Novel Reactivity of Ferrocene Derivatives toward Lewis Acids: Decomplexation with Boron Trichloride and Synthesis of a Triple-Decker-like Iron−Zinc Complex[†]

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Ferrocene derivatives bearing the 8-quinoline-tetramethyl-Cp ligand (**1**) possess a free nitrogen donor function. Because of the methyl groups at the Cp ring, the quinoline adopts an orientation that locates the N-donor above the five-membered ring. Additional molecules that are bound by the N-donor function are therefore in proximity to the π-system of the Cp ring. Zinc dichloride, which binds to the N-donor, interacts slightly with the ferrocene moiety, and the triple-decker-like complex **5** is formed. The more Lewis acidic boron trichloride interacts with the functionalized Cp ring much more strongly so that the iron(II) ion cannot compete and is eliminated. Thus the organoborane **6** with intramolecular donor coordination is formed quantitatively.

Introduction

Ferrocene and its derivatives are among the most investigated organometallic compounds due to the ease of derivatization and their pronounced stability. The connection of additional donor ligands to the rigid metallocene backbone leads to chelate ligands of great variety. Applications are for example the use of ferrocene-based ligands in catalysis[1] or the control of binding of additional metal ions by the redox properties of the metallocene.[2] As the iron center in a ferrocene derivative is coordinatively saturated, the additional donor function can only bind a second metal atom. Depending on the geometric prerequisites of the ligands used, the two metal atoms might be well separated or in close proximity.[2,3] In some cases a direct metal−metal interaction is found.[4,5] Lewis acids or H^+ may coordinate to the iron atom of ferrocene,[4−6] and in the case of the highly electrophilic boron trihalides, borylferrocenes are obtained.[7]

The liberation of functionalized Cp ligands from ferrocene derivatives is difficult. Whereas ferrocene itself can be cleaved reductively by lithium,[8] the higher substituted derivatives need stronger reducing agents[9] and in many cases the liberation of the functionalized Cp ligands does not work at all.

Results and Discussion

We use donor-functionalized cyclopentadienyl ligands, which allow for only a few coordination modes due to their rigid, predefined geometry. In the ligand **1** (C_5Me_4Q) the quinoline substituent strongly prefers a more or less orthogonal position relative to the cyclopentadienyl ring because of steric interactions with the CH_3 substituents. Therefore only two orientations of the N-heterocycle are favorable: The nitrogen donor atom either binds to the metal atom or is located at the other side of the Cp ring opposite the metal atom, as in the ferrocene derivatives **3** or **4**. Nevertheless, rotation of the quinoline around the C−C single bond is possible, as we have shown by the reactivity of several half-sandwich complexes that contain the ligand **1**.[10] The synthesis of **3** and **4** respectively follows standard methods. The intensely colored potassium salt of **1** reacts with 1 equiv of $FeCl_2$ to give a blue solution of an iron(II) half-sandwich compound (**2**). In complex **2** the iron atom is most likely coordinated by the nitrogen donor. Although we were not able to isolate the compound and fully characterize it, its composition is inferred from its reactivity and from an EI-mass spectrum. Similar complexes, stabilized by two external or internal donor groups, have been described and fully characterized.[11] Addition of C_5H_5Li or a second equivalent of **1**K leads to the ferrocene derivatives **3** and **4**, respectively.

[†] Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday.

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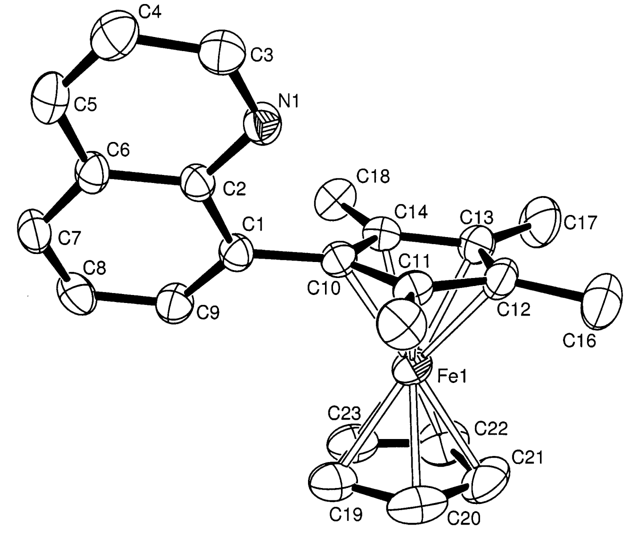

Figure 1. Solid-state structure of **3**. Selected bond lengths (Å): C14−C18 1.509(6), C11−C15 1.504(6), C14−C10 1.444(6), C11−C10 1.436(6), C14−C13 1.416(6), C11−C12 1.435(6), C12−C13 1.438(7), Fe−C14 2.049(4), Fe−C11 2.055(4), $\text{Plane}_{\text{Cp}}-\text{Plane}_{\text{Quinoline}}$ 64.1

The solid-state structure of **3** is shown in Figure 1. Due to the presence of methyl groups at the five-membered ring, the quinolyl substituent cannot lie in a coplanar position relative to the substituted cyclopentadienyl ring. The latter orientation is found in compounds with the 8-quinolylcyclopentadienyl ligand (C_5H_4Q).[5,12] The angle between the quinoline substituent in **3** and the cyclopentadienyl ring is 64°. This orientation brings the lone pair of the nitrogen atom in proximity to the π-system of the five-membered ring. Therefore the coordination of a Lewis acid by the nitrogen donor should cause an interaction with these π-electrons. To investigate such interactions caused by the ligand geometry, we treated compounds such as **3** or **4** with different Lewis acids. Zinc dichloride slowly dissolves in the presence of an orange dichloromethane solution of **3** and a pink powder precipitates. The elemental analysis shows that the new compound **5** is a 1:1 complex from **3** and $ZnCl_2$. However, the EI-MS spectra of **3** and **5** are practically identical and both show the cation $\mathbf{3}^+$ as highest mass (intensity 100%). The ^1H and ^{13}C NMR spectra of **5** and **3** are similar. Both compounds show the same number of signals, and the average symmetry in solution is C_s. Nevertheless the chemical shift values of **3** and **5** differ significantly.

Crystals of **5** were obtained from a dichloromethane solution. The X-ray analysis shows a dinuclear compound in which the zinc atom is surrounded tetrahedrally by two chlorine atoms, the nitrogen atom of the quinoline, and one carbon atom of the cyclopentadienyl ring. (Figure 2). The zinc atom is not located above the center of the five-membered ring but is shifted toward C14 with a distance of 2.407(2) Å. This value is relatively long for a zinc−carbon bond, but clearly shorter than the van der Waals radii (3.1 Å). The contacts Zn1−C10 (2.608 Å) and Zn1−C13 (2.763 Å) are long, and all other zinc carbon distances are clearly nonbonding. The interaction of the zinc atom with the π-system of the ferrocene is obvious from the arrangement of the chloride ligands. They are bent away from the cyclopentadienyl ring with angles C14−Zn−Cl of 104.1° and 124.2°, respectively, although there is no steric repulsion between the chloride atoms and methyl groups of the π-ligand.

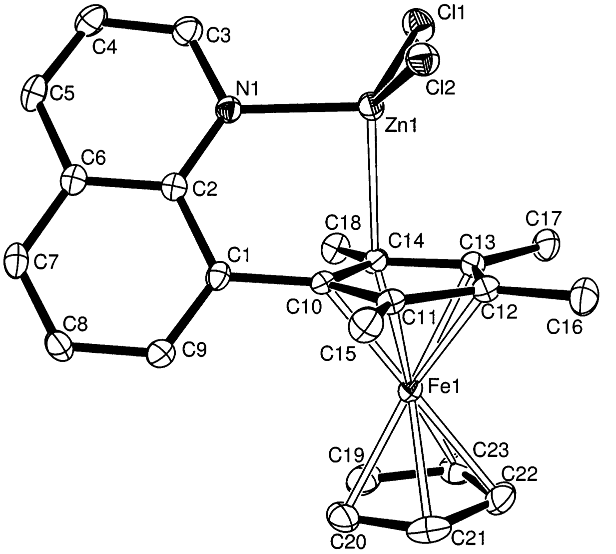

Figure 2. Solid-state structure of **5**; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−N1 2.047(2), Zn1−Cl1 2.214(1), Zn1−Cl2 2.212(1), Zn1−C14 2.407(2), Zn1−C10 2.608(2), C14−C18 1.509(3), C11−C15 1.494(3), C14−C10 1.458(3), C11−C10 1.446(3), C14−C13 1.452(3); C11−C12 1.434(3), C12−C13 1.438(3), Fe−C14 2.042(2), Fe−C11 2.036(2), $\text{Plane}_{\text{Cp}}-\text{Plane}_{\text{Quinoline}}$ 63.3, Cl1−Zn1−Cl2 116.8(1), Cl1−Zn1−N1 106.9(1), Cl2−Zn1−N1 111.5(1), N1−Zn1−C14 89.2(1).

We therefore conclude that there is a bonding interaction between the zinc atom and the cyclopentadienyl ligand. This bifacial coordination mode is rare for C_5R_5 systems.[13] The geometry of the five-membered ring is affected by this interaction. The distances between the pentacoordinated carbon atom C14 and the attached carbon atoms are slightly but significantly longer compared to the corresponding distances at C11. The differences amount to 0.012−0.018 Å (standard deviations 0.003 Å). A compound that is comparable to **5** is the polymeric ferrocene silver adduct $[Ag\{Fe(C_5H_4S_2NEt_2)_2\}]_n[ClO_4]_n$ described by Laguna et al. in 1998.[13e] The formation of analogous silver complexes with the ferrrocenes **3** or **4** is not possible. All Lewis acids that may serve as oxidizing agents (e.g., silver salts, Hg(II) salts, $TiCl_4$) led to the formation of the ferrocenium cations $\mathbf{3}^+$ and $\mathbf{4}^+$, respectively.

To obtain similar complexes with a bridging Cp ligand, boron trichloride was added to solutions of **3** or **4**, respectively. In these cases, no adduct formation was

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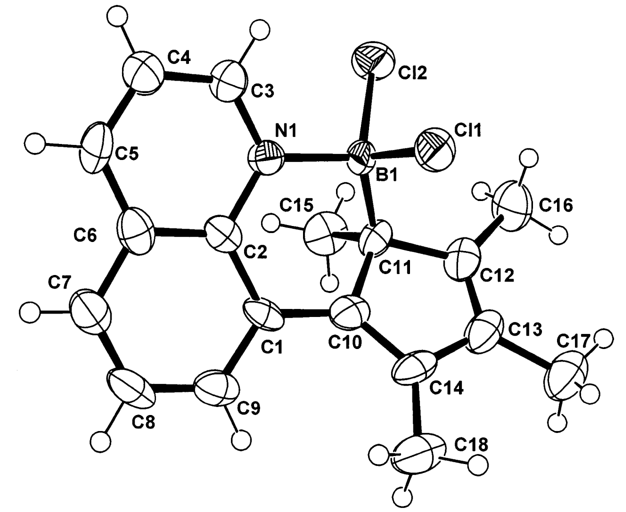


Figure 3. Solid-state structure of **6**. Selected bond lengths (Å) and angles (deg): B1−N1 1.605(8), B1−Cl1 1.857(7), B1−Cl2 1.876(7), B1−C14 1.596(8), C10−C14 1.499(9), C14−C13 1.509(9), C13−C12 1.332(9), C12−C11 1.466(9), C11−C10 1.359(8), Cl1−B1−Cl2 108.4(4), N1−B1−C11 109.4(5).

observed, but the red organoborane **6** was isolated. The other products were iron(II) chloride (reaction with **4**) or a mixture of $FeCl_2$ and ferrocene (reaction with **3**), respectively. When the reaction of BCl_3 with **4** is monitored by ^1H NMR, the new compound **6** is the only product detectable. The constitution can be inferred from mass and NMR spectra. The ^1H as well as the ^{13}C NMR spectra show the presence of four different methyl groups. No dynamic behavior was observed up to 100 °C. The ^{11}B NMR reveals the presence of a boron atom with a coordination number of four ($\delta(^{11}B) = 11.0$, $\nu_{1/2} = 107$ Hz). In addition an X-ray analysis was performed (see Figure 3). The BCl_2 unit is attached to the cyclopentadiene ring, and the coordination sphere of the boron atom is completed by the quinoline nitrogen atom. The distance to the carbon atom C11 (1.596 Å) corresponds to a normal B−C single bond.

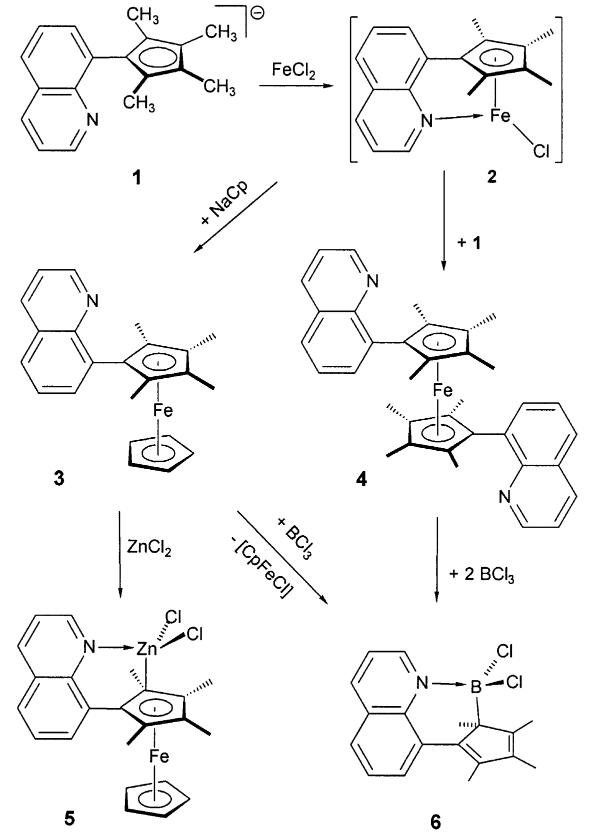
The organoborane **6** is reactive toward water, leading to the cyclopentadiene derivative H**1**. Therefore this new decomplexation reaction may be used for the liberation of functionalized Cp ligands when a suitable predefined ligand geometry is present.

It is very likely that during the formation of **6** an intermediate addition product, similar to the iron−zinc complex **5**, is formed. However, in this case the boron atom in the N−BCl_3 moiety is already coordinatively saturated, so that a sterically induced interaction with the π-system would lead to a hypercoordinated boron atom. Therefore a chloride ligand is substituted by the functionalized Cp^- ligand. The $[CpFe]^+$ ion cannot compete with the $[BCl_2]^+$ unit for the electrons of the bridging Cp^- ligand and is hence eliminated.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere with anhydrous solvents saturated with nitrogen. Glassware was heated under vacuum prior to use. The ligand **1**H was prepared according to the procedure described before.[14]

Scheme 1. Synthesis of the Ferrocene Derivatives 3 and 4 and Reactivity toward Zinc Dichloride and Boron Trichloride



$ZnCl_2$ was dried by refluxing in thionyl chloride until no evolution of gas was observed. All other reagents were used as purchased. Microanalyses: Mikroanalytisches Laboratorium des Organisch-Chemischen Instituts der Universität Heidelberg. NMR: Bruker DRX 200 (200.13 MHz for ^1H, 50.32 MHz for ^{13}C, 64.21 MHz for ^{11}B). The ^1H NMR spectra were calibrated using signals of residual protons from the solvent referenced to $SiMe_4$. The ^{13}C spectral chemical shifts are reported relative to the ^{13}C solvent signals. The ^{11}B NMR spectra were calibrated using $BF_3{\cdot}(C_2H_5)_2O$ as external standard.

η^5-1-(8-Quinolyl)-2,3,5,5-tetramethylcyclopentadienyl-η^5-cyclopentadienyliron (3). 1-(8-Quinolyl)-2,3,4,5-tetramethylcyclopentadiene (H**1**) (0.37 g, 1.5 mmol) was deprotonated with 0.06 g (1.5 mmol) of KH and treated at 0 °C with 0.19 g (1.5 mmol) of $FeCl_2$. An intensely blue solution of complex **2** was obtained, which could not be isolated in a sufficiently pure form (EI-MS: *m/z* (%) 339 (M^+ , 6), 303 (M^+ − HCl, 5), 248 (100, $[Cp^{*Q}]^+$). To a freshly prepared solution of **2** was added 0.13 g (1.5 mmol) of NaC_5H_5 in 10 mL of THF. The resulting red-brown product was purified by chromatography. Yield: 0.30 g (0.81 mmol, 54%) of **3**, orange-red crystals. Mp: 215 °C. ^1H NMR ($CDCl_3$, 200.1 MHz): δ 1.78 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 3.87 (s, 5H), 7.29 (dd, 1H, $J = 8.4$ Hz, 4.2 Hz), 7.61 (dd, 1H, $J = 7.2$ Hz, 8.1 Hz), 7.77 (dd, 1H, $J = 8.1$ Hz, 1.7 Hz), 8.13 (dd, 1H, $J = 8.4$ Hz, 1.8 Hz), 8.43 (dd, 1H, $J = 7.2$ Hz, 1.7 Hz), 8.84 (dd, 1H, $J = 4.2$ Hz, 1.8 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 12.4, 12.7 (CH_3), 72.0 (CH_{Cp}), 80.9 (CCH_3), 82.5 (CCH_3), 87.1 (quat. C_{Cp}), 120.4, 125.7, 126.8, 134.8, 136.1, 149.9 (CH_{Ar}), 128.2, 137.3, 147.9 (quat. C_{Ar}). EI-MS: (*m/z*) 369 (100%, M^+), 303 (49%, $M^+ - C_5H_6$), 248 (7%, $M^+ - FeC_5H_5$). Anal. Calcd for $C_{23}H_{23}NFe$: C 74.77, H 6.28, N 3.79. Found: C 74.76, H 6.42, N 3.74.

Bis[η^5-1-(8-quinolyl)-2,3,5,5-tetramethylcyclopentadienyl]iron (4). The procedure was analogous to the preparation

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[14] Enders, M.; Rudolph, R.; Pritzkow, H. *Chem. Ber.* **1996**, *129*, 459.

Table 1. Crystal Data and Structure Refinement Details for 3, 5, and 6

	3	**5**	**6**
empirical formula	$C_{23}H_{23}FeN$	$C_{23}H_{23}Cl_2FeNZn$	$C_{18}H_{18}BCl_2N$
fw	369.27	505.54	330.04
cryst syst	orthorhombic	triclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/a$
unit cell dimens: *a*, Å	12.360(6)	8.5871(1)	7.737(4)
b, Å	16.735(8)	8.8698(1)	17.122(10)
c, Å	17.747(9)	15.6731(2)	12.854(7)
α deg	90	106.293(1)	90
β deg	90	90.759(1)	92.84(4)
γ deg	90	114.176(1)	90
volume, $Å^3$	3671(3)	1034.06(2)	1700(2)
Z	8	2	4
density(calcd), g/cm^3	1.336	1.624	1.289
abs coeff, mm^{-1}	0.826	2.128	0.376
F(000)	1552	516	688
cryst size, mm^3	0.45 × 0.30 × 0.10	0.28 × 0.09 × 0.03	0.45 × 0.20 × 0.15
θ range for data collection, deg	2.30 to 25.00	1.37 to 28.28	1.59 to 24.99
no. of reflns collected	3234	14148	3005
no. of ind reflns	3234	5061 [*R*(int) = 0.037]	3005
no. of params	233	345	205
goodness-of-fit on F^2	1.025	0.973	0.971
final *R* indices $[I > 2\sigma(I)]$	R1 = 0.0538	R1 = 0.0271	R1 = 0.0714
R indices (all data)	wR2 = 0.1289	wR2 = 0.0694	wR2 = 0.1802
largest diff peak and hole, e $Å^{-3}$	0.288 and −0.451	0.643 and −0.452	0.268 and −0.266

of **3**. From 0.75 g (3.01 mmol) of H**1**, 0.12 g (3.01 mmol) of KH, and 0.19 g (1.50 mmol) of $FeCl_2$ a total of 0.42 g (0.76 mmol, 51%) of complex **4** was obtained. Mp: 270 °C. ^1H NMR (C_6D_6, 200.1 MHz): δ 1.91, 1.84 (s, 24H, Cp-C*H*$_3$); 6.86 (dd, 2H, *J* = 4.2 Hz, 8.2 Hz); 7.19 (dd, 2H, *J* = 8.1 Hz, 6.4 Hz); 7.52 (dd, 2H, *J* = 8.2 Hz, 1.8 Hz); 7.71 (dd, 2H, *J* = 6.6 Hz, 4.0 Hz); 7.75 (dd, 2H, *J* = 1.8 Hz, 4.0 Hz); 8.77 (dd, 2H, *J* = 8.2 Hz, 4.0 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 10.0, 11.2 (*C*H$_3$); 80.0, 81.3, 87.4 (quat., C_{Cp}); 120.1, 125.2, 126.1, 135.5, 136.0, 149.5 (*C*H$_{Ar}$), 128.2, 135.6; 147.5 (quat., *C*$_{Ar}$). MS (EI): *m*/*z* (%) 552 (100, M^+); 303 (40, $C_{18}H_{17}NFe^+$); 249 (90, $C_{18}H_{19}N^+$). Anal. Calcd for $C_{36}H_{36}N_2Fe$: C 78.26, H 6.57, N 5.07. Found: C 77.93, H 6.72 N 5.03.

Synthesis of the Iron Zinc Complex 5. A solution of 0.35 g (0.94 mmol) of **3** in 30 mL of CH_2Cl_2 was treated with 0.13 g (0.94 mmol) of anhydrous $ZnCl_2$ and stirred for 16 h. A pink powder precipitated, which was washed several times with *n*-hexane and dried in vacuo. Yield: 0.34 g (0.67 mmol, 71%). ^1H NMR (200.1 MHz, $CDCl_3$): δ 1.87 (s, 6H, C*H*$_3$), 2.19 (s, 6H, C*H*$_3$), 4.07 (s, 5H, Cp*H*), 7.64 (dd, 1H, *J* = 7 Hz, 4 Hz), 7.86 (dd, 1H, *J* = 8 Hz, 7 Hz), 8.02 (d, 1H, *J* = 8 Hz), 8.53 (d, 1H, *J* = 8 Hz), 8.57 (d, 1H, *J* = 7 Hz), 8.85 (d, 1H, *J* = 4 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 12.0, 32.7 (*C*H$_3$), 82.0 (*C*CH$_3$), 84.0 (quat. *C*$_{Cp}$), 86.5 (*C*CH$_3$), 121.9, 128.0, 128.4, 137.0, 141.5, 150.9 (*C*H$_{Ar}$), 128.9, 132.1, 143.5 (quat. *C*$_{Ar}$). MS: (EI) *m*/*z* (%) 369 (**1**$^+$, 100), 303 ($C_{18}H_{17}NFe^+$, 62), 248 ($C_{18}H_{18}N^+$, 18). Anal. Calcd for $C_{23}H_{23}NFeZnCl_2$: C 54.64, H 4.59, N 2.77, Cl 14.04. Found: C 53.48, H 4.51, N 2.55, Cl 13.25 (further purification is difficult due to the low solubility of complex **5**).

1-(8-Quinolyl)-5-dichloroboryl-2,3,5,5-tetramethylcyclopentadiene (6). A solution of 0.20 g (0.36 mmol) of **4** in 20 mL of toluene was treated at −10 °C with a solution of 0.084 g (0.72 mmol) of BCl_3 in 5 mL of toluene. A red-brown suspension was obtained, and after 24 h a small quantity of a brown solid was filtrated and washed with CH_2Cl_2. The red solutions were concentrated, and compound **6** was obtained as a red powder and was recrystallized from CH_2Cl_2. Yield: 0.21 g (0.64 mmol, 86%). Mp: 147 °C. ^1H NMR (200.1 MHz, C_6D_6): δ 1.33, 2.03, 2.13, 2.54 (4 × s, 12H, C*H*$_3$), 6.49 (dd, 1H, *J* = 5.6 Hz, 8.2 Hz), 7.01 (dd, 1H, *J* = 1.3 Hz, 3.6 Hz), 7.16 (dd, 1H, *J* = 3.6 Hz, 7.4 Hz), 7.23 (dd, 1H, *J* = 1.6 Hz, 8.2 Hz), 7.70 (dd, 1H, *J* = 7.5 Hz, 1.3 Hz), 9.75 (dd, 1H, *J* = 1.6 Hz, 5.6 Hz). ^{13}C NMR (50.3 MHz, C_6D_6): δ 10.9, 12.3, 12.6, 18.2 (Cp-*C*H$_3$), 119.2, 122.5, 127.8, 128.4, 141.8, 146.7 (*C*H$_{Ar}$); 129.8, 134.8, 135.1, 136.6, 137.8, 139.2, 149.8 (*C*$_{Ar}$ and *C*$_{Cp}$, *C*-B not detected). ^{11}B NMR: (64.2 MHz, C_6D_6): 11.0, $\nu_{1/2}$ 107 Hz. MS (EI): *m*/*z* (%) 329 (55, M^+), 294 (20, $M^+ - HCl$); 278 (100, $M^+ - HCl - CH_3$). UV/vis: (CH_2Cl_2) λ_{max} 485 (nm), ϵ 2950 (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{18}H_{18}NBCl_2$: C 65.50, H 5.50, N 4.24. Found: C 65.17, H 5.63, N 4.21.

X-ray Crystal Structure Determinations of 3, 5, and 6. Crystal data were collected for **5** on a Bruker AXS SMART 1000 diffractometer with a CCD area detector (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å) at −100 °C and for **3** and **6** on a Siemens Stoe AED2 diffractometer (λ = 0.71073 Å, ω-scan, −70 °C), respectively. An empirical absorption correction was applied.[15] The structures were solved by direct methods and refined by full-matrix least squares against F^2 with all reflections using the SHELXTL programs.[16] All non-hydrogen atoms were refined anisotropically. For **4** hydrogen atoms were located in difference Fourier maps and refined isotropically; for **3** and **6** they were inserted in calculated positions. Crystal data and experimental details are listed in Table 1.

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Supporting Information Available: Tables giving X-ray crystal structure data for **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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