Carbon(0) Compounds

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Carbodiylides $C(ECp^*)_2$ (E = B–Tl): Another Class of Theoretically Predicted Divalent Carbon(0) Compounds**

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It was recently recognized that there are organic compounds with the general formula CL_2 where the carbon atom retains its four valence electrons as two lone pairs and where the chemical bonding to the donor ligands L takes place through donor–acceptor interactions $L\rightarrow C\leftarrow L$.[1] The first example for which this bonding mode was proposed is the carbodiphosphorane (CDP) $C(PPh_3)_2$, which was synthesized in 1961[2a] and structurally characterized by an X-ray analysis in 1978.[2b] After realizing the particular bonding situation in CDPs,[1a] we carried out quantum-chemical calculations of the hitherto unknown carbodicarbenes $C(NHC)_2$ (NHC = N-heterocyclic carbene), which possess unusual $C\rightarrow C$ donor–acceptor bonds where a divalent carbon(II) atom acts as σ donor while the divalent carbon(0) atom is a σ acceptor.[1b] Carbodicarbenes have since been synthesized and structurally characterized by Bertrand et al.,[3] and they were extensively studied by Fürstner and co-workers.[4] New carbodicarbenes and related compounds have recently been calculated in a theoretical study[5] that showed that other divalent carbon(0) compounds had already been previously synthesized, but the donor–acceptor bonds had not been identified.[6] It was suggested that, in the light of recent theoretical and experimental findings, there should be a rethinking regarding the bonding of carbon.[7] The name "carbone" was coined for compounds CL_2, which, owing to the existence of two lone pairs, are σ and π donors, whereas carbenes CR_2, which have one lone pair at carbon, are σ donors and (weak) π acceptors.[1e]

Herein we present quantum-chemical calculations that suggest that there is another class of stable carbones CL_2, where L is a Group 13 diyl ligand ECp* (E = B–Tl). Transition metal complexes with ligands ECp* have been the subject of extensive experimental and theoretical investigations since the first stable complex $[(CO)_4Fe\text{-}AlCp^*]$ was isolated and characterized by X-ray analysis in 1997 by Fischer et al.[8a] Further work was reported with Group 13 homologues $[(CO)_4Fe\text{-}ECp^*]$ where E = B, Ga.[8b,c] Numerous other Group 13 complexes with ligands ER, where R is either a strong π donor or a very bulky substituent, have since been reported.[8d–o] Very recently, the first homoleptic complex with an ECp* substituent $[Mo(GaCp^*)_6]$ has been synthesized.[9] Theoretical studies clearly showed that diyl ligands ER are strong σ donors and clearly weaker π acceptors than CO.[10] This fact makes ECp* suitable candidates as ligands for stabilizing a divalent carbon(0) atom in $C(ECp^*)_2$.

Figure 1 shows the optimized geometries of $C(ECp^*)_2$ at the BP86/SVP level of theory.[11] There is a significant difference between the boron compound $C(BCp^*)_2$ and the heavier homologues. The former has a nearly linear B-C-B moiety (bending angle 178.9°) whereas the latter species are strongly bent. The bending angle E-C-E of the heavier homologues varies slightly between 101.3° for $C(GaCp^*)_2$ and 104.5° for $C(TlCp^*)_2$. The calculated bending angles are clearly smaller than in $C(NHC_{Me})_2$ (131.8°) and in $C(PPh_3)_2$ (136.9°).[1c] The wider angle in the latter compound can not be explained by steric repulsion between the more bulky substituents: The theoretically predicted bending angle in the parent compound $C(PH_3)_2$ at the same level of theory is 123.6°.[1c] A possible reason for the stronger bending in $C(ECp^*)_2$ (E = Al–Tl) is discussed below.

The geometry of $C(BCp^*)_2$ suggests that the compound can be considered as the substituted homologue of HB=C=BH, which has been synthesized by reaction of laser-ablated boron atoms with methane in a low-temperature matrix by Andrews.[12] The boron atoms are η^1-bonded to one carbon atom of the respective Cp* ligand. The calculated B1−C0 and B2−C0 bonds in $C(BCp^*)_2$ are 1.380 Å, which is slightly longer than the calculated value of 1.374 Å for the linear equilibrium structure of HB=C=BH at BP86/SVP.[13] The interatomic B−C distances to the other carbon atoms of the ring are much longer, and should not be considered as genuine boron–carbon bonds. The C−C bonds in the Cp* groups, which are rotated with respect to each other by about 90° about the C-B-C axis, show the characteristic pattern of alternating distances in a 1,3-butadiene moiety that is bonded to the carbon atoms C1a or C2a. This situation is strikingly different to the C−C bonds in the Cp* rings of $C(AlCp^*)_2$, which have nearly identical values of between 1.442–1.444 Å. The same holds true for each of the the five Al−C bonds to the carbon atoms of the Cp* ligand, which lie between 2.259–2.272 Å. The calculated equilibrium structure for $C(AlCp^*)_2$ clearly shows that the Cp* ligands are η^5-bonded to aluminum.

The optimized geometries[14] of the remaining homologues $C(ECp^*)_2$, where E = Ga, In, Tl, suggests that there is a trend toward η^3 or η^1 bonding for E-Cp* when E becomes heavier. This becomes obvious by an increasing distortion of the cyclic ligands toward bond alternation of the C−C distances in the ring and particularly by the differences among the E−C bonds to the Cp* ligand. The ligands in $C(GaCp^*)_2$ have one short (2.063 Å) Ga−C bond, two rather long Ga−C bonds (2.479 Å and 2.558 Å), and two very long

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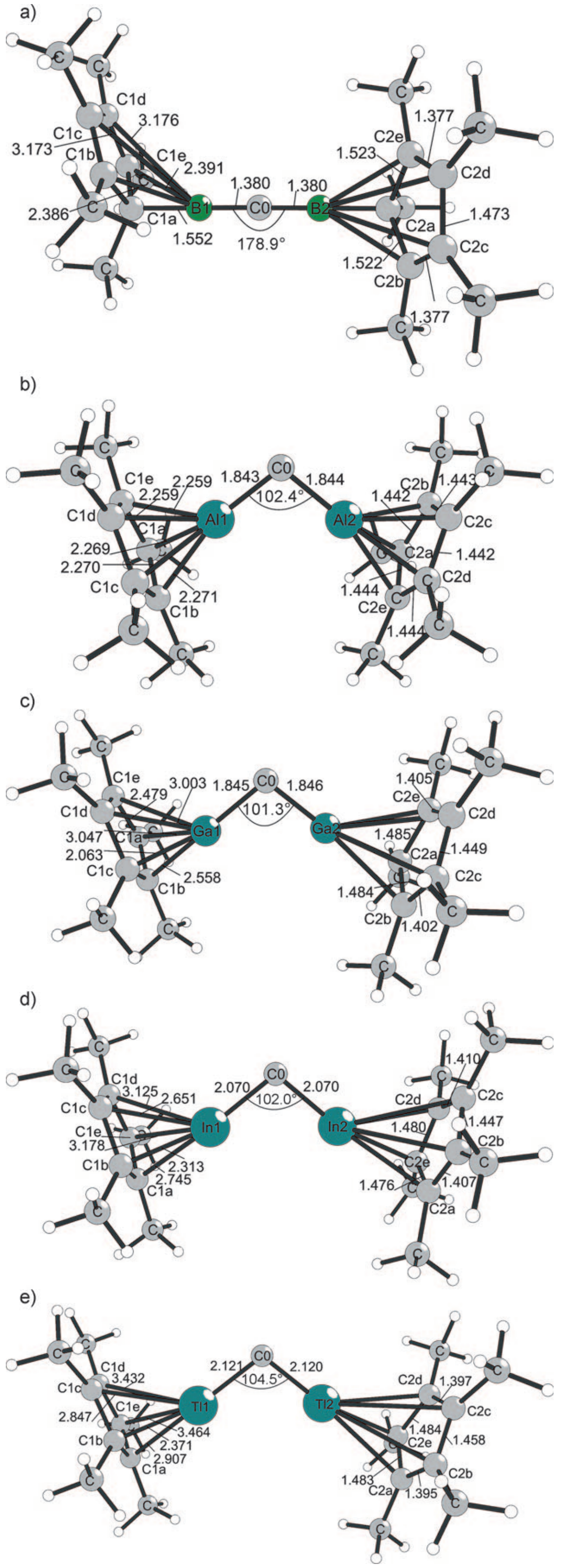

Figure 1. Optimized geometries and important bond lengths [Å] and angles [°] of $C(ECp^*)_2$ at the BP86/SVP level.

Ga–C distances (3.003 Å and 3.047 Å). The Ga–Cp* bonding can be interpreted as intermediate between η^3 and η^1. A similar situation is found for the indium and thallium carbone complexes $C(InCp^*)_2$ and $C(TlCp^*)_2$. Figure 1 shows that the In–C bonds to the Cp* ligands have one rather short (2.331 Å) In–C bond, two rather long In–C bonds (2.651 Å and 2.745 Å), and two very long In–C distances (3.125 Å and 3.178 Å). The analogous values for $C(TlCp^*)_2$ are 2.371 Å for the short Tl–C bond, 2.847 Å and 2.907 Å for the long Tl–C bonds, and 3.432 Å and 3.464 Å for the very long Tl–C distances.

A characteristic attribute of a carbone is the appearance of two carbon lone-pair orbitals and a large second proton affinity (PA).[1,15] Figure 2 shows the shape of the energetically highest-lying orbitals HOMO and HOMO−1. The occupied MOs of $C(BCp^*)_2$ exhibit the shape of a nearly degenerate pair of orbitals that have approximate π symmetry. The HOMO and HOMO−1 are strongly delocalized over the whole molecule and thus do not resemble lone-pair orbitals. In contrast, the highest-lying occupied MOs of $C(AlCp^*)_2$ are easily identified as π lone-pair (HOMO) and σ lone-pair (HOMO−1) orbitals at the central carbon atom. It should be noted that the back lobe of the carbon σ lone pair also has some bonding contributions from aluminum. We believe that this is the reason why the heavier carbone complexes $C(ECp^*)_2$ have more acute bonding angles than the carbodiphosphoranes $C(PR_3)_2$ and the carbodicarbenes $C(NHC)_2$. The ligand atoms E in the carbodiylides have formally empty p(π) orbitals. Although they are partially filled by charge donation from the Cp* π orbitals, they still serve as electron acceptor for the carbon σ lone pair by its back lobe. This weakly attractive E-C-E interaction leads to a rather acute bonding angle. A similar situation to that for $C(AlCp^*)_2$ is found for the HOMO and HOMO−1 of the heavier homologues $C(ECp^*)_2$ (E = Ga–Tl). The main difference is that the HOMO−1 in the latter species has increased contributions from the π orbitals of the Cp* moieties.

The chemically most meaningful property of carbones is the ability to serve as double Lewis base. Table 1 shows the first and second PAs of the compounds $C(ECp^*)_2$. The theoretical values for the carbones with phosphane ligands $C(PPh_3)_2$ and with carbene ligands $C(NHC_{Me})_2$ and also for the unsaturated carbene NHC_{Me} are given for comparison. The first PAs of the heavier carbodiylides $C(ECp^*)_2$, where E = Al–Tl, are very high. The calculated values (270.7–292.8 $kcal\,mol^{-1}$) are in the same range as the first PA of $C(PPh_3)_2$ (280.0 $kcal\,mol^{-1}$) and $C(NHC_{Me})_2$ (294.3 kcal mol^{-1}), which means that they are among the most basic carbon compounds. Note that even the boron compound $C(BCp^*)_2$, which has a nearly linear B-C-B moiety, has a very high first PA of 288.1 $kcal\,mol^{-1}$; this value is nearly identical to the value for the bent carbodiylide $C(AlCp^*)_2$, which has a first PA of 287.8 $kcal\,mol^{-1}$. The bending potential for Cp*B-C-BCp* is very shallow, and only 3.2 $kcal\,mol^{-1}$ are required to distort the equilibrium geometry to a bent structure, for which the bending angle is the same as in protonated molecule $C(BCp^*)_2H^+$ (135.2°).

The theoretically predicted second PAs of all the compounds $C(ECp^*)_2$ are very high. The calculated data are in a

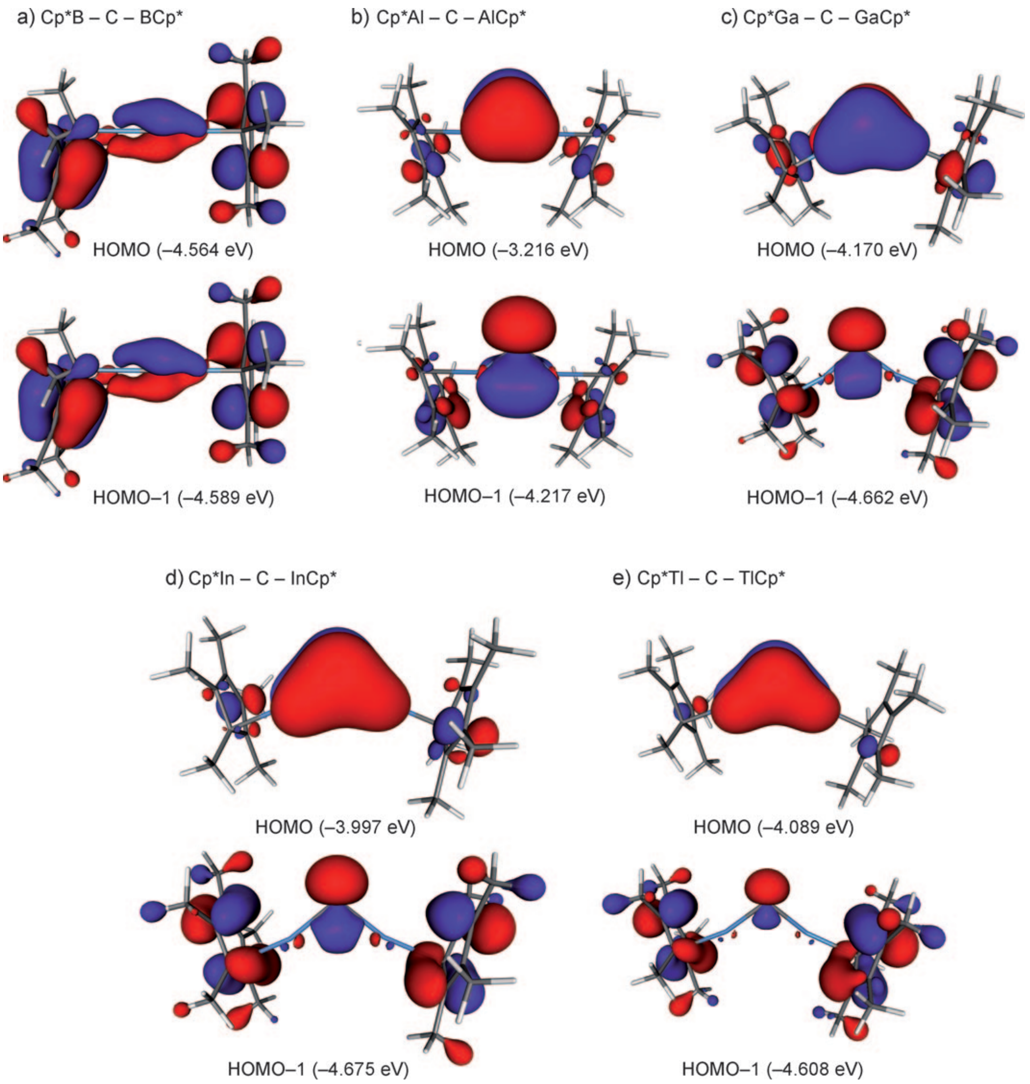

Figure 2. Highest-lying occupied molecular orbitals HOMO and HOMO−1 of C(ECp*)$_2$.

close range between 197.0 kcal mol^{-1} (E = B) and 184.9 kcal mol^{-1} (E = Tl). The calculated second PAs of C(ECp*)$_2$ are even higher than for the carbodiphosphorane C(PPh$_3$)$_2$ (185.6 kcal mol^{-1}) and the carbodicarbene C(NHC$_{Me}$)$_2$ (168.4 kcal mol^{-1}). The values for the second PA clearly distinguish a carbone from a carbene. Table 1 shows that the first PA of NHC$_{Me}$ (262.3 kcal mol^{-1}) is only slightly smaller than for the carbones, but the second PA (71.8 kcal mol^{-1}) is roughly 100 kcal mol^{-1} weaker than for the carbone CL$_2$.

The strongly bent geometries of the heavier Group 13 species C(ECp*)$_2$ (Al–Tl) and the very high second PAs clearly identify the compounds as carbones. The large value for the second PA of the boron compound C(BCp*)$_2$ suggests that it should also be considered as a carbone, even though the equilibrium structure and the shape of the frontier orbitals does not. A similar situation was found for tetraaminoallenes (TAAs) (R$_2$N)$_2$C=C=C(NR$_2$)$_2$. Calculations showed that TAAs with R = methyl or ethyl have a nearly linear C$_3$ moiety and a bonding situation that is typical for an allene. However, they also show that the second PA of the TAAs is even higher than in carbodicarbenes C(NHC)$_2$.[1b–d] The latter finding is supported by experimental work, which showed that TAAs are easily protonated twice at the central carbon but not at the amino substituents. Doubly protonated TAAs are stable species that have been structurally characterized by X-ray analysis.[16] The very strong nucleophilicity of the central carbon atom of the TAAs also comes to the fore by the observation that they easily react with CO$_2$, yielding stable donor–acceptor complexes, which feature a [(R$_2$N)$_2$C]$_2$C→CO$_2$ donor–acceptor bond.[17] It was suggested that the (quasi)linear TAAs should be considered as "hidden" divalent carbon(0) compounds because of their aptitude to serve as double Lewis base in chemical reactions.[1d] The results that are presented herein show that the

Table 1: Summary of calculations carried out on carbones CL$_2$ and the carbene NHC$_{Me}$.[a]

CL$_2$	1st PA	2nd PA	D_0^{298}	L→C(^{1}D)	q(C)
C(BCp*)$_2$	288.1	197.0	216.2	122.7	−1.29
C(AlCp*)$_2$	287.8	191.6	125.2	77.2	−1.81
C(GaCp*)$_2$	292.8	195.2	83.4	56.3	−1.57
C(InCp*)$_2$	279.0	190.0	53.7	41.4	−1.47
C(TlCp*)$_2$	270.7	184.9	26.1	27.6	−1.35
C(PPh$_3$)$_2$	280.0[c]	185.6[c]	147.8[b]	88.5[b]	−1.43[b]
C(NHC$_{Me}$)$_2$	294.3[c]	168.4[c]	177.7[b]	103.4[b]	−0.50[b]
NHC$_{Me}$	262.3[d]	71.8[d]	166.8	98.0	+0.04

[a] Calculated first and second proton affinities (PA) of carbones CL$_2$ and the carbene NHC$_{Me}$; theoretically predicted bond dissociation energies (D_0^{298}), including vibrational and thermal contributions, for the reactions CL$_2$→C(^{3}P) + 2 L and NHC$_{Me}$→C(^{3}P) + MeN=CH−CH=NMe at MP2/TZVPP//BP86/SVP; estimated strength of the L→C(^{1}D) donor–acceptor bonds in kcal mol^{-1}. The data are calculated using one-half of the D_0^{298} values, which are corrected by the excitation energy C(^{3}P)→C(^{1}D) (29.1 kcal mol^{-1}). Atomic partial charges at the divalent carbon atom q(C) calculated at the BP86/TZVPP//BP86/SVP level; all energy values in kcal mol^{-1}. [b] From reference [1c]. [c] From reference [1b]. [d] From reference [15].

carbodiylide $C(BCp^*)_2$ also belongs to the class of "hidden" carbones.

Table 1 also gives the theoretically predicted bond dissociation energies (BDEs) for the reactions $C(ECp^*)_2 \rightarrow C(^3P) + 2\,ECp^*$. It becomes obvious that the bond strength becomes significantly weaker when the Group 13 atom becomes heavier. The C−BCp* bonds have an average BDE value $D_0^{298} = 108.1\ \text{kcal mol}^{-1}$, which means that the carbon–boron double bonds are very strong. The donor–acceptor bonds of the heavier carbodiylides are weaker than the C−L bonds in $C(PPh_3)_2$ and $C(NHC_{Me})_2$. The average BDE for the C−TlCp* bonds are only $D_0^{298} = 13.1\ \text{kcal mol}^{-1}$. We believe, however, that the BDEs of the lighter homologues are sufficiently high that the compounds $C(ECp^*)_2$ may be synthesized in a condensed phase. We also calculated the strength of the donor–acceptor interactions in $C(ECp^*)_2$ by taking the BDE of D_0^{298} and adding the $C(^3P) \rightarrow C(^1D)$ excitation energy, which gives the donor–acceptor bond strength for two $L \rightarrow C(^1D)$ bonds. Table 1 gives the theoretically estimated values for one $L \rightarrow C(^1D)$ bond. The data show that even the thallium compound $C(TlCp^*)_2$ has rather strong donor–acceptor bonds compared with typical Lewis donor–acceptor complexes of main-group elements.[18]

Table 1 gives also the atomic partial charges calculated by the NBO method for the divalent carbon atoms of the carbones CL_2 and the carbene NHC_{Me}. The divalent carbon(0) atom of the carbodiylides carries a very large negative charge of between −1.29 e in $C(BCp^*)_2$ and −1.81 e in $C(AlCp^*)_2$. The negative partial charges at the divalent carbon atom in the carbones CL_2 support the donor-acceptor bonding model $L \rightarrow C \leftarrow L$. They are in striking contrast to the partial charge at the divalent carbon(II) atom in the carbene NHC_{Me}, which carries a small positive charge of +0.04 e.

In summary, we have presented quantum-chemical calculations that suggest that carbodiylides $C(ECp^*)_2$ with E = B–Tl are synthetically accessible compounds that belong to the growing numbers of divalent carbon(0) compounds (carbones). The results are a challenge for the skills of experimental chemists.

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[1] a) R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking, *Angew. Chem.* **2006**, *118*, 8206; *Angew. Chem. Int. Ed.* **2006**, *45*, 8038; b) R. Tonner, G. Frenking, *Angew. Chem.* **2007**, *119*, 8850; *Angew. Chem. Int. Ed.* **2007**, *46*, 8695; c) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260; d) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273; e) R. Tonner, G. Frenking, *Pure Appl. Chem.* **2009**, *81*, 597.

[2] a) F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1961**, *83*, 3539; b) G. E. Hardy, J. I. Zink, W. C. Kaska, J. C. Baldwin, *J. Am. Chem. Soc.* **1978**, *100*, 8001.

[3] a) C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2008**, *120*, 3250; *Angew. Chem. Int. Ed.* **2008**, *47*, 3206; b) I. Fernandez, C. A. Dyker, A. DeHope, B. Donnadieu, G. Frenking, G. Bertrand, *J. Am. Chem. Soc.* **2009**, *131*, 11875.

[4] a) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 3254; *Angew. Chem. Int. Ed.* **2008**, *47*, 3210; b) M. Alcarazo, W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nat. Chem.* **2009**, *1*, 295.

[5] S. Klein, R. Tonner, G. Frenking, *Chem. Eur. J.* **2010**, DOI: 10.1002/chem.201000174.

[6] a) J.-M. Sotiropoulos, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1987**, *109*, 4711; b) N. Dubau-Assibat, A. Baceiredo, F. Dahan, G. Bertrand, *Bull. Soc. Chim. Fr.* **1995**, *132*, 1139; c) J. M. Sotiropoulos, A. Baceiredo, G. Bertrand, *Bull. Soc. Chim. Fr.* **1992**, *129*, 367.

[7] "*Chemical Bonding: Rethinking Carbon*": C. A. Dyker, G. Bertrand, *Nat. Chem.* **2009**, *1*, 265.

[8] a) J. Weiß, D. Stetzkamp, B. Nuber, R. A. Fischer, C. Boehme, G. Frenking, *Angew. Chem.* **1997**, *109*, 95; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 70; b) J. Su, X.-W. Li, R. C. Crittendon, C. F. Campana, G. H. Robinson, *Organometallics* **1997**, *16*, 4511; c) A. H. Cowley, V. Lomeli, A. Voigt, *J. Am. Chem. Soc.* **1998**, *120*, 6401; d) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685; e) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882; *Angew. Chem. Int. Ed.* **1998**, *37*, 1786; f) R. A. Fischer, M. M. Schulte, J. Weiss, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S. F. Vyboishchikov, *J. Am. Chem. Soc.* **1998**, *120*, 1237; g) W. Uhl, M. Pohlmann, R. Wartchow, *Angew. Chem.* **1998**, *110*, 1007; *Angew. Chem. Int. Ed.* **1998**, *37*, 961; h) H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355; *Angew. Chem. Int. Ed.* **1998**, *37*, 3179; i) P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, *Organometallics* **1998**, *17*, 1305; j) S. T. Haubrich, P. P. Power, *J. Am. Chem. Soc.* **1998**, *120*, 2202; k) Q. Yu, A. Purath, A. Donchev, H. Schnöckel, *J. Organomet. Chem.* **1999**, *584*, 94; l) B. Wrackmeyer, *Angew. Chem.* **1999**, *111*, 817; *Angew. Chem. Int. Ed.* **1999**, *38*, 771; m) R. A. Fischer, J. Weiss, *Angew. Chem.* **1999**, *111*, 3002; *Angew. Chem. Int. Ed.* **1999**, *38*, 2830; n) G. Frenking, J. Uddin, W. Uhl, M. Benter, S. Melle, W. Saak, *Organometallics* **1999**, *18*, 3778; o) D. Weiss, T. Steinke, M. Winter, R. A. Fischer, N. Fröhlich, J. Uddin, G. Frenking, *Organometallics* **2000**, *19*, 4583.

[9] T. Cadenbach, T. Bollermann, C. Gemel, I. Fernández, M. von Hopffgarten, G. Frenking, R. Fischer, *Angew. Chem.* **2008**, *120*, 9290; *Angew. Chem. Int. Ed.* **2008**, *47*, 9150.

[10] a) J. Uddin, C. Boehme, G. Frenking, *Organometallics* **2000**, *19*, 571; b) C. Boehme, J. Uddin, G. Frenking, *Coord. Chem. Rev.* **2000**, *197*, 249; c) J. Uddin, G. Frenking, *J. Am. Chem. Soc.* **2001**, *123*, 1683 .

[11] Geometry optimizations without symmetry constraints were carried out using the Gaussian 03[19] optimizer together with TurboMole 6.0.2[20] energies and gradients at the BP86[21]/def2-SVP[21a] level of theory (called BP86/SVP). Small-core ECPs[21b] were used for the elements In and Tl. Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level. Thermodynamic corrections were taken from these calculations. The standard state for all thermodynamic data was 298.15 K and 1 atm. Single-point energies were calculated for some molecules with the MP2 method[23] using the def2-TZVPP[22] (called TZVPP) basis set. The resolution-of-identity method has been used for the MP2 and BP86 calculations.[24] The atomic partial charges were calculated with the NBO method[25] at BP86/TZVPP without RI approximation on the BP86/SVP geometries.

[12] P. Hassanzadeh, L. Andrews, *J. Am. Chem. Soc.* **1992**, *114*, 9239.

[13] The equilibrium structures of the heavier parent systems $C(EH)_2$, where E = Al—Tl, also have strongly bent geometries at the BP86/SVP level: the bending angle E-C-E is between

100.5° (E = Al) and 109.0° (E = Tl), which correlates with the strongly bent structures of the systems C(ECp*)$_2$. The linear structures of C(EH)$_2$ and C(ECp*)$_2$ (E = Al–Tl) are not minima on the singlet potential-energy surface. C(BH)$_2$ has a higher-lying local energy minimum at BP86/SVP, which is strongly bent (bending angle 93.4°), that is 3.4 kcal mol^{-1} less stable than the linear form. The bent form of C(BH)$_2$ has a very shallow energy minimum on the PES, which requires less than 1 kcal mol^{-1} activation energy to yield the linear energy minimum form. There are no local energy minima with linear geometry for C(EH)$_2$ and C(ECp*)$_2$ (E = Al–Tl). Preliminary calculations suggest that the preference for the bent structures of C(EH)$_2$ correlates with the singlet–triplet gap of EH.

[14] The calculated C–C and E–C bonds in C(ECp*)$_2$ are slightly different for the two ligands Ecp*, but the differences are not very large. The full set of bond lengths and angles is given in the Supporting Information, Table S1.

[15] R. Tonner, G. Heydenrych, G. Frenking, *ChemPhysChem* **2008**, *9*, 1474.

[16] M. J. Taylor, P. W. J. Surman, G. R. Clark, *J. Chem. Soc. Chem. Commun.* **1994**, 2517.

[17] H. G. Viehe, Z. Janousek, R. Gompper, D. Lach, *Angew. Chem.* **1973**, *85*, 581; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 566.

[18] a) A. Haaland, *Angew. Chem.* **1989**, *101*, 1017; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992; b) V. Jonas, G. Frenking, M. T. Reetz, *J. Am. Chem. Soc.* **1994**, *116*, 8741; c) G. Frenking, K. Wichmann, N. Fröhlich, C. Loschen, M. Lein, J. Frunzke, V. M. Rayón, *Coord. Chem. Rev.* **2003**, *238–239*, 55.

[19] a) Gaussian 03, Rev. D.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, **2004**; for the full reference, see the Supporting Information; b) C. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, *J. Comput. Chem.* **1996**, *17*, 49.

[20] R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel, *Chem. Phys. Lett.* **1989**, *162*, 165.

[21] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[22] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297; b) B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* **2000**, *113*, 2563.

[23] a) C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618; b) J. S. Binkley, J. A. Pople, *Intern. J. Quantum Chem.* **1975**, *9S*, 229.

[24] a) K. Eichkorn, O. Treutler, H. Ohm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652; b) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057; c) F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, 97, 331; d) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143.

[25] a) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066; b) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735; c) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.