ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 1839–1850

www.rsc.org/chemcomm

FEATURE ARTICLE

1,1-Carboboration

Gerald Kehr* and Gerhard Erker*

Received 12th September 2011, Accepted 24th October 2011
DOI: 10.1039/c1cc15628d

The use of very electrophilic boranes $RB(C_6F_5)_2$ widens the scope of the 1,1-carboboration reaction substantially. Simple terminal alkynes $HC{\equiv}CR$ undergo this reaction with the $RB(C_6F_5)_2$ reagents rapidly under mild conditions to give high yields of very useful new alkenylborane products. Even internal alkynes $RC{\equiv}CR$ undergo 1,1-carboboration with the $RB(C_6F_5)_2$ reagents to provide a novel way of carbon–carbon σ-bond activation. Variants of these reactions involving phosphorus substituted alkynes and more complex bisalkynyl main group and transition metal substrates give rise to the formation of very interesting functionalized metallacyclic products upon treatment with $RB(C_6F_5)_2$ reagents by means of reaction sequences involving selective 1,1-carboboration steps.

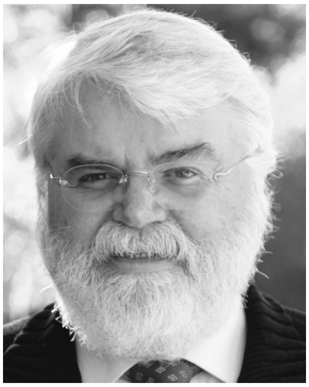
Introduction

Alkenylboranes are interesting reagents. They are boron Lewis acids and they feature a planar tricoordinate electrophilic boron substituent at an olefinic $C(sp^2)$ center which makes the system attractive for metal catalyzed cross coupling reactions.[1] 1,1-Carboboration has been an attractive way of synthesizing various types of alkenylboranes.[2,3] Topologically, the 1,1-carboboration reaction is reminiscent of the reversal of the Fritsch–Buttenberg–Wiechell (FBW) reaction,[4] where formally an *in situ* generated vinylidene type intermediate is stabilized by rearrangement to the corresponding alkyne (see Scheme 1).

Organisch-Chemisches Institut der Universität Münster, Corrensstr. 40, 48149 Münster, Germany. E-mail: erker@uni-muenster.de, kehrald@uni-muenster.de

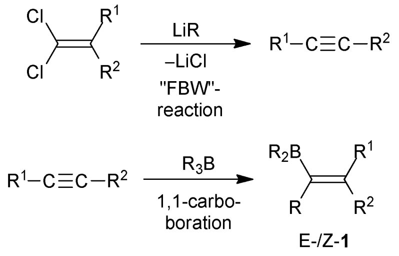
Gerald Kehr

Gerald Kehr obtained his doctoral degree at the University of Bayreuth under the guidance of Professor Bernd Wrackmeyer. After postdoctoral research with Prof. Clement Sanchez at the University "Pierre et Marie Curie" (Paris, France) and Prof. Rudolph Willem at the Free University of Brussels (Begium), he became a permanent staff member in the Organisch-Chemischen Institut at Münster. His responsibilities in the research group of Prof. Erker include, inter alia, applied state of the art NMR analyses. His current research interests are in carboboration and FLP chemistry. Dr Gerald Kehr was fellow of the "Studienstiftung des deutschen Volkes" and is an author of more than 220 publications and patents.



Gerhard Erker

Gerhard Erker did his doctoral work with Prof. Wolfgang R. Roth at the Ruhr-Universität Bochum and was a postdoc with Prof. Maitland Jones, Jr. at Princeton University. After his habilitation he joined the Max-Planck-Institut für Kohlenforschung in Mülheim a.d. Ruhr as a Heisenberg fellow and then became a C3-Professor at the Universität Würzburg. Since 1990 he is a full Professor at the Organisch-Chemisches Institut at the Universität Münster. Prof. Erker's research interests are in Organometallic Chemistry and in catalysis. He has made major contributions to the chemistry of the Group 4 metallocenes, including their utilization in olefin polymerization catalysis. His current major research interests are in frustrated Lewis pair chemistry and carboboration. Prof. Erker is the first recipient of the Krupp Award (1984) and he has recently received the Adolf-von-Baeyer-Award (2009) and the Eugen and Ilse Seibold Award (2011). He was the President of the German Chemical Society, GDCh in the years 2000 and 2001 and a member of the Senate of the Deutsche Forschungsgemeinschaft. Besides science Gerhard Erker loves art and music.



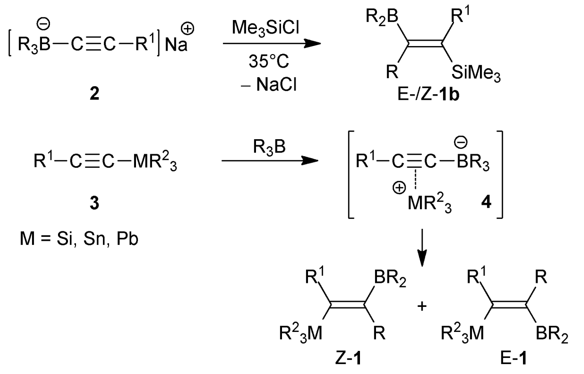
Scheme 1

The 1,1-carboboration formally resembles an insertion of a vinylidene isomer of an alkyne into a B–C bond of a borane, although mechanistically the reaction of suitable alkynes with boranes takes a very different mechanistic course to arrive at the 1,1-carboboration products **1**.

Examples of the 1,1-carboboration reactions have long been known. However, this reaction seems so far not to have been used on a large scale for a general synthesis of alkenylboranes. This is probably due to the fact that the previously described examples (with few exceptions) mostly employed 'activated' alkynes, *i.e.* substrates where R^1 or R^2 were silyl, germyl, stannyl or plumbyl[5–8] groups, respectively, or transition metal[9] containing substituents. These substituents have a high propensity for undergoing the required 1,2-migration along the alkynyl backbone, but were not overly useful synthetically. From recent work by us and others it has now become apparent that the use of the strongly electrophilic $R{-}B(C_6F_5)_2$ type borane reagents greatly facilitates the 1,1-carboboration reaction. With the use of these reagents a great variety of simple 1-alkynes (and even of internal alkynes) just bearing typical organic substituents have undergone the 1,1-carboboration reaction cleanly and rapidly. This new development will probably result in some revival of this interesting reaction type that proceeds with a remarkable combination of addition and rearrangement processes. In this feature article some recent developments are described.

1,1-Carboboration of 'activated' alkynes: the Wrackmeyer reaction

It had early on been demonstrated that trialkyl(alkynyl)borate salts **2** react readily with a variety of electrophilic silicon or tin halide reagents to form the respective alkenylborane products **1**.[5b,10,11] In the course of this reaction an alkyl group R is shifted from boron to the same carbon atom to which the remaining $-BR_2$ group is attached (see Scheme 2). Wrackmeyer *et al.* later showed with a great number of examples that 'activated' alkynes **3**, *i.e.* acetylenic substrates that were bearing a suitable potential migrating substituent at the C(sp) carbon atom, would undergo a very similar reaction when treated with a trialkylborane reagent. Typical migrating groups in the "Wrackmeyer" 1,1-carboboration reaction are main group metal centered substituents such as $-SiR_3$, $-GeR_3$, $-SnR_3$ or even $-PbR_3$ and a few selected transition metal containing groups $-ML_n$ (M = Pt or Ti).[5–9] Mechanistically, the Wrackmeyer reaction proceeds by means of a two step reaction pathway involving an alkynyl abstraction/rearrangement sequence (see Scheme 2). Variants of intermediate **4** were isolated in some special cases (see below) and even characterized by X-ray diffraction.

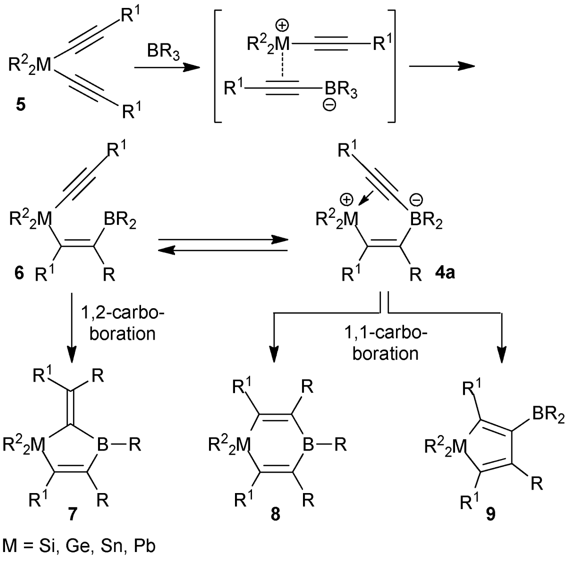


Scheme 2

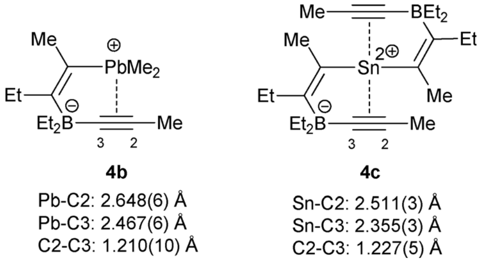
Typically, the 1,1-carboboration of such 'activated' alkynes with trialkylborane required specific reaction conditions depending on the substituents at the acetylene unit; *e.g.* ethynyltrimethylsilane reacted with triethylborane at 120 °C in an autoclave whereas the corresponding reaction of ethynyltrimethylstannane was carried out at −20 °C.[5b] Triallylborane is more reactive and undergoes the respective 1,1-carboboration reactions more easily.[12,13]

The reactions of dialkynyl group 14 metal substrates **5** with the borane reagents (*e.g.* BEt_3) were shown to provide very interesting and useful entries to important heterocyclic metal containing systems. The reaction sequences are apparently initiated by the usual 1,1-carboboration reaction at one of the acetylene units to give intermediate **6** (see Scheme 3). This then has a choice to follow one of the three principally competing pathways. 1,2-Carboboration may lead to 1-bora-3-metallacyclopent-4-enes **7**.[13a–c] Intramolecular alkynyl abstraction leads to equilibration with **4a**, which then has two choices of subsequent 1,1-carboboration to yield 1-bora-4-metallacyclohexa-2,5-dienes **8** (1,1-alkylboration)[14] or boryl-substituted metallacyclopenta-2,4-dienes **9** (1,1-alkenylboration).[15]

Wrackmeyer *et al.* were able to isolate examples of the crucial intermediates **4a** derived from each a corresponding



Scheme 3



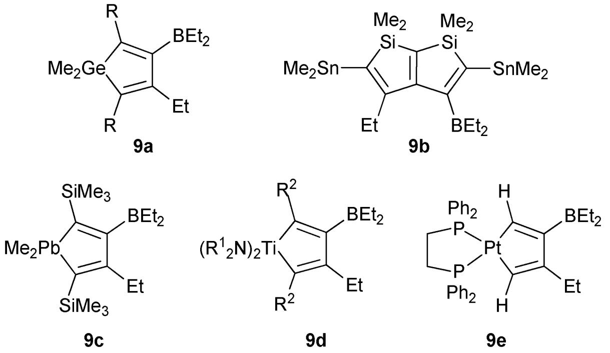
4b

Pb-C2: 2.648(6) Å
Pb-C3: 2.467(6) Å
C2-C3: 1.210(10) Å

4c

Sn-C2: 2.511(3) Å
Sn-C3: 2.355(3) Å
C2-C3: 1.227(5) Å

Scheme 4



9a **9b** **9c** **9d** **9e**

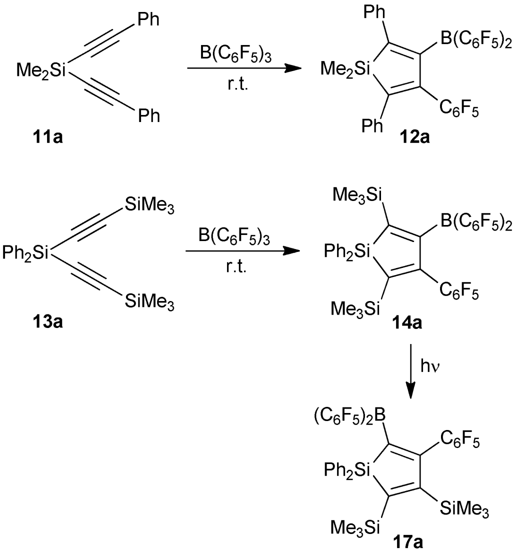
Scheme 5

lead (**4b**(Pb))[14d,16] and tin (**4c**(Sn))[14h,k,15h,j,17] system and characterize them by X-ray crystal structure analyses (see Scheme 4).

Wrackmeyer 1,1-carboboration reactions starting from group 14 metal diacetylide starting materials have been very useful for preparing a great variety of boryl-substituted metallacyclopentadiene systems. Typical examples are shown in Scheme 5, including rare examples of transition metal derived 1,1-carboboration products [**9d**(Ti)[9e] and **9e**(Pt)[9a–d]].

The B-C_6F_5 effect

Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$ (**10a**)][18] is a strongly Lewis acidic borane. It has been extensively employed as an activator component in homogenous Ziegler–Natta olefin polymerization catalysis by making use of its ability to very effectively abstract methyl anion equivalents from *e.g.* Zr or Ti centres to generate the active $Cp_2M–CH_3{}^+$ cation of these single site catalysts.[19] $B(C_6F_5)_3$ is known as a superb general Lewis acid catalyst *e.g.* in hydrosilylation reactions of ketones.[20] Lately $B(C_6F_5)_3$ has been extensively used as a Lewis acid component in frustrated Lewis pair chemistry.[21]



Scheme 6

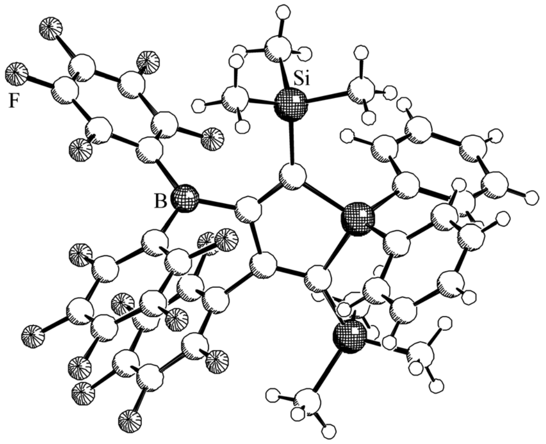
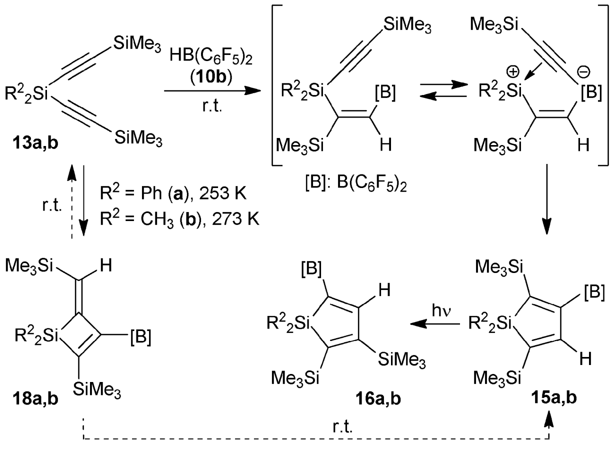


Fig. 1 Molecular structure of the $–B(C_6F_5)_2$ substituted silole derivative **14a**.

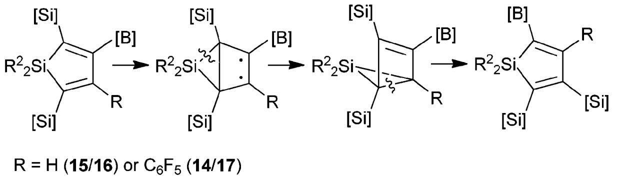
Tris(pentafluorophenyl)borane is very effectively able to undergo 1,1-carboboration reactions with *e.g.* 'activated' alkynes. The respective products are similar to the typical "Wrackmeyer products" but they are usually formed under very mild reaction conditions. The reactions of the dialkynylsilanes **11** with $B(C_6F_5)_3$ are typical examples. Treatment of bis(phenylethynyl)-dimethylsilane (**11a**) with $B(C_6F_5)$ (**10a**) gave the boryl-substituted silole product **12a** at room temperature (see Scheme 6). Similarly, silole **14a** that bears six very bulky substituents at its perimeter was analogously obtained by simply stirring the bis(alkynyl)silane starting material **13a** with $B(C_6F_5)_3$ (**10a**) at room temperature. Product **14a** was isolated and characterized by X-ray diffraction (see Fig. 1). We assume that compound **14a** is formed by a sequence of 1,1-carboboration steps similar to the reactions depicted in Scheme 3 (see above).[22]

We have also treated the dialkynylsilanes **13a** (R^2 = Ph) and **13b** ($R^2 = CH_3$) with "Piers' borane" [$HB(C_6F_5)_2$) (**10b**)[23]]. The reaction takes place smoothly at room temperature to give the silole products **15a,b** in good yields. We assume a similar sequence of abstraction/rearrangement reactions as discussed above, only that here an initial 1,1-*hydro*boration reaction must be assumed (see Scheme 7). Products **15a,b** undergo a photochemical rearrangement of their framework to give **16a,b**. Compound **16b** ($R^2 = CH_3$) was characterized by X-ray diffraction (see Fig. 2).[24] Compound **14a** was analogously isomerized photolytically to give product **17a** (see Scheme 6).[24a] The photochemical rearrangement of these silole derivatives can formally be regarded as di-π-rearrangements (see Scheme 8).[25]

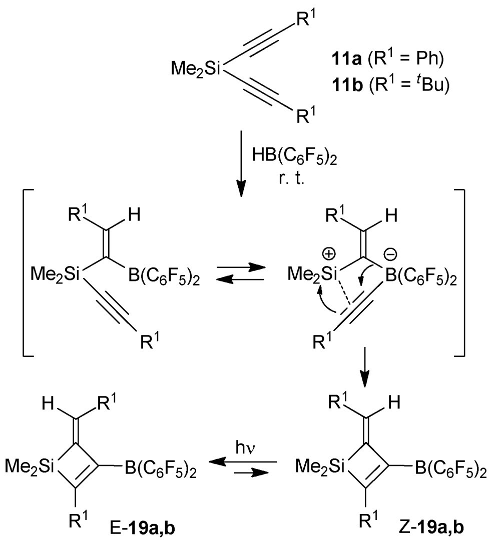
Actually we detected the formation of the borylated silacyclobutene products **18a,b** in the reactions of **13a,b** with $HB(C_6F_5)_2$ at low temperature. Their formation was probably reversible; warming the reaction mixture to room temperature eventually



Scheme 7



Scheme 8



Scheme 9

resulted in the formation of the previously observed silole derivatives **15a,b** (see Scheme 7).[24b]

In the case of the reaction of the dialkynyl silanes **11a,b** with $HB(C_6F_5)_2$ (**10b**) we observed the formation of the stable four-membered ring products Z-**19a,b** (see Scheme 9). We assume that the silacyclobutene products were formed by a sequence comprising a conventional *cis*-1,2-hydroboration reaction followed by a 1,1-carboboration.[26] Subsequent photolysis resulted in an efficient *Z*- to *E*-isomerization at the exocyclic carbon–carbon double bond leading to photostationary equilibrium mixtures that were highly enriched in the respective *E*-isomers [*E*-/*Z*-**19a** (R^1 = Ph): 10 : 1; *E*-/*Z*-**19b** (R^1 = ^{t}Bu): 3.5 : 1]. Compound *E*-**19a** was characterized by X-ray diffraction (see Fig. 3).[24b]

We used the $HB(C_6F_5)_2$ reagent (**10b**) for initiating similar coupling reactions of bis(alkynyl)group 4 metallocenes. This gave some very interesting results. The reaction of the bis(alkynyl)-zirconocene complex **20a** (M = Zr) with $HB(C_6F_5)_2$ was rapid at −40 °C. We spectroscopically identified the obtained reaction product as the initial alkynyl abstraction product **21a** [^{1}H NMR: δ −0.65 (1 : 1 : 1 : 1 quartet, B–H), ^{11}B: δ −27]. Compound **21a** was also characterized by X-ray diffraction (see Fig. 4) and shown to exhibit a very unsymmetrical Zr(π-acetylene) bonding mode [Zr–C1: δ 2.513(5) Å, Zr–C2: 2.841(5) Å, C1–C2: 1.209(7) Å].

Warming a solution of **21a** to 20 °C resulted in a 1,1-hydroboration reaction. This should actually give the reactive intermediate **22** (see Scheme 10) which we did not observe, but we observed its alkynyl shifted isomer **23a** instead by NMR spectroscopy [*e.g.* ^{11}B NMR: δ −25]. Further warming eventually resulted in the formation of the carbon–carbon coupling product **24a**. Compound **24a** (M = Zr) was characterized by X-ray diffraction (see Fig. 5). It is formally to be described as a

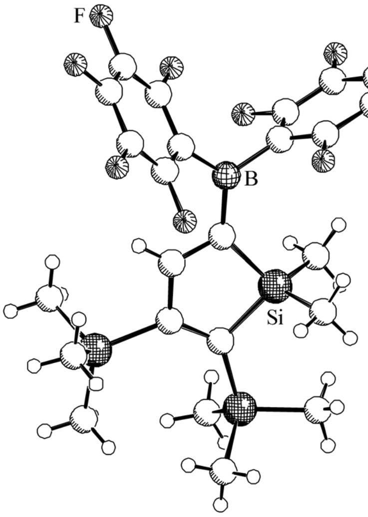


Fig. 2 A view of the molecular structure of compound **16b** (R^2 = Me).

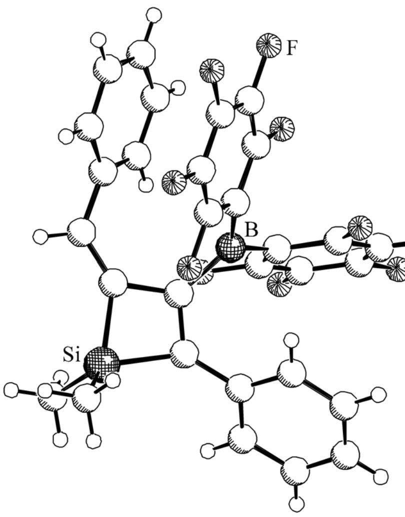


Fig. 3 Molecular structure of compound *E*-**19a** (R^1 = Ph).

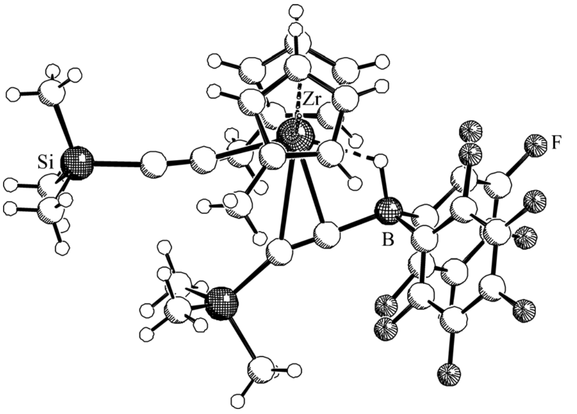
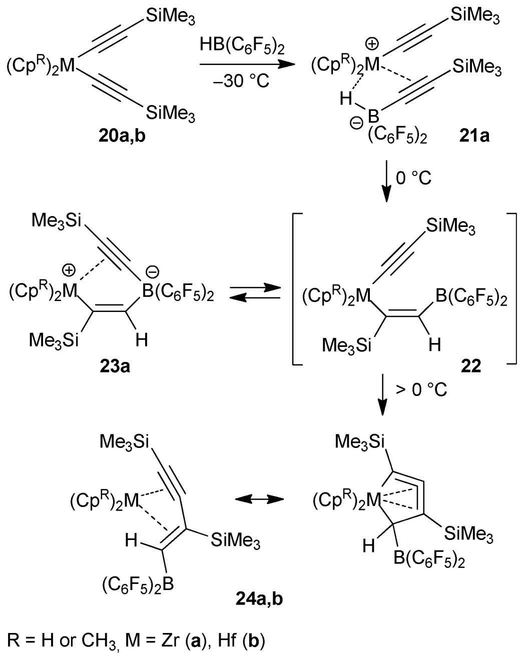


Fig. 4 A projection of the molecular geometry of complex **21a**.



Scheme 10

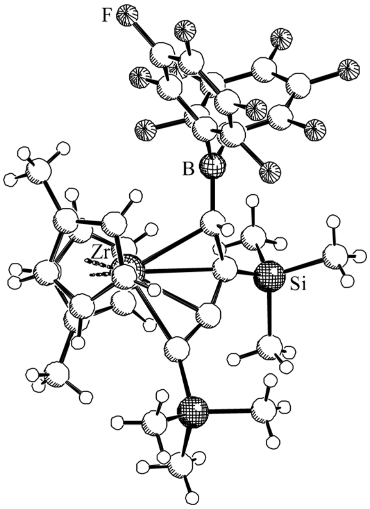
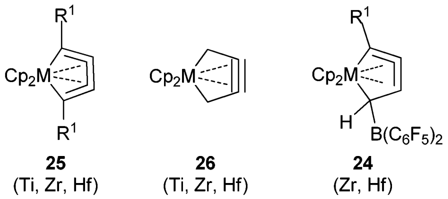


Fig. 5 A view of the molecular structure of the zirconacycloallenoid system **24a**.



Scheme 11

resonance hybrid between a metallacycloallene σ-complex structure and a metallocene (η^4-enyne) complex. The hafnocene system shows the analogous overall reaction mode (*i.e.* **20b** + **10b** → **24b**). The result of a DFT analysis has confirmed a suitable description of this type of compounds as a metallacycloallenoid exhibiting a pronounced ligand to metal σ-interaction inside the five-membered ring system.[27] This places compounds **24** alongside Rosenthal's metallacyclocumulenes **25**[28] and Suzuki's metallacyclopentynes **26**[29] (see Scheme 11).

1,1-Carboboration of 'non-activated' 1-alkynes: a conceptual alternative to alkyne hydroboration

The "Wrackmeyer" carboboration proceeds well with 'activated' alkynes that contain the metal containing substituents mentioned above as potential migrating groups. There are only very few exceptions for this behaviour when ordinary trialkylborane reagents are employed. In principle, hydrogen should be a suitable migrating group[2a,e,30] in 1,1-carboboration reactions but apparently a general realization of such a reaction requires a more electrophilic borane reagent. This is actually well met with the B(C$_6$F$_5$)$_3$ and RB(C$_6$F$_5$)$_2$ reagents. The reaction of phenylacetylene (**27a**) with B(C$_6$F$_5$)$_3$ (**10a**) is a typical example. Simple stirring of a mixture of the two reagents in a common solvent for some minutes resulted in the formation of a near to equimolar mixture of the *E*-/*Z*-**28a** 1,1-carboboration products. Crystallization gave a sample that was highly enriched in the *E*-isomer. Subsequent photolysis resulted in a very efficient *E*- to *Z*-isomerization to give a highly Z-**28a** enriched sample. The *Z*-**28a** isomer, obtained from the 1,1-carboboration reaction of phenylacetylene with B(C$_6$F$_5$)$_3$ followed by photochemical isomerization, was characterized by X-ray diffraction (see Fig. 6).[31] The reactions of the differently substituted 1-alkynes **27b–e** with B(C$_6$F$_5$)$_3$ proceeded analogously. In each case a high yield of the respective *E*-/*Z*-**28(b–e)** mixture of 1,1-carboboration products was obtained after a short reaction time under ambient conditions. Subsequent photolysis gave highly *Z*-**28** enriched samples (see Scheme 12).[32] The 1,1-carboboration reaction of 1-alkynes apparently is a good method of synthesizing specifically substituted alkenylborane products.

The 1,1-carboboration of *e.g.* 1-pentyne (**27c**) with the alkylbis(pentafluorophenyl)borane reagents RB(C$_6$F$_5$)$_2$ **10c** (R = –CH$_3$) and **10d** (R = –CH$_2$CH$_2$Ph), respectively, proceeded remarkably selective. Both these 1,1-carboboration reactions went to completion within hours at room temperature. In both cases we only observed migration of the alkyl group from boron to carbon to form the respective 1,1-carboboration products **29a,b**. These were obtained as *E*-/*Z*-mixtures. After photolysis we were able to isolate the *Z*-**29a,b** isomers in good yields (see Scheme 13).

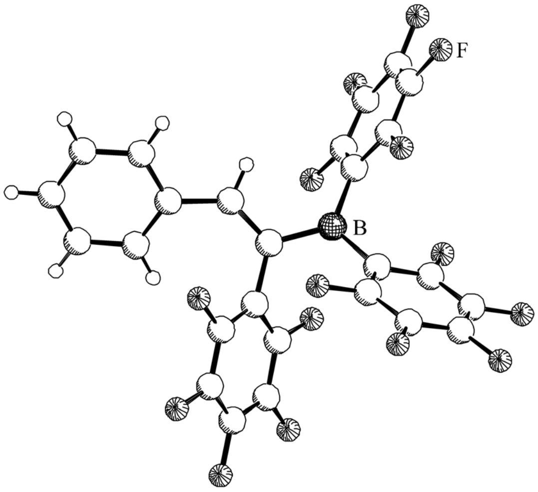
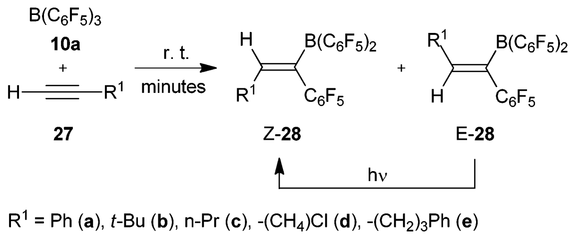
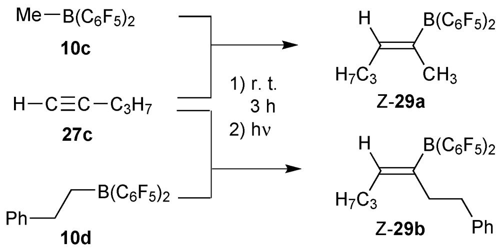


Fig. 6 Molecular structure of the 1,1-carboboration product *Z*-**28a**.



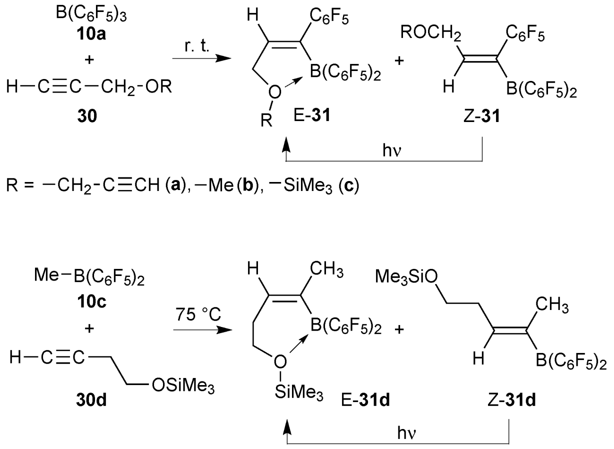
Scheme 12



Scheme 13

These examples demonstrate that the new 1,1-carboboration reaction of 1-alkynes may serve in some cases as a specifically selective conceptual alternative of the ubiquitous alkyne hydroboration reaction.

We can also selectively address the synthesis of *E*-trisubstituted olefin isomers by the 1,1-carboboration method.[32,33] Typically, the 1-alkynes **30** featuring ether substituents as part of their framework undergo facile 1,1-carboboration reactions under ambient conditions (~2 h) to yield the respective *E*-/*Z*-carboboration product mixtures **31** (see Scheme 14). However, in these cases subsequent photolysis resulted in the preferred formation of the *E*-**31** isomers that feature an internal oxygen to boron coordination. Similarly, $MeB(C_6F_5)_2$ (**10c**) reacted at elevated temperature (75 °C) with the –OTMS substituted alkyne **30d** by selective transfer of the methyl group from boron to carbon to give *E*-/*Z*-**31d**. Again, subsequent photolysis gave a good yield of *E*-**31d** (see Scheme 14). Examples of the *E*-**31** products were characterized by X-ray diffraction (see Fig. 7).



Scheme 14

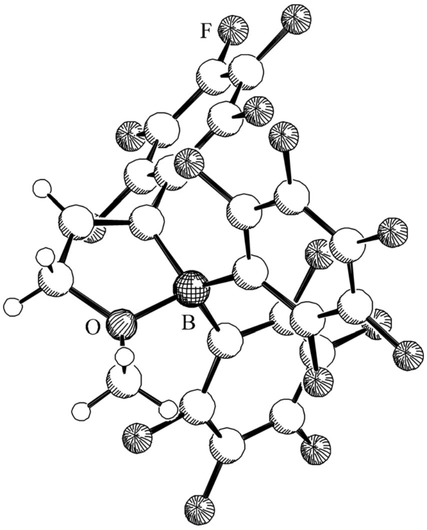
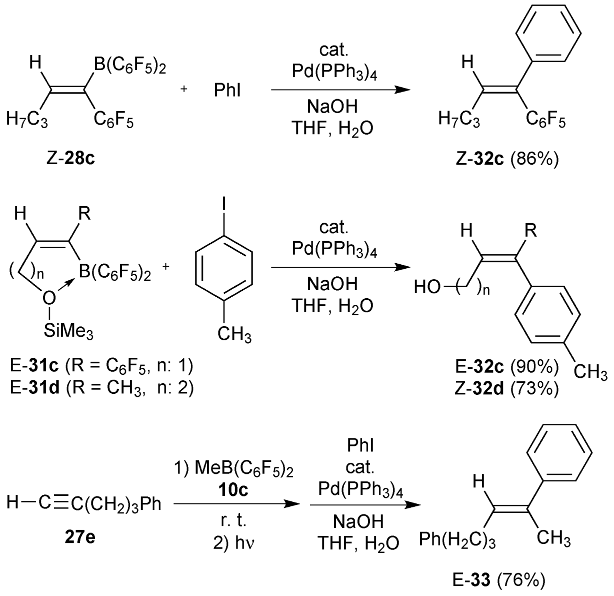


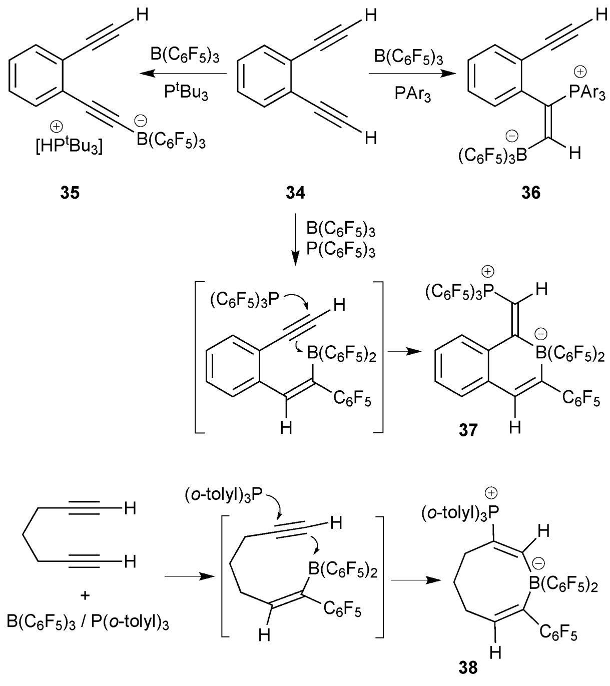
Fig. 7 Molecular structure of the 1,1-carboboration product *E*-**31b** (R = Me).

The alkenylboranes obtained by the 1,1-carboboration reactions of the strongly electrophilic $RB(C_6F_5)_2$ boranes (**10**) are interesting Lewis acids in themselves. Some have been employed as Lewis acid components for the generation of new advanced frustrated Lewis pairs, *e.g.* for utilization in catalytic hydrogenation processes.[34] The alkenylboranes were also shown to be suitable trivalent borane reagents for utilization in Pd-catalyzed Suzuki–Miyaura type carbon–carbon coupling reactions.[32] The system *Z*-**28c** is a typical example. The Pd-catalyzed coupling reaction with phenyl iodide gave the tri-substituted olefinic product *Z*-**32c** in > 80% yield. Similarly the –O-TMS containing 1,1-carboboration products *E*-**31c** and *E*-**31d** were coupled to directly give the O-deprotected products *E*-**32c** and *Z*-**32d**, respectively, in good yields (see Scheme 15). The overall reaction sequence can also be carried out as a one-pot procedure, starting from the respective 1-alkyne without specific isolation of 1,1-carboboration products to eventually give the C–C coupling products in good yields. The reaction sequence starting by treatment of the alkyne **27e** with $MeB(C_6F_5)_2$ (**10c**) to eventually yield *E*-**33** is a typical example.



Scheme 15

Frustrated Lewis Pairs (FLPs) can undergo specific reactions with 1-alkynes depending on the basicity/nucleophilicity of the Lewis base component. Typically, 1,2-diethynylbenzene (**34**) reacts by deprotonation/alkynyltransfer with the P^tBu_3/$B(C_6F_5)_3$ FLP to give salt **35** whereas the combination with a weaker triarylphosphine Lewis base leads to cooperative 1,2-FLP addition to give the zwitterion **36** (see Scheme 16). With the still weaker $P(C_6F_5)_3$ Lewis base we see a shifting of the preferred reaction pathway to the formation of product **37**, which is apparently formed by a sequence of 1,1-carboboration followed by cooperative 1,2-FLP addition of the newly formed alkenylborane/$P(C_6F_5)_3$ Lewis pair to the remaining carbon–carbon triple bond.[35] Such a situation of closely competing 1,1-carboboration and 1,2-FLP addition is frequently observed in frustrated Lewis pair chemistry. The formation of the eight-membered heterocycle **38** from 1,6-heptadiyne and the $B(C_6F_5)_3$/$P(o\text{-tolyl})_3$ pair is another typical example (see Scheme 16 and Fig. 8).[36]



Scheme 16

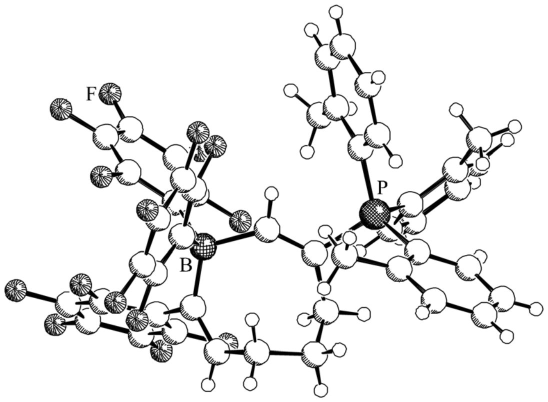
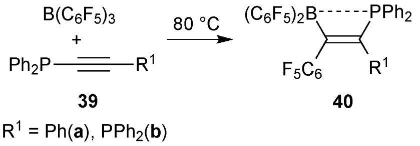


Fig. 8 Molecular structure of compound **38**.



Scheme 17

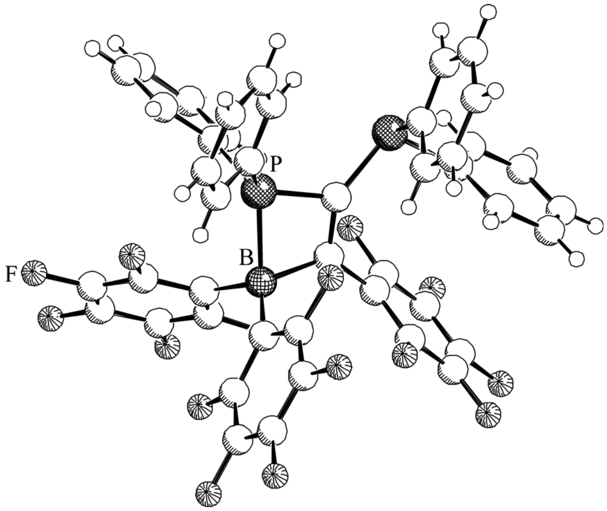


Fig. 9 A view of the molecular structure of compound **40b**.

1,1-Carboboration reactions can actually be used for the preparation of alkenylen-bridged intramolecular FLPs. Typical examples are the reactions of the phosphinyl substituted alkynes **39a,b** with $B(C_6F_5)_3$. In these cases the 1,1-carboboration requires heating. At *ca.* 80 °C these systems smoothly undergo the $-PPh_2$ migration coupled with C_6F_5 shift from boron to carbon to yield the 1,1-carboboration products **40a,b** (see Scheme 17 and Fig. 9).[37] Actually, the alkynylphosphine **39c** [$(\text{mesityl})_2P\text{–}C{\equiv}C\text{-}(p\text{-tolyl})$] reacts readily with $B(C_6F_5)_3$ at ambient temperature to give the phosphirenium–borate

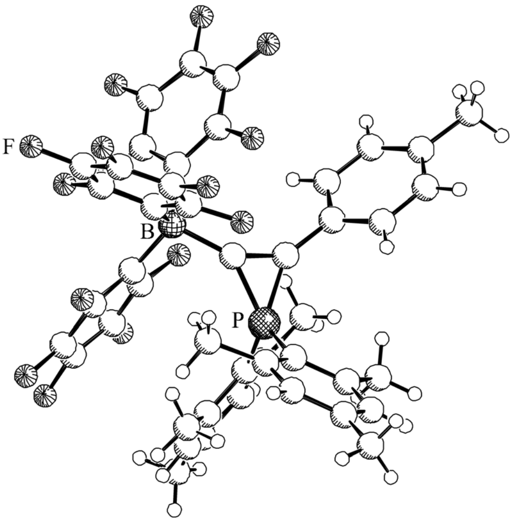
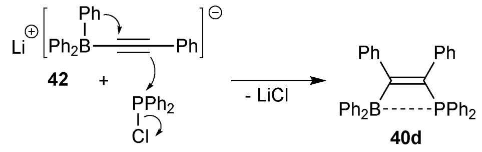


Fig. 10 Molecular geometry of the phosphirenium–borate zwitterions **41**.



Scheme 18

zwitterion **41**. Heating of **41** eventually leads to the formation of the respective B/P-system **40c**. Compound **41** was also characterized by X-ray diffraction (see Fig. 10).[38]

This work shows that these advanced 1,1-carboboration reactions provide an attractive alternative to some of the conventional preparative routes to systems **40**, which follow the pathway characterized by the early work by Köster, Binger and Balueva[10,11] (see Schemes 2 and 18), which here involves treatment of an alkenylborate salt **42** with a $Ph_2P–X$ electrophile.

Carbon–carbon σ-bond activation

There is much known about the activation of the strong H–H σ-bond.[39] Also numerous methods have successfully been developed to activate C–H bonds.[40] Although the carbon–carbon σ-bonds are thermodynamically much weaker, C–C σ-bond activation[41] is still in its infancy and far away from being a thoroughly established part of synthetic organic or organometallic chemistry. 1,1-Carboboration chemistry might turn out to provide a useful tool to contribute to the search and development of suitable activation procedures and protocols for activating some strong carbon–carbon σ-bonds.

We recently found a remarkable carbon–carbon bond cleavage process to take place upon treatment of some amino dihydropentalene systems **43** with the $RB(C_6F_5)_2$ boranes **10c** (R = CH_3) or **10d** (R = CH_2CH_2Ph). The reaction proceeded slowly at room temperature. Both products **44c** and **44d** were isolated and eventually characterized by X-ray diffraction (see Fig. 11).[42] Formally, the strong C=C double bond of the "left" carbocyclic five-membered ring of the dihydropentalene framework was

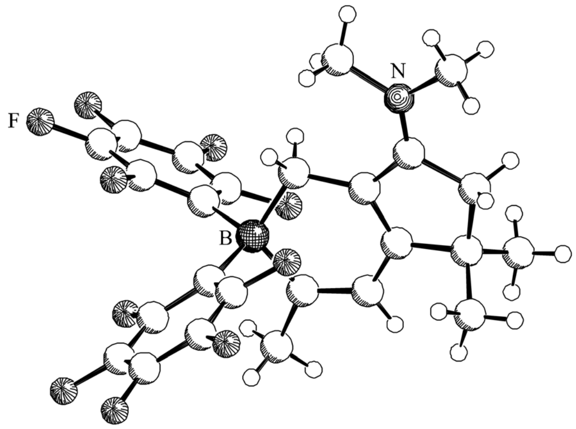
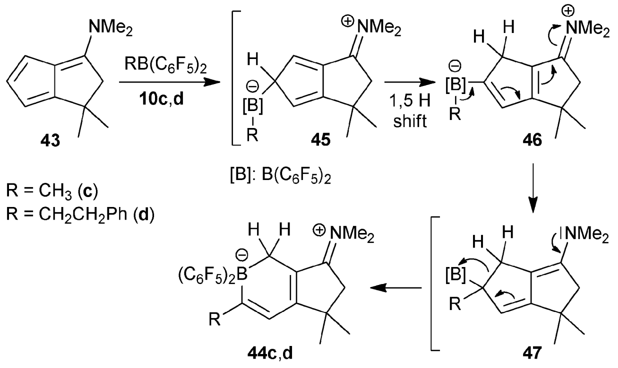


Fig. 11 A view of the molecular structure of the $B(C_6F_5)_2$ insertion product **44c**.

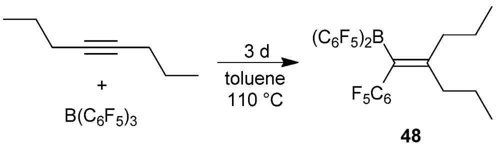


Scheme 19

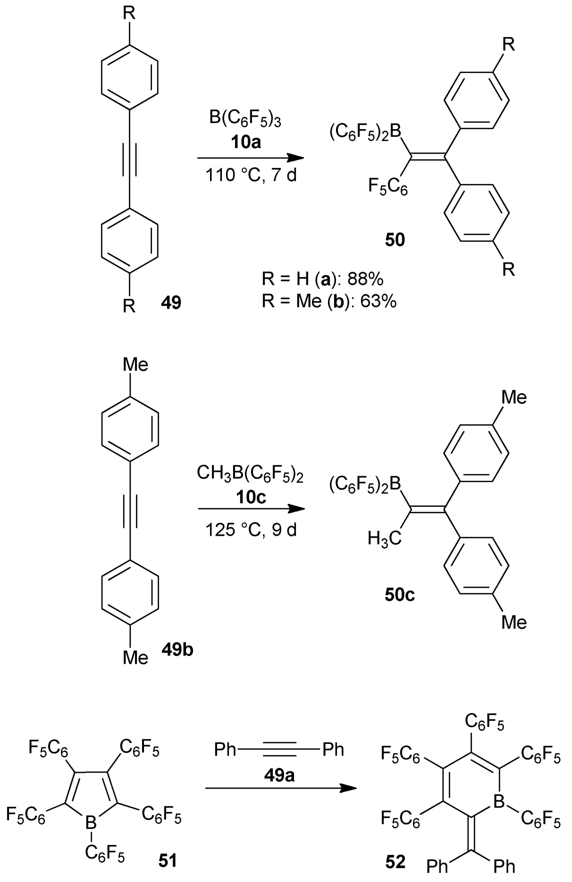
cleaved and the $B(C_6F_5)_2$ moiety inserted. A detailed study[43] indicated that the sequence started by $RB(C_6F_5)_2$ Lewis acid addition (to give **45**) followed by a rapid 1,5-H shift. In the resulting intermediate **46** the organyl substituent R at the boron atom can migrate to the adjacent carbon atom to generate **47** followed by ring-carbon migration back to the boron center to give the ring expansion products **44** (see Scheme 19). In principle this sequence is a rare example of an equivalent of a 1,1-carboboration reaction of a C=C double bond.

The 1,1-carboboration reaction can directly be used for carbon–carbon σ-bond activation. We treated the internal alkyne 4-octyne with the Lewis acid $B(C_6F_5)_3$ (**10a**). It required forcing conditions, but at 110 °C a clean 1,1-carboboration reaction ensued leading to the alkenylborane product **48**.[43] In the course of this reaction a strong C(sp)–C(sp^3) carbon–carbon σ-bond was broken and consequently one of the *n*-propyl substituents was shifted across the C≡C triple bond (see Scheme 20). Thus, it seems that the 1,1-carboboration reaction of internal acetylenes may represent an interesting novel way of cleaving a strong non-activated carbon–carbon single bond in a well defined way to actually yield a useful product (see below).

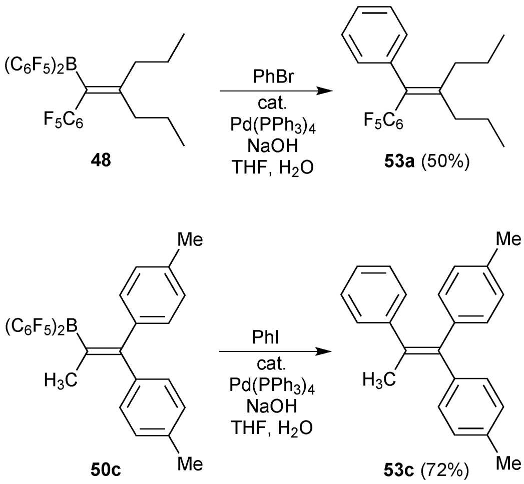
This is not a singular example. We found that the diarylacetylenes **49a** (R = H) and **49b** (R = CH_3) also underwent the 1,1-carboboration reaction, admittedly under rather forcing conditions (see Scheme 21) to yield the respective alkenylborane products **50** that each feature a geminal pair of aryl groups at



Scheme 20



Scheme 21



Scheme 22

the rehybridized distal C(sp^2) carbon center. The X-ray crystal structure analysis of product **50a** (R = H) (see Fig. 12) shows that during this process one of the strong C(sp)–C(sp^2) bonds was cleaved to allow the 1,2-migration of the phenyl substituent to take place during the 1,1-carboboration reaction sequence. As usual the –B(C_6F_5)$_2$ substituent and the remaining –C_6F_5 group, that had migrated from boron to carbon, were found bonded at the other former acetylenic carbon center that now completed the central C(sp^2)–C(sp^2) carbon–carbon double bond.[44]

The 1,1-carboboration reaction of the diarylalkynes is quite chemoselective. Treatment of bis-(*p*-tolyl)acetylene **49b** with $CH_3B(C_6F_5)_2$ (**10c**) at 125 °C eventually gave product **50c**, which was formed by selective migration of the methyl substituent from boron to carbon during the 1,1-carboboration reaction (see Scheme 21). A related acetylene C–C bond activation process was recently described by Piers *et al.* who showed that diphenylacetylene reacted with the Lewis acidic borole derivative **51** to form the 1,1-carboboration product **52** with rupture of a strong C(sp)–C(sp^2) σ-bond.[30b]

We have begun to use the very bulky alkenylboranes as Lewis acid components in frustrated Lewis pair chemistry. These products were also used as trivalent alkenylborane components for Pd-catalyzed cross-coupling reactions. System **48**

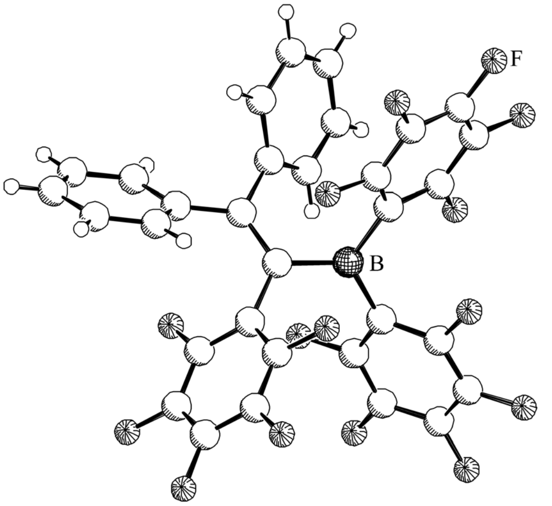


Fig. 12 Molecular structure of the C–C bond activation product **50a**.

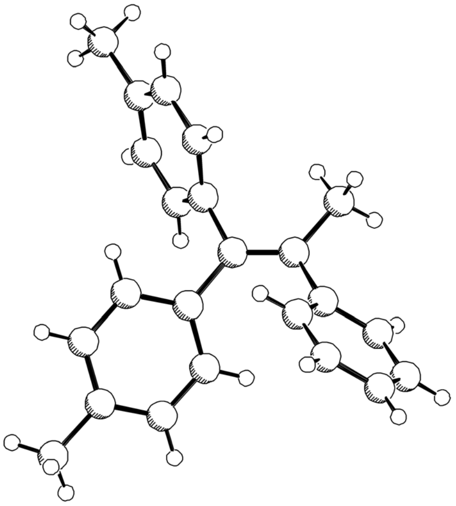


Fig. 13 Molecular structure of compound **53c**.

gave **53a** upon treatment with phenylbromide under typical Suzuki–Miyaura conditions (see Scheme 22). The alkenylborane **50c** gave product **53c** when coupled with phenyliodide under similar conditions. Product **53c** was characterized by X-ray diffraction (see Fig. 13), showing the geminal pair of *p*-tolyl groups at C1 (originating from the vicinal *p*-tolyl substituents at the diarylacetylene starting material), the methyl group at the olefinic carbon atom C2 (which originates from the methylborane reagent **10c**) and the phenyl substituent that was introduced by the Pd-catalyzed cross-coupling reaction.[44]

Conclusions and outlook

The 1,1-carboboration reaction has come a long way from early work involving the treatment of alkynylborate anions with various electrophilic reagents through the "Wrackmeyer" reaction of activated alkynes all the way to the facile 1,1-carboboration sequences of 1-alkynes with the $RB(C_6F_5)_2$ reagents that proceed easily under very mild conditions to give a variety of useful alkenylboranes and related systems. The boron Lewis acid $B(C_6F_5)_3$ is commercially available and a variety of $RB(C_6F_5)_2$ reagents can be made following well established literature pathways. These are good prerequisites from which the modern variants of the 1,1-carboboration reaction will be developed further and will become increasingly useful. In combination with some simple photochemistry the 1,1-carboboration reaction of 1-alkynes may become the method of choice as a chemo- and regioselective alternative to the ubiquitous hydroboration reaction of alkynes. It is becoming increasingly useful for the preparation of functionalized highly substituted heterocycles by one pot reaction sequences starting from readily available bisalkynyl starting materials. Remarkably, the 1,1-carboboration reaction may provide novel entries to carbon–carbon σ-bond activation chemistry, an area that will probably find increasing attention in the years to come. It seems that the 1,1-carboboration reaction has taken some remarkable development from its early stages toward an interesting and quite promising future.

Acknowledgements

G.E. thanks his group of very talented co-workers who contributed to this field over the past years. We all had a lot of fun working together, learning about the fascinating development that the 1,1-carboboration reaction took in the recent years. Generous financial support from the Deutsche Forschungsgemeinschaft, the Alexander von Humboldt-Stiftung and the Fonds der Chemischen Industrie is gratefully acknowledged.

Notes and references

1 Selected examples: (*a*) C. J. Colberg, A. Rane, J. Vaquer and J. A. Soderquist, *J. Am. Chem. Soc.*, 1993, **115**, 6065–6071; (*b*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483; (*c*) A. B. Flynn and W. W. Ogilvie, *Chem. Rev.*, 2007, **107**, 4698–4745; see also: (*d*) Y. Satoh, H. Serizawa, N. Miyaura, S. Hara and A. Suzuki, *Tetrahedron Lett.*, 1988, **29**, 1811–1814; (*e*) T. Ishiyama, M. Yamamoto and N. Miyaura, *Chem. Lett.*, 1996, **25**, 1117–1118; (*f*) A. Z. Gonzalez and J. A. Soderquist, *Org. Lett.*, 2007, **9**, 1081–1084; (*g*) N. Miyaura, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 1535–1553; (*h*) M. Daini, A. Yamamoto and M. Suginome, *J. Am. Chem. Soc.*, 2008, **130**, 2918–2919; (*i*) M. Daini and M. Suginome, *Chem. Commun.*, 2008, 5224–5226; (*j*) Y. Okuno, M. Yamashita and K. Nozaki, *Angew. Chem.*, 2011, **123**, 950–953 (*Angew. Chem., Int. Ed.*, 2011, **50**, 920–923).

2 (*a*) M. F. Lappert and B. Prokal, *J. Organomet. Chem.*, 1964, **1**, 384–400; (*b*) B. Wrackmeyer and H. Nöth, *J. Organomet. Chem.*, 1976, **108**, C21–C25; (*c*) L. Killian and B. Wrackmeyer, *J. Organomet. Chem.*, 1977, **132**, 213–221; (*d*) G. Menz and B. Wrackmeyer, *Z. Naturforsch.*, 1977, **32B**, 1400–1407; (*e*) R.-J. Binnewirtz, H. Klingenberger, R. Welte and P. Paetzold, *Chem. Ber.*, 1983, **116**, 1271–1284.

3 Reviews: (*a*) B. Wrackmeyer, *Coord. Chem. Rev.*, 1995, **145**, 125–156; (*b*) B. Wrackmeyer, *Heteroat. Chem.*, 2006, **17**, 188–208; see also: (*c*) Y. Xia, Y. Li and W. Li, *J. Organomet. Chem.*, 2008, **693**, 3722–3728; (*d*) T. Ohmura and M. Suginome, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 29–49; (*e*) M. Suginome, *Chem. Rec.*, 2010, **10**, 348–358.

4 E. Jahnke and R. R. Tykwinski, *Chem. Commun.*, 2010, **46**, 3235–3249.

5 (*a*) B. Wrackmeyer, *Polyhedron*, 1986, **5**, 1709–1721; (*b*) R. Köster, G. Seidel and B. Wrackmeyer, *Chem. Ber.*, 1989, **122**, 1825–1850; (*c*) B. Wrackmeyer, O. L. Tok and Y. N. Bubnov, *J. Organomet. Chem.*, 1999, **580**, 234–238; (*d*) B. Wrackmeyer, W. Milius, O. L. Tok and Y. N. Bubnov, *Chem.–Eur. J.*, 2002, **8**, 1537–1543; (*e*) B. Wrackmeyer, W. Milius and O. L. Tok, *Chem.–Eur. J.*, 2003, **9**, 4732–4738; (*f*) B. Wrackmeyer, K. Shahid and S. Ali, *Z. Naturforsch.*, 2005, **60B**, 590–592; (*g*) B. Wrackmeyer, K. Shahid and S. Ali, *Appl. Organomet. Chem.*, 2005, **19**, 377–382; (*h*) B. Wrackmeyer, O. L. Tok and W. Milius, *Appl. Organomet. Chem.*, 2006, **20**, 443–447.

6 (*a*) B. Wrackmeyer, O. L. Tok, E. Klimkina and Y. N. Bubnov, *Inorg. Chim. Acta*, 2000, **300–302**, 169–174; (*b*) B. Wrackmeyer, E. V. Klimkina and Y. N. Bubnov, *J. Organomet. Chem.*, 2001, **620**, 51–59.

7 (*a*) B. Wrackmeyer and R. Zentgraf, *J. Chem. Soc., Chem. Commun.*, 1978, 402–403; (*b*) B. Wrackmeyer, C. Bihlmayer and M. Schilling, *Chem. Ber.*, 1983, **116**, 3182–3191; (*c*) S. Kerschl and B. Wrackmeyer, *Z. Naturforsch.*, 1986, **41B**, 890–894; (*d*) C. Bihlmayer, S. T. Abu-Orabi and B. Wrackmeyer, *J. Organomet. Chem.*, 1987, **321**, 25–32; (*e*) B. Wrackmeyer and T. Abu-Orabi, *Chem. Ber.*, 1987, **120**, 1603–1604; (*f*) B. Wrackmeyer, K. Wagner and T. Abu-Orabi, *J. Organomet. Chem.*, 1988, **346**, 333–340; (*g*) B. Wrackmeyer, O. L. Tok, M. H. Bhatti and S. Ali, *Appl. Organomet. Chem.*, 2003, **17**, 843–850; (*h*) B. Wrackmeyer, E. V. Klimkina, W. Milius and Y. N. Bubnov, *J. Organomet. Chem.*, 2003, **687**, 108–117; (*i*) B. Wrackmeyer, B. H. Kenner-Hofmann, W. Milius, P. Thoma, O. L. Tok and M. Herberhold, *Eur. J. Inorg. Chem.*, 2006, 101–108; (*j*) B. Wrackmeyer and O. L. Tok, *Z. Naturforsch.*, 2007, **62B**, 1509–1513.

8 (*a*) B. Wrackmeyer and K. Horchler, *Organometallics*, 1990, **9**, 1881–1886; (*b*) B. Wrackmeyer and K. Horchler, *Main Group Met. Chem.*, 1990, **13**, 387–406; (*c*) B. Wrackmeyer and K. von Locquenghien Horchler, *Z. Naturforsch.*, 1991, **46B**, 1207–1213.

9 (*a*) A. Sebald and B. Wrackmeyer, *J. Chem. Soc., Chem. Commun.*, 1983, 309–310; (*b*) A. Sebald and B. Wrackmeyer, *J. Chem. Soc., Chem. Commun.*, 1983, 1293–1294; (*c*) A. Sebald and B. Wrackmeyer, *J. Organomet. Chem.*, 1986, **304**, 271–282; (*d*) A. Sebald and B. Wrackmeyer, *J. Organomet. Chem.*, 1997, **544**, 105–114; (*e*) B. Wrackmeyer, A. Pedall and J. Weidinger, *J. Organomet. Chem.*, 2002, **649**, 225–231.

10 (*a*) P. Binger and R. Köster, *Tetrahedron Lett.*, 1965, **6**, 1901–1905; (*b*) P. Binger, *Tetrahedron Lett.*, 1966, **7**, 2675–2680; (*c*) P. Binger and R. Köster, *J. Organomet. Chem.*, 1974, **73**, 205–210; (*d*) L. A. Hagelee and R. Köster, *Synth. React. Inorg. Met.-Org., Nano-Met. Chem.*, 1977, **7**, 53–67; (*e*) E. J. Corey and W. L. Seibel, *Tetrahedron Lett.*, 1986, **27**, 905–908.

11 (*a*) A. S. Balueva and O. A. Erastov, *Russ. Chem. Bull.*, 1988, **37**, 151–153 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1988, 163–165); (*b*) A. S. Balueva, G. N. Nikonov, S. G. Vul'fson, N. N. Sarvarova and B. A. Arbuzov, *Russ. Chem. Bull.*, 1990, **39**, 2367–2370 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1990, 2613–2616); (*c*) A. S. Balueva and

G. N. Nikonov, *Russ. Chem. Bull.*, 1993, **42**, 341–343 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1993, 378–380); review: (*d*) G. N. Nikonov and A. S. Balueva, *Russ. Chem. Rev.*, 1992, **61**, 335–351 (*Usp. Khim.*, 1992, **61**, 616–645).

12 (*a*) B. M. Mikhailov and Y. N. Bubnov, *Russ. Chem. Bull., Int. Ed.*, 1965, **14**, 1285 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1965, 1310); (*b*) B. M. Mikhailov, V. S. Bogdanov, G. V. Lagodzinskaya and V. F. Pozdnev, *Russ. Chem. Bull., Int. Ed.*, 1966, **15**, 366 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1966, 386); (*c*) B. M. Mikhailov, Y. N. Bubnov and S. I. Frolov, *Russ. Chem. Bull., Int. Ed.*, 1967, **16**, 2193–2199 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1967, 2290–2297); (*d*) B. M. Mikhailov, Y. N. Bubnov, S. A. Korobeinikova and S. I. Frolov, *Russ. Chem. Bull., Int. Ed.*, 1968, **17**, 1839 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1968, 1923); (*e*) S. A. Korobeinikova, Y. N. Bubnov and B. M. Mikhailov, *Russ. Chem. Bull., Int. Ed.*, 1969, **18**, 2063–2069 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1969, 2212–2219); (*f*) B. M. Mikhailov, Y. N. Bubnov and S. A. Korobeinikova, *Russ. Chem. Bull., Int. Ed.*, 1969, **18**, 2307–2313 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1969, 2465–2473); (*g*) B. M. Mikhailov, Y. N. Bubnov and S. A. Korobeinikova, *Russ. Chem. Bull., Int. Ed.*, 1970, **19**, 2480–2483 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1970, 2631–2634); (*h*) Y. N. Bubnov, S. A. Korobeinikova, G. V. Isagulyants and B. M. Mikhailov, *Russ. Chem. Bull., Int. Ed.*, 1970, **19**, 1902–1906 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1970, 2023–2028); (*i*) B. M. Mikhailov, Y. N. Bubnov and S. I. Frolov, *Russ. Chem. Bull., Int. Ed.*, 1981, **30**, 1736–1741 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1981, 2114–2119); (*j*) S. V. Ponomarev, Y. N. Bubnov and B. M. Mikhailov, *Russ. Chem. Bull., Int. Ed.*, 1981, **30**, 1528–1530 (*Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1981, 1859–1861); (*k*) Y. N. Bubnov, A. I. Grandberg, M. S. Grigorian, V. G. Kiselev, M. I. Struchkova and B. M. Mikhailov, *J. Organomet. Chem.*, 1985, **292**, 93–104; (*l*) S. Y. Erdyakov, S. V. Stefanyuk, A. V. Ignatenko, M. E. Gurskii and Y. N. Bubnov, *Mendeleev Commun.*, 2007, **17**, 139–141; see also: (*m*) Y. N. Bubnov, *Pure Appl. Chem.*, 1987, **59**, 895–906; (*n*) Y. N. Bubnov, M. E. Gruskii, S. Y. Erdyakov, O. A. Kizas, G. D. Kolomnikova, N. Y. Kuznetsov, T. V. Potapova, O. A. Varzatskii and Y. Z. Voloshim, *J. Organomet. Chem.*, 2009, **694**, 1754–1763.

13 (*a*) O. L. Tok, B. Wrackmeyer and Y. N. Bubov, in *Contemporary Boron Chemistry*, ed. M. Davidson, A. K. Hughes, T. B. Marder and K. Wade, Royal Society of Chemistry, Cambridge, 2000, p. 434–437; (*b*) B. Wrackmeyer, A. Pedall, W. Milius, O. L. Tok and Y. N. Bubnov, *J. Organomet. Chem.*, 2002, **649**, 232–245; (*c*) B. Wrackmeyer, M. H. Bhatti, S. Ali, O. L. Tok and Y. N. Bubnov, *J. Organomet. Chem.*, 2002, **657**, 146–154; (*d*) B. Wrackmeyer, O. L. Tok and Y. N. Bubnov, *Appl. Organomet. Chem.*, 2004, **18**, 43–50; (*e*) B. Wrackmeyer and O. L. Tok, *Z. Naturforsch.*, 2006, **61B**, 243–251; see also: (*f*) B. Wrackmeyer, O. L. Tok and Y. N. Bubnov, *Angew. Chem.*, 1999, **111**, 214–217 (*Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 124–126); (*g*) ref. 5*c*,5*d*,6*a*.

14 (*a*) L. Killian and B. Wrackmeyer, *J. Organomet. Chem.*, 1978, **148**, 153–164; (*b*) S. Kerschl and B. Wrackmeyer, *Z. Naturforsch.*, 1984, **39B**, 1037–1041; (*c*) C. Bihlmayer, S. T. Abu-Orabi and B. Wrackmeyer, *J. Organomet. Chem.*, 1987, **322**, 25–32; (*d*) B. Wrackmeyer, K. Horchler and R. Boese, *Angew. Chem.*, 1989, **101**, 1563–1565 (*Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1500–1502); (*e*) B. Wrackmeyer and K. Horchler, *Z. Naturforsch.*, 1990, **45B**, 437–446; (*f*) B. Wrackmeyer and G. Kehr, *Polyhedron*, 1991, **10**, 1497–1506; (*g*) R. Köster, G. Seidel, I. Klopp, C. Krüger, G. Kehr, J. Süß and B. Wrackmeyer, *Chem. Ber.*, 1993, **126**, 1385–1396; (*h*) B. Wrackmeyer, S. Kundler and R. Boese, *Chem. Ber.*, 1993, **126**, 1361–1370; (*i*) B. Wrackmeyer, G. Kehr and D. Wettinger, *Inorg. Chim. Acta*, 1994, **220**, 161–173; (*j*) B. Wrackmeyer, S. Kundler and A. Ariza-Castolo, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1994, **91**, 229–239; (*k*) B. Wrackmeyer, S. Kundler, W. Milius and R. Boese, *Chem. Ber.*, 1994, **127**, 333–342; (*l*) see also: ref. 7*i*,13*b*.

15 (*a*) L. Killian and B. Wrackmeyer, *J. Organomet. Chem.*, 1978, **148**, 137–146; (*b*) B. Wrackmeyer, *J. Organomet. Chem.*, 1981, **205**, 1–14; (*c*) B. Wrackmeyer, *J. Chem. Soc., Chem. Commun.*, 1986, 397–399; (*d*) B. Wrackmeyer, *J. Organomet. Chem.*, 1986, **310**, 151–160; (*e*) B. Wrackmeyer, *J. Organomet. Chem.*, 1989, **364**, 331–342; (*f*) B. Wrackmeyer and K. Horchler, *J. Organomet. Chem.*, 1990, **399**, 1–10; (*g*) B. Wrackmeyer and K. Horchler, *Magn. Reson. Chem.*, 1990, **28**, 56–61; (*h*) B. Wrackmeyer, G. Kehr and R. Boese, *Angew. Chem.*, 1991, **103**, 1374–1376 (*Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1370–1372); (*i*) B. Wrackmeyer, G. Kehr and R. Boese, *Chem. Ber.*, 1992, **125**, 643–650; (*j*) B. Wrackmeyer, G. Kehr, A. Sebald and J. Kümmerlen, *Chem. Ber.*, 1992, **125**, 1597–1603; (*k*) R. Köster, G. Seidel, J. Süß and B. Wrackmeyer, *Chem. Ber.*, 1993, **126**, 1107–1114; (*l*) B. Wrackmeyer, G. Kehr and J. Süß, *Chem. Ber.*, 1993, **126**, 2221–2226; (*m*) B. Wrackmeyer, G. Kehr and S. Ali, *Inorg. Chim. Acta*, 1994, **216**, 51–55; (*n*) B. Wrackmeyer, K. Horchler von Locquenghien and S. Kundler, *J. Organomet. Chem.*, 1995, **503**, 289–295; (*o*) B. Wrackmeyer, D. Wettinger and W. Milius, *J. Chem. Soc., Chem. Commun.*, 1995, 399–401; (*p*) B. Wrackmeyer, H. E. Maisel, J. Süß and W. Milius, *Z. Naturforsch.*, 1996, **51B**, 1320–1324; (*q*) B. Wrackmeyer and H. Vollrath, *Main Group Met. Chem.*, 1998, **21**, 515–525; (*r*) B. Wrackmeyer, G. Kehr, J. Süß and E. Molla, *J. Organomet. Chem.*, 1998, **562**, 207–215; (*s*) B. Wrackmeyer, H. Vollrath and S. Ali, *Inorg. Chim. Acta*, 1999, **296**, 26–32; (*t*) B. Wrackmeyer, G. Kehr, J. Süß and E. Molla, *J. Organomet. Chem.*, 1999, **577**, 82–92; (*u*) B. Wrackmeyer, W. Milius, E. V. Klimkina and Y. N. Bubnov, *Chem.–Eur. J.*, 2001, **7**, 775–782; (*v*) B. Wrackmeyer, G. Kehr, S. Willbold and S. Ali, *J. Organomet. Chem.*, 2002, **646**, 125–133; (*w*) B. Wrackmeyer, W. Milius and A. Badshah, *J. Organomet. Chem.*, 2002, **656**, 97–101; (*x*) B. Wrackmeyer and J. Süß, *Z. Naturforsch.*, 2002, **57B**, 741–745; (*y*) B. Wrackmeyer, H. E. Maisel, W. Milius and M. Herberhold, *J. Organomet. Chem.*, 2003, **680**, 271–280; (*z*) B. Wrackmeyer, O. L. Tok, K. Shahid and S. Ali, *Inorg. Chim. Acta*, 2004, **357**, 1103–1110; (*aa*) B. Wrackmeyer, O. L. Tok, A. Khan and A. Badshah, *Z. Naturforsch.*, 2005, **60B**, 251–258; (*ab*) B. Wrackmeyer, O. L. Tok, A. Khan and A. Badshah, *Appl. Organomet. Chem.*, 2005, **19**, 1249–1256; (*ac*) E. Khan, S. Bayer and B. Wrackmeyer, *Z. Naturforsch.*, 2009, **64B**, 47–57; (*ad*) E. Khan, S. Bayer and B. Wrackmeyer, *Z. Naturforsch.*, 2009, **64B**, 995–1002; (*ae*) E. Khan and B. Wrackmeyer, *Z. Naturforsch.*, 2009, **64B**, 1098–1106; (*af*) E. Khan, S. Bayer, R. Kempe and B. Wrackmeyer, *Eur. J. Inorg. Chem.*, 2009, 4416–4424; (*ag*) B. Wrackmeyer, O. L. Tok, E. V. Klimkina and W. Milius, *Eur. J. Inorg. Chem.*, 2010, 2276–2282; see also: (*ah*) ref. 2*c*,5*b*,9,13*b*,*c*,14.

16 see also: B. Wrackmeyer, K. Horchler, A. Sebald and L. H. Merwin, *Magn. Reson. Chem.*, 1990, **28**, 465–469.

17 see also: B. Wrackmeyer, G. Kehr and S. Willbold, *J. Organomet. Chem.*, 1999, **590**, 93–103.

18 (*a*) A. G. Massey, A. J. Park and F. G. A. Stone, *Proc. Chem. Soc.*, 1963, 212; (*b*) A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245–250; (*c*) G. Erker, *Dalton Trans.*, 2005, 1883–1890.

19 (*a*) T. J. Marks, *Acc. Chem. Res.*, 1992, **25**, 57–65; (*b*) X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015–10031; (*c*) G. Erker, *Dalton Trans.*, 2005, 1883–1890; (*d*) G. Erker, G. Kehr and R. Fröhlich, *J. Organomet. Chem.*, 2005, **690**, 6254–6262; (*e*) T. Beringhelli, D. Donghi, D. Maggioni and G. D'Alfonso, *Coord. Chem. Rev.*, 2008, **252**, 2292–2313.

20 (*a*) D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440–9441; (*b*) D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090–3098; (*c*) M. Oestreich, *Synlett*, 2007, 1629–1643; (*d*) S. Rendler and M. Oestreich, *Angew. Chem.*, 2008, **120**, 6086–6089 (*Angew. Chem., Int. Ed.*, 2008, **47**, 5997–6000); (*e*) W. E. Piers, A. J. V. Marwitz and L. G. Mercier, *Inorg. Chem.*, 2011, DOI: 10.1021/ic2006474.

21 (*a*) D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535–1539; (*b*) D. W. Stephan and G. Erker, *Angew. Chem.*, 2010, **122**, 50–81 (*Angew. Chem., Int. Ed.*, 2010, **49**, 46–76); (*c*) D. W. Stephan, in *Catalysis without Precious Metals*, ed. R. M. Bullock, Wiley-VCH, Weinheim, 2010, p. 261–275; (*d*) G. Erker, *Organometallics*, 2011, **30**, 358–368; (*e*) G. Erker, *Dalton Trans.*, 2011, 7475–7483; (*f*) D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch and M. Ullrich, *Inorg. Chem.*, 2011, DOI: 10.1021/ic200663v; (*g*) G. Erker, *C. R. Chim.*, 2011, **14**, 831–841.

22 G. Dierker, J. Ugolotti, G. Kehr, R. Fröhlich and G. Erker, *Adv. Synth. Catal.*, 2009, **351**, 1080–1088.

23 (*a*) D. J. Parks, R. E. v. H. Spence and W. E. Piers, *Angew. Chem.*, 1995, **107**, 895–897 (*Angew. Chem., Int. Ed.*, 1995, **34**, 809–811);

(*b*) W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345–354; (*c*) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492–5503.

24 (*a*) J. Ugolotti, G. Kehr, R. Fröhlich and G. Erker, *Chem. Commun.*, 2010, **46**, 3016–3018; (*b*) J. Ugolotti, G. Dierker, R. Fröhlich, G. Kehr and G. Erker, *J. Organomet. Chem.*, 2011, **696**, 1184–1188.

25 See for examples: (*a*) H. E. Zimmerman, R. W. Binkley, R. S. Givens and M. A. Sherwin, *J. Am. Chem. Soc.*, 1967, **89**, 3932–3933; (*b*) S. S. Hixson, P. S. Mariano and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531–551; (*c*) H. E. Zimmerman, *Science*, 1976, **191**, 523–528; (*d*) H. E. Zimmerman, *Acc. Chem. Res.*, 1982, **15**, 312–317; (*e*) U. Burger and R. Etienne, *Helv. Chim. Acta*, 1984, **67**, 2057–2062; (*f*) J. J. Eisch, B. Shafii and M. P. Boleslawski, *Pure Appl. Chem.*, 1991, **63**, 365–368; (*g*) J. D. Wilkey and G. B. Schuster, *J. Am. Chem. Soc.*, 1991, **113**, 2149–2155; (*h*) H. E. Zimmerman and D. Armesto, *Chem. Rev.*, 1996, **96**, 3065–3112; (*i*) H. E. Zimmerman, *Pure Appl. Chem.*, 2006, **78**, 2193–2203.

26 (*a*) B. Wrackmeyer, H. E. Maisel, E. Molla, A. Mottalib, A. Badshah, M. H. Bhatti and S. Ali, *Appl. Organomet. Chem.*, 2003, **17**, 465–472; (*b*) B. Wrackmeyer, O. L. Tok and R. Kempe, *Inorg. Chim. Acta*, 2005, **358**, 4183–4190; (*c*) B. Wrackmeyer, O. L. Tok, W. Milius, A. Khan and A. Badshah, *Appl. Organomet. Chem.*, 2006, **20**, 99–105; (*d*) B. Wrackmeyer, E. Khan, S. Beyer and K. Shahid, *Z. Naturforsch.*, 2007, **62B**, 1174–1182; (*e*) B. Wrackmeyer, E. Khan and R. Kempe, *Appl. Organomet. Chem.*, 2007, **21**, 39–45; (*f*) B. Wrackmeyer, E. Khan and R. Kempe, *Appl. Organomet. Chem.*, 2008, **22**, 383–388; (*g*) E. Khan and B. Wrackmeyer, *Turk. J. Chem.*, 2010, **34**, 793–803; (*h*) E. Khan and B. Wrackmeyer, *Cent. Eur. J. Chem.*, 2011, **9**, 126–132.

27 (*a*) J. Ugolotti, G. Dierker, G. Kehr, R. Fröhlich, S. Grimme and G. Erker, *Angew. Chem.*, 2008, **120**, 2662–2665 (*Angew. Chem., Int. Ed.*, 2008, **47**, 2622–2625); (*b*) J. Ugolotti, G. Kehr, R. Fröhlich, S. Grimme and G. Erker, *J. Am. Chem. Soc.*, 2009, **131**, 1996–2007.

28 (*a*) U. Rosenthal, A. Ohff, W. Baumann, R. Kempe, A. Tillack and V. V. Burlakov, *Angew. Chem.*, 1994, **106**, 1678–1680 (*Angew. Chem., Int. Ed.*, 1994, **33**, 1605–1607); (*b*) S. Pulst, P. Arndt, B. Heller, W. Baumann, R. Kempe and U. Rosenthal, *Angew. Chem.*, 1996, **108**, 1175–1178 (*Angew. Chem., Int. Ed.*, 1996, **35**, 1112–1114); (*c*) U. Rosenthal, P.-M. Pellny, F. G. Kirchbauer and V. V. Burlakov, *Acc. Chem. Res.*, 2000, **33**, 119–129; (*d*) U. Rosenthal, *Angew. Chem.*, 2004, **116**, 3972–3977 (*Angew. Chem., Int. Ed.*, 2004, **43**, 3882–3887); (*e*) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann and A. Spannenberg, *Organometallics*, 2005, **24**, 456–471; (*f*) U. Rosenthal, V. V. Burlakov, M. A. Bach and T. Beweries, *Chem. Soc. Rev.*, 2007, **36**, 719–728; (*g*) U. Rosenthal, *Angew. Chem.*, 2008, **120**, 5196–5199 (*Angew. Chem., Int. Ed.*, 2008, **47**, 5118–5121).

29 (*a*) N. Suzuki, M. Nishiura and Y. Wakatsuki, *Science*, 2002, **295**, 660–663; (*b*) N. Suzuki, N. Aihara, H. Takahara, T. Watanabe, M. Iwasaki, M. Saburi, D. Hashizume and T. Chihara, *J. Am. Chem. Soc.*, 2004, **126**, 60–61; (*c*) N. Suzuki, T. Watanabe, T. Hirose and T. Chihara, *Chem. Lett.*, 2004, **33**, 1488–1489; (*d*) N. Suzuki, T. Watanabe, M. Iwasaki and T. Chihara, *Organometallics*, 2005, **24**, 2065–2069; (*e*) N. Suzuki, T. Watanabe, H. Yoshida, M. Iwasaki, M. Saburi, M. Tezuka, T. Hirose, D. Hashizume and T. Chihara, *J. Organomet. Chem.*, 2006, **691**, 1175–1182; (*f*) N. Suzuki, D. Hashizume, H. Koshino and T. Chihara, *Angew. Chem.*, 2008, **120**, 5276–5280 (*Angew. Chem., Int. Ed.*, 2008, **47**, 5198–5202).

30 (*a*) C. Jiang, O. Blacque and H. Berke, *Organometallics*, 2010, **29**, 125–133; (*b*) C. Fan, W. E. Piers, M. Parvez and R. McDonald, *Organometallics*, 2010, **29**, 5132–5139.

31 C. Chen, F. Eweiner, B. Wibbeling, R. Fröhlich, S. Senda, Y. Ohki, K. Tatsumi, S. Grimme, G. Kehr and G. Erker, *Chem.–Asian J.*, 2010, **5**, 2199–2208.

32 C. Chen, T. Voss, R. Fröhlich, G. Kehr and G. Erker, *Org. Lett.*, 2011, **13**, 62–65.

33 (*a*) S. Kerschl and B. Wrackmeyer, *J. Chem. Soc., Chem. Commun.*, 1985, 1199–1200; (*b*) S. Kerschl and B. Wrackmeyer, *Chem. Ber.*, 1988, **121**, 1451–1453; (*c*) B. Wrackmeyer and G. Guldner, *Tetrahedron*, 1989, **45**, 1119–1130; (*d*) B. Wrackmeyer, O. L. Tok, G. Guldner and S. V. Gruener, *Appl. Organomet. Chem.*, 2003, **17**, 860–868; (*e*) B. Wrackmeyer, S. V. Gruener, A. S. Zolotareva, G. Menz and B. Wrackmeyer, *Z. Naturforsch.*, 2003, **58B**, 1035–1040; (*f*) B. Wrackmeyer, E. V. Klimkina, T. Kupcik and R. Lohwasser, *Z. Naturforsch.*, 2011, **66B**, 98–102.

34 B.-H. Xu, G. Kehr, R. Fröhlich, B. Wibbeling, B. Schirmer, S. Grimme and G. Erker, *Angew. Chem.*, 2011, **123**, 7321–7324 (*Angew. Chem., Int. Ed.*, 2011, **50**, 7183–7186).

35 R. Liedtke, R. Fröhlich, G. Kehr and G. Erker, *Organometallics*, 2011, **30**, 5222–5232.

36 C. Chen, R. Fröhlich, G. Kehr and G. Erker, *Chem. Commun.*, 2010, **46**, 3580–3582.

37 O. Ekkert, R. Fröhlich, G. Kehr and G. Erker, *J. Am. Chem. Soc.*, 2011, **133**, 4610–4616.

38 O. Ekkert, G. Kehr, R. Fröhlich and G. Erker, *Chem. Commun.*, 2011, **47**, 10482–10484.

39 (*a*) G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120–128; (*b*) R. H. Crabtree, *Acc. Chem. Res.*, 1990, **23**, 95–101; (*c*) P. G. Jessop and R. H. Morris, *Coord. Chem. Rev.*, 1992, **121**, 155–284; (*d*) R. H. Crabtree, *Angew. Chem.*, 1993, **105**, 828–845 (*Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 789–805); (*e*) G. S. McGrady and G. Guilera, *Chem. Soc. Rev.*, 2003, **32**, 383–392; (*f*) D. M. Heinekey, A. Lledós and J. M. Lluch, *Chem. Soc. Rev.*, 2004, **33**, 175–182; (*g*) R. H. Crabtree, *J. Organomet. Chem.*, 2004, **689**, 4083–4091; (*h*) G. J. Kubas, *Chem. Rev.*, 2007, **107**, 4152–4205.

40 Selected examples: (*a*) K. I. Goldberg and A. S. Goldman, *ACS Symp. Ser.*, 2004, **885**, 440; (*b*) V. Ritleng, C. Sirlin and M. Pfeffer, *Chem. Rev.*, 2002, **102**, 1731–1770; (*c*) X. Chen, K. M. Engle, D. H. Wang and J. Q. Yu, *Angew. Chem.*, 2009, **121**, 5196–5217 (*Angew. Chem., Int. Ed.*, 2009, **48**, 5094–5115); (*d*) D. H. Ess, R. J. Nielsen, W. A. GoddardIII and R. A. Periana, *J. Am. Chem. Soc.*, 2009, **131**, 11686–11688; (*e*) A. J. Vetter, R. D. Rieth, W. W. Brennessel and W. D. Jones, *J. Am. Chem. Soc.*, 2009, **131**, 10742–10752; (*f*) L. J. L. Häller, M. J. Page, S. A. Macgregor, M. F. Mahon and M. K. Whittlesey, *J. Am. Chem. Soc.*, 2009, **131**, 4604–4605; (*g*) D. Balcells, E. Clot and O. Eisenstein, *Chem. Rev.*, 2010, **110**, 749–823; (*h*) R. Jazzar, J. Hitce, A. Renaudat, J. Sofack-Kreutzer and O. Baudoin, *Chem.–Eur. J.*, 2010, **16**, 2654–2672; (*i*) S. Conejero, M. Paneque, M. L. Poveda, L. L. Santos and E. Carmona, *Acc. Chem. Res.*, 2010, **43**, 572–580; (*j*) A. Gunay and K. H. Theopold, *Chem. Rev.*, 2010, **110**, 1060–1081; (*k*) P. Lu, T. C. Boorman, A. M. Z. Slawin and I. Larrosa, *J. Am. Chem. Soc.*, 2010, **132**, 5580–5581; see also: (*l*) J. Wu, X. Cui, L. Chen, G. Jiang and Y. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 13888–13889; (*m*) H. Zhou, Y. H. Xu, W. J. Chung and T. P. Loh, *Angew. Chem.*, 2009, **121**, 5459–5461 (*Angew. Chem., Int. Ed.*, 2009, **48**, 5355–5357); (*n*) T. Nishikata, A. R. Abela, S. Huang and B. H. Lipshutz, *J. Am. Chem. Soc.*, 2010, **132**, 4978–4979; (*o*) Q. Li and Z. X. Yu, *J. Am. Chem. Soc.*, 2010, **132**, 4542–4543; (*p*) T. Nishikata, A. R. Abela and B. H. Lipshutz, *Angew. Chem.*, 2010, **122**, 793–796 (*Angew. Chem., Int. Ed.*, 2010, **49**, 781–784); (*q*) G. de Petris, A. Cartoni, A. Troiani, V. Barone, P. Cimino, G. Angelini and O. Ursini, *Chem.–Eur. J.*, 2010, **16**, 6234–6242.

41 Selected examples: (*a*) R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245–269; (*b*) M. Murakami and Y. Ito, *Topics in Organometallic Chemistry*, ed. S. Murai, Springer Verlag, New York, vol. 3, 1999, pp. 97–129; (*c*) B. Rybtchinski and D. Milstein, *Angew. Chem.*, 1999, **111**, 918–932 (*Angew. Chem., Int. Ed.*, 1999, **38**, 870–883); (*d*) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759–1792; (*e*) C.-H. Jun, *Chem. Soc. Rev.*, 2004, **33**, 610–618; (*f*) Y. J. Park, J. W. Park and C.-H. Jun, *Acc. Chem. Res.*, 2008, **41**, 222–234; (*g*) T. Li, J. J. García, W. Brennessel and W. D. Jones, *Organometallics*, 2010, **29**, 2430–2445; (*h*) Y. Nakao, A. Yada and T. Hiyama, *J. Am. Chem. Soc.*, 2010, **132**, 10024–10026.

42 B.-H. Xu, G. Kehr, R. Fröhlich and G. Erker, *Chem.–Eur. J.*, 2010, **16**, 12538–12540.

43 B.-H. Xu, G. Kehr, R. Fröhlich, S. Grimme and G. Erker, *J. Am. Chem. Soc.*, 2011, **113**, 3480–3491.

44 C. Chen, G. Kehr, R. Fröhlich and G. Erker, *J. Am. Chem. Soc.*, 2010, **132**, 13594–13595.