Cyclopropenylium−Borate Betaines: Opening an Organometallic Route to Neutral Carbocation-Like Compounds

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Treatment of bis(propynyl)zirconocene (**5**) with a stoichiometric quantity of $B(C_6F_5)_3$ leads to C–C coupling of the alkynyl ligands to form the zirconocene–(μ-hexadiyne)–borate betaine complex **11**. This apparently is in an endothermic equilibrium with a methylenecyclopropene-type isomer **13**, formed by intramolecular alkyne insertion into the (sp^2-carbon)–zirconium linkage, which is very effectively trapped by added scavenger reagents such as organic nitriles or isonitriles, to yield the stable unsaturated three-membered ring products **14** or **15**, respectively. Subsequent hydrolysis removes the zirconocene moiety from the product, but the newly formed (sp^2-carbon)–$B(C_6F_5)_3$ linkage remains intact. The resulting products **16** and **17** formally contain a central methylenecyclopropene framework, but their structural properties point to a substantial π-delocalization, that indicates a pronounced participation of an enamino-substituted cyclopropenylium–borate betaine resonance structure. The description of the neutral betaine compounds **16** and **17** as approaching cyclopropenylium cation-type compounds that have their counteranion covalently bonded to them, is further supported by the observation of low activation barriers of the rotation around the exocyclic C3–C4 bond [$\Delta G^{\neq}_{\text{CCrot}}$ (330 K) = 17.5 ± 0.5 kcal mol^{-1} for **17a**] and around the C5–N linkage [$\Delta G^{\neq}_{\text{CNrot}}$ (306 K) = 14.5 ± 0.5 kcal mol^{-1} for **16a**]. The neutral cyclopropenylium–betaine compound **17a** shows a carbocation-like chemical reactivity, and inserts *tert*-butyl isocyanide to yield the ring-expanded four-membered carbocyclic product **21**.

Introduction

Cyclopropenylium cations $C_3R_3^+$ (**1**) represent the smallest members of the carbocyclic arenes. The many reported examples of this class of compounds profit from the marked thermodynamic stabilization provided by aromaticity, but kinetically the reactivity features of many cyclopropenylium systems appear to be largely governed by their ionic nature, and hence by electrostatic effects.[1] It would be interesting to see how the cyclopropenylium arenes would behave in the absence of their positive charge. In principle, this could be achieved by covalently attaching a suitable anion as a

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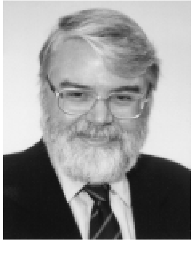

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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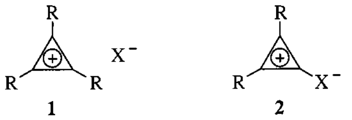
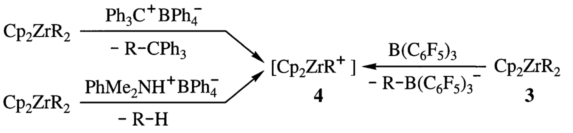
substituent to the cyclopropenylium core. Such a construction would result in the formation of a cyclopropenylium betaine **2**, a system that is neutral overall, but may be highly polarized and function chemically as a cyclopropenylium system without the electrostatic effects of the otherwise dominating positive charge, provided of course that the right combination of substituents and the internal anion moiety is used (Scheme 1).



Scheme 1. Design of a cyclopropenylium betaine **2**, a potential carbocyclic three-membered ring arene without a featured positive charge

It is well established that dialkylzirconocene complexes are easily converted into [$^{R}Cp_2ZrR^+$] cations by treatment with a variety of electrophilic reagents.[2] The reaction of $^{R}Cp_2ZrR_2$, generated in situ, with methylalumoxane is mostly used for a direct generation of the [$^{R}Cp_2ZrR^+$] species, serving as a very active homogeneous metallocene Ziegler catalyst for α-olefin polymerization.[3] Treatment of a variety of $^{R}Cp_2ZrR_2$ starting materials with either a suitable Lewis acid [e.g. $B(C_6F_5)_3$] or Brønsted acid [e.g. $PhMe_2NH^+$ BPh_4^-], or a stable carbenium ion [e.g. Ph_3C^+ BPh_4^-] has invariably resulted in the formation of stable and isolable [$^{R}Cp_2ZrR^+$] cations, albeit generally carrying σ-ligands R with sp^3-carbon atoms bonded to the transition metal center.[4] The observation of some unusual chemistry taking place with alkynyl zirconocene cations [$Cp_2Zr-C\equiv C-R^+$], generated by the Lewis acid route mentioned above, has led to the development of a simple organometallic route to a variety of examples of cyclopropenylium−betaine systems **2**, to the best of our knowledge representing the first examples of their kind. The development of this synthetic entry is reviewed in this article, along with a description of the structural features and some chemistry of the unique cyclopropenylium−borate betaines prepared by our new reaction (Scheme 2).

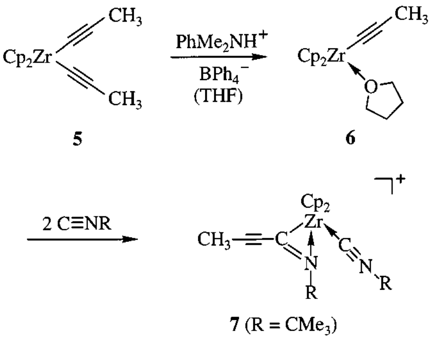


Scheme 2. Methods of [Cp_2ZrR^+] cation generation used in this study

Results and Discussion

(Propynyl)zirconocene Cation Prepared by a Protonation Route

Bis(propynyl)zirconocene (**5**) was synthesized by treatment of zirconocene dichloride with two molar equivalents of propynyllithium.[5] The X-ray crystal structure analysis of **5** revealed a Zr−C(sp) σ-bond length of 2.249(3) Å, which is only slightly shorter than the documented Zr−C(sp^3) bond length in $Cp_2Zr(CH_3)_2$ [2.277(5) Å], thus indicating that there is probably no extensive propargyl π-interaction of the $-C\equiv C-R$ unit with the 16-electron metallocene moiety in **5**.[5] Treatment of **5** with the Brønsted acid *N*,*N*-dimethylanilinium tetraphenylborate in THF, furnished the (σ-propynyl)zirconocene cation−THF adduct **6**. This turned out to be a very reactive and sensitive complex, but we were able to characterize it chemically by means of an alkyl isocyanide insertion reaction. *tert*-Butyl isocyanide inserts into the Zr−C(sp) σ-bond of **6** to form an (η^2-iminoacyl)zirconocene cation complex, which takes up another equivalent of the isonitrile reagent to form the stable product **7** that was isolated and characterized by X-ray diffraction (see Scheme 3 and Figure 1).[6]



Scheme 3. Generation and reaction of a THF-stabilized (σ-alkynyl)zirconocene cation

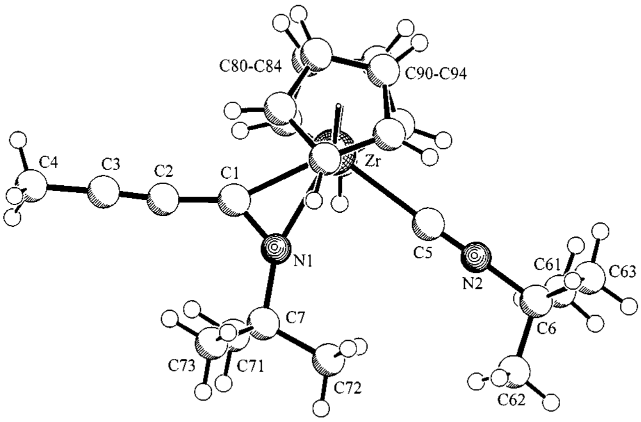
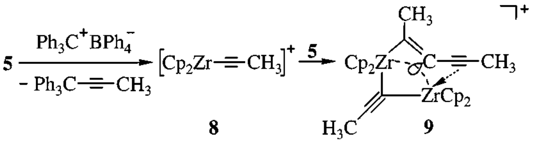


Figure 1. Molecular structure of **7** (cation only); selected bond lengths [Å] and angles [°]: Zr−C1 2.194(3), Zr−N1 2.229(3), Zr−C5 2.350(4), Zr−C(Cp) 2.501(4), C1−N1 1.264(4), C1−C2 1.412(5), C2−C3 1.191(5), C3−C4 1.453(5), N1−C7 1.499(4), C5−N2 1.148(4), N2−C6 1.464(4); C1−Zr−C5 117.36(12), C1−Zr−N1 33.20(11), N1−Zr−C5 84.17(11), Zr−C1−N1 74.9(2), Zr−C1−C2 153.7(3), Zr−N1−C1 71.9(2), Zr−N1−C7 158.8(2), Zr−C5−N2 177.3(3), C1−C2−C3 173.0(4), C2−C3−C4 177.2(4), C2−C1−N1 131.3(3), C1−N1−C7 129.0(3), C5−N2−C6 176.1(4)

(Propynyl)zirconocene Cation Generated by the Trityl Cation Route Leads to a Stable Planar-Tetracoordinated Carbon Compound

Treatment of bis(propynyl)zirconocene (**5**) with trityl tetraphenylborate led to the abstraction of a σ-$C\equiv C-CH_3$ ligand (to yield $Ph_3C-C\equiv C-CH_3$) and generation of the donor-ligand free [$Cp_2Zr-C\equiv C-CH_3^+$] cation (**8**). In contrast with the analogous [$Cp_2Zr-CH_3^+$] cation, complex **8**



Scheme 4. Formation of a stable planar-tetracoordinated carbon compound from (propynyl)zirconocene cation

is not stable under the typical reaction conditions of its generation, but instantaneously reacts with one equivalent of the bis(propynyl)zirconocene starting material.[7] Rapid carbon−carbon coupling ensues, with formation of a μ-hexadiyne ligand. The resulting dinuclear cation complex **9** contains a bridging μ-propynyl ligand and an unsymmetrically bridging μ-hexadiyne moiety (Scheme 4). The latter contains a planar-tetracoordinated carbon atom[8] (C2 in Figure 2) that features short bonds to two adjacent carbon atoms [C1−C2 1.317(8) Å, C2−C3 1.400(8) Å] as well as to the two zirconium centers [C2−Zr1 2.530(5) Å, C2−Zr2 2.434(6) Å, the sum of the bond angles at C2 is 360.0°]. The C1−C2 bond represents a C=C double bond, and the Zr1−C2−Zr2 linkage is to be regarded as a three-center two-electron bonding situation. Thus, the bonding features at carbon atom C2 are as expected for a stable *anti*-van't Hoff/LeBel compound that contains stabilizing metal substituents. Complex **9** represents just another example of an increasing number of isolated and structurally characterized examples of such types of very stable but unusually structured carbon compounds.[8b][8c]

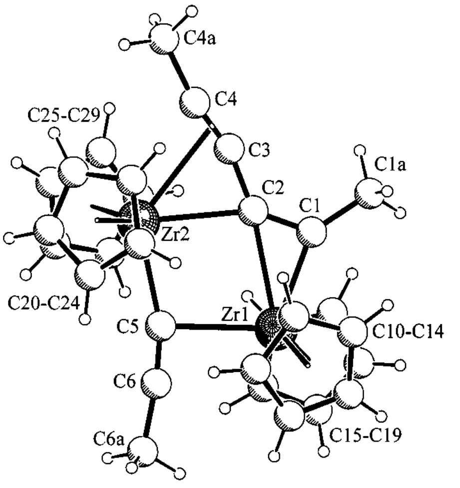
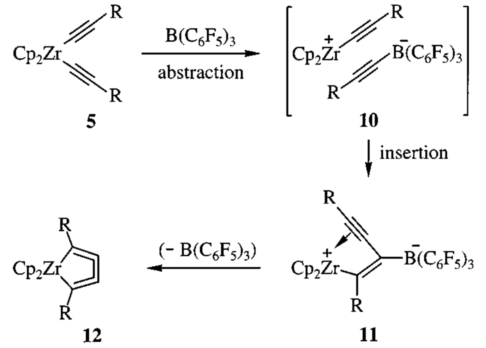


Figure 2. Molecular structure of the "*anti*-van't Hoff/LeBel compound" **9**

Reactions of Bis(alkynyl)zirconocenes with $B(C_6F_5)_3$, the Unexpected Formation of Carbocyclic Three-Membered Ring Products by Unsymmetrical Alkynyl Dimerization



Scheme 5. Products formed in the reaction of bis(alkynyl)zirconocenes with $B(C_6F_5)_3$

We have found that a variety of bis(alkynyl)zirconocenes **5** are converted into their substituted (η-butadiyne)ZrCp$_2$ isomers **12** by treatment with catalytic amounts of the strong organometallic Lewis acid $B(C_6F_5)_3$.[9,10] The likely intermediate of the catalytic C−C coupling reaction is **11**. Several examples of such zirconocene−(μ-RC$_4$R)−borate betaines were isolated from the stoichiometric reaction of a variety of bis(alkynyl)zirconocenes [as well as bis(alkynyl)hafnocenes] with $B(C_6F_5)_3$.[9,11] It is likely that the $B(C_6F_5)_3$ reagent abstracts a σ-alkynyl ligand from the metallocene to form the ion pair **10**. Subsequent rapid alkyne insertion of the $R-C\equiv C-B(C_6F_5)_3^-$ unit into the (sp-C)−Zr σ-bond of the very reactive [$Cp_2Zr-C\equiv C-R^+$] cation moiety then results in carbon−carbon coupling to directly yield the observed metallocene−(μ-diyne)−borate betaine system **11** (see Scheme 5).

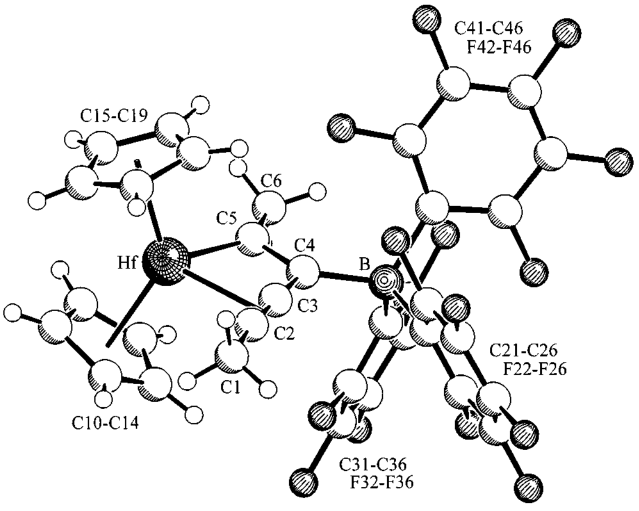


Figure 3. A view of the molecular structure of the metallocene−(μ-hexadiyne)−borate betaine complex **11′**

The hafnocene−(μ-hexadiyne)−borate betaine **11′** was characterized by X-ray diffraction (see Figure 3).[11,12] It shows the presence of a planar μ-C$_4$Me$_2$ ligand that bridges between hafnium and boron. The (sp^2-C)-to-hafnium σ-bond (C5−Hf in Figure 3) amounts to 2.150(10) Å. The C4−B bond length is 1.63(2) Å. The C4−C5 bond [1.412(13) Å] is in the range for a carbon−carbon double bond, whereas the adjacent C2−C3 bond is much shorter at 1.220(14) Å. The Hf−(C2≡C3) unit represents one of the rare examples of a structurally characterized (η^2-alkyne) group-4 metallocene moiety. The characteristic Hf−C2 and Hf−C3 bond lengths were found to be 2.671(11) Å and 2.310(10) Å, respectively.

In the crystal, the borate unit is chiral, exhibiting a $-B(C_6F_5)_3$ propeller geometry. This chirality element is persistent in many examples of the complexes **11** in solution

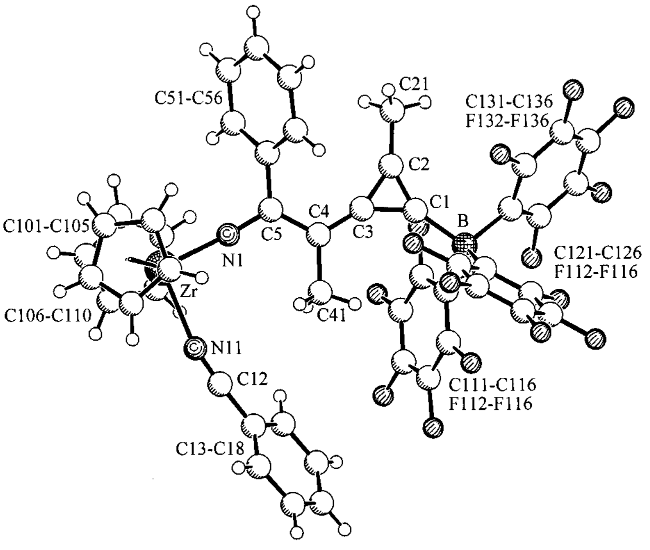
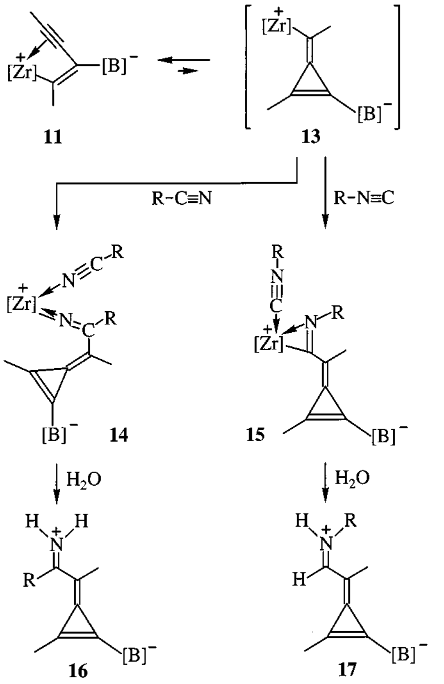


Figure 4. Molecular structure of complex **14**

on the NMR time scale. This gives rise, at sufficiently low temperature, to the observed typical NMR signals for diastereotopic pairs of Cp ligands. From the coalescence of the ^{1}H-NMR Cp resonances the Gibbs activation energies of the borate-propeller enantiomerization were obtained. The $\Delta G^{\neq}_{\text{enant}}$ values showed a marked dependence on the steric bulk of the substituents R attached at the μ-C_4 ligand (see Scheme 5) [e.g.: M = Zr, R = CH_3: $\Delta G^{\neq}_{\text{enant}}$ (292 K) = 14.3 kcal mol^{-1}; R = cyclohexyl: $\Delta G^{\neq}_{\text{enant}}$ (323 K) = 16.4 kcal mol^{-1}].[11]

A most unusual reaction took place when the zirconocene−(μ-hexadiyne)−borate betaine complex **11** was treated with benzonitrile. A rapid reaction ensued which resulted in the consumption of two molar equivalents of the nitrile reagent with formation of product **14**.[9] The X-ray crystal structure analysis (see Figure 4) showed that an unsaturated three-membered ring was formed with typical bond lengths of 1.335(3) Å (C1−C2), 1.394(3) Å (C2−C3), and 1.423(3) Å (C1−C3). The exocyclic unsaturated C3−C4 linkage features a bond length of 1.366(3) Å, and the newly formed bond (C4−C5 in Figure 4) amounts to 1.427(3) Å. The central C_4 framework of **14** in principle features a methylenecyclopropene-type structure, although a marked tendency for π-delocalization is noticed upon comparison with unperturbed methylenecyclopropene examples. The Zr$\doteq$N=CR_2 unit is almost linear [Zr−N−C 173.4(2)°], and exhibits a marked heteroallene character [Zr−N 1.955(2) Å, N=C 1.299(2) Å].[13] The second benzonitrile unit is just coordinated to zirconium, and stabilizes the electron-deficient metallocene cation substructure in the dipolar arrangement of complex **14** [Zr−N≡C angle 166.5(2)°, Zr−N 2.289(2) Å, N≡C 1.142(3) Å].

The formation of a methylenecyclopropene unit from **11** can be formulated by a reaction sequence initiated by an intramolecular insertion of the coordinated alkyne moiety into the adjacent (sp^2-C)−Zr σ-bond. Compound **13**, the methylenecyclopropene isomer of **11**, is formed in situ and may be present in an equilibrium situation, although the unsaturated three-membered ring isomer formation must be quite endothermic (by > 20−30 kcal mol^{-1}). Nevertheless, it appears that the high energy isomer **13**, which is present in only a minute equilibrium concentration, being too low for direct detection, is very efficiently trapped, e.g. by the added nitrile to yield the stable product **14**. The overall stabilization of the eventually observed product comes from the C−C and N−Zr bond formation. A variety of differently substituted nitriles have successfully been used as scavengers of **13**. Other typical insertion reagents have been used as well, such as isonitriles,[14] in which case the stable (η^2-iminoacyl)Zr derivatives **15** are obtained in good yield (see Scheme 6).[15] The structure of a typical example (**15a**), derived from $Cp_2Zr(C{\equiv}C{-}C_3H_7)_2$, $B(C_6F_5)_3$, and *tert*-butyl isocyanide, is depicted in Figure 5.



Scheme 6. Trapping of the in situ generated zirconium−(methylenecyclopropene)−borate betaine **13** with nitriles and isonitriles {[Zr] = Cp_2Zr; [B] = $B(C_6F_5)_3$; substituents used for **14** and **16**: R = C_6H_5 (**a**), *p*-$C_6H_4OCH_3$ (**b**), *p*-$C_6H_4N(CH_3)_2$ (**c**), *p*-$C_6H_4CO_2CH_3$ (**d**); for **15** and **17**: R = $C(CH)_3$ (**a**)}

Hydrolysis removes the zirconocene unit efficiently from the framework of **14** and **15**.[16,17] The borate group remains, and we have isolated the iminium−borate betaine systems **16** and **17**, respectively, in good yield (see Scheme 6) with a variety of substituent combinations. The X-ray crystal structures were determined for a number of representative examples, which revealed the remarkable structural features of this class of compounds (see Scheme 7 and Table 1). From the data compiled in Table 1 and Figure 6 it becomes apparent that compounds **16** are characterized by a very pronounced bond lengths equilibration of the C1-to-C5 core. The C1−C2 bond length is uniformly at ca. 1.35 Å. The C1−C3 bond length is ca. 1.40 Å, and the C2−C3 bond typically adopts an intermediate value of 1.37 Å. This marked bond length equilibration effect also extends to the C3−C4 linkage, which at 1.39 Å is clearly below the ex-

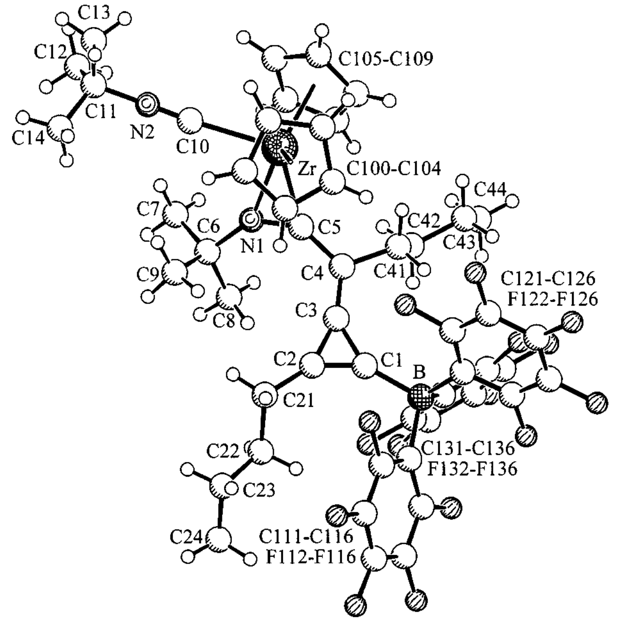


Figure 5. Molecular structure of **15a**; selected bond lengths [Å] and angles [°]: B−C1 1.609(5), C1−C2 1.328(4), C1−C3 1.432(4), C2−C3 1.417(5), C2−C21 1.474(5), C3−C4 1.353(4), C4−C41 1.523(4), C4−C5 1.430(4), C5−N1 1.277(4), N1−C6 1.482(4), C5−Zr 2.219(3), N1−Zr 2.197(3), Zr−C10 2.351(3), C10−N2 1.137(4), N2−C11 1.457(4); B−C1−C2 150.6(3), B−C1−C3 147.4(3), C2−C1−C3 61.6(2), C1−C2−C3 62.8(2), C1−C2−C21 145.9(4), C21−C2−C3 151.2(3), C1−C3−C2 55.6(2), C2−C3−C4 159.0(3), C3−C4−C41 117.7(3), C3−C4−C5 124.7(3), C41−C4−C5 116.7(3), C4−C5−N1 142.1(3), C4−C5−Zr 144.6(2), N1−C5−Zr 72.3(2), C5−N1−C6 135.7(3), C5−N1−Zr 74.1(2), C5−Zr−N1 33.6(1), C5−Zr−C10 118.2(1), N1−Zr−C10 84.6(1), Zr−C10−N2 175.1(3), C10−N2−C11 176.7(4)

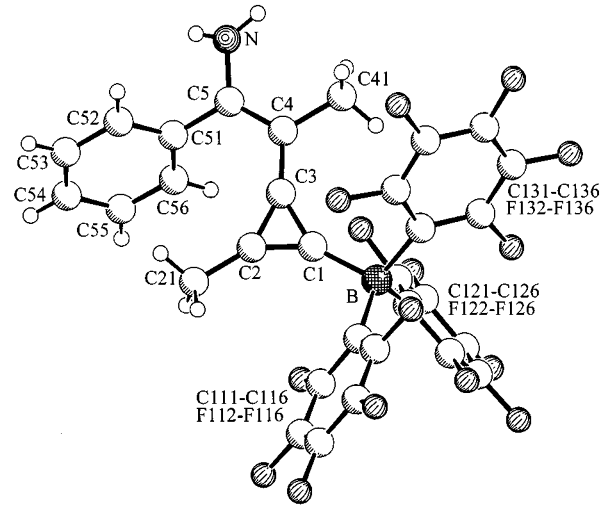
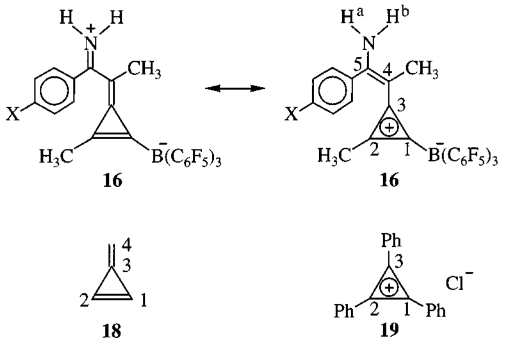


Figure 6. A view of the molecular structure of **16a**; selected bond lengths [Å] and angles [°]:C1−C2 1.341(3), C1−C3 1.399(3), C1−B 1.623(3), C2−C3 1.372(3), C2−C21 1.479(3), C3−C4 1.396(3), C4−C5 1.383(3), C4−C41 1.509(4), C5−N 1.339(3), C5−C51 1.477(4); C2−C1−C3 60.1(2), C2−C1−B 150.6(2), C3−C1−B 149.3(2), C1−C2−C3 62.1(2), C1−C2−C21 148.7(2), C3−C2−C21 149.2(2), C1−C3−C2 57.9(2), C2−C3−C4 154.2(2), C4−C3−C1 147.8(2), C3−C4−C5 118.8(2), C3−C4−C41 119.8(2), C5−C4−C41 121.4(2), C4−C5−N 121.0(3), N−C5−C51 116.0(2), C4−C5−C51 123.0(2)



Scheme 7. Resonance structures of **16** [X = H (**a**), OCH_3 (**b**), $N(CH_3)_2$ (**c**), CO_2CH_3 (**d**)]

Table 1. C−C bond lengths [Å] of the molecular core of typical examples of the compounds **16**; all compounds were prepared starting from bis(propynyl)zirconocene, see also Scheme 7

Compound	X	C1−C2	C1−C3	C2−C3	C3−C4	C4−C5
a	H	1.341(3)	1.399(3)	1.372(3)	1.396(3)	1.383(3)
b	OCH_3	1.345(3)	1.399(3)	1.376(3)	1.395(3)	1.377(3)
c	$N(CH_3)_2$	1.348(3)	1.405(3)	1.376(3)	1.393(3)	1.383(3)
d	CO_2CH_3	1.356(3)	1.405(3)	1.387(3)	1.393(3)	1.380(3)

pected $C(sp^2)-C(sp^2)$ single bond value, almost matching the C4−C5 bond length at ca. 1.38 Å (see Table 1). These values are quite atypical for a methylenecyclopropene framework, when compared with the typical C−C distances in e.g. the parent hydrocarbon methylenecyclopropene itself (C1−C2 1.323 Å, C1−C3 1.441 Å, C3−C4 1.332 Å).[18]

The observed structural π-bond delocalization probably indicates a pronounced contribution of a cyclopropenylium-type structure in the framework of compounds **16** (and of **17**, see below). The triphenylcyclopropenylium cation shows a C−C bond length of 1.373 Å inside the three-membered ring,[1] a value about which the three C1-to-C3 bond lengths of compounds **16** are closely centered (see above). Thus, compounds **16** may be structurally regarded as being very closely related to cyclopropenylium betaines bearing an enamino substituent at carbon atom C3. These unique compounds, therefore, may structurally be regarded as cyclopropenylium compounds that are devoid of their +1 charge, because they carry their counter anion covalently bonded to them.

A mandatory consequence of a description of compounds **16** and **17** as substituted cyclopropenylium betaines is that the rotational barrier about the exocyclic C3−C4 partial π-bond is low, thus allowing for a rapid *cis*/*trans* isomerization of the substituents at C2 and C4 of the framework. It must be noted that none of the *cis* isomers (e.g. *cis*-**16** or *cis*-**17**) can directly result from our synthetic scheme (see Scheme 6). Consequently, any appearance of a respective product that exhibits the former alkynyl substituents −R in a relative *cis* orientation at positions C2 and C4 at the planar central carbon framework must be considered an indication of a subsequent isomerization reaction involving rotation about the C3−C4 linkage under the applied, very mild reaction conditions. Such a *cis* product, namely the *N*-*tert*-butyl-substituted cyclopropenylium betaine *cis*-**17a**, obtained by *tert*-butyl isocyanide trapping of the metallocene−borate betaine **13a** followed by hydrolysis, was characterized structurally.[17] Compound *cis*-**17a** exhibits the typical tendency of C−C-bond length leveling in the central C_5 unit that is characteristic of the members of this larger family of compounds (see Figure 7).

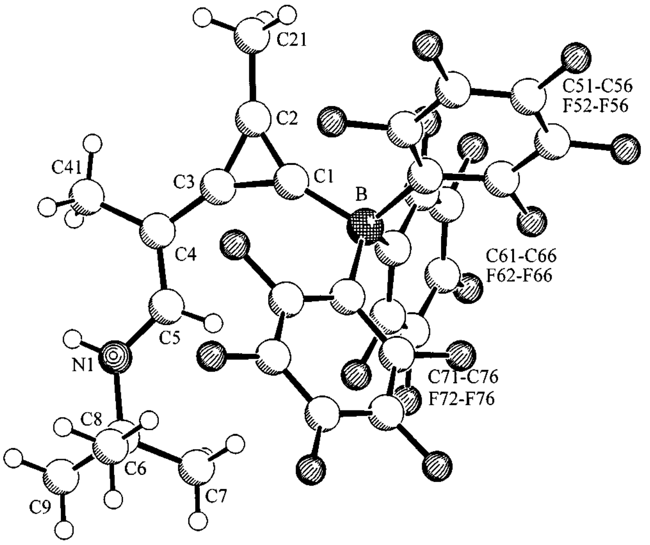
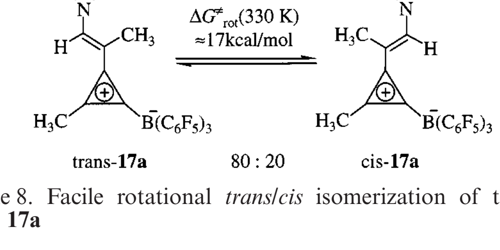


Figure 7. Molecular structure of the cyclopropenylium−borate betaine compound *cis*-**17a**; selected bond lengths [Å] and angles [°]: C1−C2 1.350(6), C1b−C2b 1.356(6), C1−C3 1.416(5), C1b−C3b 1.399(6), C1−B 1.611(6), C1b−B1b 1.610(6), C2−C3 1.383(6), C2b−C3b 1.374(6), C3−C4 1.388(6), C3b−C4b 1.394(6), C4−C5 1.380(6), C4b−C5b 1.370(6), C5−N1 1.316(5), C5b−N1b 1.325(5), N1−C6 1.484(6), N1b−C6b 1.475(6); B−C1−C2 153.5(4), B1b−C1b−C2b 152.0(4), B−C1−C3 145.3(4), B1b−C1b−C3b 147.1(4), C2−C1−C3 59.9(3), C2b−C1b−C3b 59.8(3), C1−C2−C3 62.4(3), C1b−C2b−C3b 61.7(3), C1−C3−C2 57.7(3), C1b−C3b−C2b 58.6(3), C1−C3−C4 149.1(4), C1b−C3b−C4b 149.2(4), C2−C3−C4 153.1(4), C2b−C3b−C4b 152.3(4), C3−C4−C5 116.2(4), C3b−C4b−C5b 116.5(4), C4−C5−N1 125.8(4), C4b−C5b−N1b 126.4(4), C5−N1−C6 126.0(4), C5b−N1b−C6b 125.4(4)

The rotation around the C3−C4 bond in **17a** is indeed kinetically very facile in solution. Compound **17a**, dissolved in [D$_5$]bromobenzene, exhibits typical NMR signals of the two isomers *trans*- and *cis*-**17a** in solution (Scheme 8). The compounds are present in a ca. 80:20 ratio at 270 K. Raising the temperature results in a broadening of the signals, of e.g. the methyl substituents, and eventually to coalescence. From the dynamic NMR behavior of the complex pair, *trans*-**17a** and *cis*-**17a**, a Gibbs activation energy of $\Delta G^{\neq}_{\mathrm{CCrot}}$ (330 K) = 17.0 ± 0.4 kcal mol^{-1} was obtained. Microscopically this value probably corresponds to the activation barrier of rotation around the C3−C4 [C(sp^2)−C(sp^2)] linkage in the compound **17a**. The observed value of 17 kcal mol^{-1} [17] is much lower than expected for a normal C=C double bond rotation, which strongly supports the interpretation that these complexes behave as neutral three-membered ring aromatic cyclopropenylium betaine systems.



Scheme 8. Facile rotational *trans*/*cis* isomerization of the compound **17a**

The *trans*/*cis* isomerization was observed for several other examples of this general class of compounds.[12] As a consequence of the pronounced cyclopropenylium betaine character the rotation around the enamine C5−NH$_2$ bond in the complexes listed in Table 1 is fast. Invariably, values close to $\Delta G^{\neq}_{\mathrm{CNrot}}$(306 K) ≈ 14.5 ± 0.5 kcal mol^{-1} were observed, almost independent of the arene substituents X (see Scheme 7).[12][16b,17]

First Reactions of the Cyclopropenylium−Borate Betaines

Carbenium ions react with a variety of soft neutral carbon nucleophiles by carbon−carbon coupling. The reaction with isonitriles is a typical example that may ultimately lead to products derived from intermediately formed iminium ions.[19] It is expected that the neutral betaine systems **16** and **17** should typically undergo similar reactions due to the incipient carbenium ion character of their cyclopropenylium cation-type substructural unit, and this has indeed been observed when some of the cyclopropenylium betaines were treated with alkyl isocyanide reagents.

The cyclopropenylium−borate betaine **17a** reacted rapidly with one molar equivalent of *tert*-butyl isocyanide in methanol solution to selectively yield the product **21** (see Scheme 9 and Figure 8).[17] The insertion and ring expansion is likely to be initiated by nucleophilic attack of the isonitrile to the cyclopropenylium C2 position of the betaine starting material (to generate **20**). This is probably followed by C−C σ-bond migration to the in situ formed imi-

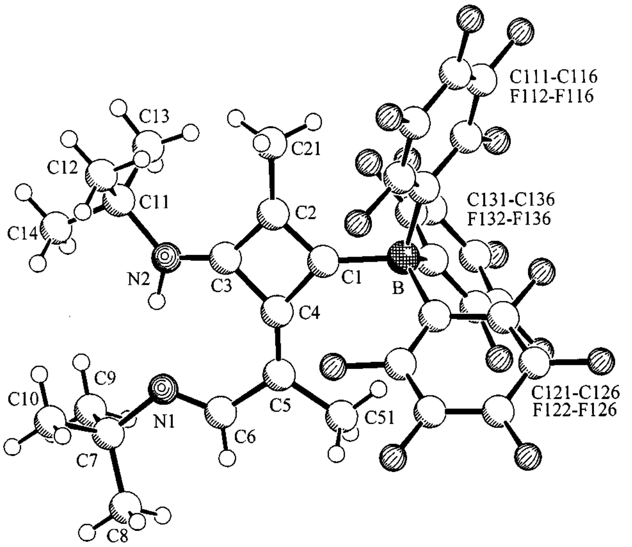
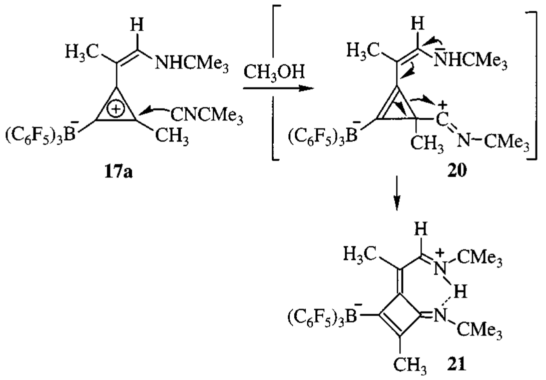


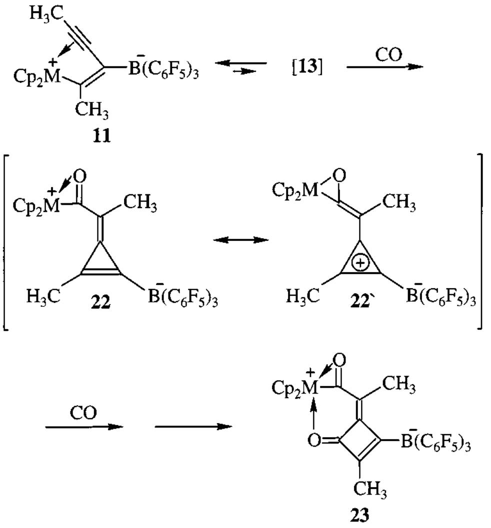
Figure 8. Molecular structure of the isonitrile insertion product **21**; selected bond lengths [Å] and angles [°]: B−C1 1.631(3), C1−C2 1.383(3), C1−C4 1.506(3), C2−C3 1.454(3), C3−N2 1.290(3), C3−C4 1.481(3), N2−C11 1.495(3), C4−C5 1.340(3), C5−C6 1.475(3), C6−N1 1.265(3), N1−C7 1.490(3); B−C1−C2 132.9(2), B−C1−C4 134.6(2), C1−C2−C3 92.2(2), C1−C4−C3 86.4(2), C2−C1−C4 91.5(2), C2−C3−C4 89.8(2), C2−C3−N2 140.6(2), C3−N2−C11 128.3(2), C1−C4−C5 138.3(2), C3−C4−C5 135.3(2), C4−C5−C6 124.4(2), C5−C6−N1 127.1(2), C6−N1−C7 121.3(2)



Scheme 9. Ring expansion reaction of **17a** upon treatment with an isonitrile

noacyl cation to give the favored expanded conjugated bis(imine) product **21** directly.

The isonitrile insertion product was characterized by X-ray diffraction.[12,17] This has revealed the presence of the unsaturated central four-membered ring structure. One of the C=N functionalities is a part of this structure, and the other is attached to it. There is a bridging hydrogen between the two imino nitrogen atoms (^{1}H NMR: $\delta = 9.98$), and the borate counter anion is again covalently bonded to the framework. In contrast to the markedly delocalized π-system of the cyclopropenylium betaine systems (**16** and **17**, see above), compound **21** contains clearly alternating single and double bonds around its completely unsaturated perimeter.



Scheme 10. Reaction of the betaine complex **11** with carbon monoxide

A related reaction probably takes place upon treatment of the betaine complex **11** with carbon monoxide (Scheme 10). It seems that initially the high-lying methylenecyclopropene intermediate **13** is trapped by C–C bond-forming insertion as usual, in this case giving rise to the formation of the corresponding (η^2-acyl)zirconocene product **22**. Its resonance structure **22′**, which consequently reacts rapidly by further CO uptake under the reaction conditions to eventually yield the methylenecyclobutenone complex **23**, seems to provide a favored description of the cyclopropenylium features of this neutral organometallic product. The product, **23**, was characterized spectroscopically,[12] and shows a variety of characteristic features similar to the closely related compound **21**.

Conclusions

We have found a simple way to make a number of examples of a new variety of unsaturated three-membered ring compounds.[20] Our organometallic route, which combines coupling of two acetylides at the zirconocene template [upon treatment with a stoichiometric quantity of the strong organometallic Lewis acid tris(pentafluorophenyl)borane], with trapping of its methylenecyclopropene isomer and subsequent hydrolysis, makes compounds **16** and **17** readily available in high yield. These compounds show a pronounced cyclopropenylium–borate betaine character, with regard to their structural properties in the solid state and their typical dynamic features in solution. Thus, it seems that such compounds represent the first series of examples that may be regarded as cyclopropenylium ions bearing their counter anion covalently bonded to their three-membered ring framework. Their structural, dynamic and, as shown in first examples, chemical behavior is the same as would be expected for the smallest carbocyclic arenes, the cyclopropenylium cations, but without the dominating effects of the charge. In some respect, systems such as **16** or **17** might be suited to the study and development of some "carbenium ion chemistry without the charge". Now that first examples have become available by easily accessible organometallic pathways, the development of the chemistry of neutral variants of a variety of charged organic species as parts of such simple betaine systems may become feasible.[21]

Acknowledgments

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[21] Details of the X-ray crystal structure analyses of complexes **16b−d** (see Table 1), that were not published previously, were deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-137521 to -137523. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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