Synthesis and Structural Characterization of the Diborylated Organometallics 1,3-Bis(dibromoboryl)-1′,2′,3′,4′,5′-(pentamethyl)-ferrocene and 1,3-Bis(dibromoboryl)cymantrene

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Diborylated organometallic complexes can function as precursors for boron-bridged organometallic macromolecules. So far, mainly ferrocenylborane polymers featuring a 1,1′-connectivity pattern have been prepared from 1,1′-bis(dibromoboryl)ferrocene. In this paper we present the optimized synthesis protocols for 1,3-bis(dibromoboryl)-1′,2′,3′,4′,5′-(pentamethyl)ferrocene and 1,3-bis(dibromoboryl)cymantrene. Both compounds have been fully characterized by NMR spectroscopy as well as X-ray diffraction techniques and possess promising potential for the preparation of boron-bridged polymers with a 1,3-connectivity pattern.

Polymeric organoboranes are of versatile use as catalysts, sensor systems, or luminescent materials.[1–9] Another important class of compounds consists of metal-containing macromolecules that show useful properties such as electronic communication or cooperative magnetic behavior between the individual metal sites.[10–23] It is thus justified to expect that the combination of both Lewis acidic boron atoms and organometallic moieties will result in particularly intriguing compounds.

So far, only a few examples of boron-bridged organometallic polymers are known in the literature, almost all of them featuring ferrocene as the key building block.[24–33] Two different types have to be distinguished: (1) The first type is poly(ferrocenylene)s containing cationic, neutral, or anionic tetra-coordinated boron linkers. In most cases, these macromolecules have been prepared via coordination polymerization of diborylated organometallics and ditopic Lewis bases (e.g., $[-BMe_2fcBMe_2-bipy-]_n$;[31] fc = $(C_5H_4)_2Fe$, bipy = 2,2′-bipyridyl). Here, the boron atoms mainly serve the purpose of providing a Lewis acidic anchor group. (2) The second class of poly(ferrocenylene)s contains three-coordinated boron atoms that offer a

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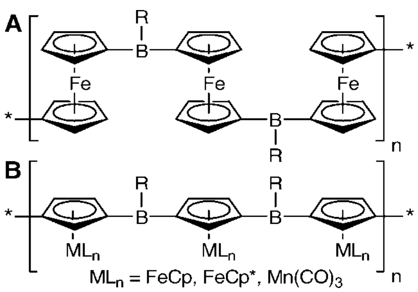


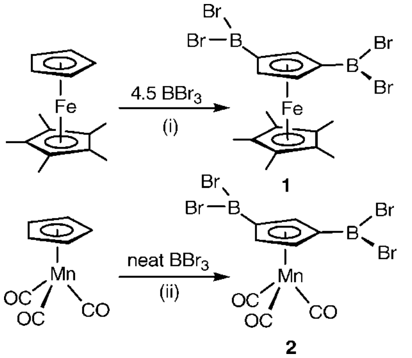
Figure 1. Boron-bridged poly(ferrocenylene)s **A** containing 1,1′-disubstituted ferrocenylene moieties and target polymers **B** containing 1,3-disubstituted organometallic fragments.

vacant p orbital for conjugative interaction between the bonded metal complexes (e.g., $[-B(Mes)fc-]_n$;[24] Mes = mesityl). Common to both types of polymers is the 1,1′-connectivity pattern at the ferrocene fragment; i.e., the polymer chain comes in at one cyclopentadienyl ring and goes out at the other (cf. **A**; Figure 1).

Our group has recently prepared various **A**-type polymers (R = Br, Mes, $O(CH_2)_4Br$) via a newly developed condensation reaction that employs 1,1′-bis(dibromoboryl)ferrocene as starting material and Et_3SiH as trigger compound.[24,25,34] According to cyclic voltammetry and UV/vis spectroscopy, these compounds show a significant degree of electronic interaction between the Fe(II) ions. Since it has been predicted that a 1,3-connectivity pattern should be superior to a 1,1′-pattern with regard to the electronic communication of the ferrocene units,[35,36] it is our aim to get access to **B**-type compounds (Figure 1) and to test this hypothesis.

Unfortunately, the synthesis of poly(ferrocenylene)s **B** is hampered by the poor availability of the required starting material 1,3-bis(dibromoboryl)ferrocene. The convenient electrophilic borylation of ferrocene with 2 equiv of BBr_3 leads almost exclusively to 1,1′-bis(dibromoboryl)ferrocene and gives only trace amounts of the 1,3-isomer.[37,38] It has, however, been shown that 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene can be prepared in reasonable yield from ferrocene and a large excess of BBr_3.[38,39] This result clearly proves that the desired 1,3-substitution pattern is electronically and sterically feasible.

Scheme 1. Synthesis of 1,3-Bis(dibromoboryl)-1′,2′,3′,4′,5′-(pentamethyl)ferrocene 1 and 1,3-Bis(dibromoboryl)cymantrene 2[a]



[a] (i) hexane, reflux, 6 h; (ii) reflux, 44 h.

To circumvent 1,1′-diborylation and to force the reaction toward 1,3-diborylation, we decided to switch from ferrocene to 1,2,3,4,5-(pentamethyl)ferrocene, in which one cyclopentadienyl ring is protected by permethylation while the other is still accessible for borylation [*Note*: In the following we will abbreviate 1,2,3,4,5-(pentamethyl)ferrocene as (pentamethyl)ferrocene]. Another possibility is to replace ferrocene by cymantrene, for which direct borylation to 1,3-bis(dibromoboryl)cymantrene has already been described.[37]

The purpose of this paper is to report the optimized synthesis and complete characterization of 1,3-bis(dibromoboryl)-1′,2′,3′,4′,5′-(pentamethyl)ferrocene (**1**; Scheme 1) and 1,3-bis(dibromoboryl)cymantrene (**2**; Scheme 1), which have promising potential as building blocks for **B**-type polymers.

Results and Discussion

Synthesis and NMR Spectroscopic Characterization. Compound **1** was synthesized in good yields from 4.5 equiv of BBr_3 and (pentamethyl)ferrocene in refluxing hexane. Since a significant degree of diborylation already occurs at ambient temperature, (pentamethyl)ferrocene appears to be more reactive toward BBr_3 than the parent ferrocene. This observation can be explained by the +I-effect of the five methyl groups.

By contrast, diborylation of cymantrene is much harder to achieve than diborylation of ferrocene due to the electron-withdrawing effect of the $Mn(CO)_3$ group. We obtained the best yields of **2** by keeping a mixture of cymantrene and neat BBr_3 at reflux temperature for about 40 h. This synthesis protocol is similar to the one employed for the preparation of 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene.[39]

Compounds **1** and **2** were characterized by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopy of C_6D_6 solutions.

The ^{11}B NMR spectrum of **1** shows one signal at 53.8 ppm, indicating the two boron atoms to be three-coordinated[40] and chemically equivalent. The chemical shift value of **1** is close to those of 1,3-bis(dibromoboryl)ferrocene ($\delta(^{11}B) = 53.0$) and 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene ($\delta(^{11}B) = 53.6$). The ^{1}H NMR spectrum of **1** reveals three signals with singlet, doublet, and triplet multiplicity (integral ratio 15:2:1), which are assigned to the five chemically equivalent methyl groups, the protons H4,5, and the H2 proton, respectively. Only four of the expected five signals are observed in the ^{13}C NMR spectrum of **1**, because the resonances of the borylated carbon atoms are broadened beyond detection due to $^{1}J_{CB}$ coupling and the fast quadrupolar relaxation of the boron nuclei.

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Table 1. Selected Crystallographic Data for 1 and 2

	1	2
formula	$C_{15}H_{18}B_2Br_4Fe$	$C_8H_3B_2Br_4MnO_3$
fw	595.40	543.30
color, shape	dark violet, block	light yellow, plate
temp (K)	173(2)	173(2)
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P-1$
a (Å)	15.0877(10)	6.7882(11)
b (Å)	18.6584(11)	10.6733(19)
c (Å)	13.8304(11)	11.313(2)
α (deg)	90	100.226(14)
β (deg)	93.375(6)	105.977(14)
γ (deg)	90	105.209(13)
V (Å^3)	3886.7(5)	732.3(2)
Z	8	2
$D_{\mathrm{calcd.}}$ (g cm^{-3})	2.035	2.464
F(000)	2272	500
μ (mm^{-1})	8.992	11.805
cryst size (mm^3)	0.29 × 0.27 × 0.24	0.21 × 0.18 × 0.07
no. of rflns collected	64 011	6497
no. of indep rflns (R_{int})	7368 (0.0999)	2722 (0.0852)
no. of data/restraints/params	7368/75/388	2722/0/164
GOF on F^2	1.096	1.076
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0709, 0.1557	0.0686, 0.1680
$R1$, $wR2$ (all data)	0.0983, 0.1701	0.0823, 0.1779
largest diff peak and hole (e Å^{-3})	0.718, −1.134	2.176, −1.532

Some trends in the chemical shift values of borylated ferrocenes are revealing in the context of the question: Are **A**-type or **B**-type compounds better suited to bring about electronic communication along the polymer chain? Introduction of BBr_2 substituents into a cyclopentadienyl ligand leads to a continuous and pronounced downfield shift of its ^{13}C (and ^1H) NMR resonances along the sequence ferrocene ($\delta(^{13}C) = 68.3$) → (dibromoboryl)ferrocene ($\delta(^{13}C) = 77.4, 78.4$) → 1,3-bis(dibromoboryl)ferrocene ($\delta(^{13}C) = 84.6, 86.1$). This deshielding of the corresponding carbon nuclei is diagnostic of a concomitant decrease of π-electron density in the ring. Contrary to that, if we compare the ^{13}C NMR data of the 1,3-$C_5H_3(BBr_2)_2$ ligand in **1**, 1,3-bis(dibromoboryl)ferrocene, and 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene, the differences in chemical shift values are negligibly small (<4 ppm). This is true, even though **1** contains an electron-rich Cp* ring whereas 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene possesses an electron-poor 1,3-bis(dibromoboryl)cyclopentadienyl moiety as second ligand. It is thus obvious that the Fe(II) ion buffers the influence of one cyclopentadienyl ligand on the other (cf. **A**) to a greater extent than the electronic interaction of a cyclopentadienyl ring with its substituents (cf. **B**).

The ^{11}B NMR signal of **2** appears at 51.0 ppm. In the ^1H NMR spectrum, the organometallic backbone gives rise to two resonances for the cyclopentadienyl protons with an integral ratio of 2:1 (d, H4,5; n.r., H2). Two ^{13}C NMR resonances are observed; the signals for the borylated carbon atoms and the CO ligands of **2** could not be detected.

In the IR spectrum, **2** has CO bands at 2038 cm^{-1} and 1967 cm^{-1}, compared to values $\tilde{\nu}$ (CO) = 2022 cm^{-1}/1934 cm^{-1} for (dibromoboryl)cymantrene and 2022 cm^{-1} (A_1)/1931 cm^{-1} (E) for parent cymantrene (toluene solutions).

X-ray Crystal Structure Determination. Crystal data and structure refinement details for **1** and **2** are compiled in Table 1.

The ferrocene derivative **1** crystallizes from hexane (monoclinic, $P2_1/c$) with two crystallographically independent molecules ($\mathbf{1_A}$, $\mathbf{1_B}$) in the asymmetric unit. In the solid state, the two cyclopentadienyl rings of $\mathbf{1_A}$ adopt a staggered conformation; the Cp* ligand of $\mathbf{1_B}$ is disordered over two positions. The molecular structures of $\mathbf{1_A}$ and $\mathbf{1_B}$ are identical within the experimental error margins so that only the structural parameters of $\mathbf{1_A}$ need to be discussed here.

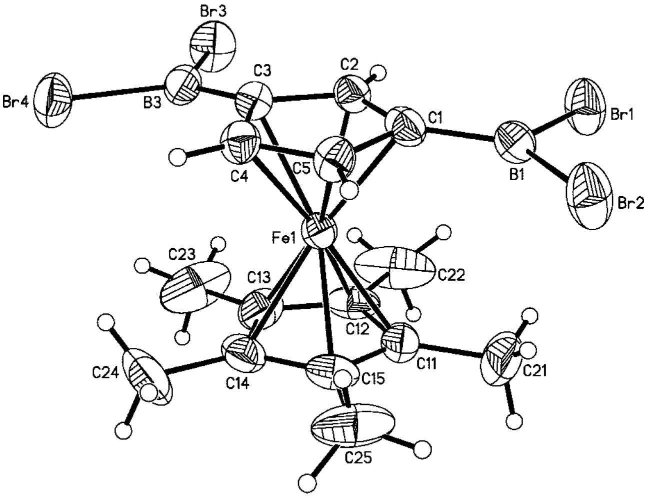

Figure 2. Molecular structure and numbering scheme of compound $\mathbf{1_A}$; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): B(1)−Br(1) = 1.912(11), B(1)−Br(2) = 1.915(11), B(1)−C(1) = 1.527(13), B(3)−Br(3) = 1.920(11), B(3)−Br(4) = 1.937(10), B(3)−C(3) = 1.478(14), C(1)−C(2) = 1.445(12), C(2)−C(3) = 1.438(12), C(3)−C(4) = 1.464(12), C(4)−C(5) = 1.403(12), C(1)−C(5) = 1.438(11), Fe(1)−COG(Cp*) = 1.679, Fe(1)−COG(Cp) = 1.667; Br(1)−B(1)−Br(2) = 117.6(5), C(1)−B(1)−Br(1) = 121.3(7), C(1)−B(1)−Br(2) = 120.9(8), Br(3)−B(3)−Br(4) = 116.1(5), C(3)−B(3)−Br(3) = 121.9(7), C(3)−B(3)−Br(4) = 121.9(7); B(1)Br(1)Br(2)//B(3)Br(3)Br(4) = 5.1, B(1)Br(1)Br(2)//Cp = 3.8, B(3)Br(3)Br(4)//Cp = 3.9, Cp//Cp* = 3.3; α*(B(1)) = 7.1, α*(B(3)) = 5.8. COG: centroid of the respective cyclopentadienyl ring.

The crystal structure analyses of **1** (Figure 2) and **2** (Figure 3) clearly prove them to be 1,3-diborylated species with three-coordinated boron atoms (sum of angles about B(1) and B(3) = 360°). In both cases, the dihedral angle between the two BBr_2 planes is smaller than 10°. The same is true for the angles between each cyclopentadienyl ring and its boryl substituents. This leads to the conclusion that there is no significant steric repulsion within the 1,3-$C_5H_3(BBr_2)_2$ ligands of **1** and **2**. Moreover, the conformations of the molecules permit a high degree of orbital overlap between the cyclopentadienyl π-electron system and the empty p orbitals of the boron atoms.

Interestingly, the C−C bond lengths of the borylated cyclopentadienyl rings vary in the comparatively broad interval between C(4)−C(5) = 1.403(12) Å and C(3)−C(4) = 1.464(12) Å in the ferrocene derivative $\mathbf{1_A}$ and C(4)−C(5) = 1.389(13) Å and C(1)−C(5) = 1.472(12) Å in the cymantrene species **2**. A similar bond alternance has been reported for the related compounds (dibromoboryl)ferrocene[41] and (dibromoboryl)cymantrene[42] and was attributed to some borafulvene character of the C_5H_4-BBr_2 moieties. If we superpose the two borafulvene resonance structures that can be drawn for each molecule of **1** and **2**, it becomes immediately apparent that C(4)−C(5) is the only bond that possesses double-bond character in *both* reso-

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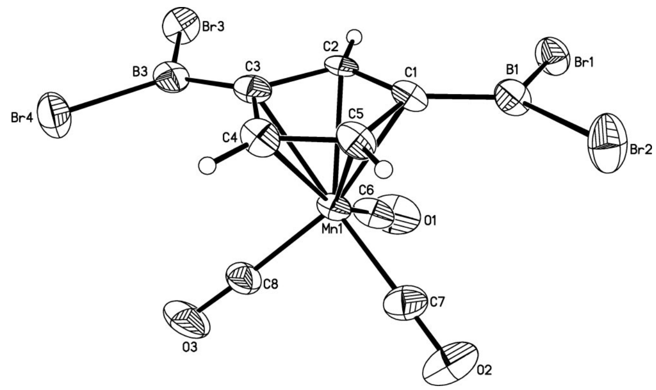

Figure 3. Molecular structure and numbering scheme of compound **2**; thermal ellipsoids are drawn at the 50% probability level. B(1)−Br(1) = 1.921(10), B(1)−Br(2) = 1.911(10), B(1)−C(1) = 1.524(14), B(3)−Br(3) = 1.921(10), B(3)−Br(4) = 1.914(10), B(3)−C(3) = 1.515(14), C(1)−C(2) = 1.452(11), C(2)−C(3) = 1.436(12), C(3)−C(4) = 1.460(12), C(4)−C(5) = 1.389(13), C(1)−C(5) = 1.472(12), Mn(1)−COG(Cp) = 1.774; Br(1)−B(1)−Br(2) = 118.4(6), C(1)−B(1)−Br(1) = 120.5(6), C(1)−B(1)−Br(2) = 121.1(7), Br(3)−B(3)−Br(4) = 117.6(5), C(3)−B(3)−Br(3) = 121.0(7), C(3)−B(3)−Br(4) = 121.4(7); B(1)Br(1)Br(2)//B(3)-Br(3)Br(4) = 9.7, B(1)Br(1)Br(2)//Cp = 8.8, B(3)Br(3)Br(4)//Cp = 2.5; α*(B(1)) = 7.6, α*(B(3)) = 3.7. COG: centroid of the cyclopentadienyl ring.

nance structures. As a consequence, one would expect C(4)−C(5) to be the shortest of all cyclopentadienyl C−C bonds, which nicely agrees with our experimental findings.

Bending of the three-coordinated boryl substituent out of the plane of the cyclopentadienyl ring toward the respective transition metal center is a regularly observed structural feature in the solid state structures of borylated ferrocenes and cymantrenes.[39,41–49] The dip angle α* = 180° − α (α = B−C_{ipso}−COG; COG: centroid of the Cp ring) has been introduced as a measure for the degree of this distortion.[45] Large values of α* are usually observed with strongly Lewis acidic boryl substituents. Moreover, α* tends to become smaller when additional boryl substituents are introduced into the organometallic core. Bending of an exocyclic BR_2 substituent is likely due to electronic interactions between filled d-type orbitals at Fe(II) or Mn(I) and the empty p orbital at boron.[45]

We determined dip angles α*(B(1)) = 7.1° and α*(B(3)) = 5.8° for $\mathbf{1_A}$; the corresponding values in $\mathbf{1_B}$ are 5.2° and 4.5°. These angles are significantly smaller than in (dibromoboryl)ferrocene (two crystallographically independent molecules in the asymmetric unit; α* = 17.7°/18.9°)[41] but compare well with the value of 1,1′-bis(dibromoboryl)ferrocene (α* = 9.1°).[48] In 1,1′,3,3′-tetrakis(dibromoboryl)ferrocene, only two of the boryl substituents show a significant bending toward the Fe(II) ion (α* = 6.8°), while the other two are not bent (α* = 0.1°).[39] It has, however, to be taken into account that the dip angles in compound **1** are not only influenced by the through-space Fe−B interaction but also by the steric repulsion between the BBr_2 fragments and the Cp* ring.

The diborylated complex **2** features dip angles α*(B(1)) = 7.6° and α*(B(3)) = 3.7°, which are again significantly smaller than the α* values of 11.4°[42] and 12.3°[44] that have been found in monoborylated cymantrenes.

Conclusion

As a result of our work, the two ditopic organometallic Lewis acids, 1,3-bis(dibromoboryl)-1′,2′,3′,4′,5′-(pentamethyl)ferrocene (**1**) and 1,3-bis(dibromoboryl)cymantrene (**2**), are now readily available. The solid state structures of **1** and **2** give no indication of steric repulsion between their two boryl substituents, and it is apparent that both molecules can adopt a conformation permitting π-electron delocalization from the cyclopentadienyl rings into both boryl substituents. Thus, complexes **1** and **2** have promising potential as building blocks for the preparation of boron-bridged organometallic polymers with a 1,3-connectivity pattern, which favors a high degree of charge delocalization along the polymer chain.

Experimental Section

General Remarks. All reactions were carried out under a nitrogen atmosphere using Schlenk tube techniques. Reaction solvents were freshly distilled under argon from Na/Pb alloy (hexane) and Na/benzophenone (toluene) prior to use; C_6D_6 was distilled under nitrogen from Na/benzophenone and stored in a Schlenk flask. NMR: Bruker AM 250, Avance 300, and Avance 400. Chemical shifts are referenced to residual solvent signals (^{1}H, ^{13}C{^{1}H}) or external $BF_3 \cdot Et_2O$ (^{11}B{^{1}H}). Abbreviations: s = singlet, d = doublet, tr = triplet, n.r. = multiplet expected in the ^{1}H NMR spectrum but not resolved, n.o. = signal not observed. BBr_3 was stored over mercury under a nitrogen atmosphere. Cymantrene and BBr_3 are commercially available; (pentamethyl)ferrocene can be synthesized according to a literature procedure.[50]

Synthesis of 1. BBr_3 (4.89 g, 1.85 mL, 19.5 mmol) was added via syringe to a suspension of (pentamethyl)ferrocene (1.11 g, 4.3 mmol) in hexane (30 mL) at room temperature. The resulting mixture was heated to reflux for 6 h and the released HBr condensed into a cold trap cooled with liquid nitrogen. The reaction mixture was filtered through a frit while still hot. The filtrate was evaporated to dryness *in vacuo* to give **1** as a red to purple microcrystalline solid; further purification was not required. Yield: 2.17 g (84%). Dark violet single crystals for X-ray diffraction analysis were grown from hexane at −30 °C over a period of 2 weeks. ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ 53.8 ($h_{1/2}$ = 340 Hz). ^{1}H NMR (300.0 MHz, C_6D_6): δ 1.56 (s, 15H, C_5Me_5), 4.47 (d, 2H, $^4J_{HH}$ = 1.1 Hz, H4,5), 4.97 (tr, 1H, $^4J_{HH}$ = 1.1 Hz, H2). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 10.4 ($C_5\mathit{Me}_5$), 83.5 (C_5Me_5), 87.1 (C4,5), 88.3 (C2), n.o. (CB). The identity of the single crystal used for the structure determination and the bulk material was confirmed by X-ray powder diffractometry.

Synthesis of 2. Cymantrene (4.92 g, 24.00 mmol) was dissolved in neat BBr_3 (20 mL) and the mixture refluxed for 44 h. The released HBr was condensed into a cold trap cooled with liquid nitrogen. The reaction mixture was allowed to cool to room temperature, a brown precipitate was removed by filtration, and the filtrate was slowly evaporated *in vacuo* to give **2** in the form of yellow crystals.

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Yield: 12.06 g (93%). IR (toluene, cm^{-1}): $\tilde{\nu}$ (CO) 2038 (s), 1967 (s). ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ 51.0 ($h_{1/2}$ = 250 Hz). ^{1}H NMR (250.1 MHz, C_6D_6): δ 4.66 (d, 2H, $^{4}J_{HH}$ = 1.0 Hz, H4,5), 5.67 (n.r., 1H, H2). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 96.5 (C4,5), 106.2 (C2), n.o. (CO, CB). The identity of the single crystal used for the structure determination and the bulk material from which the crystal was selected was confirmed by X-ray powder diffractometry.

X-ray Crystal Structure Analysis of 1 and 2. Data were collected on a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo Kα radiation. Empirical absorption corrections were performed using the MULABS[51] option in PLATON.[52] The structures were solved by direct methods using the program SHELXS[53] and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97.[54] Compound **1** crystallizes with two crystallographically independent molecules in the asymmetric unit ($\mathbf{1_A}$, $\mathbf{1_B}$). The Cp* ring of $\mathbf{1_B}$ is disordered over two sites with site occupation factors of 0.45(1) and 0.55(1). Bond lengths of the two disordered moieties were restrained to be equal to those of the ordered molecule $\mathbf{1_A}$.

CCDC reference numbers: 662925 (**1**) and 662924 (**2**).

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Supporting Information Available: Crystallographic data of **1** and **2** in the Crystallographic Information File (CIF) format. This material is available free of charge via the Internet at http://pubs.acs.org.

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