Oligonuclear Organometallic Complexes with Boron-Nitrogen Bridges

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The facile formation of boron-nitrogen bridges allows the one-step assembly of oligonuclear organometallic complexes. By the reaction of 1-(dibromoboryl)ferrocene (**1a**) and 1,1′-bis(dibromoboryl)ferrocene (**1b**) with 1-[(dimethylamino)methyl]ferrocene (**2**) and (η^6-aniline)tricarbonylchromium derivatives (**3**, **4**) dinuclear to pentanuclear units (**5**–**10**) were obtained. The homodimetallic compound $FcBBr_2-NMe_2CH_2Fc$ (**5**, Fc: ferrocene) closely resembles a propylene-bridged complex. Its dative B–N link is stable at temperatures as high as 100 °C. Each of the heterooligonuclear aggregates **7**–**10** is tied together by covalent B–N bonds, which are isoelectronic with ethylene bridges. In FcB(Br)–N(Me)Bct [**7**, Bct: $(\eta^6\text{-}C_6H_5)Cr(CO_3)$] and 1,1′-$Fc[B(Br)-N(Me)Bct]_2$ (**9**) B–N π bonding dominates over the N–Bct π interaction as indicated by spectroscopical data and an X-ray analysis of **9**. The *N*-lithiated compounds BctNRLi (**4a**, **b**; R = H, Me) possess a remarkably increased N–Bct π donation compared to the protonated parent compounds, which results in a further perturbation of the local C_{3v} symmetry of the $(C_6H_5)Cr(CO_3)$ framework.

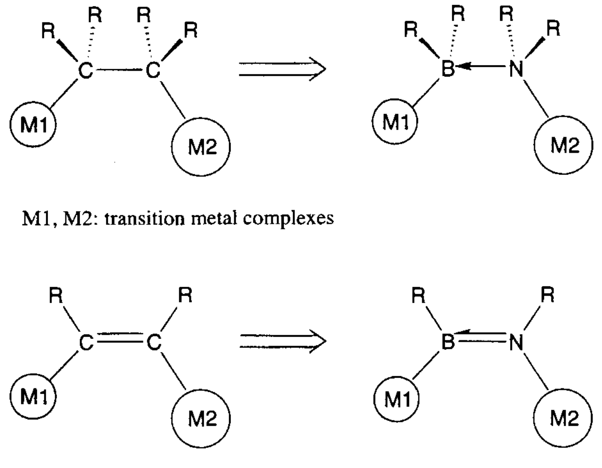
The continuing interest in polynuclear aggregates of transition metal complexes stems mainly from their electrochemical properties[1] and from potential applications in homogeneous catalysis[2]. Cooperative effects between the different transition metal centers can be envisaged to result in chemical properties of the polynuclear complex that are distinctly different from those of the constituent mononuclear specimen. Normally, these aggregates are tied together by covalent carbon-carbon bonds, which are often difficult to build under sufficiently mild conditions[3]. Salt elimination reactions, for example, a classical way of C–C coupling, often proceed via highly reactive organolithium and organomagnesium reagents that would immediately destroy any more delicate mononuclear building block.

In this paper a general concept for the facile synthesis of oligonuclear organometallic complexes is presented, which is based on the isoelectronic principle[4]. Our strategy avoids the critical step of carbon-carbon bridge formation by taking advantage of the close relationship between covalent C–C bonds and both dative and covalent boron-nitrogen links (Scheme 1).

The empty p orbital of three-coordinate boron makes this element the "natural" electrophile, while the nitrogen lone pair possesses nucleophilic character. It should therefore be possible to form bridges between mononuclear building blocks only just in the last step of aggregate formation by taking advantage of the self-assembly of B–N bonds. This is obviously a much simpler approach than to synthesize an extended ligand sphere for the entire oligonuclear molecule first and to add the required transition metals afterwards.

In addition, the Lewis acidity of a given boron center and thus the rotational barrier around a covalent B–N bond can be tuned over a wide range by choice of appropriate substituents at both boron and nitrogen. Moreover, boron centers can be switched from the three-coordinate trigonal-planar configuration to the tervalent tetragonal conformation and *vice versa* with the help of Lewis basic or Lewis acidic additives[5]. This offers a unique opportunity for the design of oligonuclear complexes with custom-tailored conformational flexibility.

Scheme 1



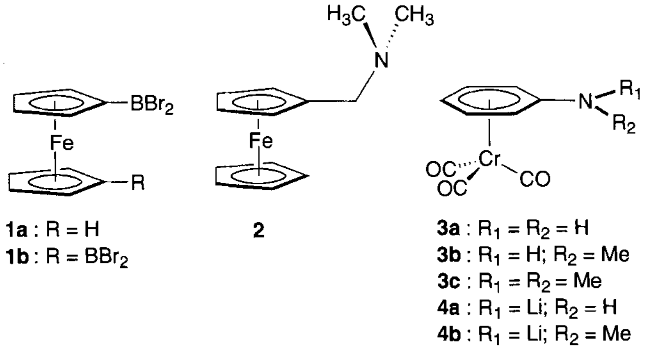
M1, M2: transition metal complexes

Up to now only very few oligonuclear complexes on the basis of similar bridging concepts have been reported[6]. We have already shown this approach to be very useful for the synthesis of organometallic compounds with *intra*molecular bridges (i.e. *ansa*-metallocenes)[7,8] and will now investigate its applicability to the *inter*molecular case.

Synthesis of Oligonuclear Complexes

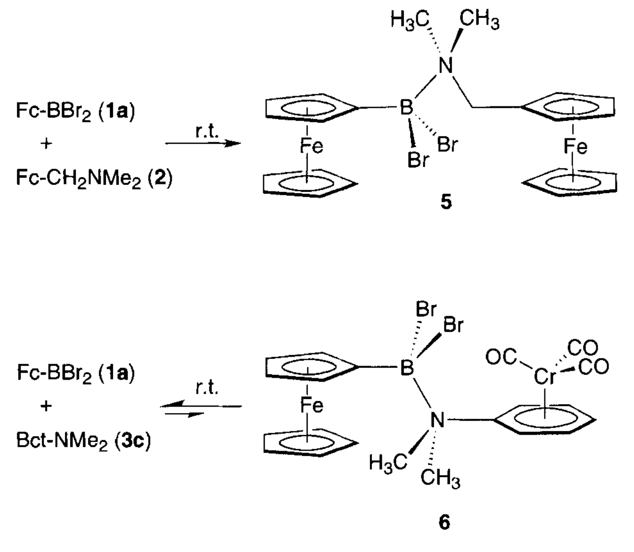
The ferrocene (Fc) derivatives 1-(dibromoboryl)ferrocene (**1a**) and 1,1'-bis(dibromoboryl)ferrocene (**1b**), which serve as the boron-containing mononuclear building blocks, are readily available according to the method of Siebert[9]. 1-[(Dimethylamino)methyl]ferrocene[10] (**2**) and (aniline)-tricarbonylchromium derivatives[11] (**3**, **4**) act as nitrogen-bearing species (Scheme 2). The latter will give valuable insights into the relative strength of the main group Lewis acid and the organometallic Lewis acid.

Scheme 2



The homodimetallic complex **5** was obtained in quantitative yield by mixing equimolar amounts of **1a** and **2**[10] in dichloromethane at ambient temperature (Scheme 3).

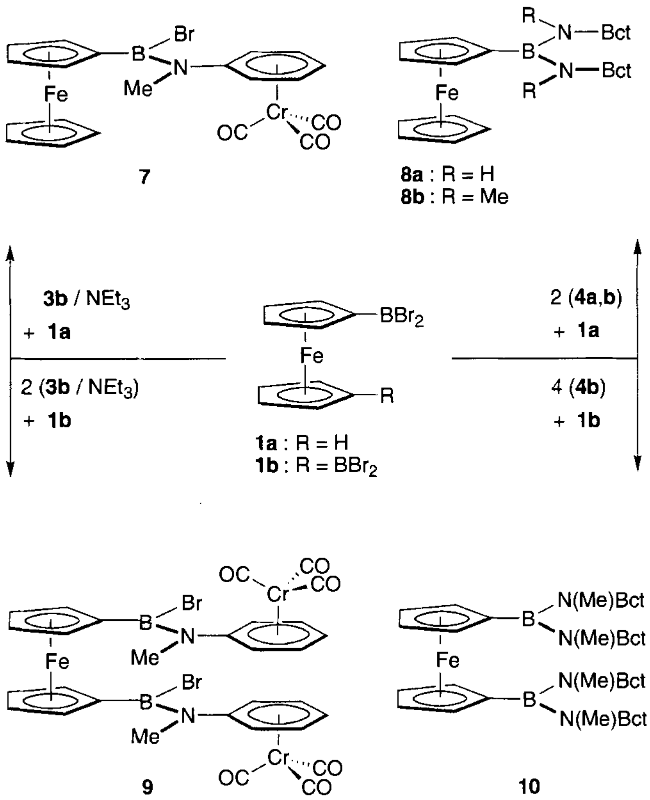
Scheme 3



On the other hand, no stable heterodimetallic adduct **6** was formed between **1a** and **3c** not even at temperatures as low as −60 °C (see below).

The covalently bridged oligonuclear aggregate **7** was synthesized by reaction of the ferrocenylborane **1a** with one equivalent of **3b** (Scheme 4).

Scheme 4



Triethylamine was used for the subsequent abstraction of HBr. The diaminoborane **8a** could be obtained from **1a** and two equivalents of $BctNH_2$ (**3a**) by prolonged stirring of both components in refluxing toluene with evaporation of HBr. A synthetic approach similar to **7** with NEt_3 as HBr trapping agent required high temperatures as well and afforded rather impure **8a** in moderate yield. Both methods failed completely in the case of the methyl derivative **8b**. These findings show that (aniline)tricarbonylchromium derivatives are sufficiently Lewis basic for an aminolysis of the highly acidic dibromoborane **1a**. A second substitution at the same boron center is far less straightforward, calls for drastic conditions and is much more dependent on steric factors.

The necessary increase in the nucleophilicity of **3a** and **3b** was achieved by lithiating their nitrogen groups by treatment with *n*-butyllithium/hexane in diethyl ether. The resulting lithium amides **4a** and **4b** reacted cleanly and smoothly with **1a** to give **8a**, **b** in high yield. The compounds **9** and **10** were obtained similar to **7** and **8** from **1b** and 2 equivalents (4 equiv.) of **3b** (**4b**) (Scheme 4).

IR and NMR Data

To our knowledge, lithiated (aniline)tricarbonylchromium compounds (BctNRLi) have not been isolated nor spectroscopically characterized before. Even their *in situ* generation and reaction were reported in only very few cases[12], which is the more surprising as Bct derivatives play an important role in synthetic organic chemistry[13].

We were interested in the consequences of *N*-lithiation concerning the π donor strength of the nitrogen atom towards the Bct moiety. A first hint at a remarkably increased N–Bct π interaction upon lithiation of the nitrogen center comes from the ^{1}H-NMR spectrum of **4b** ([D$_8$]THF). At ambient temperature, only broad signals for the *ortho* and *meta* protons of the Bct moiety are observed. The protonated parent compound **3b** shows a well-resolved doublet and pseudo triplet (pt) for these protons under the same conditions. These differences result from a dynamic effect, which at ambient temperature is weak in the lithiated compound, but strong in its protonated analog. To quantify this observation, we determined the coalescence temperatures for the resonances of the *meta* protons in **3b** ($T_c = 203 \pm 5$ K), **4a** ($T_c = 293 \pm 5$ K), and **4b** ($T_c = 300 \pm 5$ K). Since **4a, b** can be expected to form solvent-separated ion pairs in THF solution (**4b**: $\delta^7Li = 0.1$), a significant contribution of a weakly coordinated lithium ion to the observed dynamic behavior is unlikely. Therefore, its origin lies in a hindered rotation of the NMe group around the N-Bct bond in the case of **4b**, which is free at ambient temperature in **3b**. The T_c values correspond to rotational barriers of $\Delta G^{\neq} = 42 \pm 1$, 62 ± 1 and 62 ± 1 kJ · mol^{-1}, respectively ($\Delta G^{\neq} = RT_c\,[22.96 + \ln(T_c/\delta\nu)]\,[\mathrm{Jmol}^{-1}]$)[14]. Further evidence for the remarkable π donor strength of the RNLi group stems from ^{13}C-NMR and IR spectroscopical data. In electron-rich Bct derivatives, the carbon nuclei of the CO ligands are known to be deshielded[15] (Table 1). The chemical shifts of the *para* carbon atoms provide another measure of charge density in monosubstituted (benzene)tricarbonylchromium molecules. For a quantitative treatment, the term Δπ was introduced, which is defined as the chemical shift difference between the *para* and the *meta* carbon atoms of the aromatic ring under investigation[16]: $\Delta\pi = \delta_{para} - \delta_{meta}$. Electron-releasing ring substituents lead to a negative, electron-withdrawing substituents to a positive value of Δπ (Table 1). In carbonyl complexes, the IR bands of the carbonyl ligands correlate strongly with the charge density on the transition metal. The position of the ν(CO) bands is therefore sensitive to the nature of arene substituents, shifting to lower frequencies as the π donor strength of the substituent is increased[17] (Table 1).

The spectroscopic data summarized in Table 1 suggest, that *N*-lithiation of the exocyclic amino group leads to a substantial increase of charge density on the Bct fragment. The difference between LiN(R)Bct (**4a, b**) and HN(Me)Bct (**3b**) is even greater than between **3b** and the parent (benzene)tricarbonylchromium (**11**), provided an approximately linear correlation between the electron density on the Bct moiety and the values ν(CO), δ(^{13}CO) and Δπ exists. Thus, changes in the σ framework of the molecule exert a marked influence on its π electron distribution. In the carbonyl region of the IR spectrum, a splitting of the E band is observed in **4a, b**, which is far less pronounced in **3b**. It can therefore be concluded that the local C_{3v} symmetry of the Bct moiety is much more perturbed in the former than in the latter.

Table 1. Comparison of IR and ^{13}C-NMR data of selected Bct derivatives

Compnd.	ν(CO) cm^{-1}	C-m	C-p	CO	Δπ[g]
4b	1928, 1837, 1827[a]	100.6[d]	75.9[d]	239.3[d]	-24.7
3b	1954, 1869[a]	98.2[d]	83.4[d]	235.9[d]	-14.8
	1958, 1877[b]	96.6[e]	83.1[e]	234.5[e]	-13.5
8a	1965, 1885[b]	95.2[e]	86.4[e]	234.2[e]	-8.8
10	1960, 1884[b]	94.1[f]	89.2[f]	234.3[f]	-4.9
11	1974, 1894[c]	93.5[f]	93.5[f]	233.3[f]	0.0
7	1969, 1895[b]	89.8[e]	91.9[e]	233.1[e]	+2.1
9	1970, 1897[b]	89.6[e]	92.3[e]	232.5[e]	+2.7
12	1985, 1911[c]	90.2[f]	95.4[f]	231.2[f]	+5.2

[a] THF solution. – [b] Toluene solution. – [c] CH_2Cl_2 solution; see ref.[23]. – [d] [D$_8$]THF. – [e] $CDCl_3$. – [f] CD_2Cl_2[16]. – [g] $\Delta\pi = \delta_{para} - \delta_{meta}$.

The ^{11}B-NMR signal of **5** appears at $\delta = 8$ ($h_{1/2} = 150$ Hz), which is a characteristic value for tetravalent boron nuclei[18]. In the temperature range from +20 to +100 °C ([D$_8$]toluene) no changes in either its chemical shift or its line width are observed. This means that even at 100 °C the B–N link is perfectly stable on the NMR time scale and therefore meets the conditions for most applications. In contrast to **5**, the ^{11}B-NMR spectrum of an equimolar mixture of **1a** and BctNMe$_2$ (**3c**) in [D$_8$]toluene was found to be highly temperature-dependent. The chemical shift of the ^{11}B resonance changed from $\delta = 39$ ($h_{1/2} = 130$ Hz) at +20 °C to $\delta = 18$ ($h_{1/2} = 900$ Hz) at −60 °C, which means that the components do not form a stable adduct in this temperature range. The ^{11}B-NMR resonances observed represent the weighted averages of the chemical shift values of pure **1a** and the dimetallic complex **6** in the dynamic equilibrium at the respective temperatures. The main reason for the weak Lewis base strength of **3c** lies in the strongly electron-withdrawing effect of the Bct moiety.

The ^{11}B-NMR resonances of **7** ($\delta = 39$) and **9** ($\delta = 39$) fall in the typical range for monoaminoboranes[18]. However, there are some indications of a diminished π-donating ability of the BctNR unit compared to e.g. alkylamino substituents. In the ^{1}H-NMR spectra of **7** and **9**, only one set of signals is observed at ambient temperature both for the Bct moieties and for the NCH$_3$ groups. Consequently, there is no restricted rotation around the B–N bond at ambient temperature, which is unusual for compounds R$_2$NB(Br)R′ (R, R′ = alkyl, aryl). Normally, these species show significant rotational barriers due to a pronounced N–B π interaction ($\Delta G^{\neq}$: about 80 kJ mol^{-1})[19]. It has to be concluded, therefore, that in both molecules **7** and **9** the electron-withdrawing Bct moiety competes to some extent with the Lewis-acidic boron center for the nitrogen lone pair. In the case of the diaminoboranes **8a**, **8b** and **10** the ^{11}B-NMR shifts are found at $\delta = 31$, 39 and 40, respectively. The deshielding of the two latter derivatives may result from the fact that these are more hampered by sterical overcrowding than **8a**, so that they cannot adopt the conformation required for optimal N–B π overlap. As for other diaminoboranes, no rotational barrier around the B–N bond is observed.

The same diagnostic criteria that were employed for the comparison of **3b** and **4b** are valid for an estimation of N–B versus N–Bct π bonding in **7**–**10**. Table 1 shows the ν(CO) and Δπ values of these compounds together with their ^{13}CO resonances in comparison with other donor- or acceptor-substituted Bct derivatives (**12**: BctCOOEt). According to these data, the borylation of the nitrogen atoms leads to a significant decrease in the N-Bct π interaction. If again a linear correlation between the electron density on the Bct moiety and the values ν(CO), δ(^{13}CO) and Δπ is assumed, the following conclusions may be drawn:

In the diaminoboryl derivatives **8** and **10**, the π donor strength of each nitrogen atom towards the Bct group is about half its value in the parent (aniline)tricarbonylchromium complexes. Two nitrogen substituents at the same boron center lead to a resonance saturation of its p_z orbital. As a result, the amino groups do not exert their full donor capacity towards boron and there is electron density left, which is delocalized into the Bct fragment. In the case of the monoaminoboryl derivatives **7** and **9**, the nitrogen lone pair is almost exclusively delocalized into the empty p orbital of boron. Therefore, the electronic properties of the Bct moiety in these compounds closely resemble those of unsubstituted (benzene)tricarbonylchromium (**11**; see Table 1).

Molecular Structure

The molecular structure of the trinuclear complex **9** was determined by X-ray methods (Figure 1). The compound crystallizes from toluene/pentane with two molecules of toluene in the unit cell in the triclinic space group $P\bar{1}$ (No. 2).

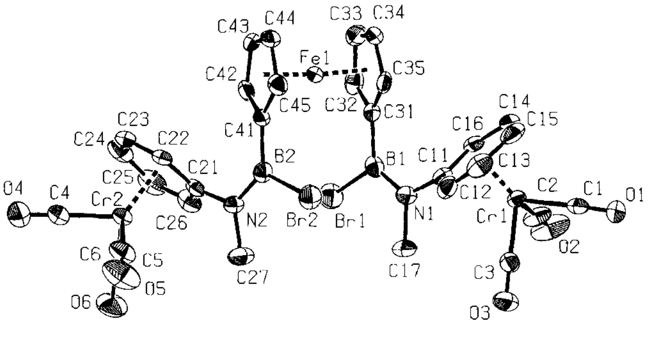


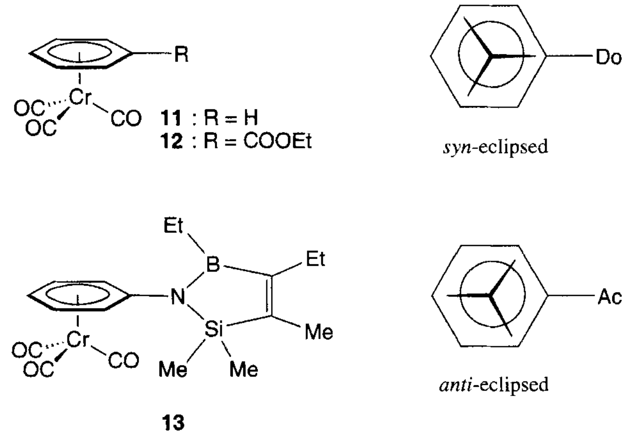
Figure 1. Molecular structure of **9** (thermal ellipsoids at 50% probability level)[a]

[a] Selected bond lengths [Å], angles [°] and angles between planes [°]: B1–N1 1.384(7), B2–N2 1.380(7), B1–C31 1.548(7), B2–C41 1.555(7), B1–Br1 1.977(5), B2–Br2 1.977(5), N1–C11 1.431(6), N2–C21 1.431(6), N1–C17 1.490(6), N2–C27 1.487(6); N1–B1–C31 125.9(4), N2–B2–C41 126.4(4), N1–B1–Br1 117.8(4), N2–B2–Br2 117.3(3), Br1–B1–C31 116.2(3), Br2–B2–C41 116.3(3), B1–N1–C11 120.5(4), B2–N2–C21 119.8(4), B1–N1–C17 124.4(4), B2–N2–C27 124.8(4), C11–N1–C17 115.1(4), C21–N2–C27 115.3(4); N1–COG^1–Cr1–C1 149.5, N2–COG^2–Cr2–C4 179.0; [C11–C16]/[B1N1C17] 56.5, [C21–C26]/[B2N2C27] 53.2, [C31–C35]/[N1B1Br1] 26.0, [C41–C45]/[N2B2Br2] 26.4, [C31–C35]/[C41–C45] 5.7

A remarkable feature of the molecular structure of **9** is the almost eclipsed conformation of both boryl substituents (dihedral angle B1-COG^1-COG^2-B2 = 6.7°; COG: center of gravity of the respective cyclopentadienyl ring). It is not clear, why a *syn* conformation with respect to the COG^1-COG^2 line is preferred to the sterically less encumbered *anti* conformation. Only two other unbridged derivatives of 1,1′-diborylferrocene were structurally characterized so far[20]; these [i.e. 1,1′-Fc(BBr$_2$)$_2$; 1,1′-Fc(B(N*i*Pr$_2$)$_2$)$_2$] adopt an *anti* and a *gauche* conformation of the boryl groups. From the limited data available it cannot be decided, whether crystal lattice effects are responsible for the peculiar conformation of **9** or whether a more fundamental electronic effect on the molecular scale plays a role.

Both boron and both nitrogen atoms show a trigonal-planar conformation. The planes B1N1C17/N1B1Br1 and B2N2C27/N2B2Br2 meet at an angle of about 10°, whereas an angle of 56.5° (53.2°) is observed between the planes B1N1C17/[C11–C16] (B2N2C27/[C21–C26]). Therefore, an efficient π interaction is possible for the N–B bonds only, while a pronounced N–Bct π donation can be excluded in the solid state. Consequently, the N1–C11 [1.431(6) Å] and N(2)–C(21) [1.431(6) Å] bond lengths are 0.07 Å longer than in the analogous compound BctNEt$_2$ [1.357(3) Å][21]. The bond lengths B1–N1 [1.384(7) Å] and B2–N2 [1.380(7) Å] are rather short compared to the commonly accepted value of 1.41 Å for $R_2B{-}NR_2$ bonds with pronounced B–N π interaction[4] [**13**: d(B–N) = 1.427(6) Å[22]].

Scheme 5



11 : R = H
12 : R = COOEt

syn-eclipsed

13

anti-eclipsed

π-Donor substituents at the Bct core are known to be bent away from the Cr(CO)$_3$ center[23]. The Lewis-acidic BBr$_2$ groups in 1,1′-Fc(BBr$_2$)$_2$, on the other hand, were found to be bent towards the central iron atom[20]. In the case of **9**, no deviation of both the boron and the nitrogen atoms from the best planes of their adjacent Cp and phenyl rings was observed. This again shows the B–N π interaction in **9** to eliminate efficiently both the electron deficiency of the boron atoms and any significant N–Bct back bonding.

(η^6-Arene)tricarbonylchromium complexes can adopt several conformations of the Cr(CO)$_3$ fragment relative to the arene ligand. For unsubstituted π-arene compounds, the staggered conformer is energetically preferred to the eclipsed one, while electron-donating arene substituents lead to a *syn*-eclipsed and electron-withdrawing substituents to an *anti*-eclipsed situation (Scheme 5)[23]. In **9**, one Bct moiety was found to possess an *anti*-eclipsed and the other a staggered conformation. These data suggest the rotational barrier of the $Cr(CO)_3$ moiety in **9** to be unusually low, which points to an electronic situation of the Bct units similar to that in unsubstituted (benzene)tricarbonylchromium.

Conclusion

The facile connection of mononuclear organometallic building blocks by boron-nitrogen bridges provides a straightforward method for the synthesis of oligonuclear complexes. Both dative and covalent B−N links can be employed to bring different transition metal centers into close proximity. The stability of dative B−N bridges with tervalent boron and nitrogen atoms is remarkably decreased when the nitrogen atoms are attached to electron-withdrawing complex fragments [e.g. $(C_6H_5)Cr(CO)_3$]. In contrast, covalent B−N bonds were found to be strong and less perturbed by a similar environment. A pronounced double bond character is preserved with the N−B π interaction dominating over N−Bct π bonding.

Work is in progress to build larger B−N-bridged organometallic networks and "molecular trees" by using multiply boron- and amino-functionalized transition metal complexes. Four-membered (diazadiboretidines)[24] and six-membered (borazines)[25] B−N heterocycles are known to be particularly stable compounds and are therefore ideally suited as backbones for oligonuclear complex aggregates. The reaction of **1a** with **3a** stops at the stage of the trinuclear compound **8a**. In this special case, the reason lies in the low Lewis basicity of (aniline)tricarbonylchromium derivatives. First preliminary results indicate a possibility of overcoming this problem either by doubly *N*-lithiating **8a** or by using amino-functionalized organometallic compounds of greater basicity [e.g. (amino)alkylferrocenes].

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Experimental

All reactions and manipulations were carried out in dry, oxygen-free argon using standard Schlenk ware or in an argon-filled drybox. Solvents were freshly distilled under N_2 from Na/K alloy-benzophenone (toluene, hexane, THF, Et_2O) or from CaH_2 (CH_2Cl_2) prior to use. − IR: solvent toluene or THF (organic and organometallic compounds), Perkin-Elmer 1650 FTIR. − NMR: Jeol JMN-GX 400 and Bruker DPX 400. ^{11}B-NMR spectra were referenced to external $BF_3 \cdot Et_2O$, ^7Li NMR spectra to external $LiCl/H_2O$. The assignment of NMR resonances follows the common numbering scheme for substituted ferrocenes (Fc), whereas the *ortho, meta, para* nomenclature is used for the phenyl rings. − MS (CI mode): Finnigan MAT 90. − Elemental analyses: Microanalytical laboratory of the Technische Universität München.

The compounds **1**[9], **2**[10] and **3**[11] were synthesized according to literature procedures.

1. *Tricarbonyl(η^6-N-lithioaniline)chromium(0)* (**4a**): *n*-Butyllithium/hexane (1.45 ml, 2.32 mmol) was added dropwise with stirring to a solution of 0.53 g (2.32 mmol) of **3a** in 40 ml of diethyl ether at −78 °C. The reaction mixture was slowly warmed to room temp. and stirred for 3 h to give a pale yellow precipitate and an almost colorless supernatant. The precipitate was collected on a fine-porosity frit, washed twice with diethyl ether (10 ml) and dried for 12 h in vacuo. According to its ^1H-NMR spectra and elemental analysis, **4a** still contained about 0.5 equiv. of coordinated diethyl ether. The lithiation proceeded almost quantitatively, giving the *N*-lithiated compound only. After all volatile components had been removed from the filtrate in vacuo, only traces of a yellow oily byproduct were detected. − IR (THF): ν(CO) 1929 cm^{-1}, 1838/1830. − ^1H NMR ($[D_8]$THF, +20 °C, 400 MHz): δ = 5.14 (br., 2H, *m*-H), 4.39 [t, *J*(HH) = 6 Hz, 1H, *p*-H], 4.17 (br., 2H, *o*-H), 3.63 (br., 1H, NH); ($[D_8]$THF, −90 °C, 400 MHz): δ = 5.28, 5.22 [pt, pt, *J*(HH) = 6 Hz, 1H, 1H, *m*-H], 4.44 [pt, *J*(HH) = 6 Hz, 1H, *p*-H], 4.20, 4.18 [d, d, *J*(HH) = 6 Hz, 1H, 1H, *o*-H], 3.98 (br., 1H, NH). − ^{13}C NMR ($[D_8]$THF, −90 °C, 100.6 MHz): Due to coalescence at room temp., the ^{13}C resonances are very broad and the signal-to-noise ratio is poor; therefore, the spectrum at −90 °C is given: δ = 239.4 (CO), 158.1 (C-*i*), 101.4, 100.5 (C-*m*), 78.8, 77.6 (C-*o*), 75.3 (C-*p*). − $C_9H_6CrLiNO_3$ (235.1) · 0.5 $C_4H_{10}O$ (74.1): calcd. C 48.56, H 4.04, Li 2.60, N 5.14; found C 48.06, H 4.14, Li 3.00, N 4.92.

2. *Tricarbonyl(η^6-N-lithio-N-methylaniline)chromium(0)* (**4b**): The lithiation of **3b** was achieved in the same way as described for **3a**. − IR (THF): ν(CO) 1928 cm^{-1}, 1837/1827. − ^7Li NMR ($[D_8]$THF, +20 °C, 155.4 MHz): δ = 0.1. − ^1H NMR ($[D_8]$THF, +20 °C, 400 MHz): δ = 5.23 (br., 2H, *m*-H), 4.45 [t, *J*(HH) = 6 Hz, 1H, *p*-H], 4.25 (br., 2H, *o*-H), 2.53 (s, 3H, CH_3); ($[D_8]$THF, −90 °C, 400 MHz): δ = 5.40, 5.28 [pt, pt, *J*(HH) = 6 Hz, 1H, 1H, *m*-H], 5.51 [pt, *J*(HH) = 6 Hz, 1H, *p*-H], 4.34, 4.12 [d, d, *J*(HH) = 6 Hz, 1H, 1H, *o*-H], 2.50 (s, 3H, CH_3). − ^{13}C NMR ($[D_8]$THF, −90 °C, 100.6 MHz): Due to coalescence at room temp., the ^{13}C resonances are very broad and the signal-to-noise ratio is poor; therefore, the spectrum at −90 °C is given: δ = 239.3 (CO), 153.8 (C-*i*), 101.9, 100.6 (C-*m*), 79.9 (C-*o*), 75.9 (C-*p*), 70.0 (C−*o*), 36.0 (CH_3). − $C_{10}H_8CrLiNO_3$ (249.1) · 0.5 $C_4H_{10}O$ (74.1): calcd. C 50.36, H 4.58, Li 2.43, N 4.89; found C 49.61, H 4.84, Li 2.67, N 4.57.

3. *Dibromo(ferrocenyl)borane−(Ferrocenylmethyl)dimethylamine Adduct* **5**: A solution of **1a** (0.58 g, 1.63 mmol) in CH_2Cl_2 was added slowly with stirring to a solution of **2** (0.40 g, 1.63 mmol) in CH_2Cl_2 at room temp; the resulting orange solution was concentrated in vacuo to 5 ml and then stored at −78 °C for 12 h, whereupon a yellow microcrystalline precipitate of **5** formed. After filtration at −78 °C, the solid material was washed with pentane and dried in vacuo; yield 0.86 g (88%). − ^{11}B NMR ($[D_8]$toluene, 128.3 MHz): δ = 8 ($h_{1/2}$ = 150 Hz; +20 °C), 8 ($h_{1/2}$ = 110 Hz; +100 °C). − ^1H NMR (C_6D_6, 400 MHz): δ = 4.59 [pt, 2H, *J*(H,H) = 1.8 Hz, BC_5H_4], 4.51 (s, 5H, $C_5\mathit{H}_5FeC_5H_4B$), 4.28 [pt, 2H, *J*(H,H) = 1.8 Hz, BC_5H_4], 3.82 (s, 5H, $C_5\mathit{H}_5FeC_5H_4C$), 3.77 [pt, 2H, *J*(H,H) = 1.8 Hz, CC_5H_4], 3.57 (br., 4H, CC_5H_4/CH_2), 2.22 (s, 6H, CH_3). − ^{13}C NMR (C_6D_6, 100.5 MHz): δ = 76.1 (C_5H_4B), 75.3 (C_5H_4C), 72.1 (C_5H_4B), 70.6 ($\mathit{C}_5H_5FeC_5H_4B$), 70.2/69.7 (C_5H_4C), 69.2 ($\mathit{C}_5H_5FeC_5H_4C$), 59.5 (CH_2), 44.6 (CH_3). − $C_{23}H_{26}BBr_2Fe_2N$ (598.8): calcd. C 46.24, H 4.39, Br 26.44, N 2.35; found C 45.83, H 4.62, Br 27.29, N 2.40.

4. *Preparation of a Mixture of Fc−BBr_2 and Bct−NMe_2* (**6**): Solutions of 0.32 g (1.24 mmol) of **3c** and 0.44 g (1.24 mmol) of

1a in CH_2Cl_2 were mixed at room temp. with stirring. The color of the mixture was temperature-dependent and changed from red (+20°C) to yellow (−90°C). After evaporation of the solvent in vacuo, a yellow microcrystalline solid was obtained. – ^{11}B NMR ([D$_8$]toluene, 128.3 MHz): δ = 39 (+20°C; $h_{1/2}$ = 130 Hz), 31 (0°C; $h_{1/2}$ = 190 Hz), 23 (−20°C; $h_{1/2}$ = 260 Hz), 19 (−40°C; $h_{1/2}$ = 450 Hz), 18 (−60°C; $h_{1/2}$ = 900 Hz), broad (−80°C).

5. *Dinuclear Complex* **7**: A toluene solution of **1a** (0.50 g, 1.41 mmol) was added slowly with stirring to a toluene solution of **3b** (0.34 g, 1.40 mmol) at −78°C. Neat triethylamine (0.14 g, 1.40 mmol) was then added and the orange reaction mixture was slowly warmed to room temp. and stirred for 12 h. After filtration from the precipitated Et_3NHBr, the orange filtrate was concentrated to 5 ml and treated with 60 ml of pentane to afford a small amount of an orange solid, which was removed by filtration. The filtrate was stored at −25°C for several hours to give orange crystals of **7**; yield: 0.52 g (71%). – IR (toluene): ν(CO) = 1969 cm^{-1}, 1895. – ^{11}B NMR (C_6D_6, 128.3 MHz): δ = 39 ($h_{1/2}$ = 580 Hz). – ^{1}H NMR (C_6D_6, 400 MHz): δ = 4.65 [d, 2H, J(H,H) = 5.5 Hz, *o*-H], 4.29–4.27 (m, 3H, *m,p*-H), 4.13 (br., 2H, 3,4-H), 4.04 (br., 2H, 2,5-H), 3.97 (s, 5H, C_5H_5), 3.17 (s, 3H, CH_3). – ^{13}C NMR (C_6D_6, 100.5 MHz): δ = 233.1 (CO), 129.3 (C-1), 93.1 (C-*o*), 91.9 (C-*p*), 89.8 (C-*m*), 77.0 (C-2,5), 73.4 (C-3,4), 69.9 (C_5H_5), 44.8 (CH_3). – MS (CI), *m/z* (%): 517 (3) [M$^+$], 433 (10) [M$^+$ − 3 CO], 381 (100) [M$^+$ − Cr(CO)$_3$], 186 (40) [FeCp$_2^+$]. – $C_{20}H_{17}BBrCrFeNO_3$ (517.9): calcd. C 46.38, H 3.31, Br 15.43, N 2.70; found C 46.57, H 3.53, Br 15.07, N 2.68.

6. *Trinuclear Complex* **8a**: *n*-Butyllithium/hexane (1.6 ml, 2.56 mmol) was added dropwise with stirring to a solution of **3a** (0.59 g, 2.59 mmol) in diethyl ether at −78°C. A pale yellow precipitate formed immediately. The suspension was warmed to room temp. and stirred for 1 h. The solvents were removed by filtration, and the solid residue was washed with 10 ml of diethyl ether, dried in vacuo and suspended in 40 ml of toluene. The suspension was then cooled to −78°C, and a solution of **1a** (0.46 g, 1.29 mmol) in 10 ml of toluene was added slowly with stirring. The resulting orange suspension was warmed to room temp., stirred for 12 h and filtered through a fine-porosity frit. The filtrate was concentrated in vacuo until a yellow solid precipitated and stored at −25°C for 24 h. The mother liquor was separated by filtration at −25°C and the yellow, microcrystalline material was washed twice with 5 ml of pentane. Red crystals were obtained from toluene, which contained 1 eq. of toluene (^{1}H NMR, elemental analysis); yield: 0.48 g (57%). – IR (toluene): ν(CO) = 1965 cm^{-1}, 1885. – ^{11}B NMR ($CDCl_3$, 128.3 MHz): δ = 31 ($h_{1/2}$ = 650 Hz). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.56 [pt, 4H, J(H,H) = 6.4 Hz, *m*-H], 5.32 [d, 4H, J(H,H) = 6.4 Hz, *o*-H], 5.28 (br., 2H, NH), 4.99 [t, 2H, J(H,H) = 6.4 Hz, *p*-H], 4.45 [pt, 2H, J(H,H) = 1.8 Hz, 3,4-H], 4.28 [pt, 2H, J(H,H) = 1.8 Hz, 2,5-H], 4.18 (s, 5H, C_5H_5). – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 234.2 (CO), 124.5 (C-*i*), 95.2 (C-*m*), 86.4 (C-*p*), 84.8 (C-*o*), 73.9 (C-2,5), 72.1 (C-3,4), 69.4 (C_5H_5). – $C_{28}H_{21}BCr_2FeN_2O_6$ (652.2) · 1 C_7H_8 (92.1): calcd. C 56.49, H 3.93, N 3.76; found C 56.15, H 3.70, N 3.55.

7. *Trinuclear Complex* **8b** was prepared in the same way as **8a** from **3b** (0.51 g, 2.10 mmol), *n*-butyllithium/hexane (1.31 ml, 2.10 mmol) and **1a** (0.37 g, 1.04 mmol). Recrystallization of the crude product from toluene/pentane (1:1) gave orange crystals of **8b**; yield: 0.52 g (72%). – IR (toluene): ν(CO) = 1958 cm^{-1}, 1888. – ^{11}B NMR (C_6D_6, 128.3 MHz): δ = 39 ($h_{1/2}$ = 770 Hz). – ^{1}H NMR (C_6D_6, 400 MHz): δ = 4.48 [pt, 4H, J(H,H) = 6.4 Hz, *m*-H], 4.32 [d, 4H, J(H,H) = 6.4 Hz, *o*-H], 4.28 (br., 2H, 3,4-H), 4.22 (pt, 2H, 2,5-H), 4.10 [t, 2H, J(H,H) = 6.4 Hz, *p*-H], 4.02 (s, 5H, C_5H_5), 2.72 (s, 6H, CH_3). – ^{13}C NMR (C_6D_6, 100.5 MHz): δ = 234.1 (CO), 130.3 (C-*i*), 92.7 (C-*m*), 88.0 (C-*p*), 85.2 (br., C-*o*), 76.6 (C-2,5), 72.9 (C-3,4), 68.9 (C_5H_5), 38.5 (CH_3). – MS (CI), *m/z* (%): 680 (25) [M$^+$]; 596 (25) [M$^+$ − 3 CO]; 544 (100) [M$^+$ − Cr(CO)$_3$]; 460 (25) [M$^+$ − 3 CO − Cr(CO)$_3$]. – $C_{30}H_{25}BCr_2FeN_2O_6$ (680.2): calcd. C 52.98, H 3.70, N 4.12; found C 53.21, H 3.91, N 3.96.

8. *Trinuclear Complex* **9**: A toluene solution of **1b** (0.63 g, 1.20 mmol) was added at −78°C with stirring to a toluene solution of **3b** (0.58 g, 2.39 mmol). To the resulting suspension neat NEt_3 (0.24 g, 2.40 mmol) was added. The color of the reaction mixture turned from orange to yellow. The solution was slowly warmed to room temp., stirred for 5 h and subsequently filtered through a fine-porosity frit. Volatile material was removed in vacuo to yield an orange-red oil. After extraction with 20 ml of pentane, the crude product was recrystallized from toluene/pentane (1:2) at −25°C. The resulting orange crystals contained 2 equiv. of toluene (NMR, X-ray structure, elemental analysis); yield: 0.97 g (78%). – IR (toluene): ν(CO) = 1970 cm^{-1}, 1897. – ^{11}B NMR ($CDCl_3$, 128.3 MHz): δ = 39 ($h_{1/2}$ = 900 Hz). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.47 [d, 4H, J(H,H) = 5.5 Hz, *o*-H], 5.33 [t, 2H, J(H,H) = 5.5 Hz, *p*-H], 5.27 (m, 4H, *m*-H), 4.42 (br., 4H, 3,4-H), 4.11 (br., 4H, 2,5-H), 3.48 (s, 6H, CH_3). – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 232.5 (CO), 125.3 (C-*i*), 93.0 (C-*o*), 92.3 (C-*p*), 89.6 (C-*m*), 78.0 (C-2,5), 73.9 (C-3,4), 21.4 (CH_3). – MS (CI), *m/z* (%): 576 (10) [M$^+$ − 2 Cr(CO)$_3$], 433 (10) [M$^+$ − BBr−NMe−Bct, − 3 CO], 381 (100) [M$^+$ − BBr−NMe−Bct, − Cr(CO)$_3$]. – $C_{30}H_{24}B_2Br_2Cr_2FeN_2O_6$ (849.8) · 2 C_7H_8 (92.1): calcd. C 51.11, H 3.90, Br 15.45, N 2.71; found C 51.36, H 3.94, Br 15.67, N 2.80.

9. *Pentanuclear Complex* **10** was prepared in the same way as **8b** from **3b** (1.45 g, 5.96 mmol), *n*-butyllithium/hexane (3.8 ml, 6.08 mmol) and **1b** (0.79 g, 1.50 mmol). – IR (toluene): ν(CO) = 1960 cm^{-1}, 1884. – ^{11}B NMR (CD_2Cl_2, 128.3 MHz): δ = 40 ($h_{1/2}$ = 1200 Hz). – ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 5.35 [pt, 8H, J(H,H) = 6.4 Hz, *m*-H], 5.08 [d, 8H, J(H,H) = 6.4 Hz, *o*-H], 5.01 [t, 4H, J(H,H) = 6.4 Hz, *p*-H], 4.67 (br., 4H, 3,4-H), 4.50 (br., 4H, 2,5-H), 3.26 (s, 12H, CH_3). – ^{13}C NMR (CD_2Cl_2, 100.5 MHz): δ = 234.3 (CO), 131.0 (C-*i*), 94.1 (C-*m*), 89.2 (C-*p*), 86.3 (C-*o*), 77.3 (C-2,5), 74.0 (C-1), 73.3 (C-3,4), 39.5 (CH_3). – A satisfactory C, H, N analysis was not obtained due to the presence of varying amounts of trapped toluene (NMR), which could not be removed completely. However, a ratio of Fe to Cr of 1:4 was determined and the absence of bromine confirmed.

10. *X-ray Structure of* **9**[26]: Crystal data: $C_{30}H_{24}B_2Br_2Cr_2FeN_2O_6 \cdot 2\,C_7H_8$, M = 849.8, a = 1253.3(3), b = 1293.0(3), c = 1467.7(5) pm, α = 101.90(2), β = 105.48(1), γ = 102.79(1)°, V = 2144 · 10^6 pm^3, crystal size 0.16 · 0.28 · 0.49 mm, measurement at 193 K, ρ_{calc} = 1.602 gcm^{-3}, μ = 27.4 cm^{-1}, F_{000} = 1040, Z = 2, triclinic crystal system, space group $P\bar{1}$ (No. 2), two disordered molecules of toluene in the unit cell, Enraf-Nonius CAD4, λ = 71.07 pm (Mo-K_α, graphite monochromator), range of measurement 1.0° < Θ < 25°, ω scan, scan width (1.1 + 0.2 tanΘ)° (± 25% before and after each reflection to determine the background), t_{max} = 60 s, 7883 measured reflections (h, $\pm k$, $\pm l$), 7479 independent reflections of which 5831 with $I > 2 \cdot \sigma(I)$ were used for refinement, structure determination with Patterson methods and difference Fourier syntheses, empirical absorption correction based on Ψ-scan data, transmission coefficients 0.66–1.0, 532 least-squares parameters, all 59 heavy atoms refined with anisotropic thermal parameters, all 40 hydrogen atoms placed in ideal geometry, included into the structure factor calculations, but not refined. Anomalous dispersion[27] was accounted for, shift/error < 0.0001 in the last cycle of refinement, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ =

0.0514, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.0528$, reflection-to-parameter ratio 11, residual electron density $+1.08$ ΔeÅ^{-3} (100 pm besides Br2)/-0.61 ΔeÅ^{-3}, weighting scheme according to Tukey and Prince[28] with five refined parameters. All calculations were performed on a DECstation 5000/25 using the programs CRYSTALS[29] and PLATON[30].

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