DOI: 10.1002/chem.201000372

Planar Chiral Organoborane Lewis Acids Derived from Naphthylferrocene

Jiawei Chen,[a] Krishnan Venkatasubbaiah,[a] Thilagar Pakkirisamy,[a, b] Ami Doshi,[a] Andrej Yusupov,[a] Yesha Patel,[a] Roger A. Lalancette,[a] and Frieder Jäkle*[a]

Abstract: Enantiomerically pure metalated 2-(1-naphthyl)ferrocene (NpFc) derivatives NpFcM (M = $SnMe_3$, HgCl) were prepared and characterized by multinuclear NMR and UV/Vis spectroscopy, cyclic voltammetry, and elemental analysis. Optical rotation measurements were performed and the absolute configuration of the new planar chiral ferrocene species was confirmed by single-crystal X-ray diffraction analysis. The mercuriated species NpFcHgCl proved suitable as a reagent for the preparation of the chiral organoborane Lewis acid $NpFcBCl_2$, which can in turn be converted to other ferrocenylboranes by replacement of Cl with nucleophiles. The highly Lewis acidic perfluoroarylborane derivatives $NpFcB(C_6F_5)Cl$ and $NpFcB(C_6F_5)_2$ were successfully prepared by treatment with CuC_6F_5. The structures were studied by single-crystal X-ray diffraction and variable-temperature ^{19}F NMR spectroscopy, which suggested that π stacking of a C_6F_5 group on boron with the adjacent naphthyl group is energetically favorable. UV/Vis absorption spectroscopy and cyclic voltammetry measurements were performed to examine the electronic properties of these novel redox-active chiral Lewis acids.

Keywords: boron · chirality · ferrocenes · ferrocenylboranes · Lewis acids

Introduction

Highly Lewis acidic organoboranes play key roles as reagents and catalysts in organic synthesis.[1] Especially important for organic transformation are chiral derivatives;[2] early examples include Brown's pinene-based organohaloboranes,[3] Hawkins' naphthylcyclohexyl-dichloroboranes,[4] and organoboron-modified binaphthyl species first studied by Kaufmann and later by Yamamoto and Piers.[5–7] These and related chiral Lewis acidic organoboranes serve as excellent catalysts for enantioselective Diels–Alder reactions.[4,6,8] More recently, Piers et al. showed that a $B(C_6F_5)_2$-substituted binaphthyl derivative effectively catalyzes the stereoselective allylstannation of aromatic aldehydes.[7] In an effort to enhance the Lewis acidity of the boron sites, a backbone-perfluorinated binaphthylborane derivative has also been introduced by Piers and co-workers.[9] Soderquist et al. prepared enantiomerically pure 9-borabicyclo-[3.3.2]decane derivatives and studied their applications in various organic transformations, including asymmetric allyl-, crotyl-, allenyl-, propargyl-, and hydroboration reactions.[10] Finally, highly Lewis acidic organoboranes are of much interest for transition-metal-free hydrogenation reactions. Stephan et al. first demonstrated that frustrated Lewis pairs consisting of a combination of a strong Lewis acid and sterically hindered Lewis base are capable of activating dihydrogen and other small molecules.[11] Recent studies have been aimed at utilizing this unusual reaction for stereoselective hydrogenation reactions.[12]

We have focused our attention on ferrocenylborane-based Lewis acids.[13–16] One motivation has been that preparation of planar chiral derivatives could open up a new entry into enantioselective Lewis acid catalysts.[17] Attractive is also that the Lewis acidity of the borane moiety can be tuned through reversible redox chemistry at the metal centers.[18,19] Prior efforts by our group involved studies on the binding properties of heteronuclear bidentate 1-stannyl-2-borylferrocene derivatives, which are obtained in their racemic form by a rearrangement reaction from 1,1′-bis(trimethylstannyl) ferrocene and boron halides $RBCl_2$ (R = Cl, Ph, C_6F_5).[13,14] We have demonstrated that the bidentate Lewis acid 1,2-Fc-

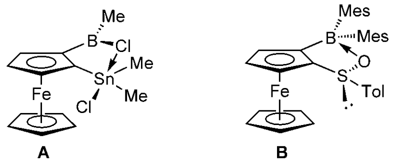
---

[a] J. Chen, Dr. K. Venkatasubbaiah, Dr. T. Pakkirisamy, Dr. A. Doshi,
A. Yusupov, Y. Patel, Prof. Dr. R. A. Lalancette, Prof. Dr. F. Jäkle
Department of Chemistry, Rutgers University-Newark
73 Warren Street, Newark, NJ 07102 (USA)
Fax: (+1) 973-353-1264
E-mail: fjaekle@rutgers.edu

[b] Dr. T. Pakkirisamy
Current address: Inorganic and Physical Chemistry Department
Indian Institute of Science, Bangalore, 560 012 (India)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000372.

(BClMe)($SnMe_2Cl$) (**A**, Fc = ferrocene) can be resolved into its constituent planar chiral enantiomers and that these can be subsequently employed in the enantioselective allylation of ketones.[20] In this context, we would like to also note that Aldridge and co-workers recently obtained compound **B** in enantiomerically pure form by regioselective *ortho*-metalation and subsequent diastereomer separation by recrystallization (see Scheme 1).[21]

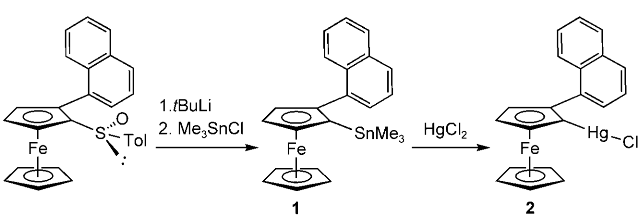


Scheme 1. Examples of enantiomerically pure planar chiral ferrocenylboranes (Mes = 2,4,6-trimethylphenyl, Tol = 4-methylphenyl).

Herein, we describe a high-yielding enantioselective synthesis route to the planar chiral napththyl ferrocenylborane 1,2-Fc(Np)(BCl_2) (Np = naphthyl), which in turn serves as a versatile precursor to other chiral organoborane Lewis acids through subsequent transmetalation reactions.

Results and Discussion

(S_p)-2-(1-Naphthyl)-1-(trimethylstannyl)ferrocene (**1**) was prepared in analogy to a literature procedure for the synthesis of (S_p)-2-(1-naphthyl)-1-(tributylstannyl)ferrocene.[22,23] Reaction of (S_p,S_S)-2-(1-naphthyl)-1-(*p*-tolylsulfinyl)ferrocene with *tert*-butyllithium followed by quenching with Me_3SnCl gave **1** in 60 % yield after recrystallization from methanol (Scheme 2). The ^1H and ^{13}C NMR spectra of **1** show patterns that are consistent with a 1,2-disubstituted ferrocene derivative, and a signal at $\delta = -7.1$ ppm in the ^{119}Sn NMR spectrum confirms the attachment of the trimethylstannyl group. The absolute configuration of **1** as the S_p isomer was assigned from the single-crystal X-ray structure, which confirms stereoselective replacement of the sulfinate moiety (Figure 1 a). Two independent molecules are found in the unit cell. The angle between the cyclopentadienyl (Cp) and the naphthyl group is 72.27(9)° and 83.22(10)°, respectively, and the orientation of the naphthyl group matches that proposed for related compounds[23] based on NMR studies.



Scheme 2. Synthesis of the enantiomerically pure organometallic naphthylferrocene derivatives **1** and **2**.

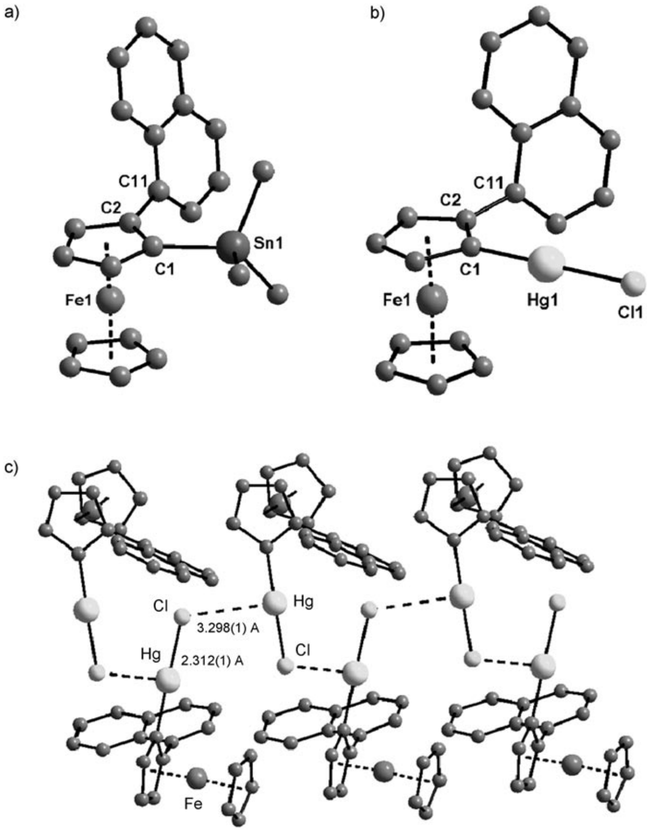
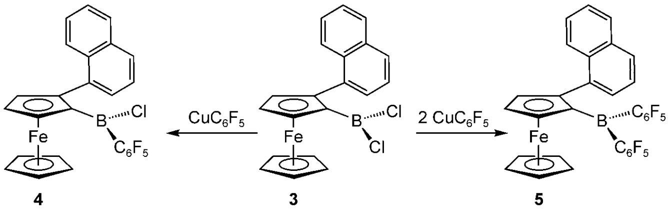


Figure 1. a) X-ray crystal structure plot of one of two independent molecules of **1**. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1−C1 2.135(3), C2−C11 1.488(4), C1-C2-C11 124.7(3), Sn1-C1-C2 125.6(2). b) X-ray crystal structure plot of **2**. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Hg1−C1, 2.024(5), Hg1−Cl1 2.312(1), C2−C11 1.489(7), C1-Hg1-Cl1 179.0(1), C1-C2-C11 122.4(4), Hg1-C1-C2 123.0(3). c) Illustration of the extended structure of **2** in the solid state.

Treatment of aryltin species with $HgCl_2$ is generally known to lead to highly selective tin–mercury exchange.[16,24] Indeed, reaction of **1** with $HgCl_2$ in acetone led to facile formation of **2** in 84 % isolated yield. The ^1H NMR spectrum shows three signals at $\delta = 4.82$ (dd), 4.64 (pst (pseudo triplet)), and 4.30 ppm (dd), as expected for a 1,2-disubstituted Cp ring, and a singlet at $\delta = 4.33$ ppm for the free Cp ring. Single-crystal X-ray analysis confirmed that the S_p stereochemistry is unchanged relative to that of the Sn precursor (Figure 1 b). The angle between the Cp ring and the naphthyl group of 77.1(1)° is similar to that found for **1**. The Hg1−C1 and Hg1−Cl1 bond lengths [(2.024(5) and 2.312(1) Å, respectively] are comparable to those found in chloromercury ferrocene and other related organomercury compounds.[25] The C1-Hg1-Cl1 angle of 179.0° indicates an almost perfect linear coordination geometry at Hg. In the solid state, **2** exhibits an interesting supramolecular structure with infinite helical chains that arise from weak intermolecular Hg1···Cl1 interactions (3.298(1) Å) as shown in Figure 1c.

We then studied the reactivity of these organometallic naphthylferrocene derivatives towards boron halides. Reaction of **1** with BBr_3 in $CDCl_3$ at −35 °C resulted in the formation of a mixture of the 1,1′- and 1,3-disubstituted species according to ^1H NMR spectroscopy analysis of the crude product mixture (ratio of 57:43; see the Supporting Information). Presumably, rearrangement occurs through interannular proton transfer, as previously reported for the reaction of 1,1′-bis(trimethylstannyl)ferrocene with boron halides.[14] In contrast, reaction of **2** with one equivalent of BCl_3 at −30 °C in hexane resulted in clean conversion to the chiral Lewis acid (R_p)-1,2-NpFcBCl$_2$ (**3**) in a good yield of 82 %. The formation of **3** was confirmed by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, high resolution MS, and elemental analysis. In the Cp region of the ^1H NMR spectrum of **3** the pattern of a 1,2-disubstituted ferrocene was retained with three signals at $\delta = 4.63$ (dd), 4.57 (brs), and 4.38 ppm (brs) for the substituted Cp ring and a singlet at $\delta = 4.02$ ppm for the free Cp ring. The ^{11}B NMR spectrum shows a signal at $\delta = 49$ ppm, which is in a similar range as that reported for the achiral analogue FcBCl$_2$ ($\delta = 50.5$ ppm).[26]

The novel planar chiral diarylchloroborane (R_p)-1,2-NpFcBCl(C_6F_5) (**4**) and triarylborane (R_p)-1,2-NpFcB(C_6F_5)$_2$ (**5**) were obtained by treatment of **3** with one and two equivalents of pentafluorophenyl copper,[27] respectively (Scheme 3). Compounds **4** and **5** were isolated as dark red microcrystalline solids in 80 and 84 % yield, respectively. Their structures were confirmed by multinuclear NMR spectroscopy, high-resolution MALDI-TOF MS or elemental analysis, and single-crystal X-ray analysis. The ^{11}B NMR shifts of **4** ($\delta = 55$ ppm) and **5** ($\delta = 54$ ppm) are in a similar range as that reported by Piers et al. for the achiral analogue FcB(C_6F_5)$_2$ ($\delta = 53$ ppm),[19] which is consistent with the presence of a weak Fe→B interaction (see below).[28] At room temperature, the ^{19}F NMR spectrum of **4** shows three slightly broadened resonances at $\delta = -130$, −154.1, and −162.7 ppm. In contrast, the spectrum of **5** shows two sets of strongly broadened ^{19}F NMR peaks (see Figure 2), one of which is attributed to the C_6F_5 ring (A) adjacent to the naphthyl moiety and the other to the C_6F_5 ring (B) that is pointing away. The apparent signal broadening suggests hindered rotation around the B−C(Cp) and/or the B−C(C_6F_5) bonds. We performed variable temperature ^{19}F NMR studies to further examine the fluxional behavior of compounds **4** and **5**.



Scheme 3. Synthesis of highly Lewis acidic planar chiral ferrocenylboranes.

For compound **5**, two distinct sets of resonances of equal intensity were observed for the C_6F_5 moieties at −60 °C (Figure 2). They were assigned based on 2D ^{19}F–^{19}F NMR spectroscopy (see Figure S7 in the Supporting Information). Ring A shows five ^{19}F NMR resonances due to hindered rotation about the B−C(C_6F_5) bond, which is a result of the presence of the adjacent naphthyl moiety. In contrast, ring B shows only one signal for the *meta* fluorines and strongly broadened signals for the *ortho* fluorines, indicating a much lower barrier of rotation. The energy barriers were determined from line shape analysis[29] and coalescence temperature methods[30] (see Figure S8 in the Supporting Information, which shows a detailed variable-temperature (VT) NMR plot for compound **5**). Analysis of the temperature dependency of the line shape of the *para* fluorines provides information on the rotation barrier of the B−C(Cp) bond, whereas information on the rotational barrier of the B−C(C_6F_5 ring A) bond can be obtained from line shape analysis for the *ortho* or *meta* fluorines (Table 1). A similar barrier was deduced for exchange of the *meta*-fluorines of ring A ($\Delta G^{\neq}_{298} = 58.9(1)$ kJ mol^{-1}) and the *para*-fluorines of rings A/B ($\Delta G^{\neq}_{298} = 58.3(6)$ kJ mol^{-1}), which indicates that the rotation of ring A and interchange between rings A and B require about the same energy, whereas rotation of ring B is comparatively much more facile ($\Delta G^{\neq}_{228} = 39.8(6)$ kJ mol^{-1} on the basis of the coalescence temperature method applied to *ortho*-F in ring B versus $\Delta G^{\neq}_{228} = 55.3(8)$ kJ mol^{-1} on the basis of line shape analysis applied to *ortho*-F in ring A; see the Supporting Information).

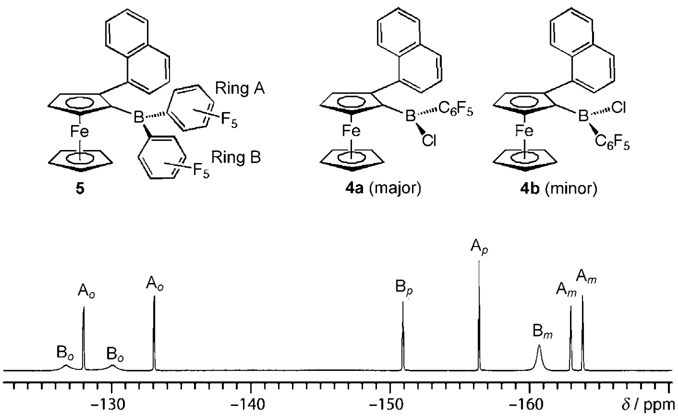


Figure 2. Low-temperature ^{19}F NMR spectrum of **5** ($CDCl_3$, 470.4 MHz, −60 °C).

Compound **4** also shows two sets of ^{19}F NMR peaks at −60 °C, but their relative intensity is different (Figure 3). Hence, a major and a minor rotational isomer are formed (**4a** and **4b**). Based on a comparison with the NMR data for **5**, we can confidently assign the major isomer to be that with the C_6F_5 group pointing toward the naphthyl group. The free energy barriers for interconversion of isomer **4a**

Table 1. Results from line-shape analysis and coalescence temperatures for **4** and **5**.

Compd	Probe	$\Delta H^{\neq[a]}$ [kJ mol^{-1}]	$\Delta S^{\neq[a]}$ [J mol^{-1} K^{-1}]	$\Delta G^{\neq}_{298}$[a] [kJ mol^{-1}]	T_c[b] [K]	$\Delta G^{\neq}_{T_c}$[b] [kJ mol^{-1}]
4a→**4b**	*p*-F(A)	37.1(6)	−45.5(8)	50.6(4)		
4b→**4a**	*p*-F(B)	37.0(3)	−36.9(3)	48.0(3)		
4a	*m*-F(A)	22.1(6)	−110(3)	55.0(4)	265(3)	50.0(6)
4b	*o*-F(B)	34(1)	−41(2)	45.9(8)	248(3)	44.1(6)
5 ring A→ring B	*p*-F(A)	52.5(7)	−19.4(3)	58.3(6)		
5 ring A	*m*-F(A)	30(1)	−97(4)	58.9(1)	308(3)	58(2)
5 ring B	*o*-F(B)	[c]	[c]	[c]	228(3)	39.8(6)

[a] Data from line-shape analysis by using the fitting program DNMR. [b] Data from coalescence temperature method by using the approximation $\Delta G^{\neq} = 19.1T_c[9.97+\lg(T_c\Delta\nu^{-1})]$ for estimation of $\Delta G^{\neq}$ at T_c.[30] [c] Data were not well resolved.

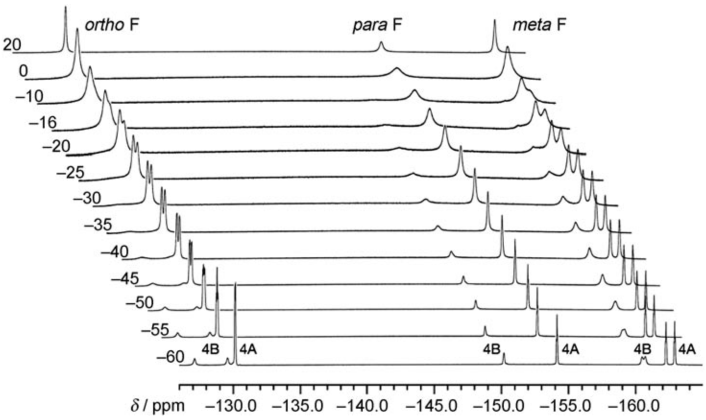


Figure 3. Variable-temperature ^{19}F NMR spectra of **4** (CDCl$_3$, 470.4 MHz).

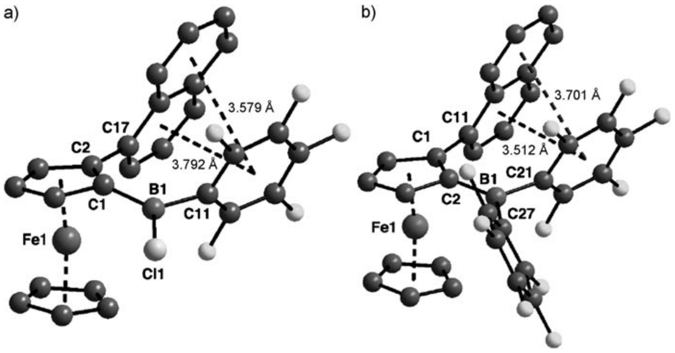


Figure 4. a) X-ray crystal structure plot of **4**. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: B1−C1 1.511(3), B1−C11 1.587(4), B1−Cl1 1.787(3), C1-B1-C11 123.9(2), C1-B1-Cl1 119.5(2), C11-B1-Cl1 115.95(18), Cp//Cp 7.0, Cp//Np 59.2, C$_6$F$_5$//Np 14.7. b) X-ray crystal structure plot of one of two independent molecules of **5**. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: B1−C2 1.521(6), B1−C27 1.578(7), B1−C21 1.598(7), C2-B1-C27 123.0(4), C2-B1-C21 122.2(4), C27-B1-C21 114.3(4), Cp//Cp 7.6, Cp//Np 65.1, C$_6$F$_5$//Np 7.6.

into **4b** and vice versa were calculated to be $\Delta G^{\neq}_{298}$ = 50.6(4) and 48.0(3) kJ mol^{-1}, respectively, suggesting that the isomer with the pentafluorophenyl group pointing toward the naphthyl group is energetically favorable by about 2–3 kJ mol^{-1}.

The solid-state structures were examined by single-crystal X-ray diffraction. The X-ray analysis of **5** revealed two independent molecules with similar structural features in the asymmetric unit, whereas only one molecule of **4** was found (Figure 4). For **4**, the isomer with the C$_6$F$_5$ moiety pointing toward the naphthyl group crystallized, which is consistent with our findings that this isomer is energetically favorable in solution. The boryl moieties are bent away from the plane of the substituted Cp ring of the ferrocenyl unit in both **4** and **5**, with interplanar angles of Cp//BC$_2$Cl = 21.4° for **4** and Cp//BC$_3$ = 14.8 and 16.0° for the independent molecules of **5**, respectively. This tilting of the boryl group toward the iron atom and the comparatively short B−C bond lengths (B−C$_{Cp}$ = 1.511(3) for **4** and B−C$_{Cp}$ = 1.521(6), 1.501(6) Å for **5**) indicate a considerable degree of electronic delocalization between the electron-rich ferrocene and the electron-deficient boron atom.[28] In comparison, the angle in the structure from Piers et al. is about 16°[19] and those for the two independent molecules in the asymmetric unit of FcBBr$_2$ are 17.7 and 18.9°.[31] The observation that the tilting of the boryl group is much more pronounced in **4** than in **5** may suggest increased steric strain in the latter due to the additional C$_6$F$_5$ group, which is preventing even closer contact between Fe and B. Indeed, considerable strain is evident for both molecules from the Cp//Cp tilt angles, which range from 7.0 to 7.6°. Noteworthy is also an intramolecular π-stacking interaction between the naphthyl moiety and the pentafluorophenyl ring (centroid–centroid distances in **4**: 3.792 and 3.579 Å, **5**: 3.512 and 3.701 Å). The interplanar angle between the C$_6$F$_5$ moiety and the naphthyl ring ranges from 7.6° for **5** to 14.7° for **4**. In the solid state, both **4** and **5** reveal an interesting supramolecular 3D network structure as a result of multiple CH⋯π and CF⋯π interactions (see Figures S5 and S6 in the Supporting Information).

We examined the electronic structures of the ferrocenylborane Lewis acids by UV/Vis spectroscopy and cyclic voltammetry (CV) measurements. The longest wavelength absorption occurs at lowest energy for the bisperfluorophenyl-substituted compound **5** (λ = 491 nm, ε = 1680), followed by **4** (λ = 475 nm, ε = 1280) and **3** (λ = 455 nm, ε = 1120) (Figure 5). This band can be attributed to a d–d transition of the ferrocene moieties with significant charge-transfer character. The particular order may suggest that electronic interactions between the π orbitals of the ferrocenyl and the empty p orbitals on boron are promoted by the electron-deficient C$_6$F$_5$ groups more effectively than by the electronegative chlorine atoms.

Finally, we explored the possibility of **5** to undergo reversible oxidation. The cyclic voltammogram of **5** shows a re-

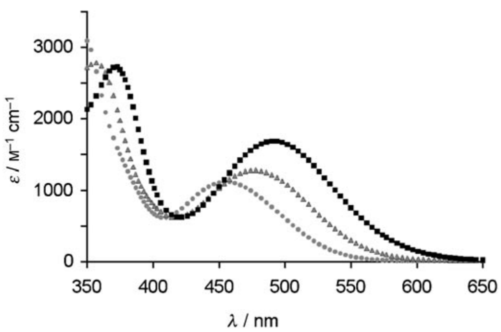


Figure 5. UV/Vis absorption spectra of chiral ferrocenylboranes **3** (ball), **4** (triangle), and **5** (square).

versible redox process at $E_{1/2} = +460$ mV versus the Fc/Fc$^+$ couple (Figure 6), which is considerably more anodic than those determined for **1** (+6 mV) and **2** (+127 mV). The higher oxidation potential for **5** is in good agreement with data reported by Piers et al. for FcB(C_6F_5)$_2$ (+450 mV in trifluorotoluene/$Bu_4N[B(C_6F_5)_4]$)[19] and attributed to the electron withdrawing nature of the B(C_6F_5)$_2$ moiety. Addition of the Lewis base pyridine, which binds to boron and thus, renders the boryl group more electron rich, shifts the redox potential of **5** to +90 mV. The fact that **5** undergoes a reversible electrochemical oxidation clearly suggests the possible use of this new class of compounds as redox-active chiral Lewis acid.

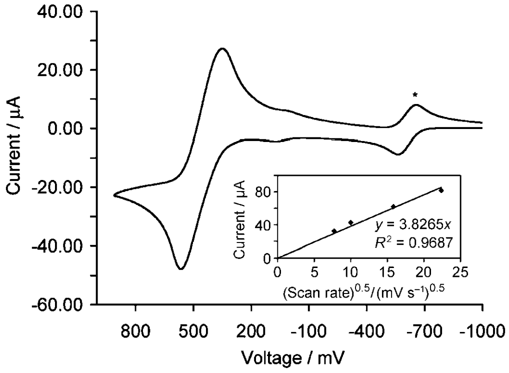


Figure 6. Cyclic voltammogram of compound **5** (CH_2Cl_2, 0.05 M $Bu_4N[B(C_6F_5)_4]$, reported versus Fc/Fc$^+$, which is taken as +610 mV versus Cp*$_2$Fe/Cp*$_2$Fe$^+$ (indicated with an asterisk, Cp* = pentamethylcyclopentadienyl) as an internal reference). The small peak at approximately +50 mV is due to trace amounts of naphthylferrocene that is formed as a result of the reaction of **5** with traces of water (Inset: plot of current versus square root of scan rate).

Conclusion

In conclusion, we describe the first examples of highly Lewis acidic planar chiral ferrocenylborane Lewis acids. Compounds **4** and **5** are structurally closely related to the important class of chiral binaphthyl species, which have found abundant use in catalysis applications. Importantly, the ferrocenyl group not only provides a rigid chiral environment, but the redox-active nature of the central iron atom may allow for tuning and further enhancement of the Lewis acidity. Additional studies in this regard and on the application of compounds **4** and **5**, as well as related planar chiral Lewis acids, in stereoselective organic synthesis are in progress. To explore the combination of these chiral Lewis acids with sterically-hindered Lewis bases in the context of so-called frustrated Lewis pairs will also be of interest.

Experimental Section

BCl_3 (1 M in hexanes), *t*-butyl lithium (1.7 M in hexanes), and mercuric chloride were purchased from Acros. BBr_3 (99+%) was obtained from Aldrich and distilled prior to use. (S_P,S_S)-2-(1-naphthyl)-1-(*p*-tolylsulfinyl)ferrocene,[22] pentafluorophenyl copper,[32] and $(C_6F_5)_2BCl$[33] were prepared according to literature procedures. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (MBraun). 499.9 MHz ^{1}H NMR, 125.7 MHz ^{13}C NMR, 470.4 MHz ^{19}F NMR, 160.4 MHz ^{11}B NMR, and 186.4 MHz ^{119}Sn NMR spectra were recorded on a Varian INOVA NMR spectrometer (Varian Inc., Palo Alto, CA) equipped with a 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). GC–MS spectra were acquired on a Hewlett Packard HP 6890 Series GC system equipped with a series 5973 mass selective detector and a series 7683 injector. MALDI-TOF measurements were performed either on an Applied Biosystems 4700 Proteomics Analyzer in reflectron (+) mode with delayed extraction or an Apex Ultra 7.0 Hybrid FTMS (Bruker Daltonics). UV/Vis absorption data were acquired on a Varian Cary 500 UV/Vis/NIR spectrophotometer. Optical rotation analysis was performed on an Autopol III polarimeter, Rudolph Research Analytical, using a tungsten-halogen light source operating at λ = 589 nm. Cyclic voltammetry measurements were carried out on a BAS CV-50W analyzer. The three-electrode system consisted of an Au disk as working electrode, a Pt wire as secondary electrode, and an Ag wire as the pseudo-reference electrode. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ. X-ray data for **1**, **2**, **4**, and **5** were collected on a Bruker SMART APEX CCD Diffractometer using Cu$_{K\alpha}$ (1.54178 Å) radiation. Details of X-ray diffraction experiments and crystal structure refinements are provided in the Supporting Information. CCDC-765783, 765784, 765785, and 765786 contain the supplementary data for the structures of **1**, **2**, **4**, and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 3: To a suspension of (S_p)-2-(1-naphthyl)-1-(chloromercurio)ferrocene (**2**) (0.56 g, 0.118 mmol) in hexane (30 mL) at −30 °C was added BCl_3 (1.24 mL, 1 M solution in hexane) inside a glove box. The reaction mixture was stirred for 2 h. The color of the solution turned orange and a grey solid formed, which was removed by filtration. The filtrate was kept at −37 °C for two days to give an orange crystalline solid. The product was recrystallized once more from warm hexane. A second fraction was obtained upon concentration of the combined mother liquors. Isolated yield: 380 mg (82 %); ^{1}H NMR (499.9 MHz, C_6D_6, 25 °C): $\delta = 7.94$ (br d, $J = 7.0$ Hz, 1H; Np), 7.74 (br d, $J = 6.5$ Hz, 1H; Np), 7.69–7.65 (m, 2H; Np), 7.37 (br pst, $J = 6.5$ Hz, 1H; Np), 7.21 (br pst, $J = 8.0$ Hz, 1H; Np), 7.14 (br s, 1H; Np), 4.63 (dd, $J = 2.5$, 1.0 Hz, 1H; Cp-3/5), 4.57 (br s, 1H; Cp-3/5), 4.38 (br pst, 1H; Cp-4), 4.02 ppm (s, 5H; free Cp); ^{13}C NMR (125.69 MHz, $CDCl_3$, 25 °C): $\delta = 135.2$, 134.1, 133.3, 128.4, 128.3, 128.0, 126.2, 125.9 (2 signals), 125.2 (Np), 97.9, 82.9, 77.3, 75.4, (substituted Cp), 72.6 ppm (C_5H_5) (the *ipso*-Cp-B signal was not observed); ^{11}B NMR (160.4 MHz, C_6D_6, 25 °C): $\delta = 49.4$ ppm ($w_{1/2} = 350$ Hz); UV/Vis (CH_2Cl_2, 1.00×10^{-3} M): $\lambda_{max} = 455$ nm ($\varepsilon = 1120$); MALDI-TOF (+ reflector mode, benzopyrene/pyridine) *m*/*z*: calcd for

$C_{20}H_{15}BCl_2Fe$: 391.9993; found: 392.0023; elemental analysis calcd (%) for $C_{20}H_{15}BCl_2Fe$: C 61.14, H 3.85; found C 61.30, H 3.49.

Synthesis of 4: A precooled solution of $[C_6F_5Cu]_4$ (18 mg, 20 μmol) in toluene (3 mL, −37 °C) was added dropwise to a precooled solution of **3** (31 mg, 79 μmol) in toluene (5 mL, −37 °C) under stirring. The reaction mixture was stirred for 3 h at RT and then filtered. All volatile components were removed under high vacuum. The crude product was purified by recrystallization from hexane at −37 °C to give a dark red microcrystalline solid. Isolated yield: 39 mg (80 %); ^{1}H NMR (499.9 MHz, $CDCl_3$, 25 °C): $\delta = 7.71$ (d, $J = 8.5$ Hz, 1H; Np), 7.66 (d, $J = 8.5$ Hz, 2H; Np), 7.47 (br s, 1H; Np), 7.39 (t, $J = 7.1$ Hz, 1H; Np), 7.31 (m, $J = 7.5$ Hz, 2H; Np), 5.15 (pst, $J = 2.5$ Hz, 1H; Cp), 5.02 (br, 1H; Cp), 4.9 (br, 1H; Cp), 4.53 ppm (s, 5H; free Cp); ^{13}C NMR (125.69 MHz, $CDCl_3$, 25 °C): $\delta =$ 150–130 (*ortho*-, *meta*-, *para*-C_6F_5 signals are broad and not resolved), 115.1 (br, *ipso*-C_6F_5), 132.5, 129.1, 127.6, 127.5, 125.8, 125.7, 124.2, 98.1 (*ipso*-Cp-B), 77.7 (Cp), 81.5 (Cp), 75.9 (br, Cp), 71.7 ppm (C_5H_5); ^{11}B NMR (160.4 MHz, C_6D_6, 25 °C): $\delta = 55.3$ ppm ($w_{1/2} = 500$ Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$, 25 °C): $\delta = -130$ (2F; *ortho*-F), −154.1 (1F; *para*-F), −162.7 ppm (2F; *meta*-F); UV/Vis (CH_2Cl_2, 1.00×10^{-3} M): $\lambda_{max} = 475$ nm ($\varepsilon = 1280$); elemental analysis calcd (%) for $C_{26}H_{15}BClF_5Fe$: C 59.54, H 2.88; found C 59.41, H 2.88.

Synthesis of 5: A solution of $[C_6F_5Cu]_4$ (117 mg, 127 μmol) in toluene (5 mL) was added dropwise at RT to a solution of **3** (100 mg, 255 μmol) in toluene (5 mL) under stirring. The mixture was stirred for 3 h at 80 °C and then cooled to RT and filtered. All volatile components were removed under high vacuum. The crude product was purified by repeated recrystallization from hot hexane to give a dark red microcrystalline solid. Isolated yield: 140 mg (84 %); $[\alpha]_D^{20}$ ($c = 0.072$, hexane) $= -132°$; ^{1}H NMR (499.9 MHz, $CDCl_3$, 25 °C): $\delta = 7.71$ (d, $J = 6.5$ Hz, 1H; Np), 7.62 (m, 2H; Np), 7.53 (d, $J = 8.5$ Hz, 1H; Np), 7.40–7.25 (m, 3H; Np), 5.28 (pst, $J = 2.5$ Hz, 1H; Cp-4), 5.26 (dd, $J = 2.5$, 1.0 Hz, 1H; Cp-5), 4.61 (s, 5H; free Cp), 4.17 (br s, 1H; Cp-3), 2.0–0.8 ppm (ca. 10H; hexane); ^{13}C NMR (125.69 MHz, $CDCl_3$, 25 °C): $\delta = 150$–130 (*ortho*-, *meta*-, *para*-C_6F_5 signals are broad and not resolved), 115.1 (br, *ipso*-C_6F_5), 133.4, 133.3, 132.4, 129.4, 127.8, 127.4, 126.1, 126.0, 125.8, 124.6 (Np), 100.0 (*ipso*-CpC), 83.3 (*ipso*-Cp-B), 77.7 (Cp), 77.5 (Cp), 75.8 (br, Cp), 71.6 ppm (C_5H_5); ^{11}B NMR (160.4 MHz, C_6D_6, 25 °C): $\delta = 54$ ppm ($w_{1/2} =$ 900 Hz); ^{19}F NMR (470.4 MHz, $CDCl_3$, 25 °C): $\delta = -127.5$ (br, 1F; *ortho*-F_{A2}), −132.8 (br, 1F; *ortho*-F_{A6}), −128.7 (br, 2F; *ortho*-$F_{B3,5}$), −151.8 (br, 1F; *para*-F_{A4}), −156.5 (br, 1F, *para*-F_{B4}), −161.5 (br, 2F; *meta*-$F_{B3,5}$), −163.3 (pst, 1F; *meta*-F_{A5}), −163.8 ppm (pst, 1F; *meta*-F_{A3}). ^{19}F NMR (470.4 MHz, $CDCl_3$, −60 °C): $\delta = -128.0$ (d, J(F,F) = 23 Hz, 1F; *ortho*-F_{A2}), −133.1 (d, J(F,F) = 24 Hz, 1F; *ortho*-F_{A6}), −126.7, −130.1 (very br, *ortho*-$F_{B3,5}$), −150.9 (t, J(F,F) = 18 Hz, 1F; *para*-F_{B4}), −156.4 (t, J(F,F) = 21 Hz, 1F; *para*-F_{A4}), −160.7 (br, 2F; *meta*-$F_{B3,5}$), −162.9 (pst, 1F; *meta*-F_{A5}), −163.8 ppm (pst, 1F; *meta*-F_{A3}); UV/Vis (CH_2Cl_2, 1.00×10^{-3} M): $\lambda_{max} = 491$ nm ($\varepsilon = 1680$); CV (CH_2Cl_2, 1.9×10^{-3} M): $E_{1/2} = 460$ mV ($\Delta E_p =$ 214 mV); CV of complex with pyridine (CH_2Cl_2, 1.9×10^{-3} M): $E_{1/2} =$ 93 mV ($\Delta E_p = 98$ mV); high-resolution MALDI-TOF (+ mode, benzopyrene/picoline) m/z: calcd for $C_{32}H_{15}BF_{10}Fe$: 656.0457; found: 656.0455.

Descriptions of the syntheses of compounds **1** and **2**, the reaction of **1** with BBr_3, and additional details on experimental instrumentation and results are provided in the Supporting Information.

Acknowledgements

We gratefully acknowledge support by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-0809642, CRIF-0443538). F.J. thanks the Alfred P. Sloan Foundation for a research fellowship and the Alexander von Humboldt foundation for a Friedrich Wilhelm Bessel research award. We thank Dr. Kakalis for acquisition of 2D NMR data and Prof. Malhotra for providing access to a polarimeter.

---

[1] H. Yamamoto, *Lewis Acids in Organic Synthesis*, Wiley-VCH, Weinheim, **2000**; W. E. Piers, G. J. Irvine, V. C. Williams, *Eur. J. Inorg. Chem.* **2000**, 2131; E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391; W. E. Piers, *Adv. Organomet. Chem.* **2004**, *52*, 1.

[2] K. Ishihara in *Lewis Acids in Organic Synthesis, Vol. 1* (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, **2000**, p. 135.

[3] H. C. Brown, P. V. Ramachandran, *J. Organomet. Chem.* **1995**, *500*, 1; U. P. Dhokte, R. Soundararajan, P. V. Ramachandran, H. C. Brown, *Tetrahedron Lett.* **1996**, *37*, 8345; U. P. Dhotke, H. C. Brown, *Organometallics* **1998**, *17*, 2891.

[4] J. M. Hawkins, S. Loren, M. Nambu, *J. Am. Chem. Soc.* **1994**, *116*, 1657; J. M. Hawkins, M. Nambu, S. Loren, *Org. Lett.* **2003**, *5*, 4293.

[5] B. Schilling, V. Kaiser, D. E. Kaufmann, *Chem. Ber.* **1997**, *130*, 923; G. Bir, C. Ernst, U. M. Gross, C. Rehwinkel, B. Schilling, S. Thormeier, V. Kaiser, D. Kaufmann, *Spec. Publ. R. Soc. Chem.* **1997**, *201*, 193; B. Schilling, D. E. Kaufmann, *Eur. J. Org. Chem.* **1998**, 701.

[6] K. Ishihara, K. Inanaga, S. Kondo, M. Funahashi, H. Yamamoto, *Synlett* **1998**, 1053.

[7] D. J. Morrison, W. E. Piers, M. Parvez, *Synlett* **2004**, 2429.

[8] G. Bir, D. Kaufmann, *Tetrahedron Lett.* **1987**, *28*, 777; D. Kaufmann, R. Boese, *Angew. Chem.* **1990**, *102*, 568; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 545; M. Reilly, T. Oh, *Tetrahedron Lett.* **1994**, *35*, 7209; K. Ishihara, H. Kurihara, M. Matsumoto, H. Yamamoto, *J. Am. Chem. Soc.* **1998**, *120*, 6920; K. Ishihara, H. Yamamoto, *Eur. J. Org. Chem.* **1999**, 527; S. Thormeier, B. Carboni, D. E. Kaufmann, *J. Organomet. Chem.* **2002**, *657*, 136.

[9] D. J. Morrison, S. D. Riegel, W. E. Piers, M. Parvez, R. McDonald, *Chem. Commun.* **2006**, 2875.

[10] C. H. Burgos, E. Canales, K. Matos, J. A. Soderquist, *J. Am. Chem. Soc.* **2005**, *127*, 8044; E. Canales, K. G. Prasad, J. A. Soderquist, *J. Am. Chem. Soc.* **2005**, *127*, 11572; E. Hernandez, J. A. Soderquist, *Org. Lett.* **2005**, *7*, 5397; C. Lai, J. A. Soderquist, *Org. Lett.* **2005**, *7*, 799; E. Canales, E. Hernandez, J. A. Soderquist, *J. Am. Chem. Soc.* **2006**, *128*, 8712; A. Z. Gonzalez, E. Canales, J. A. Soderquist, *Org. Lett.* **2006**, *8*, 3331; E. Hernandez, E. Canales, E. Gonzalez, J. A. Soderquist, *Pure Appl. Chem.* **2006**, *78*, 1389; E. Hernandez, C. H. Burgos, E. Alicea, J. A. Soderquist, *Org. Lett.* **2006**, *8*, 4089; J. G. Román, J. A. Soderquist, *J. Org. Chem.* **2007**, *72*, 9772; A. Z. Gonzalez, J. G. Roman, E. Gonzalez, J. Martinez, J. R. Medina, K. Matos, J. A. Soderquist, *J. Am. Chem. Soc.* **2008**, *130*, 9218; J. R. Gonzalez, A. Z. Gonzalez, J. A. Soderquist, *J. Am. Chem. Soc.* **2009**, *131*, 9924; L. Munoz-Hernandez, J. A. Soderquist, *Org. Lett.* **2009**, *11*, 2571; B. Soto-Cairoli, J. A. Soderquist, *Org. Lett.* **2009**, *11*, 401.

[11] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124; D. W. Stephan, *Dalton Trans.* **2009**, 3129; D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50; *Angew. Chem. Int. Ed.* **2010**, *49*, 46.

[12] D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, 2130.

[13] F. Jäkle, A. J. Lough, I. Manners, *Chem. Commun.* **1999**, 453; R. Boshra, A. Sundararaman, L. N. Zakharov, C. D. Incarvito, A. L. Rheingold, F. Jäkle, *Chem. Eur. J.* **2005**, *11*, 2810.

[14] J. A. Gamboa, A. Sundararaman, L. Kakalis, A. J. Lough, F. Jäkle, *Organometallics* **2002**, *21*, 4169.

[15] K. Venkatasubbaiah, L. N. Zakharov, W. S. Kassel, A. L. Rheingold, F. Jäkle, *Angew. Chem.* **2005**, *117*, 5564; *Angew. Chem. Int. Ed.* **2005**, *44*, 5428; K. Venkatasubbaiah, A. G. DiPasquale, A. L. Rheingold, M. Bolte, F. Jäkle, *Angew. Chem.* **2006**, *118*, 6992; *Angew. Chem. Int. Ed.* **2006**, *45*, 6838; R. Boshra, K. Venkatasubbaiah, A. Doshi, R. A. Lalancette, L. Kakalis, F. Jäkle, *Inorg. Chem.* **2007**, *46*, 10174; K. Venkatasubbaiah, T. Pakkirisamy, R. A. Lalancette, F. Jäkle, *Dalton Trans.* **2008**, 4507; R. Boshra, A. Doshi, F. Jäkle, *Organometallics* **2008**, *27*, 1534.

[16] K. Venkatasubbaiah, J. W. Bats, A. L. Rheingold, F. Jäkle, *Organometallics* **2005**, *24*, 6043.

[17] J. Tweddell, D. A. Hoic, G. C. Fu, *J. Org. Chem.* **1997**, *62*, 8286; G. C. Fu, *J. Org. Chem.* **2004**, *69*, 3245; S.-Y. Liu, I. D. Hills, G. C. Fu, *J. Am. Chem. Soc.* **2005**, *127*, 15352.

[18] C. Dusemund, K. R. A. S. Sandanayake, S. Shinkai, *Chem. Commun.* **1995**, 333; B. E. Carpenter, W. E. Piers, R. McDonald, *Can. J. Chem.* **2001**, *79*, 291; K. Venkatasubbaiah, I. Nowik, R. H. Herber, F. Jäkle, *Chem. Commun.* **2007**, 2154; K. Venkatasubbaiah, A. Doshi, I.

Nowik, R. H. Herber, A. L. Rheingold, F. Jäkle, *Chem. Eur. J.* **2008**, *14*, 444; K. Parab, F. Jäkle, *Macromolecules* **2009**, *42*, 4002; L. Kaufmann, H. Vitze, M. Bolte, H. W. Lerner, M. Wagner, *Organometallics* **2008**, *27*, 6215; S. Aldridge, C. Bresner, I. A. Fallis, S. J. Coles, M. B. Hursthouse, *Chem. Commun.* **2002**, 740; C. Bresner, J. K. Day, N. D. Coombs, I. A. Fallis, S. Aldridge, S. J. Coles, M. B. Hursthouse, *Dalton Trans.* **2006**, 3660; J. K. Day, C. Bresner, I. A. Fallis, L. L. Ooi, D. J. Watkin, S. J. Coles, L. Male, M. B. Hursthouse, S. Aldridge, *Dalton Trans.* **2007**, 3486; J. K. Day, C. Bresner, N. D. Coombs, I. A. Fallis, L. L. Ooi, S. Aldridge, *Inorg. Chem.* **2008**, *47*, 793; A. E. J. Broomsgrove, D. A. Addy, C. Bresner, I. A. Fallis, A. L. Thompson, S. Aldridge, *Chem. Eur. J.* **2008**, *14*, 7525; A. E. J. Broomsgrove, D. A. Addy, A. Di Paolo, I. R. Morgan, C. Bresner, V. Chislett, I. A. Fallis, A. L. Thompson, D. Vidovic, S. Aldridge, *Inorg. Chem.* **2010**, *49*, 157.

[19] B. E. Carpenter, W. E. Piers, M. Parvez, G. P. A. Yap, S. J. Rettig, *Can. J. Chem.* **2001**, *79*, 857.

[20] R. Boshra, A. Doshi, F. Jäkle, *Angew. Chem.* **2008**, *120*, 1150; *Angew. Chem. Int. Ed.* **2008**, *47*, 1134; R. Boshra, K. Venkatasubbaiah, A. Doshi, F. Jäkle, *Organometallics* **2009**, *28*, 4141.

[21] I. R. Morgan, A. Di Paolo, D. Vidovic, I. A. Fallis, S. Aldridge, *Chem. Commun.* **2009**, 7288.

[22] O. Riant, G. Argouarch, D. Guillaneux, O. Samuel, H. B. Kagan, *J. Org. Chem.* **1998**, *63*, 3511; J. G. Seitzberg, C. Dissing, I. Sotofte, P.-O. Norrby, M. Johannsen, *J. Org. Chem.* **2005**, *70*, 8332.

[23] H. L. Pedersen, M. Johannsen, *J. Org. Chem.* **2002**, *67*, 7982.

[24] C. Eaborn, *J. Organomet. Chem.* **1975**, *100*, 43; N. Rot, F. J. J. de Kanter, F. Bickelhaupt, W. J. J. Smeets, A. L. Spek, *J. Organomet. Chem.* **2000**, *593*, 369.

[25] K. Sünkel, T. Kießling, *J. Organomet. Chem.* **2001**, *637–639*, 796; S. Q. Huo, Y. Zhu, Y. J. Wu, *J. Organomet. Chem.* **1995**, *490*, 243; Y. J. Wu, X. L. Cui, Y. H. Liu, H. Z. Yuan, X. A. Mao, *J. Organomet. Chem.* **1997**, *543*, 63; K. Lin, M. Song, Y. Zhu, Y. Wu, *J. Organomet. Chem.* **2002**, *660*, 139.

[26] T. Renk, W. Ruf, W. Siebert, *J. Organomet. Chem.* **1976**, *120*, 1.

[27] A. Sundararaman, F. Jäkle, *J. Organomet. Chem.* **2003**, *681*, 134.

[28] M. Scheibitz, M. Bolte, J. W. Bats, H.-W. Lerner, I. Nowik, R. H. Herber, A. Krapp, M. Lein, M. Holthausen, M. Wagner, *Chem. Eur. J.* **2005**, *11*, 584.

[29] J. I. Kaplan, G. Fraenkel in *NMR of Chemically Exchanging Systems*, Academic Press, New York, **1980**, p. 71; J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, **1982**, p. 77.

[30] M. Hesse, H. Meier, B. Zeeh, *Spectroscopic Methods in Organic Chemistry*, Thieme, Stuttgart, **1997**.

[31] A. Appel, F. Jäkle, T. Priermeier, R. Schmid, M. Wagner, *Organometallics* **1996**, *15*, 1188.

[32] A. Cairncross, W. A. Sheppard, E. Wonchoba, W. J. Guildford, C. B. House, R. M. Coates, *Org. Synth.* **1979**, *59*, 122–131; A. Sundararaman, R. A. Lalancette, L. N. Zakharov, A. L. Rheingold, F. Jäkle, *Organometallics* **2003**, *22*, 3526–3532.

[33] D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492–5503.

Received: February 11, 2010