof. Dr. G. Bertrand
Joint UCSD-CNRS Research Chemistry Laboratory (UMI 3555),
Department of Chemistry and Biochemistry
University of California San Diego
La Jolla, CA 92093-0343 (USA)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201600765.

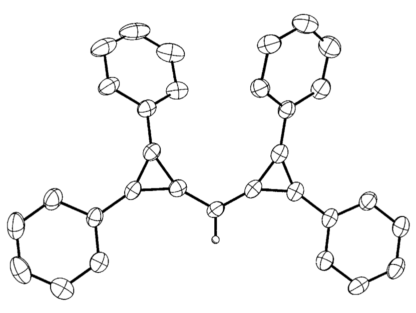
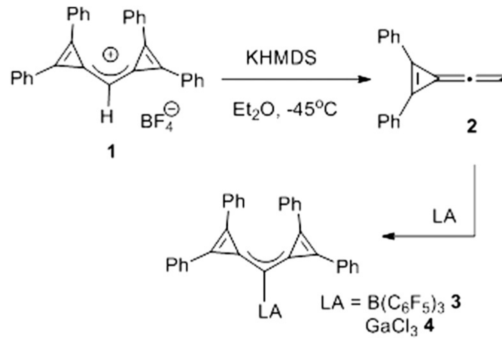


Figure 1. Molecular structure of the cation **1** with thermal ellipsoids set at 50% probability. Hydrogen atoms on phenyl groups are removed for clarity.

respect to each other, owing to the steric interaction of the axially disposed phenyl groups. The distances of the central carbon atom to the adjacent rings are 1.378(3) Å and 1.381(3) Å respectively, supporting the presence of a 3-center–2-electron (3c–2e) π bond. The backbone 1,2-cyclopropene C−C bonds are 1.350(3) Å and 1.356(3) Å, indicating localized double bonds at these positions. These observations support ground state resonance structure depicted in Scheme 2. Restricted rotation about the 3c–2e bond is observed in the room temperature ^{1}H and ^{13}C NMR spectra, giving rise to two inequivalent phenyl rings.

Combination of **1·BF$_4$** with an equimolar portion of potassium hexamethyldisilazide (KHMDS) at −45 °C in Et$_2$O resulted in immediate consumption of the starting material and formation of a deep red solution. However, upon extended stirring at −45 °C, or upon warming to room temperature the solution blackened, and room temperature ^{1}H NMR analysis revealed the presence of numerous decomposition products. Nevertheless, when the reaction was performed in a J-Young NMR tube in [D$_8$]THF and maintained at −60 °C, a single product was observed, consistent with the formulation of **2** (Scheme 3). A single set of phenyl resonances are observed in the ^{1}H NMR spectrum acquired at −60 °C in [D$_8$]THF, suggesting an allene-like conformation. Seven signals are observed in the ^{13}C NMR spectrum at −60 °C (Figure 2). HSQC and DEPTQ-135 experiments indicated that three signals correspond to aryl C-Hs, and the other four to quaternary centers, as would be anticipated for compound **2** (Figure 2).



Scheme 3. Synthesis of tetraphenylcarbodicyclopropenylidene **2** and the main-group adducts **3** and **4**.

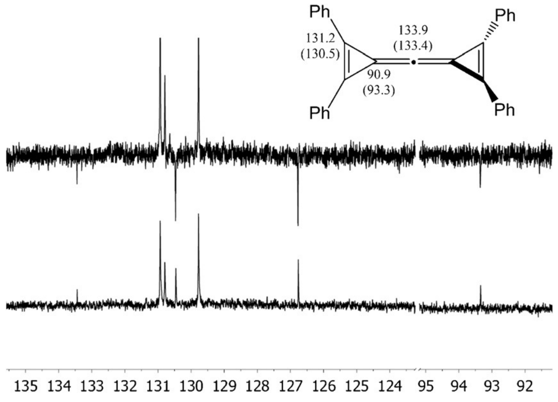


Figure 2. DEPTQ-135 (top) and ^{13}C NMR spectrum (bottom) of **2** generated in situ acquired at −60 °C in [D$_8$]THF. Antiphase signals in the top spectrum indicate quaternary carbon atoms. Calculated ^{13}C NMR resonances (GIAO-B97-2/Def2-TZVP//M06-2X/Def2-SVP) are indicated in the structural drawing of **2**, and observed resonances are indicated in parentheses.

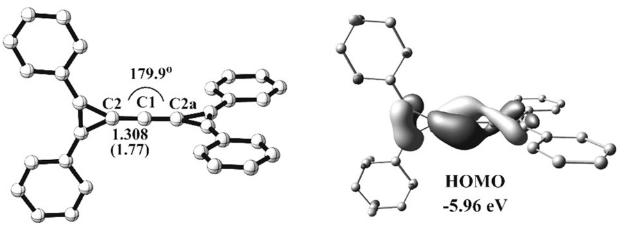


Figure 3. Left: Optimized geometry of **2**. Right: HOMO of **2**.

The molecular structure of **2** was investigated computationally (Figure 3). The density functional theory (DFT) calculations at M06-2X/Def2-SVP level of theory reveal that the central carbon is in an almost linear environment (C2-C1-C2a angle of 179.9°). The C1−C2 (1.308 Å) and C1−C2a (1.308 Å) distances are shorter than those in **1** (1.378 and 1.381 Å). The highest occupied molecular orbital (HOMO) and HOMO−1 of **2** are degenerate and incorporate the π orbitals of the C2-C1-C2a fragment. Furthermore, the Wiberg bond indices (WBIs) of the central C−C bonds from the natural bond orbital (NBO) calculations (M06-2X/TZVP//M06-2X/Def2-SVP level) are both 1.77, indicating C−C double bond character. The C1 atom (−0.19 a.u.) is more negatively charged than those of C2 (−0.04 a.u.) or C2a (−0.04 a.u.), suggesting nucleophilicity of C1 atom. The first and second proton affinities of **2** were determined to be 282.7 and 153.3 kcal mol^{-1}, respectively, similar to those calculated for compound **B** (Scheme 1).[1e] The bending potential of the central allenic moiety of **2** was also investigated. It was found that while the potential is generally shallow (6.6 kcal mol^{-1} to 140° and 10.0 kcal mol^{-1} to 130°; see Supporting Information), it is somewhat deeper than that calculated for **B** (5.6 kcal mol^{-1} to 136.9°).[1c]

^{13}C NMR prediction was also performed (GIAO-B97-2/Def2-TZVP//M06-2X/Def2-SVP level of theory) and was found to correlate well with the resonances observed for **2** at −60 °C in in [D$_8$]THF (Figure 2). The resonance for the central carbon atom was observed at δ = 133.4 ppm and the two flanking carbons at $\delta = 93.3$ ppm, while the corresponding calculated resonances are 133.9 and 90.9 ppm, respectively. Compound **2** decomposes slowly at −60 °C in [D$_8$]THF solution and very rapidly at ambient temperature, forming a complex mixture of products.

The formulation of **2** and its nucleophilic nature was confirmed by its capture with $B(C_6F_5)_3$, which yields the η^1 adduct **3** in 47% yield. Room temperature ^{1}H NMR analysis of **3** reveals very broad signals assignable to two inequivalent phenyl moieties, which sharpen upon cooling to −40 °C. The room temperature ^{19}F NMR spectrum reveals only broad uninformative resonances. However, upon cooling to −40 °C, ^{19}F NMR signals sharpen to reveal restricted rotation about the B–CDC bond and additional restricted rotation in two of the three C_6F_5 rings, giving rise to three sets of *ortho* and *meta* C–F resonances integrating to two fluorine atoms each, and two *para* resonances integrating to two and one fluorine atom, respectively (see supporting information). A very broad signal centered at $\delta = 89.3$ ppm is observed in the ^{13}C NMR at −40 °C, which is assigned to the central carbon atom. The two equivalent flanking carbon atoms give a sharper resonance at $\delta = 154.2$ ppm. Crystals of **3** suitable for X-Ray diffraction were grown from Et_2O at −45 °C (Figure 4). In the solid state, the planes of the two three-membered rings are canted with respect to one another by 28.7(2)°. The central C–B bond in is 1.643(3) Å, and the distances to the flanking carbon atoms are 1.389(3) Å and 1.392(3) Å. Compound **3** is stable at room temperature toward both air and moisture.

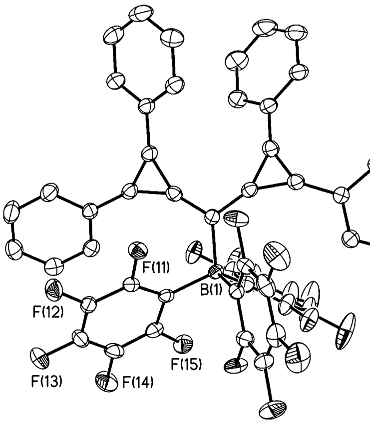


Figure 4. Molecular structure of **3** with thermal ellipsoids set at 50% probability. Hydrogen atoms are removed for clarity.

The analogous, but much more fragile, $GaCl_3$ complex **4** can also be accessed by addition of a $GaCl_3$ solution in Et_2O to freshly generated **2** at −45 °C, and crystals suitable for X-ray diffraction were grown from CH_2Cl_2/Et_2O solution (Figure 5). In the solid state, the canting of the two three-membered rings with respect to one another is 27.1(3)°. The central C–Ga distance in is 1.960(3) Å, and the distances to the flanking carbon atoms are 1.387(4) Å and 1.394(4) Å. Very broad resonances for **4** are observed in the room temperature ^{1}H NMR spectra, which appears to show a single phenyl environment. Cooling to −80 °C in [D$_8$]THF was necessary to achieve decoalescence and sharpening of the two inequivalent phenyl environments anticipated from the solid-state structure. Compound **4** gives a ^{71}Ga NMR signal at $\delta = 251.3$ ppm at −80 °C in [D$_8$]THF, similar to resonances observed for other NHC–$GaCl_3$ adducts.[10] Compound **4** decomposes if exposed to air.

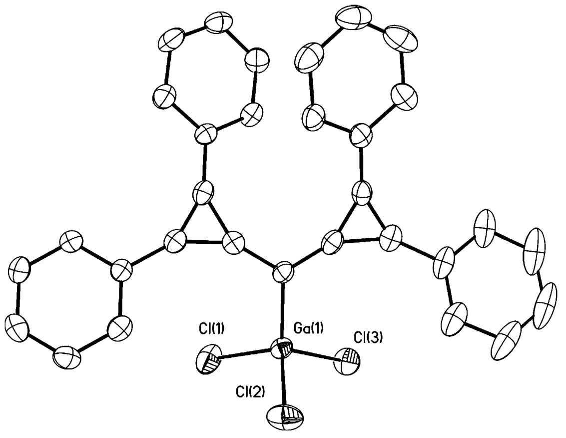
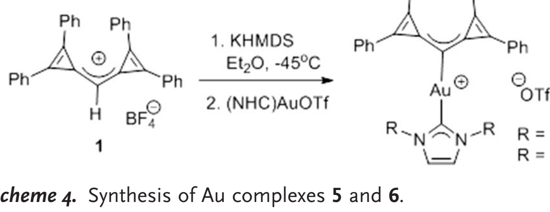


Figure 5. Molecular structure of **4** with thermal ellipsoids set at 50% probability. Hydrogen atoms are removed for clarity.

Recently, Gandon and co-workers reported a "gallium scale" whereby the degree of pyramidalization of $GaCl_3$ in a series of adducts L–$GaCl_3$ was shown to correlate with the Tolman electronic parameter (TEP) of the ligand L, with good correlation across a range of 26 phosphine, NHC, cyclic alkylamino carbene (CAAC), and CDC/carbodiphosphorane derivatives.[11] Placing **2** on the gallium scale, we find that $\Sigma_{ClGaCl} = 320.7°$, which correlates to a TEP of 2044.5. This indicates that **2** is a stronger donor than both NHCs and CAACs, placing it among the strongest electron donors. However, **2** is a weaker donor than other members of the carbone family (TEP typically 2039–2027).

Transition-metal complexes of **2** have also been accessed. Combination of an Et_2O solution of (NHC)AuOTf (NHC = IDipp, IAd) and a freshly generated solution of **2** at −45 °C results in the formation of compounds **5** and **6**, respectively (Scheme 4). The molecular structure of **6** was determined by single-crystal X-ray diffraction, and confirmed the η^1 coordination of **2** to the Au center, as is predicted for members of the carbone family.[1p] This is in contrast to conventional allenes in which the resting state is typically η^2 coordination to Au.[1p,12] Two molecules of **6** are present in an asymmetric unit, which have somewhat different metrical parameters. The Au–C_{CDC} bond lengths are 2.071(6) Å and



Scheme 4. Synthesis of Au complexes **5** and **6**.

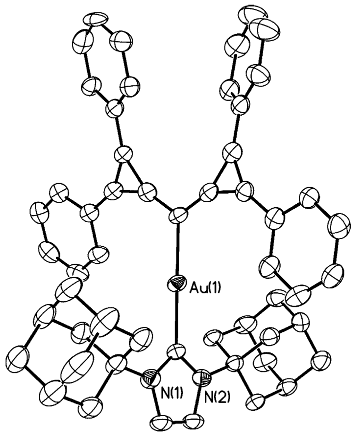


Figure 6. Molecular structure of the cation **6** with thermal ellipsoids set at 50% probability. Hydrogen atoms are removed for clarity.

2.047(6) Å (Figure 6), while the corresponding Au$-$C$_{NHC}$ bond lengths are 2.073(6) Å and 2.042(7) Å, respectively. We attribute this variation to packing effects within the crystal lattice. The angles of the flanking cyclopropenyliene groups with respect to one another are quite similar at 24.2(8)° and 24.3(7)°, respectively.

The room temperature ^{13}C NMR spectrum of **5** reveals a sharp resonance at $\delta = 98.0$ ppm, which is assigned to the central carbon atom, an additional resonance for the flanking cyclopropenylidene carbons is observed at $\delta = 155.8$ ppm. Interestingly, a single set of sharp phenyl resonances is observed for Au bound carbodicyclopropenylidene in **5** in the ^{1}H NMR spectrum acquired at room temperature in [D$_8$]THF. Upon cooling, these signals gradually broaden and finally decoalesce to give two very broad but inequivalent phenyl environments at -80°C (Figure 7), supporting the η^1 binding mode. Similar ^{1}H and ^{13}C NMR resonances are also observed for **6** (see Supporting Information).

It is interesting that compounds **3**–**6** all display some degree of fluxionality in their NMR spectra at room temperature. We postulate that this is due to varying degrees of free rotation in the flanking 1,2-diphenylcyclopropenylidene moieties. In support of this assertion, high temp variable temperature (VT) ^{1}H NMR was carried out on **1·BF$_4$** in $C_2D_2Cl_4$. Above 40°C, the sharp inequivalent phenyl environments begin to broaden, and coalescence to a single broad phenyl environment is observed at 120°C, suggesting that free rotation of the flanking groups is occurring (see Supporting Information). It is reasonable that increasing the π-acceptor ability of the coordination center decreases the barrier to rotation in these flanking groups by delocalization of the electrons in the 3c–2e π bond to the coordination center (Scheme 5), thereby resulting in fast rotation and the equivalent phenyl resonances as observed in **4**, **5** and **6** at room temperature (See Supporting Information for discussion of **3**). This suggests the ability of **2** to act as a four-electron donor to unsaturated centers, as has been observed with other members of the CDC family. Interestingly, **1·BF$_4$** can be protonated at the central carbon by excess HOTf to form the methylene bridged dicyclopropenium salt[9] **7** (Scheme 6), confirming the double basicity of the central carbon atom in **2**. As expected, a single sharp phenyl environment is observed for **7** in the ^{1}H NMR spectrum acquired in CDCl$_3$ solution, indicating fast rotation of the flanking cyclopropenium groups. The central methylene resonance is observed at·$\delta = 5.95$ ppm.

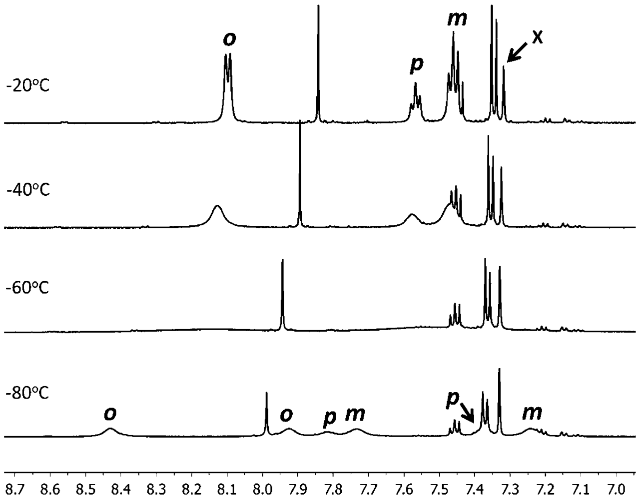
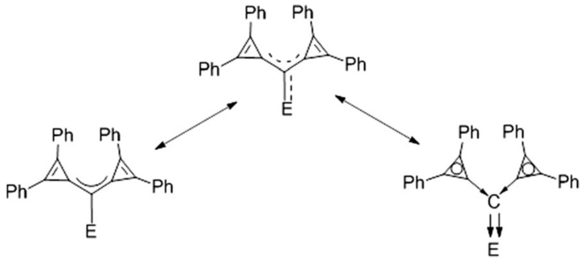
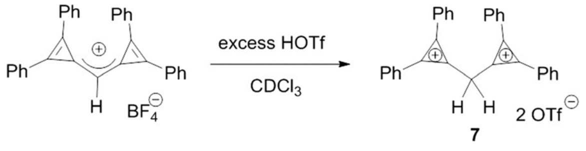


Figure 7. Variable temperature ^{1}H NMR ([D$_8$]THF) spectrum of **5**. *o* = *ortho*, *m* = *meta*, *p* = *para*. X = C_6H_6 impurity.



Scheme 5. Resonance structures of complexes of compound **2**.



Scheme 6. Protonation of **1·BF$_4$**.

In summary, we have reported the first example of a carbodicyclopropenylidene, which is also the first example of a CDC based entirely on carbon. Tetraphenylcarbodicyclopropenylidene (**2**) has been observed to form stable η^1 complexes with both main-group Lewis acids and transition metals. A logical extension of this chemistry would be the study of the corresponding tetra-amino derivative, which is currently under investigation.

Acknowledgements

We acknowledge the financial support of NSERC of Canada and D.W.S. is grateful for the award of a Canada Research Chair. C.P. acknowledges a Walter and Margery Warren QEII-GSST Scholarship for funding. We wish to acknowledge the Canadian Foundation for Innovation, project number 19119, and the Ontario Research Fund for funding of the Centre for Spectroscopic Investigation of Complex Organic Molecules and Polymers. L.L. thanks the China Scholarship Council for a graduate fellowship. G.B. thanks the DOE (DE-FG02-13ER16370) for financial support. Dmitri Ptchugin, Dr. Darcy Burns, and Dr. Jack Sheng at the Centre for Spectroscopic Investigation of Complex Organic Molecules and Polymers are also gratefully acknowledged for their invaluable assistance with the variable-temperature NMR experiments.

Keywords: bent allenes · carbodicarbenes · carbon donors · carbones · gold complexes

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 5536–5540
Angew. Chem. **2016**, *128*, 5626–5630

---

[1] a) R. Tonner, G. Frenking, *Angew. Chem. Int. Ed.* **2007**, *46*, 8695; *Angew. Chem.* **2007**, *119*, 8850; b) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273; c) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260; d) R. Tonner, G. Frenking, *Organometallics* **2009**, *28*, 3901; e) R. Tonner, G. Heydenrych, G. Frenking, *ChemPhysChem* **2008**, *9*, 1474; f) M. Alcarazo, *Dalton Trans.* **2011**, *40*, 1839; g) G. Frenking, R. Tonner, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 869; h) O. Kaufhold, F. E. Hahn, *Angew. Chem. Int. Ed.* **2008**, *47*, 4057; *Angew. Chem.* **2008**, *120*, 4122; i) S. Klein, R. Tonner, G. Frenking, *Chem. Eur. J.* **2010**, *16*, 10160; j) W. Petz, *Coord. Chem. Rev.* **2015**, *291*, 1; k) M. M. Deshmukh, S. R. Gadre, R. Tonner, G. Frenking, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2298; l) G. Frenking, R. Tonner, *Pure Appl. Chem.* **2009**, *81*, 597; m) C. A. Dyker, G. Bertrand, *Nat. Chem.* **2009**, *1*, 265; n) M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nat. Chem.* **2009**, *1*, 295; o) D. S. Patel, P. V. Bharatam, *J. Org. Chem.* **2011**, *76*, 2558; p) C. Esterhuysen, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 9944; q) E. Kleinpeter, P. Werner, A. Koch, *Tetrahedron* **2013**, *69*, 2436; r) H. V. Huynh, G. Frison, *J. Org. Chem.* **2013**, *78*, 328; s) D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics* **2011**, *30*, 5304; t) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389; u) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810; *Angew. Chem.* **2010**, *122*, 8992.

[2] a) W.-C. Chen, Y.-C. Hsu, C.-Y. Lee, G. P. A. Yap, T.-G. Ong, *Organometallics* **2013**, *32*, 2435; b) W.-C. Chen, C.-Y. Lee, B.-C. Lin, Y.-C. Hsu, J.-S. Shen, C.-P. Hsu, G. P. A. Yap, T.-G. Ong, *J. Am. Chem. Soc.* **2014**, *136*, 914; c) C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2008**, *47*, 3206; *Angew. Chem.* **2008**, *120*, 3250; d) Y.-C. Hsu, J.-S. Shen, B.-C. Lin, W.-C. Chen, Y.-T. Chan, W.-M. Ching, G. P. A. Yap, C.-P. Hsu, T.-G. Ong, *Angew. Chem. Int. Ed.* **2015**, *54*, 2420; *Angew. Chem.* **2015**, *127*, 2450; e) D. A. Ruiz, M. Melaimi, G. Bertrand, *Chem. Asian J.* **2013**, *8*, 2940.

[3] a) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2008**, *47*, 3210; *Angew. Chem.* **2008**, *120*, 3254; b) C. M. Weinstein, C. D. Martin, L. Liu, G. Bertrand, *Angew. Chem. Int. Ed.* **2014**, *53*, 6550; *Angew. Chem.* **2014**, *126*, 6668.

[4] a) I. Fernández, C. A. Dyker, A. DeHope, B. Donnadieu, G. Frenking, G. Bertrand, *J. Am. Chem. Soc.* **2009**, *131*, 11875; b) A. DeHope, B. Donnadieu, G. Bertrand, *J. Organomet. Chem.* **2011**, *696*, 2899; c) C. Pranckevicius, D. W. Stephan, *Organometallics* **2013**, *32*, 2693; d) C. Pranckevicius, L. Fan, D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 5582; e) C. C. Roberts, D. M. Matías, M. J. Goldfogel, S. J. Meek, *J. Am. Chem. Soc.* **2015**, *137*, 6488; f) M. J. Goldfogel, C. C. Roberts, S. J. Meek, *J. Am. Chem. Soc.* **2014**, *136*, 6227; g) V. Lavallo, C. A. Dyker, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2008**, *47*, 5411; *Angew. Chem.* **2008**, *120*, 5491; h) M. Melaimi, P. Parameswaran, B. Donnadieu, G. Frenking, G. Bertrand, *Angew. Chem. Int. Ed.* **2009**, *48*, 4792; *Angew. Chem.* **2009**, *121*, 4886.

[5] V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722.

[6] a) L. E. Johnson, D. B. DuPré, *J. Phys. Chem. A* **2007**, *111*, 11066; b) W. Scherer, M. Tafipolsky, K. Öfele, *Inorg. Chim. Acta* **2008**, *361*, 513.

[7] a) D. F. Wass, M. F. Haddow, T. W. Hey, A. G. Orpen, C. A. Russell, R. L. Wingad, M. Green, *Chem. Commun.* **2007**, 2704; b) W. A. Herrmann, K. Öfele, C. Taubmann, E. Herdtweck, S. D. Hoffmann, *J. Organomet. Chem.* **2007**, *692*, 3846; c) D. F. Wass, T. W. Hey, J. Rodriguez-Castro, C. A. Russell, I. V. Shishkov, R. L. Wingad, M. Green, *Organometallics* **2007**, *26*, 4702; d) C. Taubmann, E. Tosh, K. Öfele, E. Herdtweck, W. A. Herrmann, *J. Organomet. Chem.* **2008**, *693*, 2231; e) R. Chotima, T. Dale, M. Green, T. W. Hey, C. L. McMullin, A. Nunns, A. Guy Orpen, I. V. Shishkov, D. F. Wass, R. L. Wingad, *Dalton Trans.* **2011**, *40*, 5316.

[8] J. T. DePinto, W. A. deProphetis, J. L. Menke, R. J. McMahon, *J. Am. Chem. Soc.* **2007**, *129*, 2308.

[9] K. Komatsu, K. Masumoto, Y. Waki, K. Okamoto, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470.

[10] a) S. Tang, J. Monot, A. El-Hellani, B. Michelet, R. Guillot, C. Bour, V. Gandon, *Chem. Eur. J.* **2012**, *18*, 10239; b) A. H. Cowley, F. P. Gabbaï, C. J. Carrano, L. M. Mokry, M. R. Bond, G. Bertrand, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 578; *Angew. Chem.* **1994**, *106*, 584.

[11] A. El-Hellani, J. Monot, S. Tang, R. Guillot, C. Bour, V. Gandon, *Inorg. Chem.* **2013**, *52*, 11493.

[12] M. Paz Muñoz, C. Hurtado-Rodrigo in *PATAI'S Chemistry of Functional Groups*, Wiley, Hoboken, **2009**.

Received: January 22, 2016