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Alkene conversions with early transition metal catalysts

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Chapter 5

Early Transition Metal-catalyzed
Hydroboration of Alkenes[#]

5.1. Introduction.

For organic synthesis, hydroboration of alkenes forms an interesting synthetic methodology for the conversion of alkenes to other functionalities, since the products can conveniently be transformed into alcohols,[1] amines[2] or halides.[3] In addition, a nucleophilic boron-carbon bond can react with an electrophilic carbonyl group to form a higher alcohol.[4] The potential application of the hydroboration reaction has greatly been enhanced by rhodium- and ruthenium-catalyzed processes which afford good chemoselectivity,[5] regioselectivity (usually Markovnikov),[6] diastereoselectivity,[7] enantioselectivity[8] and high reaction rates. However, there are some drawbacks, such as the formation of relatively large amounts (~5%) of hydrogenated alkenes, decomposition of the borane reagent and diborated products,[9] which limit the usefulness of this catalytic system. Recently, efficient and selective organolanthanide-catalyzed hydroboration of alkenes using catecholborane, $HB(1,2-O_2C_6H_4)$, was reported by Harrison and Marks.[10] Mechanistically, this catalytic reaction follows a different path (regioselectivity anti-Markovnikov) than for rhodium, while side reactions (diboration, isomerization, hydrogenation) are negligible. The catalytic cycle proposed by Harrison and Marks is given in Scheme 1;[10] the key step is generation of a metal-hydride from the catalyst precursor, which is followed by insertion of an alkene. Subsequent σ-bond metathesis forms the hydroboration product and regenerates the metal-hydride catalyst.[10] The latter reaction is proposed to be the rate determining step of the alkene hydroboration reaction, as alkene insertion into a organolanthanide-hydride bond is well-known to be rapid and exothermic.[10] It must be noted here that the uncatalyzed hydroboration reaction is very slow and results in addition of the boron functionality at the least substituted carbon of the alkene (regioselectivity anti-Markovnikov).[11]
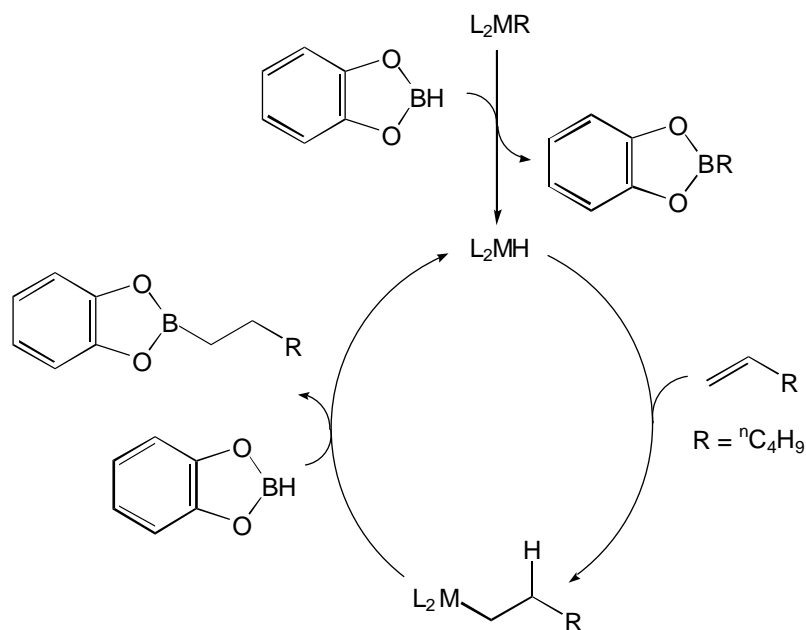
Scheme 1. *Proposed mechanism of organolanthanide-catalyzed alkene hydroboration.*[10]

Considering the proposed mechanism, it seems to be that coordinative and electronic unsaturation (16 or lower electron system) and facile (re)generation of an M-H bond are essential for a successful catalytic system for anti-Markonikov alkene hydroboration. Our group has available a wide range of well-characterized early transition metal complexes with various auxiliary ligand systems, which meet the requirements for catalytic hydroboration. We decided to explore their potential as catalyst in the hydroboration of 1-hexene and compare the results with those published for the η^5-C$_5$Me$_5$)$_2$LnR systems (Ln = La, Sm; R = H, CH(SiMe$_3$)$_2$).[10]

5.2. Outline of the Investigation.

We have concentrated on a model hydroboration system using catecholborane and 1-hexene earlier used with organolanthanide catalysts by Harrison and Marks (Scheme 2).[10] The early transition metal complexes tested are listed in Table 1 and have been selected on the basis of their analogy with the (η^5-C$_5$Me$_5$)$_2$LnR systems used by Marks with variations in the auxiliary ligand system, the metal and the nature of the active ligand. The (η^5-C$_5$Me$_5$)$_2$ group has been replaced either by (η^5-C$_5$H$_5$)$_2$, (η^5,σ^1-C$_5$Me$_4$)-aryloxide, (η^5,η^3-C$_5$H$_4$)-amide, (η^5-C$_5$H$_5$)-benzamidinate or bis(benzamidinate). Also, several metals (Y, La, Ti, Zr) and two active ligands (hydride or carbyl) have been used. All complexes studied meet the criteria for possible catalytic activity, as mentioned in the introduction. Two reactions have been investigated: (1) stoichiometric reactions between the precatalysts (**1-29**) and catecholborane and (2) catalytic hydroboration of 1-hexene using catecholborane as hydroboration agent (Table 1).
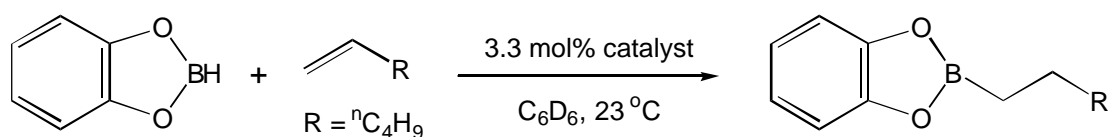
Scheme 2. *Reaction of catecholborane with 1-hexene catalyzed by early transition metal complexes.*

5.3. Reactions between the Precatalyst (1-29) and Catecholborane in a 1 : 1 ratio.

The reactions between the precatalysts (**1**-**29**) and catecholborane in 1 : 1 ratio have been studied in benzene-d_6 at room temperature. In all cases, catecholborane-R was formed rapidly as concluded from ^{11}B-NMR spectroscopy (δ = 37-35 ppm (s)), which is in line with the observations from Harrison and Marks.[10] From this it can be assumed that an M-H compound has been generated.

The precatalysts **9**, **10**, and **17** reacts very slowly with catecholborane. In some other cases (**5**, **6** and **15**) catalyst deactivation took place due to a rapid side reaction of catecholborane with the precursors under transfer of ligands; this aspect will be discussed further on (see 5.4.2.).

5.4. Catalytic Alkene Hydroboration.

The alkene hydroboration reaction was studied by dissolving one equivalent precatalyst in benzene-d_6, followed by addition of 120 equivalents of catecholborane and 60 equivalents of 1-hexene at room temperature. The consumption of 1-hexene was monitored via the alkene resonances in the ^{1}H-NMR spectrum. The general features of the observed conversion plots are those of an S-curve like those frequently found in catalysis (Figure 1). After rapid initiation (*i.e.* formation of the catalyst from the precursor and catecholborane), a period of maximal catalytic activity starts, which lasts until deactivation of the catalyst becomes notable whereupon the catalysis gradually slows down. At last only the uncatalyzed reaction proceeds after complete deactivation of the catalyst has occurred.[11]

In some cases (**6**, **9**, **10** and **15**), in addition to catalytic hydroboration, decomposition of catecholborane has been observed as well (*vide infra*). It could be of interest to study this reaction in more detail. However, after considering the results of the work by Marks *et al.*, further attempts in this area have not been undertaken.[12] They obtain very complex NMR spectra for the reaction between the catalyst and catecholborane either in the absence of alkene or in the case of a sterically hindered alkene, making it difficult to obtain good data on

the decomposition of catecholborane.[13] These competing processes also hampered full analysis of the kinetics of the alkene hydroboration by NMR spectroscopy.[12]
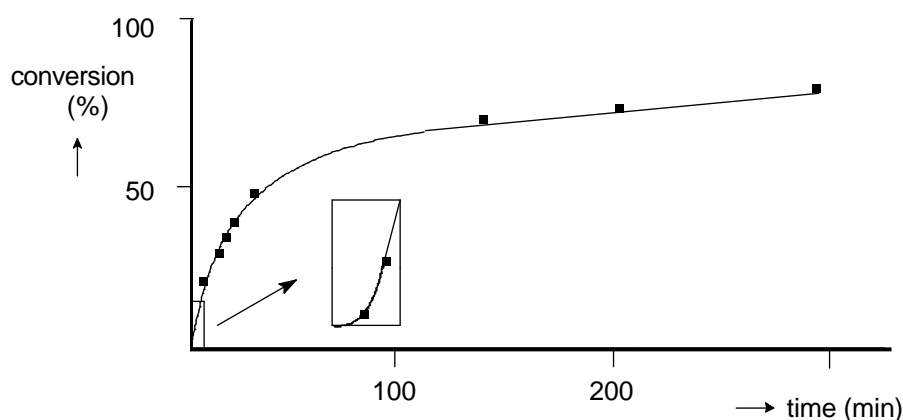

Figure 1. *Conversion versus time plot for the hydroboration of 1-hexene with Cp$_2$YCH(SiMe$_3$)$_2$ (5) as catalyst.*

Table 1. *Observed conversions of 1-hexene (mol product per mol precatalyst after one hour) for the hydroboration of 1-hexene with selected early transition metal complexes.*

Precatalyst	Act.	Precatalyst	Act.
(η^5-C$_5$Me$_5$)$_2$LaCH(SiMe$_3$)$_2$ (**1**)	60	[C$_6$H$_5$C(NCMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ (**16**)	2.0[a]
(η^5-C$_5$Me$_5$)$_2$YCH(SiMe$_3$)$_2$ (**2**)	1.3	[C$_6$H$_5$C(NSiMe$_3$)$_2$]$_3$La (**17**)	0.6
(η^5-C$_5$Me$_5$)$_2$YMe.THF (**3**)	1.1	[C$_6$H$_5$C(NCMe$_3$)$_2$]$_2$TiMe$_2$ (**18**)	1.5[a]
[(η^5-C$_5$Me$_5$)$_2$YH]$_2$ (**4**)	1.3	[C$_6$H$_5$C(NCMe$_3$)$_2$]$_2$ZrMe$_2$ (**19**)	5.0[a]
(η^5-C$_5$H$_5$)$_2$YCH(SiMe$_3$)$_2$ (**5**)	20[a]	(η^5-C$_5$H$_5$)[C$_6$H$_5$C(NCMe$_3$)$_2$]TiMe$_2$ (**20**)	2.2[a]
(η^5-C$_5$H$_5$)$_2$YCH(SiMe$_3$)$_2$.Et$_2$O (**6**)	15[a+b]	(η^5-C$_5$H$_5$)[C$_6$H$_5$C(NCMe$_3$)$_2$]TiNp (**21**)	1.8[a]
(η^5-C$_5$Me$_5$)$_2$TiMe$_2$ (**7**)	0.2[c]	(η^5-C$_5$H$_5$)[C$_6$H$_5$C(NCMe$_3$)$_2$]Zr(CH$_2$Ph)$_2$ (**22**)	4.8[a]
(η^5-C$_5$Me$_5$)$_2$ZrMe$_2$ (**8**)	0.2[c]	[C$_6$H$_5$C(NCMe$_3$)$_2$]$_2$Ti(allyl) (**23**)	5.0[a]
(η^5-C$_5$H$_5$)$_2$TiMe$_2$ (**9**)	4.7[a+b]	(η^5-C$_5$H$_5$)[C$_6$H$_5$C(NCMe$_3$)$_2$]Ti(allyl) (**24**)	3.6[a]
(η^5-C$_5$H$_5$)$_2$ZrMe$_2$ (**10**)	2.0[a+b]	[η^5,η^3-C$_5$H$_4$(CH$_2$)$_3$NMe]Zr(BH$_4$)$_2$ (**25**)	1.4
(η^5-C$_5$Me$_5$)$_2$Ti(allyl) (**11**)	0.1[c]	[η^5,η^3-C$_5$H$_4$(CH$_2$)$_3$NMe]Zr(CH$_2$Ph)$_2$ (**26**)	0.2[c]
(η^5-C$_5$H$_5$)$_2$Ti(allyl) (**12**)	0.2[c]	[η^5,η^3-C$_5$H$_4$(CH$_2$)$_3$NMe]TiMe$_2$ (**27**)	1.8
{[C$_6$H$_5$C(NSiMe$_3$)$_2$]$_2$YH}$_2$ (**13**)	5.0[a]	[η^5,σ^1-C$_5$Me$_4$(2-O)(6-OMe)C$_6$H$_3$]TiNp$_2$ (**28**)	0.7
[C$_6$H$_5$C(NSiMe$_3$)$_2$]$_2$YCH(SiMe$_3$)$_2$ (**14**)	4.4[a]	[η^5,σ^1-C$_5$Me$_4$(2-O)(6-OMe)C$_6$H$_3$]Ti(allyl) (**29**)	0.9
[C$_6$H$_5$C(NSiMe$_3$)$_2$]$_2$YCH$_2$Ph.THF (**15**)	1.6[a+b]	none	0.1

[a] Quick catalyst deactivation was observed. [b] Decomposition of HB(1,2-O$_2$C$_6$H$_4$) to B$_2$(1,2-O$_2$C$_6$H$_4$)$_3$ took place, see ref 29. [c] Reaction rate comparable with the uncatalyzed hydroboration of 1-hexene.

In all cases where catalytic hydroboration has taken place, except those using (η^5-C$_5$H$_5$)$_2$TiMe$_2$ (**9**) and (η^5-C$_5$H$_5$)$_2$ZrMe$_2$ (**10**), high regioselectivity (anti-Markovnikov >99%) and low substrate hydrogenation (<2%) have been observed. With group 4 compounds **9** and **10** the regioselectivity (anti-Markovnikov) decreased to 93% and 95%, respectively. After one hour the gross activity (Act.) was calculated by dividing the amount of converted 1-hexene by the amount of precatalyst started with (Table 1).

For a number of catalytic systems (*e.g.* **1**, **5**, **13**, **20** and **23**) the maximum rate of the reaction was calculated from the slope of the tangent at the observed linear part at the beginning of the conversion curve. From this, the amount of hydroboration product formed per mol precatalyst can be estimated after one hour reaction time to give the turnover frequency (T.O.F.) (Table 2, Figure 1). For other catalyst precursors, rapid catalyst deactivation or catalytic decomposition of catecholborane made this impossible.

Table 2. *Estimated maximum turnover frequencies (mol product per mol precatalyst after one hour) for the hydroboration of 1-hexene for selected early transition metal complexes.*

Precatalyst	T.O.F.	Precatalyst	T.O.F.
(η^5-C$_5$Me$_5$)$_2$LaCH(SiMe$_3$)$_2$ (**1**)	130	(η^5-C$_5$H$_5$)[C$_6$H$_5$C(NCMe$_3$)$_2$]TiMe$_2$ (**20**)	8.0
(η^5-C$_5$H$_5$)$_2$YCH(SiMe$_3$)$_2$ (**5**)	50	[C$_6$H$_5$C(NCMe$_3$)$_2$]$_2$Ti(allyl) (**23**)	14
{[C$_6$H$_5$C(NSiMe$_3$)$_2$]$_2$YH}$_2$ (**13**)	7.0		

5.4.1. Bis(cyclopentadienyl) systems. First, we tested (η^5-C$_5$Me$_5$)$_2$LaCH(SiMe$_3$)$_2$ (**1**) to check the system and compare with the work by Harrison and Marks.[10] Indeed, high activity and selectivity were observed and the results are in agreement with those reported. (η^5-C$_5$Me$_5$)$_2$YCH(SiMe$_3$)$_2$ (**2**) turned out to be much less active, which is in line with the observation in other catalytic systems *e.g.* alkene hydrogenation and ethene polymerization that lanthanide metals show quite a large spread in activity. This can be related to the steric aspects of the various metal centers.[14,15]

The rate determining step is proposed to be formation of the hydroboration product with regeneration of the M-H catalyst (Scheme 1).[10] The reduction of space around the metal center when going from La to Y apparently raises the energy for the concerted σ-bond metathetical transition state. Permethylyttrocene complexes (η^5-C$_5$Me$_5$)$_2$YMe(THF) (**3**), and [(η^5-C$_5$Me$_5$)$_2$YH]$_2$ (**4**) proved to be moderately active as well. The view that the final step in the cycle is indeed rate determining is supported by the observation that for dimeric hydride **4**, combination of the reagents leads to immediate loss of the characteristic hydride resonances. This indicates a rapid dissociation into monomers and consequent fast hexene insertion (this step is well-documented),[16] while the catalytic activity is the same as found for the other (η^5-C$_5$Me$_5$)$_2$Y-compounds **2** and **3**.

The sterically more accessible yttrium complexes (η^5-C$_5$H$_5$)$_2$YCH(SiMe$_3$)$_2$ (**5**) and (η^5-C$_5$H$_5$)$_2$YCH(SiMe$_3$)$_2$·Et$_2$O (**6**) showed a marked increase in activity, although this did not reach the value found for **1**. Unfortunately, rapid, concurrent, catalyst deactivation was observed, which limits the overall catalytic performance of the complexes. The decomposition of catecholborane to (1,2-O$_2$C$_6$H$_4$)$_3$B$_2$ during the alkene hydroboration in the presence of diethylether complex **6** is remarkable, while this was not found for **5**. Reaction of **5** and catecholborane in 1 : 1 ratio in benzene-d_6 at room temperature gave a complex mixture of boron compounds. On the basis of ^{11}B-NMR spectroscopy we could identify (1,2-O$_2$C$_6$H$_4$)BCH(SiMe$_3$)$_2$ (δ = 36 ppm (s)), but two other signals (δ = 8.4 (s) and -26.3 (q, J_{B-H}= 90 Hz) ppm) remain unassigned. Efforts to isolate these products were not successful and identification was not possible.

The d^0, 16 electron systems (η^5-C$_5$Me$_5$)$_2$TiMe$_2$ (**7**) and (η^5-C$_5$Me$_5$)$_2$ZrMe$_2$ (**8**) did not effect the catalytic hydroboration. For (η^5-C$_5$H$_5$)$_2$TiMe$_2$ (**9**) only transient activity was observed. The initial orange-yellow solution changed to dark brown. This indicates that reduction of titanium(IV) to low valent species took place, resulting in catalytically inactive species (*vide infra*).[17] (η^5-C$_5$H$_5$)$_2$ZrMe$_2$ (**10**) itself seems not active for alkene hydroboration at all.[18] Compound **10** reacts with catecholborane stoichiometrically to give (1,2-O$_2$C$_6$H$_4$)$_3$B$_2$, Cp$_2$Zr(BH$_4$)$_2$, methylcatecholborane and BH$_3$ (NMR spectroscopy).[19] Remarkable is that for both **9** and **10** small amounts of the Markovnikov hydroboration product are present in the mixtures (7% and 5%, respectively). This can be rationalized by assuming reaction of 1-hexene with BH$_3$,[20] which is present according to ^{11}B-NMR spectroscopy, similar as observed by Marks and Burgess in closely related alkene hydroboration systems.[13,21]

The d^1, 15 electron, systems (η^5-C$_5$Me$_5$)$_2$Ti(allyl) (**11**) and (η^5-C$_5$H$_5$)$_2$Ti(allyl) (**12**) were not catalytically active at all.[22] The ^{11}B-NMR spectrum showed that allylcatecholborane (1,2-O$_2$C$_6$H$_4$)B(allyl) (δ = 37 ppm (s)) was formed quickly.[23] Therefore, it is reasonable to assume that the titanium-hydride necessary to start the catalytic cycle has been generated. Then alkene insertion should be possible.[24] However, the catalytic hydroboration reaction is blocked, probably due to a very slow reaction of the titanium-hexyl species with catecholborane, and catalyst deactivation competes effectively. It is well-known that (η^5-C$_5$H$_5$)$_2$Ti(alkyl) compounds decompose rapidly at -30 °C.[25] Considering the decrease in size of metal going from yttrium to titanium, it is expected that for the latter a higher activation energy will be encountered in the last step (Scheme 1). Consequently, the M-H catalyst will be regenerated more slowly and a lower catalytic activity will be observed. The titanium(III) systems were not studied in detail by NMR spectroscopy, because the complexes formed are paramagnetic.

5.4.2. Alternative ligand systems. Our group is exploring the chemistry of early transition metal and lanthanide complexes that have an alternative coordination environment around the metal center to compare their properties with those of known bis(pentamethylcyclopentadienyl)

systems. We decided to concentrate on two types of ligands, namely benzamidinates (Figure 2)[26] and (bidentate) ligands combining a cyclopentadienyl with a pendant anionic (aryloxide or amide) functionality.[27] Benzamidinate ligands are "harder" Lewis bases than cyclopentadienyl ligands.[26] Therefore the metal-center will be more Lewis acidic, which will influence the metal-alkyl bonding and the transition state of the final σ-bond metathesis step. Although the steric aspects of dish-shaped ((η^5-C$_5$H$_5$), (η^5-C$_5$Me$_5$)) and wedge-shaped (benzamidinate) ligands are difficult to assess exactly, a molecular modelling study of (η^5-C$_5$Me$_5$)$_2$YR, [C$_6$H$_5$C(NSiMe$_3$)$_2$]$_2$YR and (η^5-C$_5$H$_5$)$_2$YR (R = H, alkyl), assuming freely rotating ligands, suggests that the steric bulk of benzamidinates is between that of cyclopentadienyl and pentamethylcyclopentadienyl groups.[28]
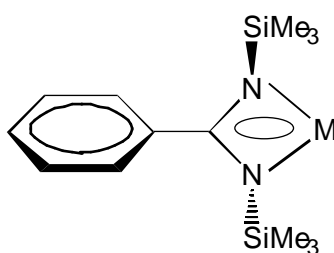
Figure 2. Benzamidinate metal complexes.

All benzamidinate complexes tested (**13**-**24**) proved to be catalytically active, but the activity is considerably lower than found for lanthanum complex **1**. All runs proceeded with concurrent fast deactivation of the catalyst due to reaction between catecholborane and the benzamidinate ligands, possibly to give products with B-N containing bonds. Nevertheless, bis(benzamidinate)yttrium systems (**13**, **14**) showed a catalytic activity substantially higher than the bis(pentamethylcyclopentadienyl)yttrium compounds (**2**-**4**), but lower than the bis(cyclopentadienyl)yttrium complexes (**5**, **6**). This indicates that a more open metal center increases the rate of reaction. From this, it may be anticipated that bis(benzamidinate)lanthanum systems will have a much higher hydroboration rate. To test this, we attempted the synthesis of [C$_6$H$_5$C(NSiMe$_3$)$_2$]$_2$LaR complexes. Unfortunately, only tris(benzamidinate)lanthanum (**17**) could be obtained and the planned comparison was not possible. Nevertheless, [C$_6$H$_5$C(NSiMe$_3$)$_2$]$_3$La (**17**) was tested as well. The complex slowly reacts with catecholborane probably under transfer of the benzamidinate ligands to boron. The resulting lanthanum compounds proved to be slightly catalytically active.

Remarkably, decomposition of catecholborane to (1,2-O$_2$C$_6$H$_4$)$_3$B$_2$ has been observed when Lewis bases (THF and diethylether) are present (Scheme 3), but only in combination with a metal complex (*e.g.* **6** and **15**). This process has also been observed for reaction between catecholborane and tertiary phosphines.[29] In the systems under study here, other decomposition products could not be identified unequivocally. BH$_3$, a likely product, could not be observed, nor its hexene insertion product B(hexyl)$_3$ (^{11}B-NMR spectroscopy).[20] For the

titanium systems **18**, **20** and **21** a dark colored reaction mixture developed. This color change indicates reduction to low valent titanium species. The catalytic activity of the mixed cyclopentadienyl-benzamidinate titanium(III) compounds **21** and **24** is comparable with that of the bis(benzamidinates) (**13**-**16**, **18**-**19**, **23**), but significantly higher than that of bis(cyclopentadienyl)titanium(III) allyls (**11** and **12**).
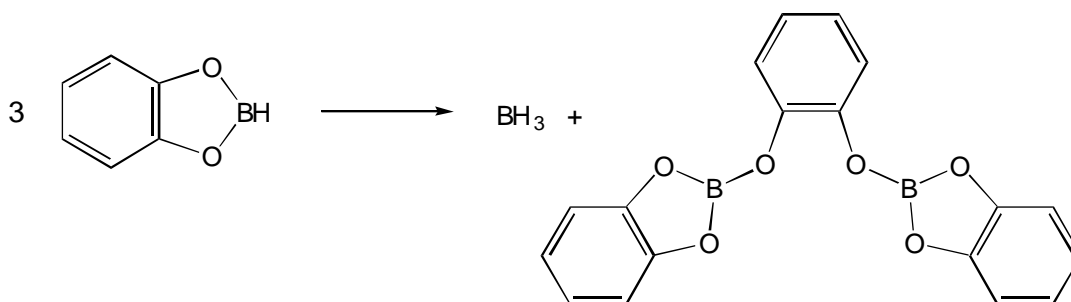
Scheme 3. *Decomposition of catecholborane.*[29]

In addition to the benzamidinate systems, we explored new bidentate ligands which combine a cyclopentadienyl with a pendant anionic function X (Figure 3).[27] Both steric and electronic effects can be tuned, if desired *e.g.* by varying the coordinating group X (X = amide, alkoxide, phosphide, sulfide) and/or by introducing substituents R' (R' = H, alkyl, silyl, aryl) on the cyclopentadienyl group. Unfortunately, so far only group 4 complexes of this class of ligands are available.[30] There is one exception at the moment: Bercaw studied catalytic properties of some related scandium compounds, including polymerization and oligomerization of 1-alkenes.[31] The open structure around the metal center suggests less steric hindrance during the catalytic conversions, which should enhance activity for sterically more demanding substrates.
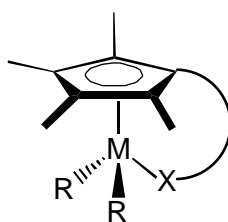
Figure 3. *Bidentate cyclopentadienyl ligand with a pendant anionic ligand X.*

Monomeric zirconium or titanium cyclopentadienyl-amide (**25-27**) and titanium tetramethylcyclopentadienyl-aryloxide (**28**, **29**) complexes showed a catalytic activity comparable to other Ti and Zr compounds tested, but less active than the lanthanum compound **1**. Apparently, for these systems the reaction rate is decreased by electronic effects, since sterically there is more space available at the metal center. A remarkable feature of these systems is that catecholborane is not decomposed and also that the bidentate cyclopentadienyl anionic ligand system is not attacked. From this point, it seems attractive to focus on group 3 complexes containing these bifunctional, bidentate ligands since the larger space available there suggests a much higher catalytic activity.

5.5. Conclusions.

Catalytic alkene hydroboration with group 3 and group 4, 10 - 16 electron organometallic compounds as catalyst strongly depends on the size of the metal and the stabilizing auxiliary ligand system present. For bis(pentamethylcyclopentadienyl) complexes the highest activity and stability of the catalyst is found for lanthanum, the largest metal. For smaller metal centers (Y, Zr, Ti) catalytic activity is low, while catalyst deactivation by reaction of the complex with the boron hydride reagent can compete effectively. Other ligand systems (bis(cyclopentadienyl), bis(benzamidinate) and mixed cyclopentadienyl-benzamidinate) are less effective in stabilizing the catalysts. For benzamidinate complexes, the ligands seem to be transferred to the hydroboration reagent. Bidentate ligand systems based on cyclopentadienyl ligands with pending anionic functions (aryloxo, amido) form stable catalysts. The catalytic performance is moderate, but could possibly be improved by using larger metal centers. For this, lanthanides seem the elements of choice.

5.6. Experimental Section.

5.6.1. General Considerations. General procedures, techniques and instrumentation were described in Chapter 2. ^{11}B-NMR spectra were recorded on a Varian VXR-300 (^{11}B, 96.2 MHz). ^{11}B-NMR spectra were referenced externally to $BF_3 \cdot Et_2O$. Catecholborane (Aldrich) was distilled under reduced pressure and stored under nitrogen. P.-J. Sinnema and J. Vogelzang are gratefully acknowledged for supplying the complexes **25-27** and **28-29**, respectively.

5.6.2. Synthesis of Catalyst Precursors. The syntheses of the following early transition metal complexes have been published or will be reported elsewhere: $(\eta^5\text{-}C_5Me_5)_2LaCH(SiMe_3)_2$ (**1**),[14] $(\eta^5\text{-}C_5Me_5)_2YCH(SiMe_3)_2$(**2**),[32] $(\eta^5\text{-}C_5Me_5)_2YMe \cdot THF$ (**3**),[33] $[(\eta^5\text{-}C_5Me_5)_2YH]_2$ (**4**),[34] $(\eta^5\text{-}C_5H_5)_2YCH(SiMe_3)_2$ (**5**),[35] $(\eta^5\text{-}C_5H_5)_2YCH(SiMe_3)_2 \cdot Et_2O$ (**6**),[35] $(\eta^5\text{-}C_5Me_5)_2TiMe_2$ (**7**),[36] $(\eta^5\text{-}C_5Me_5)_2ZrMe_2$ (**8**),[36] $(\eta^5\text{-}C_5H_5)_2TiMe_2$ (**9**),[37] $(\eta^5\text{-}C_5H_5)_2ZrMe_2$(**10**),[36] $(\eta^5\text{-}C_5Me_5)_2Ti(allyl)$ (**11**) (allyl = $\eta^3\text{-}C_3H_5$),[38] $(\eta^5\text{-}C_5H_5)_2Ti(allyl)$ (**12**),[38] $\{[C_6H_5C(NSiMe_3)_2]_2YH\}_2$ (**13**),[26] $[C_6H_5C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**14**),[26] $[C_6H_5C(NSiMe_3)_2]_2YCH_2Ph \cdot THF$ (**15**),[39] $[C_6H_5C(NCMe_3)_2]_2YCH(SiMe_3)_2$ (**16**),[39] $[C_6H_5C(NSiMe_3)_2]_3La$ (**17**),[40] $[C_6H_5C(NSiMe_3)_2]_2TiMe_2$ (**18**),[35] $[C_6H_5C(NSiMe_3)_2]_2ZrMe_2$ (**19**),[35] $(\eta^5\text{-}$

C$_5$H$_5$)[C$_6$H$_5$C(NSiMe$_3$)$_2$]TiMe$_2$ (**20**),[41] (η^5-C$_5$H$_5$)[C$_6$H$_5$C(NSiMe$_3$)$_2$]TiNp (Np = CH$_2$C(CH$_3$)$_3$) (**21**),[35] (η^5-C$_5$H$_5$)[C$_6$H$_5$C(NSiMe$_3$)$_2$]Zr(CH$_2$Ph)$_2$ (**22**),[42] [C$_6$H$_5$C(NSiMe$_3$)$_2$]$_2$Ti(allyl) (**23**),[43] (η^5-C$_5$H$_5$)[C$_6$H$_5$C(NSiMe$_3$)$_2$]Ti(allyl) (**24**),[35] [η^5,η^3-C$_5$H$_4$(CH$_2$)$_3$NMe]Zr(BH$_4$)$_2$ (**25**),[27b] [η^5,η^3-C$_5$H$_4$(CH$_2$)$_3$NMe]Zr(CH$_2$Ph)$_2$ (**26**),[27b] [η^5,η^3-C$_5$H$_4$(CH$_2$)$_3$NMe]TiMe$_2$ (**27**),[44] [η^5,σ^1-C$_5$Me$_4$(2-O)(6-OMe)C$_6$H$_3$]TiNp$_2$ (**28**),[45] [η^5,σ^1-C$_5$Me$_4$(2-O)(6-OMe)C$_6$H$_3$]Ti(allyl) (**29**).[45]

5.6.3. General Procedure for the Catalyzed Hydroboration of Alkenes. A 5-mm NMR tube, equipped with a Teflon needle valve, was charged with 0.30 mmol of 1-hexene, 0.60 mmol of catecholborane, 0.3 mL benzene-d_6, and 10 μmol of catalyst precursor (**1-29**) at room temperature. Progress of the reaction was monitored following the intensity of the alkene resonances in the ^{1}H NMR spectrum. The alkylborane ester formed was identified by ^{1}H and ^{11}B NMR spectroscopy. After all 1-hexene had been consumed, the mixture was quenched with 0.25 mL 3N NaOH and 0.50 mL 30% H$_2$O$_2$ and warmed to 50 °C for 3 hours. The organic layer was separated and analyzed with ^{1}H-NMR spectroscopy, GC and GC-MS.

5.6.4. Reactions of Catecholborane with the Precatalyst. A 5-mm NMR tube, equipped with a Teflon needle valve, was charged with 10 μmol of catalyst precursor (**1-29**), 0.3 mL benzene-d_6, and 10 μmol of catecholborane at room temperature. The resulting mixture was characterized spectroscopically by ^{1}H, ^{11}B and ^{13}C NMR.

5.6.5. Determination of Gross Activity. The conversion of 1-hexene to the alkylborane ester was determined after one hour reaction time by ^{1}H-NMR spectroscopy (Table 1). The gross activity was calculated by dividing the amount of formed hydroboration product by the amount of precatalyst started with. Runs for a number of selected complexes (**1**, **2**, **3**, **5**, **11**, **13**, **18**, **19**, **20** and **23**) were reproducible (within 5-10%), indicating that uncontrolled, trivial inactivation (air, water) of the catalyst did not occur.

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