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Calcium-mediated hydroboration of alkenes: "Trojan horse" or "true" catalysis?

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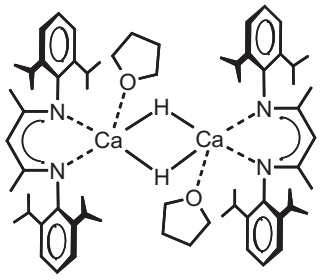
ABSTRACT

The hydroboration of 1,1-diphenylethylene (DPE) with catecholborane (HBcat) proceeds at 100 °C. For conversion at room temperature three different organocalcium catalysts have been investigated: the calcium hydride complex [DIPPnacnacCaH·(THF)]$_2$ (**1**, DIPPnacnac = CH{(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)}$_2$), Ca[2-Me$_2$N-α-Me$_3$Si-benzyl)$_2$·(THF)$_2$ (**2**) and DIPPnacnacCa(H-BBN)·(THF) (**3**, BBN = 9-borabicyclo[3.3.1.]nonane). Although up to 96% conversion of DPE is found, the product of the reaction is not the expected Ph$_2$CHCH$_2$Bcat but (Ph$_2$CHCH$_2$)$_3$B is formed instead. Organocalcium compounds catalyze the decomposition of HBcat to B$_2$(cat)$_3$ and BH$_3$ (or B$_2$H$_6$) and the latter is involved in hydroboration of DPE. The calcium-catalyzed decomposition of HBcat was investigated with ^{11}B NMR and the signals were assigned to the following species: B$_2$(cat)$_3$, B(cat)$_2^-$, HBcat, BH$_3$(THF), BH$_4^-$ and B$_2$H$_7^-$. A tentative mechanism for the formation of these species was proposed. The intermediate DIPPnacnacCa(BH$_4$)·(THF)$_2$ (**5**) was independently prepared by reaction of **1** and BH$_3$(Me$_2$S) and was structurally characterized by X-ray diffraction. Stoichiometric reaction of **1** with pinacolborane (HBpin) gave a trimeric complex [DIPPnacnacCa(H$_2$Bpin)]$_3$ (**6**) which was structurally characterized by X-ray diffraction. This complex does not react with DPE, also not at elevated temperatures. The possible equilibrium between **6** and **1**/HBpin is therefore fully at the side of **6**. As **6** is unstable in the presence of HBpin, no further catalytic conversions have been investigated.

1. Introduction

Classical hydroboration [1] is an important synthetic tool for the conversion of alkenes to boron-functionalized organics which subsequently offer various possibilities for further transformation into alcohols [2], amines [3] or halogenated organics [4]. Although the hydroboration of alkenes with B$_2$H$_6$ generally proceeds smoothly and under mild conditions there has been increased interest in alkene hydroboration with heteroatom-substituted boranes like catecholborane (HBcat; Scheme 1). As such a stabilized borane is less Lewis-acidic, it shows better functional group tolerance and is easier to store and handle. Alkene hydroboration with HBcat, however, generally needs the assistance of a catalyst [5,6]. Although this might seem a disadvantage, it is inherently coupled to the crucial advantage of organometallic catalysis, *i.e.* control over the course of the reaction by metal and/or ligand choice. Transition metal-catalyzed addition of catecholborane to carbon–carbon multiple bonds produced some remarkable chemo- [5], regio- [7–9], diastereo- [7,9–12] and enantioselectivities [13,14]. The catalytic toolbox contains late transition metal catalysts that recently also includes an Au complex [15]. Early group 3 and 4 transition metal compounds have been used as catalysts already at a preliminary stage [16–21]. Marks et al. [16] proposed that lanthanide-catalyzed alkene hydroboration could proceed through a succession of steps typical for organolanthanide chemistry, *i.e.* alkene insertion and σ-bond metathesis (Scheme 2). The actual catalyst in this cycle is proposed to be a highly reactive lanthanide-



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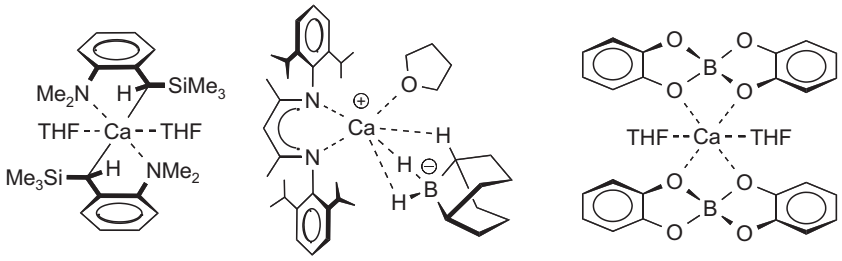

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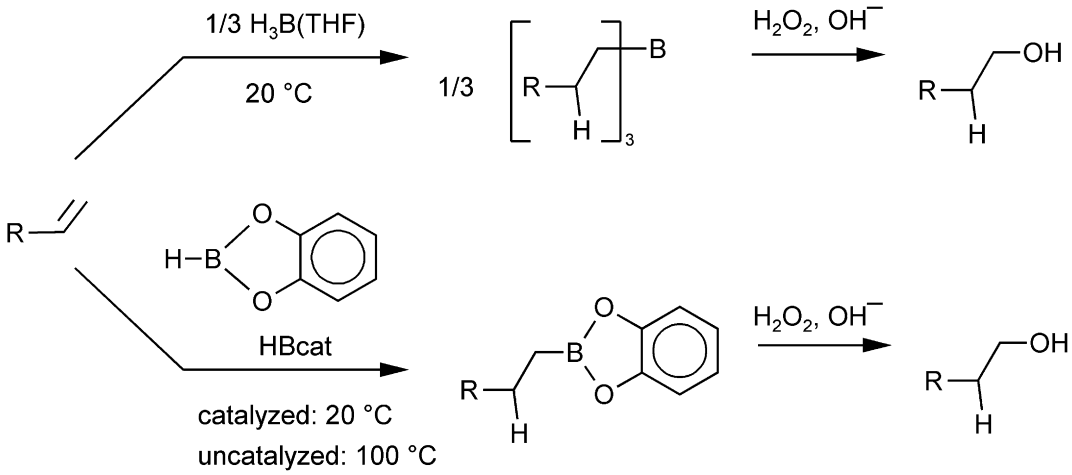
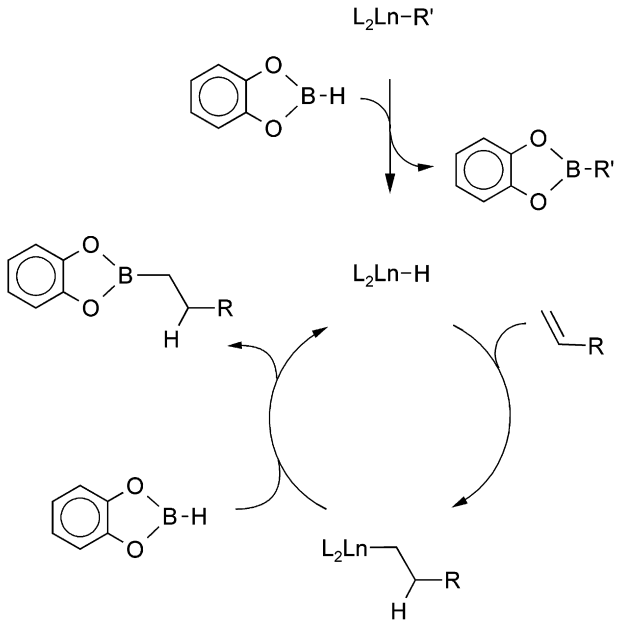


Scheme 1.

hydride complex. The formulation of an intermediate highly nucleophilic lanthanide-hydride complex in the presence of a Lewis-acidic borane seems contradictory. The borane HBcat, however, should be regarded as a resonance-stabilized less Lewis-acidic borane and, based on metal-ligand bond enthalpies, the reaction of a lanthanide-alkyl complex with HBcat to give a lanthanide-hydride and alkylBcat has been estimated to be slightly exothermic (−3 kcal/mol) [16]. In addition, Marks et al. do not rule out the possibility that the lanthanide-hydride catalyst is present as a lanthanide borate species containing the $(H_2Bcat)^-$ ion.

We recently introduced the well-defined calcium hydride complex $[DIPPnacnacCaH\cdot(THF)]_2$ (**1**) [22] (DIPPnacnac = CH{(CMe)(2,6-*i*$Pr_2C_6H_3N$)}$_2$) and could show that such a species is an actual catalyst for alkene hydrosilylation [23] and hydrogenation [24]. As the key steps in catalysis based on organolanthanide and organocalcium chemistry are similar [25,26], we posed the question whether calcium-catalyzed alkene hydroboration would be feasible and efficient. Use of calcium compounds in catalysis has important economical advantages (Ca is globally available and is one of the cheapest metals) as well as environmental advantages (Ca is biocompatible and non-poisonous). Herein we describe preliminary investigations of alkene hydroboration with organocalcium catalysts and extend our earlier studies [27] on the reactivity of the calcium hydride complex **1** with boranes.



Scheme 2.

Table 1
Catalytic hydroboration of DPE with HBcat.

Entry	catalyst	[cat]/[DPE] (%)	solvent	temperature (°C)	time (hrs)	conversion (%)
1	–	–	–	25	72	–
2	–	–	–	100	20	96
3	**1**	2.5	–	25	72	95
4	**2**	2.5	–	50	20	90
5	**1**	2.5	benzene	25	72	38
6	**3**	5	benzene	25	192	43

2. Results and discussion

The calcium hydride complex **1** does not react with isolated alkenes but shows addition to conjugated alkenes like butadienes and styrenes. Therefore we chose 1,1-diphenylethylene (DPE) as a model substrate. This alkene has the additional advantage to be inert to anionic polymerization, a possible side reaction for which organocalcium compounds have been shown to be highly effective initiators [28]. Hydroboration experiments were run in the temperature range of 25–100 °C, either without solvent or in benzene and with or without the use of three different catalysts (**1**–**3**). The results are summarized in Table 1.

The first two entries confirm that HBcat does not react with DPE at room temperature. Heating to 100 °C is a necessity and this gave near to full conversion to Ph_2CHCH_2Bcat within 20 h. With calcium hydride as a catalyst, however, already at room temperature 95% conversion of DPE is observed but the reaction is slow (entry 3). Use of catalyst **2** at the slightly raised temperature of 50 °C gave a faster conversion (entry 4). Whereas this set of experiments has been run without solvent, use of benzene as a solvent led to slower conversion (entry 5) which is likely attributed to a dilution effect. The last experiment (entry 6) shows that also the calcium borate complex **3** catalyzes the hydroboration of DPE, albeit much slower. In all cases oxidative work-up under basic conditions gave the expected alcoholic product Ph_2CHCH_2OH.

Given these results, it seems that organocalcium compounds can function as a catalyst for the hydroboration of DPE with HBcat. Careful analysis of the products by ^1H NMR before oxidative work-up, however, showed that the intermediate product in question is not the boronic ester Ph_2CHCH_2Bcat but the *tris*-alkyl borane $(Ph_2CHCH_2)_3B$. This compound was independently prepared by reaction of excess DPE with $BH_3(Me_2S)$. It is therefore likely that organocalcium compounds catalyze the decomposition of HBcat in BH_3 (or the diborane B_2H_6) and further products. This is followed by selective addition of BH_3 to the 1,1-substituted alkene DPE. Such behaviour has been pointed out earlier in Ti-catalyzed alkene hydroboration [17,18]. The organocalcium species is therefore not a "true" catalyst but could be regarded a "Trojan horse", as was described earlier by Burgess et al. for Nb-mediated alkene hydroboration [29].

Table 2
^{11}B NMR signals for the reaction of **1** with HBcat (THF-d_8, 160 Mhz, 25 °C) and their comparison with literature data.

δ (ppm)	Multiplicity, $^1J_{B,H}$	Possible species	Literature values	Ref.
−36.5	quint, 82.0 Hz	$Ca[BH_4]_2$	−35.8, quint 82.0 Hz, in monoglyme	[31]
−23.9	q, 68.2 Hz	$[B_2H_7]^-$	−22.7, q, in diglyme	[32]
			−25.3, q 102 Hz, in monoglyme	[33]
−0.6	q, 101.6 Hz	$BH_3(THF)$	−0.6, q 103 Hz, in THF	[33]
9.2	s	$[B(cat)_2]^-$	15.2, s, in CD_2Cl_2	[34a]
			15.1, s, in toluene-d_8	[35]
			14.6, s, in diglyme	[32]
23.9	d, 185.8 Hz	HBcat	29.9, d, in $CDCl_3$	[36]
			28.8, d 193.0 Hz, in benzene-d_6	[this work]
25.2	s, broad	$B_2(cat)_3$	22.7, s (broad), in CD_2Cl_2	[34a]

In order to uncover the species involved in these catalytic reactions, we measured ^{11}B NMR spectra of the reaction mixture in benzene-d_6 after catalysis. The very broad signal at 87.6 ppm can be assigned to the product $(Ph_2CHCH_2)_3B$ (this was supported by comparison with the independently prepared sample). The doublet at 28.8 ppm ($^1J_{B,H} = 191.6$ Hz) corresponds to unreacted substrate HBcat. Minor signals at 23.2 and 9.2 have been assigned to $B_2(cat)_3$ and $[B(cat)_2]^-$ (*vide infra*).

Earlier work from Nöth et al. showed that HBcat is also not stable in the presence of group 4 metal hydrides like Cp_2ZrH_2 [30]. In order to learn more about the catalytic decomposition of HBcat we followed the reaction of **1** with excess HBcat in THF-d_8 by ^{11}B NMR. The reaction mixture became after a short time at room temperature already viscous. The ^{11}B NMR signals (Fig. 1) can be

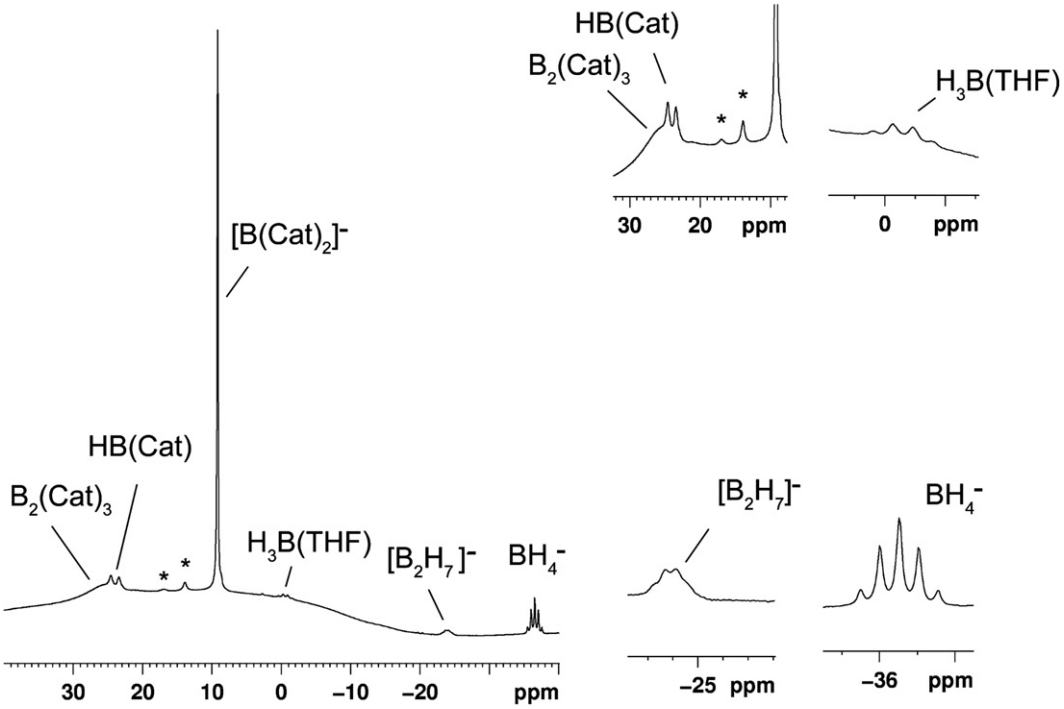
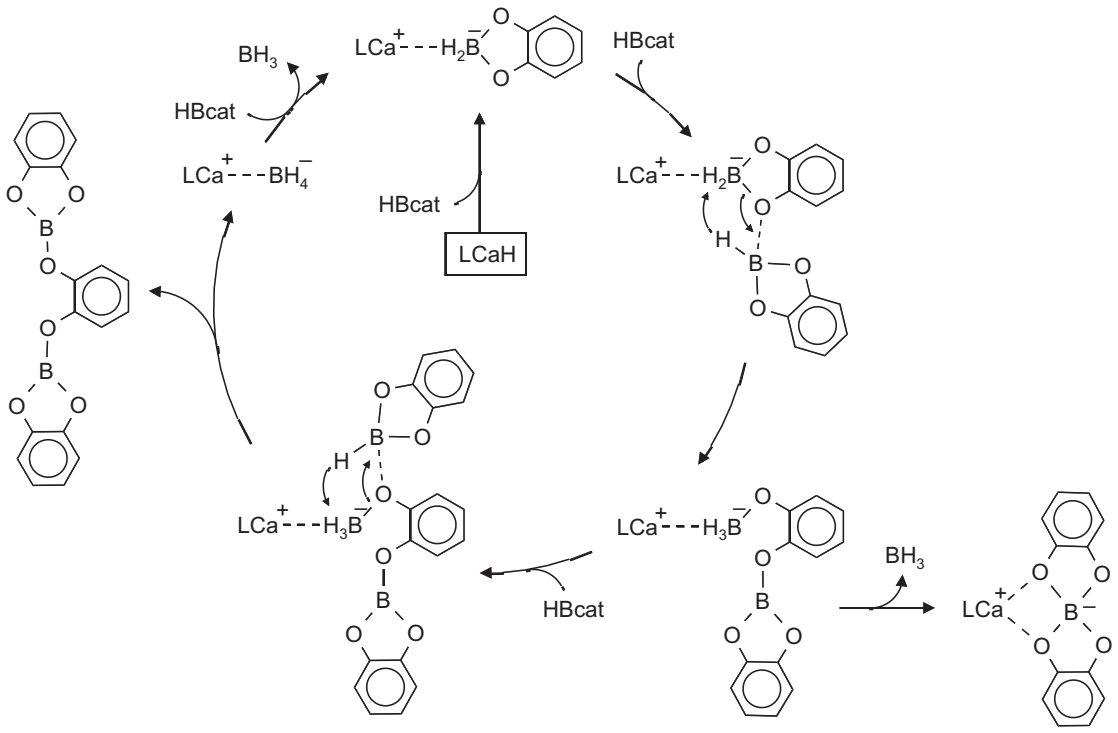


Fig. 1. The ^{11}B NMR spectrum (THF-d_8, 160 Mhz, 25 °C) for the reaction of 1 with excess HBcat. See Table 2 for assignments of signals (* indicates unknown species).



Scheme 3.

compared to literature values for various boron species (Table 2). The signal for the main decomposition product is a sharp singlet at 9.2 ppm. This is assigned to the $B(cat)_2^-$ ion that in the presence of Ca^{2+} likely forms the complex DIPPnacnacCaB(cat)$_2$ or Ca$[B(cat)_2]_2\cdot(THF)_2$ in which the Ca^{2+} is chelated by two $B(cat)_2^-$ ions (**4**). This binding mode would be in agreement with the crystal structure of $Cp_2Ti[B(cat)_2]$ that also contains a chelating $B(cat)_2^-$ ligand [21]. In contrast, the $B(cat)_2^-$ ligand binds Rh via the aromatic ring [37]. The ^{1}H NMR of the reaction mixture is in agreement with the proposed structure for **4**: it shows an AA′XX′ pattern for the aromatic protons. We were not able to crystallize this major species from solution. Further ^{11}B signals can be assigned to residual HBcat (doublet at 23.9 ppm), $B_2(cat)_3$ (broad signal at 25.2 ppm), $BH_3(THF)$ (characteristic quartet at −0.6 ppm), BH_4^- (characteristic quintet at −36.5 ppm) and $B_2H_7^-$ (broad multiplet at −23.9 ppm).

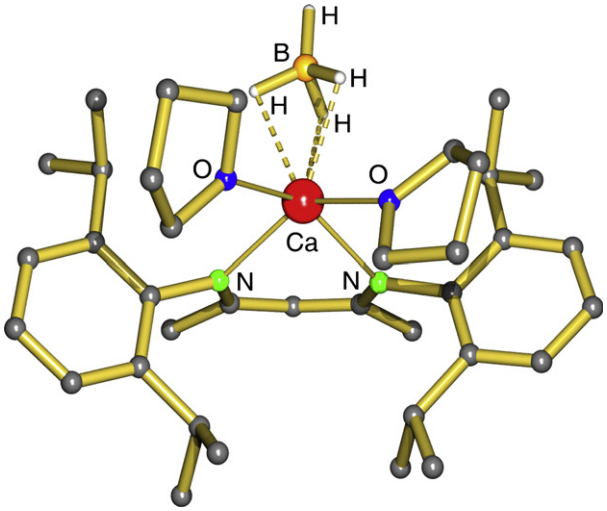


Fig. 2. Crystal structure of DIPPnacnacCa$(BH_4)\cdot(THF)_2$ (**5**); hydrogen atoms, except those for BH_4, are not shown for clarity. The range of selected bond distances in Å (average values for two independent molecules are given in square brackets): Ca–N 2.371(3)–2.404(3) [2.399(3)], Ca–O 2.410(2)–2.429(2) [2.419(2)], Ca···H 2.27(4)–2.46(3) [2.37(3)], Ca···B 2.596(5)–2.604(5) [2.600(5)].

The mechanism of HBcat decomposition in the presence of an organocalcium compound likely shows parallels with that proposed for the phosphine promoted degradation of HBcat [34]. The tentatively proposed scheme contains all species observed in the ^{11}B NMR spectrum (Scheme 3).

One of the key species in this catalytic cycle is DIPPnacnacCa(BH_4), a compound we could prepare by reaction of **1** with $BH_3(Me_2S)$. Considering the strong Lewis-basicity and acidity of **1** and BH_3, respectively, it is not likely that this compound is in equilibrium with a calcium hydride complex and BH_3 (as suggested for the lanthanide-catalyzed cycle, Scheme 2). Indeed, ^{1}H NMR spectra of DIPPnacnacCa(BH_4) in aromatic solvents do not show any indication for such equilibria.

Crystals obtained from a THF solution have the composition DIPPnacnacCa$(BH_4)\cdot(THF)_2$ and the crystal structure could be determined by X-ray diffraction. It crystallizes as a monomeric complex with two nearly identical molecules in the asymmetric unit (Fig. 2). The BH_4^- ion caps the Ca^{2+} ion via three bridging B–H units (hydrogen atoms have been observed in the difference-Fourier map and could be refined isotropically). A similar κ^3-BH_4 bonding mode is found in other known crystal structures of calcium tetrahydroborate complexes like Ca$(BH_4)_2\cdot$(DME) [38a], Ca$(BH_4)_2\cdot$(diglyme) [38b] and a series of cationic complexes [39]. The Ca···B distance of 2.600(5) Å is significantly shorter than that in Ca$(BH_4)_2\cdot$(DME) and Ca$(BH_4)_2\cdot$(diglyme) (range: 2.643(5)–2.884(5) Å) but is similar to that observed in the cationic complexes (2.580(2)–2.610(4) Å). The coordination around the five-coordinate Ca centre could be described as a tetragonal pyramid. Complex DIPPnacnacCa$(BH_4)\cdot(THF)_2$ was also fully characterized by ^{1}H, ^{13}C and ^{11}B NMR. The ^{11}B signal at −35.0 ppm (quint, $^1J_{B,H}$ = 82.2 Hz) fits well the signal observed in the decomposition studies (Fig. 1, Table 2).

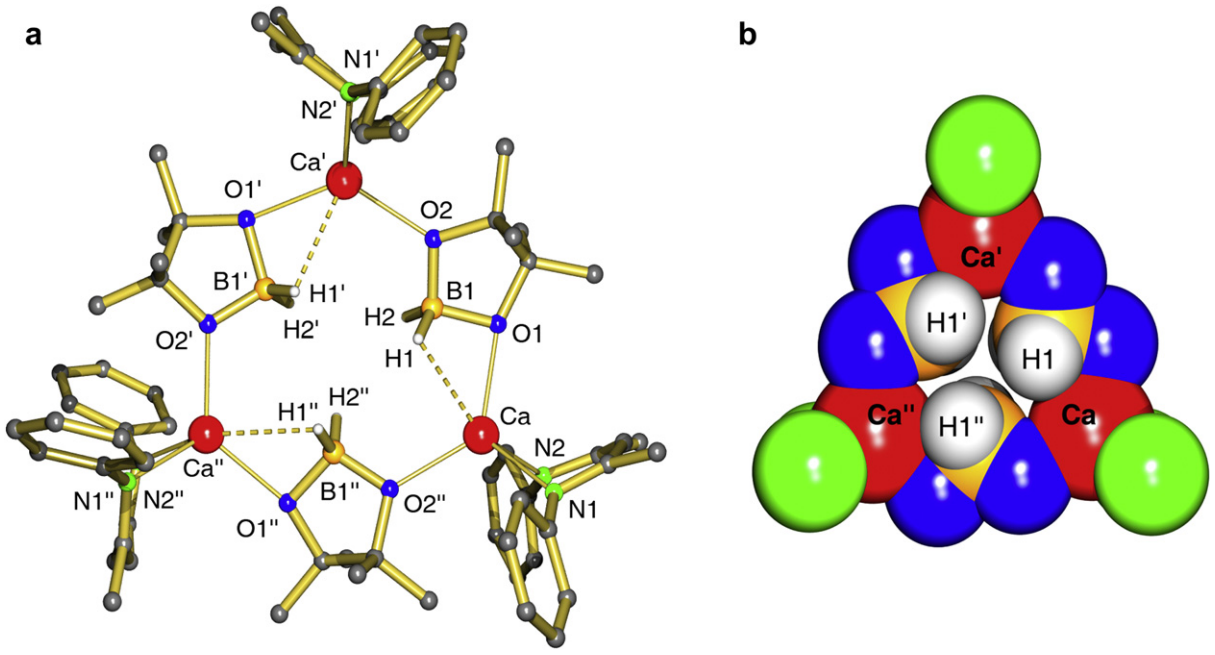


Fig. 3. Crystal structure of $[DIPPnacnacCa(H_2Bpin)]_3$ (**6**); *i*Pr substituents and hydrogen atoms, except those on B, are not shown for clarity. Symmetry operations: X′ = 1/2 + z, 3/2 − x, 1 − y; X″ = 3/2 − y, 1 − z, −1/2 + x.

Results described above show that the Ca-mediated hydroboration of DPE with HBcat is not "true" organometallic catalysis. The overall catalytic decomposition, 3 HBcat → $B_2(cat)_3$ + BH_3, generates BH_3 which is the actual reactive species in the alkene hydroboration. This "Trojan horse"-like behaviour also renders any control of chemo-, regio- or enantioselectivity by catalyst design. For these reasons we also investigated the reactivity of the calcium hydride complex **1** with other boranes.

In previous work we could isolate and structurally characterize the borate complex **3** from the reaction of **1** and 9-BBN (9-borabicyclo[3.3.1.]nonane) [27]. This complex was simultaneously prepared and characterized by Hill et al. [40]. Compound **3** is also catalytically active in the hydroboration of DPE with HBcat but the reaction is very slow (Table 1, entry 6). Complex **3** itself does not react with DPE even under forcing conditions (benzene, 80 °C). Complex **3** likely functions as hydride transfer reagent and forms H_2Bcat^- which starts the catalytic degradation of HBcat. As 9-BBN already reacts with DPE at room temperature, a Ca-controlled catalytic system based on **4** and 9-BBN would not be feasible (at least not at room temperature).

We directed further attention to Knochel's pinacolborane HBpin [41], a borane that similar to HBcat, displays reduced Lewis-acidity and hydroboration reactivity due to partial O(*p*)–B(*p*) overlap. Alkene hydroboration with HBpin needs the presence of a catalyst. The borane HBpin, however, is based on a tertiary alkyl ether instead of a phenolic ether which makes it less prone to decomposition via ring opening reactions [41,42].

From the reaction of **1** with HBpin in benzene we could isolate crystals of $[DIPPnacnacCa(H_2Bpin)]_3$ (**6**). The crystal structure shows a trimeric aggregate with crystallographic C_3-symmetry (Fig. 3, Table 3) which is unusual in organocalcium chemistry [43]. The origin for the formation of trimeric units lies in the bonding mode of the H_2Bpin^- ion: instead of bonding through a $BH_2\cdots Ca$ interaction, the ether O atoms interact with the metal. Hitherto there is no precedence for this coordination mode but there are few isolated examples for $R(H)Bcat^-\cdots$metal coordination [44]. The star-like structure results from the bridging behaviour of the H_2Bpin^- ion. Although the primary bonding between the anion and the metal cation proceeds through $O\cdots Ca^{2+}$ interaction, there is

Table 3
Selected bond distances (Å) in the crystal structure of $[DIPPnacnacCa(H_2Bpin)]_3$ (**6**).

Ca–N1	2.367(3)	Ca···O2″	2.299(3)	Ca··· B″	3.259(5)
Ca–N2	2.372(3)	Ca···H1	2.60(4)	B–O1	1.489(6)
Ca···O1	2.313(3)	Ca···B	2.830(5)	B–O2	1.459(6)

Table 4
Crystal data for $DIPPnacnacCa(BH_4)\cdot(THF)_2$ (**5**) and $[DIPPnacnacCa(H_2Bpin)]_3$ (**6**).

Compound	$DIPPnacnacCa(BH_4)\cdot(THF)_2$	$[DIPPnacnacCa(H_2Bpin)]_3$
Formula	$C_{37}H_{61}BCaN_2O_2$	$C_{105}H_{165}B_3Ca_3N_6O_6$, $3(C_6H_6)$
MW	616.77	1994.43
Size (mm^3)	0.2 × 0.3 × 0.5	0.2 × 0.2 × 0.2
Crystal system	triclinic	cubic
Spacegroup	*P*−1	*Pa*−3
a (Å)	14.6759(3)	29.2765(10)
b (Å)	15.6628(3)	29.2765(10)
c (Å)	17.7136(4)	29.2765(10)
α	75.614(1)	90
β	81.328(1)	90
γ	70.817(1)	90
V ($Å^3$)	3714.42(14)	25,093.3(15)
Z	4	8
ρ ($g.cm^{-3}$)	1.103	1.056
$\mu(Mo_{K\alpha})$ (mm^{-1})	0.201	0.183
T (°C)	−123	−70
θ(max)	23.0	27.5
Refl. total independent	36,582, 10,295	242,723, 9612
R_{int}	0.089	0.098
Obsd refl.($I > 2\sigma(I)$)	5963	7253
Parameter	845	481
R_1	0.0511,	0.0779
wR2	0.1416	0.2190
GOF	1.11	1.16
min/max residual e-density ($e.Å^{-3}$)	−0.23/0.32	−0.46/0.60

a tendency for BH···Ca bonding (H1···Ca). The bridging H_2Bpin^- ion is rotated to one of the Ca^{2+} ions which is demonstrated by unequal B–O–Ca angles (B1–O1–Ca 93.7(1)°; B1–O2–Ca′ 118.5(1)°). This brings H1 in close vicinity of one of the Ca^{2+} ions. Although the H1···Ca distance of 2.60(1) Å is significantly longer than that of 2.45(1) Å in DIPPnacnacCa(BH_4)·$(THF)_2$, it is well within the sum of the van der waals radii for B and H (3.33 Å). All other BH···Ca distances are well over 3 Å. The bonding interaction between H1 can be clearly seen in the space-filling model (Fig. 3b). The hole in the middle of the ring is too small for interaction with metal cations, however, ring enlargement could produce crown ether-like species for entrapment of cations through BH_2···metal interactions. Another feature is the extreme side-on coordination of the DIPPnacnac ligand: the C(H)–C(Me)–N–Ca torsion angles are 45.1(1)° and 51.6(1)°.

Trimeric [DIPPnacnacCa(H_2Bpin)]$_3$ (**6**) dissolves well in aromatic solvents and was characterized by ^1H, ^{13}C and ^{11}B NMR. It likely retains its trimeric structure in this solvent. The ^1H NMR spectrum shows two singlet signals for the Me groups of H_2Bpin and four signals for the *i*Pr groups of DIPPnacnac. The ^{13}C NMR spectrum shows two CH_3 signals and two quaternary signals for the carbon atoms in H_2Bpin. If one assumes fast exchange between ring-puckering conformations in H_2Bpin, these data are in agreement with the crystal structure.

NMR investigations on **6** do not show any sign of this species being in equilibrium with **1** and HBpin. A benzene solution of **6** in benzene-d_6 is even stable for several days at 60 °C. As addition of DPE and heating to 80 °C for several days did not result in reaction of the hydride with the C=C bond, it can be ruled out that **6** is in equilibrium with small amounts of **1** and HBpin (**1** reacts smoothly with DPE at 60 °C [24]). Reaction of **1** with HBpin seems therefore irreversible. The high stability of calcium borate complexes has been reported earlier by Hanusa et al.: attempted synthesis of a calcium hydride complex by decomposition of $(Me_3Si)_3CpCa(HBEt_3)$ into $(Me_3Si)_3CpCaH$ and BEt_3 failed [45].

Failure of **6** and DPE to react, inherently means that the borate anion H_2Bpin^- does not react directly with DPE. However, a benzene solution of complex **6** is unstable in the presence of HBpin. Therefore, any crystals obtained by reaction of **1** with HBpin must be isolated immediately. Prolonged crystallization times lead to decomposition of **6** and HBpin. Although we did not analyze this decomposition reaction in detail, it is likely that similar ring opening mechanisms apply as for HBcat (Scheme 3). For these reasons catalytic conversions with HBpin were not further considered.

3. Conclusion

Several organocalcium compounds, the hydride **1**, the benzyl complex **2** and the borate **3**, are catalytically active in the hydroboration of DPE with HBcat. The products, however, are not the expected boronic ester Ph_2CHCH_2OBcat but the borane $(Ph_2CHCH_2)_3B$. Therefore, Ca-catalyzed alkene hydroboration should not be regarded as "true" catalysis but as a "Trojan horse"-type of reaction [29]: *i.e.* the organocalcium compounds catalyze the decomposition of HBcat to mainly $B_2(cat)_3$ and BH_3 (or B_2H_6) and the latter is the actual reagent. NMR studies on the reaction solutions and stoichiometric reactions between **1** and HBcat indeed indicate the formation of several new species including $B(cat)_2^-$, $B_2(cat)_3$, $BH_3(THF)$, BH_4^- and $B_2H_7^-$. The organometallic complex with the BH_4 ion as a ligand was prepared via a different route and DIPPnacnacCa(BH_4)·$(THF)_2$ (**5**) could be fully characterized. Hydroboration according to this protocol does not have the advantage of chemo-, regio- or enantiocontrol by catalyst design. In addition, the less sensitive pinacolborane HBpin was investigated in reactivity studies. Reaction of **1** with HBpin gave a trimeric organocalcium complex [DIPPnacnacCa(H_2Bpin)]$_3$ (**6**) which in benzene solution is invariably stable also at higher temperatures (60–80 °C). However, in the presence of excess of HBpin the complex and the borane decompose already at room temperature and therefore this system is not useful for "true" catalytic conversion. Complex **6** does not react with DPE even at higher temperatures (80 °C). This demonstrates that there is no equilibrium between **6** and **1** + HBpin. It is possible that more Lewis-acidic metals like the lanthanide 3+ cations may give an equilibrium between borate and hydride. Therefore, also more Lewis-acidic organomagnesium might be productive in alkene hydroboration catalysis. We will address this possibility in future investigations.

4. Experimental

4.1. General procedures

All experiments were carried out under argon using dry solvents and Schlenk techniques. The following complexes have been prepared according to literature procedures: **1** [22], **2** [28a] and **3** [27]. Crystals were measured on a Siemens Smart diffractometer with APEXII area detector system. The structures were solved by Direct Methods (SHELXS-97) and refined with SHELXL-97 [46]. All geometry calculations and graphics were performed with PLATON [47].

4.2. General procedure for catalytic hydroboration of DPE with HBcat

Catecholborane (HBcat) and pinacolborane (HBpin) were purified by distillation prior to use. 1,1-Diphenylethylene (DPE) was dried by overnight heating to 60 °C over finely powdered CaH_2 and subsequently isolated by centrifugation. NMR spectra were recorded on a Bruker DPX300 (300 MHz) spectrometer. The indicated amount of an organocalcium catalyst (Table 1) was added to a solution of HBcat (360 mg, 3.00 mmol) in DPE (360 mg, 2.00 mmol) which previously had been brought to the indicated temperature. The conversion was followed by taking samples and analyzing these with ^1H NMR. For experiments in benzene solution, 3.0 ml of benzene was added prior to catalyst addition.

Reactions without organocalcium catalyst (entry 2) gave Ph_2CHCH_2Bcat. ^1H NMR (300 MHz, benzene-d_6 + THF-d_8, 25 °C): δ = 1.95 (d, $^3J_{H,H}$ = 8.1 Hz, 2H, CH_2), 4.52 (t, $^3J_{H,H}$ = 8.1 Hz, 1H, CH), 6.70 (m, 2H, cat), 6.93 (m, 2H, cat), 6.98 (m, 2H, aryl), 7.07 (m, 2H, aryl), 7.20 (m, 2H, aryl); ^{11}B NMR (160 MHz, benzene-d_6 + THF-d_8, 25 °C): δ = 35.1 ppm (br).

Reactions in the presence of an organocalcium catalyst gave $(Ph_2CHCH_2)_3B$. ^1H NMR (300 MHz, benzene-d_6, 25 °C): δ = 1.97 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, CH_2), 4.28 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, CH), 7.02 (m, 4H, aryl), 7.10 (m, 2H, aryl), 7.02 (m, 4H, aryl); ^{11}B NMR (160 MHz, benzene-d_6, 25 °C): δ = 87.8 ppm (br).

4.3. Stoichiometric reaction of [(DIPPnacnac)CaH·(THF)]$_2$ (**1**) with HBcat

A J. Young NMR tube was charged with [(DIPPnacnac)CaH·(THF)]$_2$ (30 mg, 0.028 mmol) and 0.6 ml of THF-d_8. After addition of HBcat (68 mg, 0.56 mmol) the solution became viscous. The reaction was followed by ^1H and ^{11}B NMR spectroscopy. Major species: ^1H NMR (300 MHz, THF-d_8, 25 °C): δ = 6.22 (m, AA′XX′ spin system, 2H), 6.38 (m, AA′XX′ spin system, 2H), 6.65 (m, AA′XX′ spin system, 2H), 6.71 (m, AA′XX′ spin system, 2H). ^{11}B NMR (160 MHz, THF-d_8, 25 °C): δ = 9.2 ppm (sharp). The

signal for the major species was assigned to the $B(cat)_2^-$ ion. Asymmetry in the ^1H NMR spectrum is caused by coordination to Ca^{2+} (like in **4**). See Table 2, Fig. 1 and the discussion for the assignment of other ^{11}B signals.

4.4. Synthesis of DIPPnacnacCa(BH$_4$)·(THF)$_2$ (**5**)

[(DIPPnacnac)CaH·(THF)]$_2$ (**1**, 212 mg; 0.40 mmol) were dissolved in 1.3 ml of THF. To this solution was slowly added $BH_3(Me_2S)$ (33 mg, 0.43 mmol). Slow cooling of the resulting solution to 8 °C gave the crystalline product in the form of large colourless blocks. Yield: 148 mg, 0.24 mmol, 60%. Anal. (%): Calcd. for $C_{37}H_{61}BCaN_2O_2$ (616.78): C, 72.05; H, 9.97. Found: C, 71.71; H 9.71. ^1H NMR (300 MHz, benzene-d_6, 25 °C): $\delta = -0.14$ (q, $^1J_{B,H} = 82.2$ Hz, 4H, BH_4), 1.23 (d, $^3J_{H,H} = 6.8$ Hz, 12H, *i*Pr), 1.25 (d, $^3J_{H,H} = 6.8$ Hz, 12H, *i*Pr), 1.33 (m, 8H, THF), 1.68 (s, 6H, Me backbone), 3.24 (sept, $^3J_{H,H} = 6.8$ Hz, 4H, *i*Pr), 3.53 (m, 8H, THF), 4.80 (s, 1H, backbone), 7.13 (m, 6H, aryl); ^{11}B NMR (160 MHz, benzene-d_6, 25 °C): $\delta = -33.3$ (quint, $^1J_{B,H} = 82.2$ Hz); ^{11}B NMR (160 MHz, THF-d_8, 25 °C): $\delta = -35.0$ (quint, $^1J_{B,H} = 82.2$ Hz); ^{13}C NMR (300 MHz, benzene-d_6, 25 °C): $\delta = 24.8$ (*i*Pr), 25.0 (*i*Pr), 25.1 (Me backbone), 25.5 (*i*Pr), 28.4 (THF), 69.0 (THF), 94.5 (backbone), 123.8 (aryl), 124.5 (aryl), 142.1 (aryl), 146.9 (aryl), 165.8 (backbone).

4.5. Synthesis of [DIPPnacnacCa(H$_2$Bpin)]$_3$ (**6**)

A solution of [(DIPPnacnac)CaH·(THF)]$_2$ (**1**, 200 mg; 0.38 mmol) and excess of HBpin (191 mg; 1.49 mmol) in 3.0 ml of benzene was stirred for 40 min at room temperature and then cooled to 8 °C. After circa 30 min crystals of [(DIPPnacnac)Ca(H$_2$Bpin)]$_3$ in the form of colourless blocks appeared. These were immediately isolated from the cloudy mother liquor. Prolonged crystallization times led to decomposition of the product. Yield: 120 mg, 0.18 mmol, 48%. Anal. (%): Calcd. for $C_{35}H_{55}BCaN_2O_2\cdot(C_6H_6)$ (664.45): C, 74.07; H, 9.25. Found: C, 74.52; H 8.92. ^1H NMR (300 MHz, benzene-d_6, 25 °C): $\delta = 0.89$ (s, 6H, Me H_2Bpin), 0.90 (s, 6H, Me H_2Bpin), 1.19 (d, $^3J_{H,H} = 6.4$ Hz, 6H, *i*Pr), 1.26 (d, $^3J_{H,H} = 6.7$ Hz, 6H, *i*Pr), 1.34 (d, $^3J_{H,H} = 6.9$ Hz, 6H, *i*Pr), 1.46 (d, $^3J_{H,H} = 6.9$ Hz, 6H, *i*Pr), 1.68 (s, 6H, Me backbone), 3.07 (sept, $^3J_{H,H} = 6.9$ Hz, 2H, *i*Pr), 3.33 (br, 2H, H_2B), 3.42 (sept, $^3J_{H,H} = 6.9$ Hz, 2H, *i*Pr), 4.74 (s, 1H, backbone), 7.17–7.14 (m, 4H, aryl); ^{11}B NMR (160 MHz, benzene-d_6, 25 °C): $\delta = 2.1$ (t br, $^1J_{B,H} = 91$ Hz); ^{13}C NMR (300 MHz, benzene-d_6, 25 °C): $\delta = 25.6$ (*i*Pr), 25.8 (*i*Pr), 25.8 (*i*Pr), 26.0 (*i*Pr), 26.7 (Me backbone), 29.5 (*i*Pr), 29.8 (H_2Bpin), 29.9 (H_2Bpin), 81.5 (H_2Bpin), 82.5 (H_2Bpin), 95.0 (backbone), 125.1 (aryl), 125.1 (aryl), 125.9 (aryl), 129.1 (aryl), 142.7(aryl), 143.4 (aryl), 148.9 (aryl), 166.9 (backbone).

4.6. Crystal structure determinations for DIPPnacnacCa(BH$_4$)·(THF)$_2$ (**5**) and [DIPPnacnacCa(H$_2$Bpin)]$_3$ (**6**)

Crystal data for both structures are summarized in Table 4.

Details for the refinement of DIPPnacnacCa(BH$_4$)·(THF)$_2$ (**5**): The asymmetric unit contains two independent molecules. Pseudo *C*-symmetry was confirmed by the presence of weak but significant h + k = 2n reflections and refinement has been done in a *P*-lattice with two nearly equal independent molecules in the asymmetric unit. The asymmetric unit contains one cocrystallized THf molecule which was severely disordered. This molecule was treated with the SQUEEZE procedure (hole around *i*: 230 Å^3, 98 electrons) incorporated in PLATON [44]. All H atoms, except those on the THF ligands, could be found in the Difference-Fourier map and were refined isotropically. The hydrogen atoms on the THF ligands were placed on calculated positions and were refined in a riding mode.

Details for the refinement of [DIPPnacnacCa(H$_2$Bpin)]$_3$ (**6**): The H_2Bpin^- ligand shows strong disorder due to ring-puckering in the five-membered ring. This was solved with an appropriate disorder model but affects the quality of the structure. All hydrogen atoms, except those on B, have been placed on calculated positions and were refined in a riding mode. The hydrogen atoms on B have been found in the Difference-Fourier map and were refined isotropically. The asymmetric unit contains two cocrystallized benzene molecules. One is relatively ordered and was refined with large anisotropic displacement parameters, the other is completely disordered and was treated with the SQUEEZE procedure (hole: 250 Å^3, 59 electrons) incorporated in PLATON [47].

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structure of DIPPnacnacCa(BH$_4$)·(THF)$_2$ (**5**) (CCDC 836486) and [DIPPnacnacCa(H$_2$Bpin)]$_3$ (**6**) (CCDC 836485) can be obtained free of charge from the Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.ck).

References

[1] H.C. Brown, Isr. J. Chem. 25 (1985) 84.
[2] H.C. Brown, M.M. Midland, G.W. Kabalka, J. Am. Chem. Soc. 93 (1971) 1024.
[3] M.W. Rathke, N. Inoue, K.R. Varma, H.C. Brown, J. Am. Chem. Soc. 88 (1966) 2870.
[4] G.W. Kabalka, E.E. Gooch III, J. Org. Chem. 45 (1980) 3578.
[5] First example of catalytic hydroboration with catecholborane D. Mannig, H. Nöth, Angew. Chem. Int. Ed. Engl. 24 (1985) 878.
[6] Reviews: (a) K. Burgess, M.J. Ohlmeyer, Chem. Rev. 91 (1991) 1179; (b) H. Wadepohl, Angew. Chem. Int. Ed. Engl. 36 (1997) 2441; (c) I. Beletskaya, A. Pelter, Tetrahedron 53 (1997) 4957; (d) C.M. Crudden, D. Edwards, Eur. J. Org. Chem. (2003) 4695; (e) C.M. Vogels, S.A. Westcott, Curr. Org. Chem. 9 (2005) 687.
[7] D.A. Evans, G.C. Fu, A.H. Hoveyda, J. Am. Chem. Soc. 110 (1988) 6917.
[8] S.A. Westcott, H.P. Blom, T.B. Marder, R.T. Baker, J. Am. Chem. Soc. 114 (1992) 8863.
[9] D.A. Evans, G.C. Fu, A.H. Hoveyda, J. Am. Chem. Soc. 114 (1992) 6671.
[10] K. Burgess, M.J. Ohlmeyer, Tetrahedron Lett. 30 (1989) 395.
[11] K. Burgess, J. Cassidy, M.J. Ohlmeyer, J. Org. Chem. 56 (1991) 1020.
[12] K. Burgess, M.J. Ohlmeyer, J. Org. Chem. 56 (1991) 1027.
[13] J. Zhang, B. Lou, G. Guo, L. Dai, J. Org. Chem. 56 (1991) 1670.
[14] A. Schnyder, L. Hintermann, A. Togni, Angew. Chem. Int. Ed. Engl. 34 (1995) 931.
[15] A. Leyva, X. Zhang, A. Corma, Chem. Commun. (2009) 4947.
[16] K.N. Harrison, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 9221.
[17] K. Burgess, W.A. van der Donk, Organometallics 13 (1994) 3616.
[18] K. Burgess, W.A. van der Donk, J. Am. Chem. Soc. 116 (1994) 6561.
[19] E.A. Bijpost, R. Duchateau, J.H. Teuben, J. Mol. Catal. A.: Chem. 95 (1995) 121.
[20] S. Pereira, M. Srebnik, Organometallics 14 (1995) 3127.
[21] X. He, J.F. Hartwig, J. Am. Chem. Soc. 118 (1996) 1696.
[22] S. Harder, J. Brettar, Angew. Chem. Int. Ed. Engl. 45 (2006) 3474.
[23] F. Buch, J. Brettar, S. Harder, Angew. Chem. Int. Ed. Engl. 45 (2006) 2741.
[24] J. Spielmann, F. Buch, S. Harder, Angew. Chem. Int. Ed. Engl. 47 (2008) 9434.
[25] S. Harder, Chem. Rev. 110 (2010) 3852.
[26] A.G.M. Barrett, M.R. Crimmin, M.S. Hill, P.A. Procopiou, Proc. R. Soc. A. 466 (2010) 927.
[27] J. Spielmann, S. Harder, Chem. Eur. J. 13 (2007) 8928.
[28] (a) S. Harder, F. Feil, A. Weeber, Organometallics 20 (2001) 1044; (b) S. Harder, F. Feil, K. Knoll, Angew. Chem. Int. Ed. 40 (2001) 4261; (c) S. Harder, F. Feil, Organometallics 21 (2002) 2268; (d) F. Feil, C. Müller, S. Harder, J. Organomet. Chem. 683 (2003) 56; (e) F. Feil, S. Harder, Eur. J. Inorg. Chem. (2003) 3401; (f) D.F.-J. Piesik, K. Häbe, S. Harder, Eur. J. Inorg. Chem. (2007) 5652.
[29] K. Burgess, M. Jaspars, Tetrahedron Lett. 34 (1993) 6813.
[30] D. Männig, H. Nöth, J. Organomet. Chem. 275 (1984) 169.
[31] E. Hanecker, H. Nöth, J. Moll, Z. Naturforsch. B. 38 (1983) 424.

[32] D. Männig, H. Nöth, Dalton Trans. (1985) 1689.
[33] H. Nöth, B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds. Springer, Heidelberg, 1978.
[34] (a) S.A. Westcott, H.P. Blom, T.B. Marder, R.T. Baker, J.C. Calabrese, Inorg. Chem. 32 (1993) 2175;
(b) K. Burgess, W.A. Van der Donk, S.A. Westcott, T.B. Marder, R.T. Baker, J.C. Calabrese, J. Am. Chem. Soc. 114 (1992) 9350.
[35] S.A. Westcott, N.J. Taylor, T.B. Marder, R.T. Baker, N.J. Jones, J.C. Calabrese, Chem. Commun. (1991) 304.
[36] R. Goetze, H. Nöth, H. Pommerening, D. Sedlak, B. Wrackmeyer, Chem. Ber. 114 (1981) 1884.
[37] (a) C. Dai, E.G. Robins, A.J. Scott, W. Clegg, D.S. Yufit, J.A.K. Howard, T.B. Marder, Chem. Commun. (1998) 1983;
(b) D.A. Kanas, S.J. Geier, C.M. Vogels, A. Decken, S.A. Westcott, Inorg. Chem. 47 (2008) 8727.
[38] (a) E. Hanecker, J. Moll, H. Nöth, Z. Naturforsch, B. J. Chem. Sci. 39 (1984) 424;
(b) E.B. Lobkovsky, A.N. Chekhlov, M.D. Levicheva, L.V. Titov, Koord. Khim. 14 (1988) 543.
[39] M.G. Cushion, P. Mountford, Chem. Commun. 47 (2011) 2276.
[40] A.G.M. Barrett, M.R. Crimmin, M.S. Hill, P.B. Hitchcock, P.A. Procopiou, Organometallics 26 (2007) 4076.
[41] C.E. Tucker, J. Davidson, P. Knochel, J. Org. Chem. 57 (1992) 3482.
[42] (a) W.H. Lam, S. Shimada, A.S. Batsanov, Z. Lin, T.B. Marder, J. Cowan, J.A.K. Howard, S.A. Mason, G.J. McIntyre, Organometallics 22 (2003) 4557;
(b) J. Zhu, Z. Lin, T.B. Marder, Inorg. Chem. 44 (2005) 9384;
(c) L. Dang, H. Zhao, Z. Lin, T.B. Marder, Organometallics 27 (2008) 1178.
[43] Another established example of a trimeric structure is [DIPPnacnac-CaCN·(THF)]$_3$ C. Ruspic, S. Harder, Inorg. Chem. 46 (2007) 10426.
[44] (a) J. Knizek, H. Nöth, M. Warchhold, Z. Naturforsch. B61 (2006) 1079;
(b) A. Takaoka, A. Mendiratta, J.C. Peters, Organometallics 28 (2009) 3744.
[45] M.J. Harvey, T.P. Hanusa, M. Pink, Chem. Commun. (2000) 489.
[46] (a) G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution. Universität Göttingen, Göttingen, Germany, 1997;
(b) G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement. Universität Göttingen, Göttingen, Germany, 1997.
[47] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool. Utrecht University, Utrecht, Netherlands, 2000.