934 *Organometallics* **2010**, *29*, 934–938
DOI: 10.1021/om9009813

ORGANOMETALLICS
Article

1,1-Diboration of Isocyanides with [2]Borametalloarenophanes

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Received November 10, 2009

A series of new [3]diboracarbametalloarenophanes was synthesized by reaction of [2]borametalloarenophanes or [3]diboraplatinametalloarenophanes with isocyanides and was fully characterized by multinuclear NMR spectroscopy and, in the case of [Fe{η^5-$C_5H_4B(NMe_2)$}$_2$C=N-*t*-Bu], additionally by X-ray diffraction analysis.

Introduction

Over the past two decades transition-metal-catalyzed hydroboration starting from moderately reactive boranes such as CatBH and PinBH (Cat = 1,2-$O_2C_6H_4$, Pin = $OCMe_2CMe_2O$) has become a well-established protocol for the functionalization of organic substrates.[1] Likewise, the use of diboranes(4) $R_2B{-}BR_2$ for the borylation or diboration of unsaturated hydrocarbons represents a facile method for the generation of organoboranes, many of which are key intermediates in organic synthesis.[2] This method commonly employs a catalytic protocol involving rather stable diboranes(4) such as CatB−BCat (**1**) or PinB−BPin (**2**) (Figure 1) and a late-transition-metal catalyst.[3] The list of possible substrates ranges from alkynes[3a,4] to alkenes,[4b,e,5] CO,[5d,6] NN,[7] and α,β-unsaturated carbonyl compounds.[4f,8] It is noteworthy that in one case an unusual 1,1-diboration of a vinylboronate was observed.[5l] In contrast to these well-established transformations, very little is known about the corresponding diboration of isocyanides and only from instances where the B−B bond of the diboration reagent is part of a strained heterocycle rather than an acyclic diborane(4).

Paetzold et al. reported the insertion of isocyanides[9] and of the isoelectronic CO[10] into the highly strained B−B bond of tri-*tert*-butylazadiboriridine (**3**) (Figure 1). Depending on the size of the isocyanide, monomeric or dimeric products were isolated, whereas in the case of the smaller CO only dimeric compounds were obtained. The postulated mechanism for the formation of the latter includes initial generation of the monomeric insertion product and subsequent intermolecular attack at one of the boron atoms by the nucleophilic oxygen or nitrogen center (Scheme 1).

A similar reactivity with respect to the insertion of CO and isocyanides, respectively, into a B−B bond was reported

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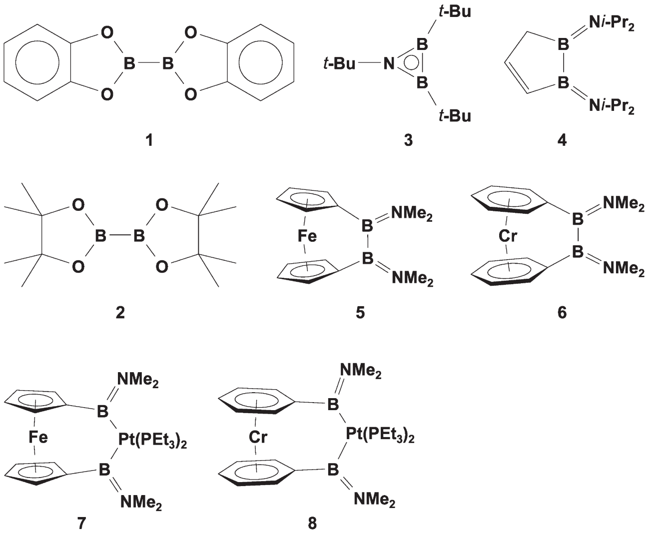
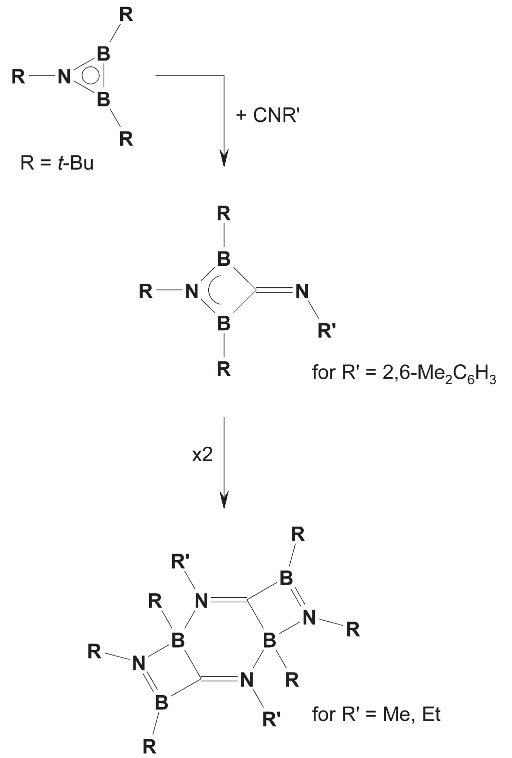


Figure 1. Precursors for diboration reactions.

Scheme 1. Reaction of Tri-*tert*-butylazadiboriridine with Isocyanides



by Siebert et al. in 1998.[11] They presented corresponding reactions of the strained 1,2-diboracyclopent(3)ene **4** (Figure 1), which led to monomeric products due to the steric demand of the isocyanides and the boron-bound moiety. Again, insertion of CO into the B−B bond afforded dimeric products. While few of these dimeric species have been structurally characterized, the constitution of the initial insertion products was only derived from multinuclear NMR spectroscopy in solution. The insertion of small molecules such as alkynes in particular was also observed for [2]silametalloarenophanes. Thus, transition-metal-catalyzed 1,2-disilation of C−C triple bonds by [2]disilaferrocenophanes was first reported by Manners et al. in 1992,[12] whereas our group studied the insertion of propyne into the Si−Si bond of [2]silachromoarenophanes in 2007.[13]

In recent years, a number of [2]borametalloarenophanes have been reported and their reactivity toward insertion reactions into the B−B bond has been studied. The [2]boraferrocenophane **5** (Figure 1), initially synthesized by Wrackmeyer and Herberhold in 1997[14] and subsequently structurally characterized,[15] constitutes the first example of these species, followed by the [2]borachromoarenophane **6** (Figure 1), which we synthesized in 2004.[16] Since then, various [2]borametalloarenophanes have been synthesized from different transition metals such as V,[17] Cr,[18] and Mn.[19] It was revealed that [2]borametalloarenophanes display a certain degree of molecular strain that renders the B−B bond very reactive, in particular with respect to oxidative addition to low-valent transition metals: i.e., platinum. Therefore, they have already proven ideal precursors for the functionalization of organic substrates such as alkynes[4g] or diazo compounds[7] via transition-metal-catalyzed diboration.

Results and Discussion

Herein we present a series of new [3]diboracarbametalloarenophanes that were obtained (i) by reaction of isocyanides with [2]borametalloarenophane and alternatively (ii) from a [3]diboraplatinametalloarenophane. We also present the first molecular structure of a monomeric 1,1-diborated isocyanide.

The new complexes **9**−**12** are formed by adding the isocyanide to a solution of the respective [2]borametalloarenophane

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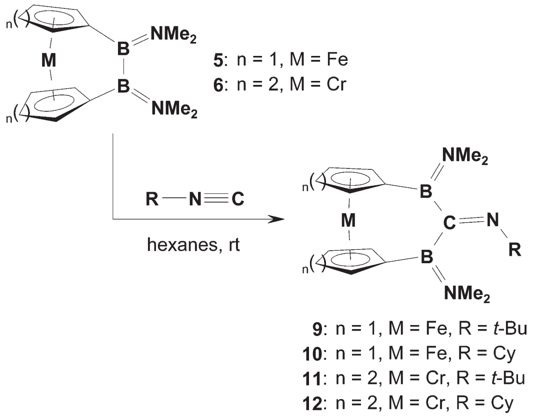
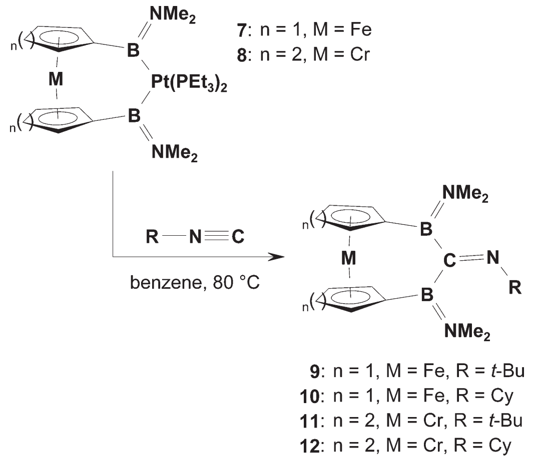
Scheme 2. Syntheses of 9−12 Starting from [2]Borametalloarenophanes



Scheme 3. Syntheses of 9−12 Starting from [3]Diboraplatinametalloarenophanes



in hexanes at room temperature (Scheme 2). It should be noted that according to multinuclear NMR spectroscopy no soluble side products are formed during these reactions, thus indicating quantitative conversion of the starting materials. The pure compounds can be obtained in yields of 28−55% as orange to reddish brown crystals by cooling the respective reaction solution to −30 °C. Nonetheless, complete removal of the reaction solvent or concentration of the reaction solution in vacuo has to be omitted, as it leads partially to a powdery material of poor solubility, which probably suggests the formation of an oligomeric compound, comparable to the dimeric species depicted in Scheme 1. However, attempts to generate a defined dimerization product of **9** or **10** by drying the reaction mixture and redissolving the solid residue repeatedly led to product mixtures. The aforementioned pure, crystalline compounds **9**−**12** proved to be inert toward oligomerization in the solid state and are readily soluble in aliphatic and aromatic solvents. Likewise, dilute solutions of these species showed no tendency toward aggregation at ambient temperature over a period of several days. Compounds **9** and **10** also display a moderate stability to air and moisture, whereas **11** and **12** tend to undergo rapid hydrolysis.

An alternative access to **9**−**12** is provided by the reaction of [3]diboraplatinametalloarenophanes **7** and **8** (Figure 1) with the corresponding isocyanides (Scheme 3). Surprisingly, this reaction is not facilitated by the precoordination of the boryl groups to the platinum center (i.e., the metal-induced activation of the B−B bond), as commonly observed for the metal-mediated 1,2-diboration of alkynes. In fact, the use of **7** or **8** as diborane(4) precursors requires harsher conditions and the reaction mixtures have to be heated to 80 °C so as to achieve completion. This finding indicates that the release of molecular strain, as observed for the conversion of **5** and **6** (but not in the case of **7** and **8**) into the final products, contributes to the driving force of this reaction (vide infra).

Insertion of an isocyanide with its stereochemically active lone pair at the nitrogen center into the B−B bond of the [2]borametallocenophanes leads to an unsymmetrical bridge and thus a decrease of the molecular symmetry from C_{2v} to C_1. Hence, in contrast to only two singlets for the NMe_2 protons at 2.78 and 2.82 ppm found for **5**, complexes **9** and **10** display four singlets each in the ^1H NMR spectra between 2.57 and 2.84 ppm (**9**) and between 2.62 and 2.88 ppm (**10**). The Cp-bound protons of **9** and **10** show eight multiplets ranging from 4.04 to 4.38 ppm and from 4.02 to 4.38 ppm, respectively. The protons of the *t*-Bu group of **9** show a singlet at 1.44 ppm which is shifted downfield with respect to the resonance at 0.91 ppm for *t*-BuNC.[20] Likewise, the CH proton of **10** can be detected at 3.31 ppm and thus appears deshielded with respect to the corresponding signal at 2.91 ppm for CyNC,[21] while the remaining protons of the cyclohexyl ring show four complex multiplets between 1.35 and 2.04 ppm.

As discussed before in the cases of **9** and **10**, the ^1H NMR spectra of **11** and **12** also exhibit four resonances for the NMe_2 protons between 2.60 and 2.83 ppm (**11**) and between 2.65 and 2.89 ppm (**12**), respectively, in contrast to only two signals found for **6** at 2.80 and 2.84 ppm.

In the ^{13}C NMR spectra of all new complexes the ipso carbon atoms of the metal-bound aromatic rings could not be detected, due to quadrupolar broadening induced by the neighboring boron nuclei. This has already been observed in the corresponding [4]diboradicarbametalloarenophanes.[4g] However, the quaternary carbon atoms of the imine group were detected as very broad signals between 198 and 204 ppm in long-range $^{13}C-^1H$ NMR correlation experiments. As expected and already discussed for the ^1H NMR spectra, the decrease of symmetry in the products with respect to the starting materials **5** and **6** leads to a corresponding multitude of resonances in the ^{13}C NMR spectra.

With regard to the ^{11}B NMR spectra, one should also expect to see two different signals due to C_1 symmetry of the products. That is indeed the case for **9**, which shows two signals at 38.9 and 42.1 ppm, and **11**, which displays two signals at 40.0 and 43.8 ppm. However, for **10** and **12** only one very broad signal at 40.6 and 41.1 ppm, respectively, could be resolved. As expected, the ^{11}B NMR resonances of all four compounds exhibit a slight upfield shift compared to those of the starting compounds **5** at 44.4 ppm and **6** at 46.3 ppm, as already observed in case of the [4]diboradicarbametalloarenophanes mentioned before.[4g]

Single crystals of **9** suitable for X-ray analysis were obtained by crystallization from hexanes (Figure 2). The structural data prove that the isocyanide substrate is diborated in a 1,1-fashion, in contrast to corresponding reactions with alkynes that are diborated in a 1,2-fashion.

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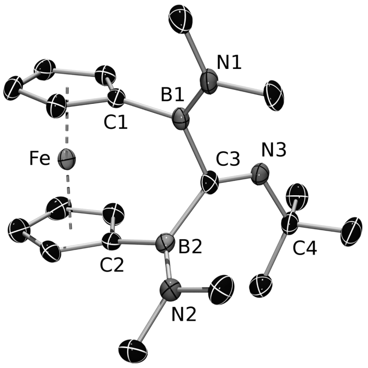

Figure 2. Molecular structure of **9**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability. Selected bond lengths (Å) and angles (deg): C1−B1 = 1.582(5), C2−B2 = 1.569(5), B1−N1 = 1.386(4), B2−N2 = 1.387(5), B1−C3 = 1.597(5), B2−C3 = 1.606(5), C3−N3 = 1.291(4), N3−C4 = 1.478(4); C1−B1−C3 = 117.3(3), C2−B2−C3 = 116.6(3), B1−C3−B2 = 111.5(3), B1−C3−N3 = 115.7(3), B2−C3−N3 = 132.7(3), C3−N3−C4 = 123.9(3), α = 5.4, δ = 176.2 (see text).

As expected, the degree of molecular strain in **9** is less pronounced than in the starting material **5**, due to the extension of the bridge from two to three atoms. Thus, the tilt angle α, which describes the mutual inclination of the metal-bound cyclopentadienyl rings, is reduced from 12.8° for **5** to 5.4°. This value is comparable to that of 5.0° found for the [3]diboraplatinaferrocenophane **7**, which is also characterized by a bridging unit consisting of three atoms.[4g] Likewise, the angle centroid(1)−Fe−centroid(2) of 176.2° is enlarged in comparison to that of **5** (170.1°), thus resembling the corresponding value of **7** (175.7°) and indicating an almost nonstrained, ferrocene-like geometry. The cyclopentadienyl rings exhibit a slightly staggered conformation, as indicated by a torsion angle Cp centroid(1)−C1−C2−Cp centroid(2) of 12.2° that falls between the corresponding values for **5** (16.0°) and **7** (6.0°). The B−C−B bridge adopts a folded conformation: i.e., the N1 and N2 atoms are situated opposite to the C3 center with respect to the plane defined by B1, Fe, and B2. The C−N bond length of 1.291(4) Å and the C3−N3−C4 angle of 123.9(3)° lie in the expected range for a corresponding imine double bond.[22] The overall geometry of the cyclopentadienyl rings is normal, and likewise, the atoms B1, B2, and C3 display the expected planar coordination, as indicated by angle sums of 359.9, 359.0, and 359.9°, respectively.

Conclusions

To conclude, we have described the four new, fully characterized [3]diboracarbametalloarenophanes [M{η^n-C$_n$H$_{n-1}$B(NMe$_2$)}$_2$C=NR] (M = Fe, n = 5, R = *t*-Bu, Cy; M = Cr, n = 6, R = *t*-Bu, Cy). These new species were synthesized by two different ways: i.e., by 1,1-diboration of the isocyanide RNC (R = *t*-Bu, Cy) with a [2]borametalloarenophane [M{η^n-C$_n$H$_{n-1}$B(NMe$_2$)}$_2$] (M = Fe, n = 5; M = Cr, n = 6) or a [3]diboraplatinametalloarenophane [M{η^n-C$_n$H$_{n-1}$B(NMe$_2$)}$_2$Pt(PEt$_3$)$_2$] (M = Fe, n = 5; M = Cr, n = 6). In addition to that, the first X-ray diffraction study of a monomeric diborated isocyanide, i.e.[Fe{η^5-C$_5$H$_4$B(NMe$_2$)}$_2$C=N-*t*-Bu], was conducted.

Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk and glovebox techniques. Solvents were distilled from molten alkali metal, degassed, and stored over molecular sieves (4 Å) under argon. Deuterated solvents were degassed by three freeze−pump−thaw cycles and stored under argon. [Fe{η^5-C$_5$H$_4$B(NMe$_2$)}$_2$] (**5**),[14] [Cr{η^5-C$_6$H$_5$B(NMe$_2$)}$_2$] (**6**),[16] [Fe{η^5-C$_5$H$_4$B(NMe$_2$)}$_2$Pt(PEt$_3$)$_2$] (**7**),[4g] and [Cr{η^6-C$_6$H$_5$B(NMe$_2$)}$_2$Pt(PEt$_3$)$_2$] (**8**)[4g] were prepared according to known methods. The isocyanides were purchased from Aldrich and used without further purification.

NMR experiments were performed on a Bruker Avance 200 (^{1}H, 200.130 MHz; ^{11}B, 64.210 MHz; ^{31}P, 81.014 MHz) or a Bruker Avance 500 (^{1}H, 500.130 MHz; ^{11}B, 160.462 MHz; ^{13}C, 125.758 MHz). ^{1}H NMR and ^{13}C NMR spectra were calibrated to TMS; in the case of ^{11}B NMR experiments BF$_3$·OEt$_2$ was used as the external standard. Elemental analyses were performed on a Vario Micro Cube elemental analyzer.

Due to the toxicity and the very unpleasant odor of the isocyanides, all glassware was washed with HCl$_{aq.}$/EtOH (1:10) after use.

Synthesis of [Fe{η^5-C$_5$H$_4$B(NMe$_2$)}$_2$C=N-*t*-Bu] (9). (a) To a stirred solution of 100 mg (0.340 mmol) of [Fe{η^5-C$_5$H$_4$B(NMe$_2$)}$_2$] (**5**) in 5 mL of hexanes was added 39 μL (28.3 mg) of *t*-BuNC via syringe. In doing so, the color of the solution changed from orange-red to orange. The solution was filtered and cooled to −30 °C for 3 d. The precipitate was isolated by decanting the cooled mother liquor, predried under a stream of argon, and subsequently dried in vacuo. The product was isolated as an orange powdery solid (53 mg, 0.139 mmol, 41%) and analyzed by multinuclear NMR spectroscopy. Single crystals suitable for X-ray diffraction analysis were obtained by redissolving the solid in hexanes and allowing the solvent to evaporate slowly.

(b) A 20 mg portion (0.028 mmol) of [Fe{η^5-C$_5$H$_4$B(NMe$_2$)}$_2$Pt(PEt$_3$)$_2$] (**7**) was dissolved in 0.5 mL of benzene-d_6, and a drop of *t*-BuNC was added. The solution was heated to 80 °C, and the reaction progress was monitored by NMR spectroscopy. The color of the solution thereby changed from orange-red to orange. After 1 h no signals for **7** could be observed.

^{1}H NMR (500.130 MHz, C$_6$D$_6$): δ 1.44 (s, C(CH_3)$_3$, 9H), 2.57 (s, NCH_3, 3H), 2.61 (s, NCH_3, 3H), 2.64 (s, NCH_3, 3H), 2.84 (s, NCH_3, 3H), 4.04 (m, C$_5H_4$, 1H), 4.08 (m, C$_5H_4$, 1H), 4.18 (m, C$_5H_4$, 1H), 4.20 (m, C$_5H_4$, 1H), 4.29 (m, C$_5H_4$, 1H), 4.30 (m, C$_5H_4$, 1H), 4.33 (m, C$_5H_4$, 1H), 4.38 ppm (m, C$_5H_4$, 1H). ^{11}B{^{1}H} NMR (160.462 MHz, C$_6$D$_6$): δ 38.9 (br), 42.1 ppm (br). ^{13}C{^{1}H} NMR (125.758 MHz, C$_6$D$_6$): δ 30.3 (C(CH$_3$)$_3$), 39.6 (NCH$_3$), 40.5 (NCH$_3$), 40.7 (NCH$_3$), 41.7 (NCH$_3$), 61.5 (C(CH$_3$)$_3$), 69.9 (C_5H$_4$), 70.5 (C_5H$_4$), 70.7 (C_5H$_4$), 71.4 (C_5H$_4$), 71.6 (C_5H$_4$), 72.0 (C_5H$_4$), 74.4 (C_5H$_4$), 76.6 (C_5H$_4$), 199 ppm (B$_2$$C$N-*t*-Bu). Anal. Calcd for C$_{19}$H$_{29}$B$_2$FeN$_3$ (376.92): C, 60.54; H, 7.75; N, 11.15. Found: C, 60.44; H, 7.57; N, 10.58.

Synthesis of [Fe{η^5-C$_5$H$_4$B(NMe$_2$)}$_2$C=NCy] (10). (a) A 100 mg portion (0.340 mmol) of **5** was dissolved in 5 mL of hexanes. When 42 μL (37.2 mg) of CyNC was added via syringe, the color of the solution changed from orange-red to orange. The solution was filtered and cooled to −30 °C for 3 d. The cooled mother liquor was decanted, and the formed solid was predried under a stream of argon and then dried in vacuo. The product was isolated as an orange-red solid (75 mg, 0.187 mmol, 55%) and analyzed by multinuclear NMR spectroscopy.

(b) A 20 mg (0.028 mmol) portion of **7** was dissolved in 0.5 mL of benzene-d_6, and 1 drop of CyNC was added. The solution was heated to 80 °C, and the reaction progress was monitored by NMR spectroscopy. The color of the solution changed thereby from orange-red to orange. After 1 h no signals for **7** could be observed.

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^{1}H NMR (500.130 MHz, C_6D_6): δ 1.35−1.49 (m, Cy_{CH_2}, 3H), 1.65 (m, Cy_{CH_2}, 1H), 1.90 (m, Cy_{CH_2}, 1H), 1.93−2.04 (m, Cy_{CH_2}, 6H), 2.62 (s, $\mathrm{NC}H_3$, 3H), 2.65 (s, $\mathrm{NC}H_3$, 3H), 2.67 (s, $\mathrm{NC}H_3$, 3H), 2.88 (s, $\mathrm{NC}H_3$, 3H), 3.31 (m, Cy_{CH}, 1H), 4.02 (m, $\mathrm{C_5}H_4$, 1H), 4.05 (m, $\mathrm{C_5}H_4$, 1H), 4.22 (m, $\mathrm{C_5}H_4$, 2H), 4.28 (m, $\mathrm{C_5}H_4$, 2H), 4.36 (m, $\mathrm{C_5}H_4$, 1H), 4.38 ppm (m, $\mathrm{C_5}H_4$, 1H). ^{11}B{^{1}H} NMR (160.462 MHz, C_6D_6): δ 40.6 ppm (vbr). ^{13}C{^{1}H} NMR (125.758 MHz, C_6D_6): δ 25.0 ($\mathrm{Cy}_{\mathit{C}\mathrm{H_2}}$), 25.0 ($\mathrm{Cy}_{\mathit{C}\mathrm{H_2}}$), 26.6 ($\mathrm{Cy}_{\mathit{C}\mathrm{H_2}}$), 34.3 ($\mathrm{Cy}_{\mathit{C}\mathrm{H_2}}$), 35.8 ($\mathrm{Cy}_{\mathit{C}\mathrm{H_2}}$), 39.9 ($\mathrm{N}C\mathrm{H_3}$), 40.4 ($\mathrm{N}C\mathrm{H_3}$), 40.6 ($\mathrm{N}C\mathrm{H_3}$), 41.6 ($\mathrm{N}C\mathrm{H_3}$), 70.0 ($C_5\mathrm{H_4}$), 70.0 ($C_5\mathrm{H_4}$), 70.5 ($C_5\mathrm{H_4}$), 71.0 ($\mathrm{Cy}_{\mathit{C}\mathrm{H}}$), 71.2 ($C_5\mathrm{H_4}$), 71.4 ($C_5\mathrm{H_4}$), 71.9 ($C_5\mathrm{H_4}$), 74.4 ($C_5\mathrm{H_4}$), 75.6 ($C_5\mathrm{H_4}$), 203 ppm (vbr, $\mathrm{B_2}C\mathrm{NCy}$). Anal. Calcd for $C_{21}H_{31}B_2FeN_3$ (402.96): C, 62.59; H, 7.75; N, 10.43. Found: C, 62.58; H, 7.77; N, 10.31.

Synthesis of [Cr{$\boldsymbol{\eta^6}$-$\mathbf{C_6H_5B(NMe_2)}$}$_\mathbf{2}$C=N-*t*-Bu] (11). (a) To a stirred solution of 100 mg (0.316 mmol) of [Cr{η^5-$C_6H_5B(NMe_2)$}$_2$] (**6**) in 5 mL of hexanes was added 36 μL (26.3 mg) of *t*-BuNC via syringe. In doing so, the color of the solution changed from red to orange-red. The solution was filtered and cooled to −30 °C for 3 d. The cooled mother liquor was decanted, and the precipitate was first dried under a stream of argon and then in vacuo, yielding the product as a reddish brown powdery solid (39 mg, 0.098 mmol, 31%) that was analyzed by multinuclear NMR spectroscopy.

(b) A 20 mg portion (0.027 mmol) of [Cr{η^6-$C_6H_5B(NMe_2)$}$_2$Pt(PEt_3)$_2$] (**8**) was dissolved in 0.5 mL of benzene-d_6, and 1 drop of *t*-BuNC was added. The solution was then heated to 80 °C, and the reaction progress was monitored by NMR spectroscopy. The color of the solution changed thereby from dark red to red. After 1 h no signals for **8** could be observed.

^{1}H NMR (500.130 MHz, C_6D_6): δ 1.45 (s, $\mathrm{C(C}H_3)_3$, 9H), 2.60 (s, $\mathrm{NC}H_3$, 3H), 2.62 (s, $\mathrm{NC}H_3$, 3H), 2.69 (s, $\mathrm{NC}H_3$, 3H), 2.83 (s, $\mathrm{NC}H_3$, 3H), 4.23 (m, $\mathrm{C_6}H_5$, 2H), 4.40 (m, $\mathrm{C_6}H_5$, 6H), 4.56 ppm (m, $\mathrm{C_6}H_5$, 2H). ^{11}B{^{1}H} NMR (160.462 MHz, C_6D_6): δ 40.0 (br), 43.8 ppm (br). ^{13}C{^{1}H} NMR (125.758 MHz, C_6D_6): δ 30.4 ($\mathrm{C(}C\mathrm{H_3)_3}$), 39.6 ($\mathrm{N}C\mathrm{H_3}$), 40.5 ($\mathrm{N}C\mathrm{H_3}$), 41.0 ($\mathrm{N}C\mathrm{H_3}$), 42.0 ($\mathrm{N}C\mathrm{H_3}$), 61.7 ($C\mathrm{(CH_3)_3}$), 75.3 ($C_6\mathrm{H_5}$), 76.4 ($C_6\mathrm{H_5}$), 76.4 ($C_6\mathrm{H_5}$), 76.5 ($C_6\mathrm{H_5}$), 76.7 ($C_6\mathrm{H_5}$), 76.8 ($C_6\mathrm{H_5}$), 76.9 ($C_6\mathrm{H_5}$), 77.6 ($C_6\mathrm{H_5}$), 78.0 ($C_6\mathrm{H_5}$), 81.0 ($C_6\mathrm{H_5}$), 197 ppm ($\mathrm{B_2}C$N-*t*-Bu). Anal. Calcd for $C_{21}H_{31}B_2CrN_3$ (399.11): C, 63.19; H, 7.83; N, 10.53. Found: C, 62.66; H, 7.74; N, 10.15.

Synthesis of [Cr{$\boldsymbol{\eta^6}$-$\mathbf{C_6H_5B(NMe_2)}$}$_\mathbf{2}$C=NCy] (12). (a) A 100 mg portion (0.316 mmol) of **6** was dissolved in 5 mL of hexanes, and 39 μL (34.5 mg) of CyNC was added via syringe, whereupon the color of the solution changed from red to orange-red. The solution was filtered and cooled to −30 °C for 3 d. The cooled mother liquor was decanted, and the precipitate was predried under a stream of argon and afterward dried in vacuo. The product was isolated as a dark red solid in a yield of 38 mg (0.088 mmol, 28%) and analyzed by multinuclear NMR spectroscopy.

(b) A 20 mg portion (0.027 mmol) of **8** was dissolved in 0.5 mL of benzene-d_6, and a drop of CyNC (excess) was added. The solution was heated to 80 °C, and the reaction progress was monitored by NMR spectroscopy. The color of the solution changed thereby from dark red to red. After 1 h no signals for **8** could be observed.

^{1}H NMR (500.130 MHz, C_6D_6): δ 1.35−1.48 (m, Cy_{CH_2}, 3H), 1.64 (m, Cy_{CH_2}, 1H), 1.86−2.14 (m, $\mathrm{C}H_{2\,\mathrm{Cy}}$, 6H), 2.65 (s, $\mathrm{NC}H_3$, 3H), 2.70 (s, $\mathrm{NC}H_3$, 3H), 2.70 (s, $\mathrm{NC}H_3$, 3H), 2.89 (s, $\mathrm{NC}H_3$, 3H), 3.41 (m, Cy_{CH}, 1H), 4.20 (m, $\mathrm{C_6}H_5$, 1H), 4.30 (m, $\mathrm{C_6}H_5$, 1H), 4.42 (m, $\mathrm{C_6}H_5$, 6H), 4.55 (m, $\mathrm{C_6}H_5$, 1H), 4.75 ppm (m, $\mathrm{C_6}H_5$, 1H). ^{11}B{^{1}H} NMR (160.462 MHz, C_6D_6): δ 41.1 ppm (vbr). ^{13}C{^{1}H} NMR (125.758 MHz, C_6D_6): δ 25.0 ($C_6\mathrm{H_{11}}$), 25.2 ($C_6\mathrm{H_{11}}$), 26.6 ($C_6\mathrm{H_{11}}$), 34.2 ($C_6\mathrm{H_{11}}$), 36.2 ($C_6\mathrm{H_{11}}$), 40.0 ($\mathrm{N}C\mathrm{H_3}$), 40.5 ($\mathrm{N}C\mathrm{H_3}$), 40.5 ($\mathrm{N}C\mathrm{H_3}$), 41.8 ($\mathrm{N}C\mathrm{H_3}$), 71.1 ($C_6\mathrm{H_{11\,CH}}$), 75.3 ($C_6\mathrm{H_5}$), 75.6 ($C_6\mathrm{H_5}$), 76.3 ($C_6\mathrm{H_5}$), 76.5 ($C_6\mathrm{H_5}$), 76.6 ($C_6\mathrm{H_5}$), 76.6 ($C_6\mathrm{H_5}$), 76.7 ($C_6\mathrm{H_5}$), 77.5 ($C_6\mathrm{H_5}$), 78.4 ($C_6\mathrm{H_5}$), 79.9 ($C_6\mathrm{H_5}$), 201 ppm (vbr, $\mathrm{B_2}C\mathrm{NCy}$). Anal. Calcd for $C_{23}H_{33}B_2CrN_3$ (415.15): C, 64.97; H, 7.82; N, 9.89. Found: C, 64.02; H, 7.82; N, 9.89.

Crystal Structure Determination. The crystal data of **9** were collected on a Bruker D8 diffractometer with an Apex CCD area detector and graphite-monochromated Mo Kα radiation. The structure was solved using direct methods, refined with the Shelx software package,[23] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations.

Crystal data for **9**: $C_{19}H_{29}B_2FeN_3$, $M_r = 376.92$, yellow plate, $0.24 \times 0.15 \times 0.03$ mm^3, monoclinic, space group $P2_1/n$, $a = 9.8191(10)$ Å, $b = 20.866(2)$ Å, $c = 9.8839(10)$ Å, $\beta = 106.474(2)°$, $V = 1941.9(3)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.289$ g cm^{-3}, $\mu = 0.782$ mm^{-1}, $F(000) = 800$, $T = 168(2)$ K, R1 = 0.0843, wR2 = 0.1304, 3873 independent reflections ($2\theta \leq 52.34°$), 233 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-753234. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der chemischen Industrie (FCI) for financial support.

Supporting Information Available: A CIF file giving crystallographic data for compound **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112–122.