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Synthesis of borylindenides. Complexes with iron and rhenium moieties

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Abstract

Borylation of lithium indenide with $BBrMe_2$ gives the allylic 1-indenyl derivative $(1\text{-Ind})BMe_2$ (**1c**) together with the bis-allylic connected species $(1\text{-Ind})_2BMe$ (**3**) and with BCl^iPr_2, the allylic 1-indenyl $(1\text{-Ind})B^iPr_2$ (**1d**); the latter, with Et_3N or Py added, rearranges to the vinylic 3-indenyl isomer $(3\text{-Ind})B^iPr_2$ (**2d**). The disubstituted indene $C_9H_6Ind(SiMe_3)B(O_2C_2Me_4)$ (**5**) was prepared from $Li[C_9H_6B(O_2C_2Me_4)]$ (**4b**) and Me_3SiCl. Both $(1\text{-Ind})BMe_2$ and $(1\text{-Ind})B^iPr_2$ readily undergo metalation when treated with LiTMP or LiInd to give pure 1-borylindenides $Li(C_9H_6BMe_2)$ (**4c**) and $Li(C_9H_6B^iPr_2)$ (**4d**). A barrier to internal rotation for the BMe_2 group of **4c** of $\Delta G^\ddagger = 65.4 \pm 2.3$ kJ mol^{-1} was deduced from variable temperature ^{1}H-NMR spectra. ^{13}C-NMR spectra of the lithium salts $Li[C_9H_6B(NMe_2)_2]$ (**4a**), **4b**, **4c** and **4d** display a deshielding of the carbon atoms of the Cp ring according to **4a** < **4b** < **4c**, **4d**. The salts **4a** and **4b** were used to prepare the complexes $Cp^*Fe[C_9H_6B(NMe_2)_2]$ (**8**), $Cp^*Fe[C_9H_6B(O_2C_2Me_4)]$ (**9**), $Fe[C_9H_6B(O_2C_2Me_4)]_2$ (**10**) and $Re(CO)_3[C_9H_6B(O_2C_2Me_4)]$ (**11**), characterized by spectroscopic methods (^{1}H-, ^{13}C-, ^{11}B-NMR) and mass spectrometry. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Boron; Boranes; Borylindene; Borylindenide; Internal rotation

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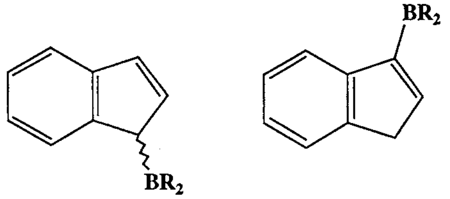
1. Introduction

In a previous report [1], the synthesis and properties of the two indenylboranes $(3\text{-Ind})B(NMe_2)_2$ (**2a**) and $(1\text{-Ind})B(O_2C_2Me_4)$ (**1b**) and their lithium salts **4a** and **4b** were described. The salts **4a** and **4b** are the first borylindenides that were made and characterized.

Hereafter, the authors describe two dialkylboryl derivatives, the (1-indenyl)dimethylborane (**1c**) and the (1-indenyl)di*iso*propylborane (**1d**), the corresponding lithium salts, lithium [1-(dimethylboryl)indenide] (**4c**) and lithium[1-(di*iso*propylboryl)indenide] (**4d**), and furthermore, the silylation product of **4b**, 2-[1-(trimethylsilyl)inden-3-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**). They also present four representative transition metal complexes with borylindenyl ligands.



1a	**R = NMe_2**	**2a**	**R = NMe_2**
1b	**R = $1/2(O_2C_2Me_4)$**	**2b**	**R = $1/2(O_2C_2Me_4)$**
1c	**R = Me**	**2c**	**R = Me**
1d	**R = $CHMe_2$**	**2d**	**R = $CHMe_2$**

The new boryl derivatives of indenes and indenides are of interest as building blocks in organic and organometallic syntheses. The high reactivities of the B–C, B–N and B–O bonds open the route to a large

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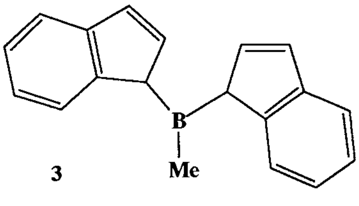
variety of potential later modifications and thus add to the synthetic value of these compounds.

2. Results and discussion

2.1. Indenylboranes

The reaction of 1-(trimethylsilyl)indene, (1-Ind)SiMe$_3$, with BBrMe$_2$ failed to give the desired (1-Ind)BMe$_2$. This failure is not surprising since the related cyclopentadienyl compound 5-(Me$_3$Si)Cp is known to undergo this type of substitution only with the most Lewis acidic boron halides [2]. When BBrMe$_2$ is treated with LiInd in hexane at low temperature (THF as solvent would undergo fast ether cleavage), the allylic isomer **1c** is readily obtained as the main product. However, the ^{1}H-NMR spectra of the mixture discloses the presence of a small amount of indene, and displays additional peaks in the range of vinylic, allylic, and boron-bonded methyl protons, at ca. 6.32, 6.19, 3.69 and 0.64 ppm with approximate intensities 2/2/2/3, respectively. These signals cannot belong to the vinylic isomer **2c** since in the ^{13}C-NMR spectra, broad signals are observed at ca. 54.89, 55.01 and 57.76 ppm, i.e. in a range typical for an allylic carbon bonded to boron, instead of 145–150 ppm for a vinylic carbon bonded to boron [3]. Furthermore, the ^{13}C-NMR spectrum displays 24 peaks in the aromatic region clearly indicative of three different indenyl units, eight for the main product **1c** and 16 additional ones. By careful integration of the ^{1}H-NMR spectrum, it became clear that in the by-product, one boron-bonded methyl group was lost. Accordingly, the formula for the by-product should be $(C_9H_7)_2BMe$ (**3**) with a boron–methyl group connecting two indenyl units with the boron in the allylic position. Since compound **3** contains two stereocenters, it should be an approximate 1:1 mixture of *rac* (C_2 symmetry) and *meso* (C_s symmetry) isomers, thus accounting for the 16 ^{13}C signals observed. Mass spectral data are in agreement with this interpretation, a single boron-containing pattern being observed at m/e 256 [$M^+ = 256$ for $C_{19}H_{17}B$ (**3**)], and further support was obtained by COSY and NOE experiments. Since the starting material BBrMe$_2$ did not contain any BBr$_2$Me, one has to assume a dismutation during the course of the reaction as often observed in boron chemistry [4].



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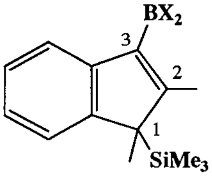
When BCl^{i}Pr$_2$ is treated with LiInd in hexane at low temperature, the product obtained is the allylic isomer **1d** with minute amounts of the vinylic compound **2d**. Thus, as previously observed [1], the 1-indenyl or allylic isomer **1d** appears as the kinetic compound, readily obtained at low temperature, while the more stable 3-indenyl compound or vinylic isomer **2d** is the thermodynamically more stable compound (see below).

The disubstituted indene $C_9H_6(SiMe_3)[B(O_2C_2Me_4)]$ (**5**) was also prepared from the reaction of the salt **4b** with Me$_3$SiCl.

$$\mathbf{4b} + Me_3SiCl \rightarrow \mathbf{5} + LiCl$$

This case is more complex since for a disubstituted compound, a total of seven isomers could be expected formally. If the less likely 2-position is excluded, three isomers, **5**, **6** and **7**, remain. In fact, from COSY and NOE experiments the major component of the product mixture (ca. 80%) was identified as isomer **5** with the boron moiety BX$_2$ [X = 1/2(O$_2$C$_2$Me$_4$)] in the vinylic position and the SiMe$_3$ group in the allylic position. A second minor isomer **6** (ca. 20%) is also found where both substituents are bound to the allylic carbon atom. Isomer **7** with the SiMe$_3$ in the vinylic position and the boron moiety in the allylic position was not detected. Since allyl boranes generally interconvert by a fast allylic rearrangement [5], the two isomers **6** and **7** are thought to be in thermodynamic equilibrium, and **6** should be the more stable isomer because of hyperconjugation effect. As a consequence, only isomer **6** is observed experimentally. Similar results were reported for $C_9H_6(SiMe_3)BX_2$ ($X = C_6F_5$) [6].



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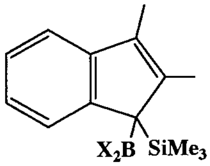

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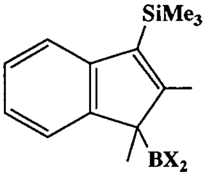

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2.1.1. Isomerization of 1d

As described above, the borylation of LiInd in hexane yields the allylic isomers **1c** and **1d** after the classical work-up. When the allylic isomer **1d** is treated with triethylamine at ambient temperature, a fast isomerization takes place to give the vinylic isomer **2d**. The ^{11}B chemical shift changes from $\delta = 87$ ppm for **1d** to $\delta = 54$ ppm for **2d** (CDCl$_3$). These observations prove the earlier notion that the allylic isomers are the products of kinetic control while the vinylic isomers are thermodynamically more stable.

If pyridine is used as a tertiary amine, the same type of isomerization takes place, easily monitored by ^{13}C-NMR: in particular, the broad signal at 52.13 ppm ascribed to the allylic boron–carbon bond disappears

Table 1
^{1}H-NMR shifts of Li[1-$C_9H_6BX_2$] in THF-d_8

Atom	LiInd	**4a**	**4b**	**4c**	**4d**
X		2.72	1.25	0.70; 0.90	1.36; 2.20
2	6.51	6.70	6.96	7.15	7.27
3	5.90	6.00	6.01	6.00	5.99
4	7.29	7.30	7.27	7.17	7.11
5	6.43	6.50	6.49[a]	6.45	6.49
6	6.43	6.54	6.53[a]	6.52	6.42
7	7.29	7.28	7.82	7.78	7.76

[a] These assignments are tentative and should possibly be reversed.

and a broad new signal at ca. 146.5 ppm appears that is clearly indicative of a vinylic boron–carbon bond. Both isomers could be characterized by their ^{13}C-NMR spectra (see Section 3). Interestingly, the ^{11}B-NMR ($CDCl_3$) signal is observed at ca. 5 ppm in this case, indicating the presence of tetracoordinated boron. Thus, the sterically less demanding base pyridine not only functions as an isomerization catalyst but also forms adducts with the isomers **1d** and **2d**.

2.2. Metalation of the boranes **1c** and **1d**

In a previous report the authors had described the metalation of the indenylboranes **2a** and **1b**. In much the same manner, the 1-indenyl compound **1c** can be readily metalated with more or less bulky bases, such as lithium-2,2,6,6-tetramethylpiperidide (LiTMP) in THF to produce the borylindenide **4c** in good yields. While the indenylborane **1c** was contaminated by the bridged species **3**, the lithium salt **4c** obtained was quite pure according to its ^{1}H-NMR spectrum. In the di*iso*propyl series, the salt **4d** was also readily obtained with LiTMP as the base as well as with $LiN(SiMe_3)_2$ in hexane or with LiInd.

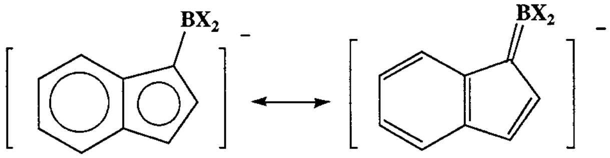
2.2.1. ^{1}H-NMR spectra

The ^{1}H-NMR chemical shifts of the borylindenides **4c** and **4d** are reported in Table 1 together with those previously measured for **4a** and **4b** and compared with LiInd in the same solvent. The assignments (except for **4a**) were deduced from (^{1}H–^{1}H) COSY and NOE experiments.

From the values reported in Table 1, proton 2, close to the boron atom, is seen to be shifted to low field, the deshielding increasing according to **4a** < **4b** < **4c** < **4d**. The same trend has been observed for borylcyclopentadienides [7]. It can be attributed to the combined influences of resonance interactions and the diamagnetic anisotropy of the boron center. A related deshielding is experienced by proton 7.

2.2.2. ^{13}C-NMR spectra

^{13}C-NMR chemical shifts are reported in Table 2. A downfield shift is observed for the five cyclopentadienyl carbon atoms 1, 2, 3, 8 and 9 increasing according to the sequence **4a** < **4b** < **4c**, **4d**. This is in line with the trend previously observed with Cp derivatives [7]. In as much as carbon chemical shifts of monocyclic aromatic rings are correlated with the π-electron density per carbon atom [8], the downfield shifts observed are direct evidence for the electron-withdrawing abilities of the boryl substituents. In contrast to this situation, the ^{13}C chemical shifts of the arene carbon atoms 4, 5, 6 and 7 are much less influenced by the nature of the boryl substituents. These observations indicate that the boratafulvene resonance formula II with a B=C bond is of large weight, and is especially important for the dialkylboryl species **4c** and **4d**.



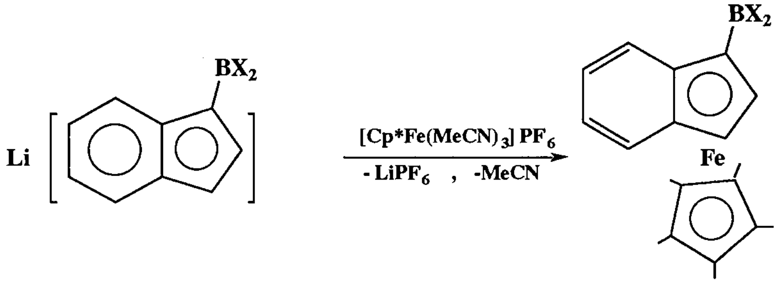
I **II**

Table 2
^{13}C-NMR shifts of Li[1-$C_9H_6BX_2$] in THF-d_8

Atom	LiInd	**4a**	**4b**	**4c**[a]	**4d**
1	91.34	102.2 (br)	Not observed	119.0 (br)	117.3 (br)
2	120.05	127.13	126.98	132.23	133.49
3	91.34	95.06	98.50	103.12	103.63
3a,7a	129.98	135.87	138.43	141.10	141.29
		132.87	134.19	138.86	139.11
4	115.82[b]	119.19	119.10	118.17	118.08
5	114.54[b]	114.22[b]	115.14[b]	114.67	114.72
6	114.54	114.62[b]	115.52[b]	115.49	115.58
7	115.82	122.12	122.22	121.41	122.08

[a] These assignments were deduced from (^{1}H–^{13}C) HETCOR experiments.

[b] These assignments are tentative and possibly should be reversed.



4a $X = NMe_2$ **8**

4b $X = 1/2(O_2C_2Me_4)$ **9**

Scheme 1.

2.2.3. *Variable temperature ^{1}H-NMR spectra*

The boratafulvene resonance formula II with a B=C bond implies the presence of a barrier to rotation around this bond. Indeed, the ^{1}H-NMR spectra of **4c** in THF-d_8 are temperature-dependent. At r.t. (25°C), two signals are observed for the two methyl groups of the BMe_2 at 0.70 and 0.90 ppm. On warming the sample, these signals broaden, and coalesce at 52°C. When dioxane-d_8 was used as solvent only a single signal was detected for the two methyl groups, even at r.t. Lineshape analysis [9,10] was used to analyze the spectra of the THF-d_8 solutions and to derive a barrier to internal rotation of $\Delta G^{\ddagger} = 65.4 \pm 2.3$ kJ mol^{-1}. Interestingly, such a barrier to rotation was only observed for the dimethylboryl compound where the contribution of the boratafulvene formula II should be most pronounced.

The barrier to rotation reported here is of course lower than the barrier for borataethene ions. Thus, the barrier for $(Mes_2BCHPh)^-$ was estimated to be >92 kJ mol^{-1} [11], and the related ions $(Mes_2BCHSiMe_3)^-$ and $(Mes_2BCHSPh)^-$ were found to be static on the NMR time scale at temperatures up to 140°C [12].

2.3. *Syntheses of transition metal complexes*

The lithium salts **4a** and **4b** were used to prepare the iron complexes $Cp^*Fe[C_9H_6B(NMe_2)_2]$ (**8**) and $Cp^*Fe[C_9H_6B(O_2C_2Me_4)]$ (**9**) (Scheme 1), the bis(ligand) complex $Fe[C_9H_6B(O_2C_2Me_4)]_2$ (**10**) (Scheme 2), and the rhenium complex $Re(CO)_3[C_9H_6B(O_2C_2Me_4)]$ (**11**) (Scheme 3). The new complexes are moderately sensitive to air and moisture.

The complexes **8**–**11** were mainly characterized by their ^{1}H-NMR data (Table 3) and their ^{13}C-NMR data (Table 4). Note that the compounds **8**, **9** and **11** are chiral and hence are racemates. On the other hand, complex **10** can exist as two diastereoisomers, as a *meso* isomer (of averaged C_s symmetry) and a racemic isomer (of averaged C_2 symmetry). In this case, the primary product mixture contained the diastereoisomers in a 4/1 ratio, and after fractional crystallization, the major isomer was isolated as purple needles. Unfortunately, the crystals so obtained were not suitable for an X-ray structure determination, and so an assignment of the product stereochemistry was not possible. Reported NMR data concern the major isomer (see Section 3).

The NMR spectra of the complexes **8**–**11** show common features. In each case, the proton and carbon atoms belonging to the Cp moieties are observed at very highfield relative to the lithium salts, while the arene protons and the carbon atoms C(4) to C(7) are rather unaffected. These observations clearly indicate an η^5-co-ordination and all four complexes are classical 18-electron species.

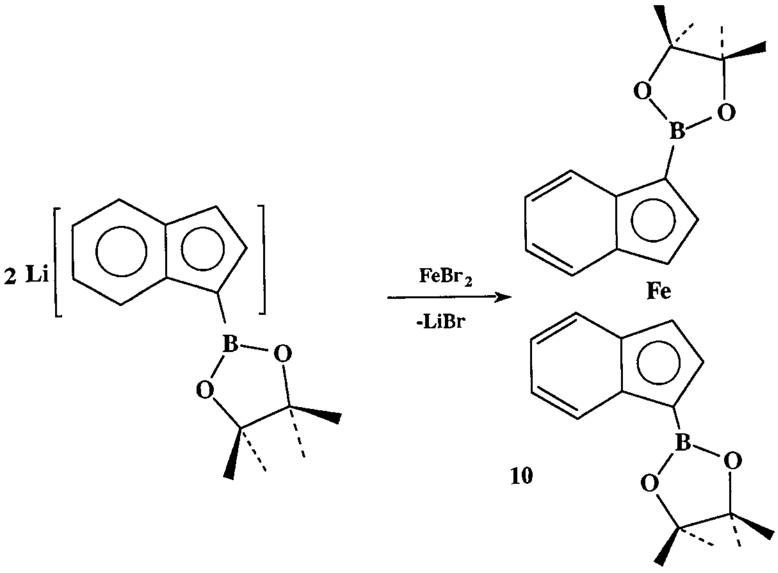
3. Experimental

Reactions were carried out under an atmosphere of nitrogen by means of conventional Schlenk techniques. Hexane was distilled from potassium, toluene from Na/K alloy, and THF from sodium benzophenone ketyl. NMR spectra were used to judge the purity of the new compounds.

NMR spectra were recorded on a Varian Unity 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125.7 MHz; ^{11}B, 160.4 MHz) and on a Varian EM 390A (^{11}B, 27.8 MHz). Mass spectra were recorded on a Finnigan MAT-95 spectrometer.

3.1. *(1-Indenyl)dimethylborane (**1c**)*

$BBrMe_2$ [13] (3.76 g, 31.15 mmol) in hexane (10 ml) was added dropwise to a stirred suspension of lithium indenide (LiInd) [14] (3.61 g, 29.59 mmol) in hexane (60 ml) at −78°C. A color change from white to a light yellow was taken to indicate the equivalence point.



Scheme 2.

After the solution had warmed to ambient temperature, the lithium bromide formed was filtered off and carefully washed with several portions of hexane. The solvent was then removed in a vacuum to leave **1c** (1.84 g, 40%) as a yellowish oil. Caution: if the amount of solvent was insufficient, the synthesis of **1c** was unsuccessfull and the reaction mixture was spontaneously flammable.

MS (EI, 70 eV): m/z $(I_{rel}) = 156$ (3, M$^+$), 141 (11, M$^+$-Me), 116 (100, $C_9H_6^+$).

^{1}H-NMR ($CDCl_3$): $\delta = 0.64$ (s, 6H), 4.06 (s, 1H), 6.55 (dd, 1H), 6.96 (ddd, 1H), 7.16 (m, 1H), 7.25 (m, 1H), 7.37 (m, 1H), 7.46 (m, 1H). ^{13}C-NMR ($CDCl_3$): $\delta = 10.00$, 55.01, 121.13, 123.55, 124.14, 125.47, 131.14, 135.39, 144.99, 145.18. ^{11}B-NMR ($CDCl_3$): $\delta = 90$.

3.2. *Lithium[1-(dimethylboryl)indenide] (4c)*

Compound **1c** (4.94 g, 31 mmol) in THF (40 ml) was added dropwise to a stirred solution of LiTMP [15] (4.67 g, 31 mmol) in THF (80 ml) at −78°C within 5 min. After the solution had warmed to ambient temperature, the solid was transferred onto a frit and washed twice with hexane. Drying in a vacuum gave **4c** (3.26 g, 65%) as a light pink powder, highly sensitive to air and humidity. A small amount of deborylated compound, LiInd, was also observed, and complete deborylation occurred with LDA and $LiN(SiMe_3)_2$.

^{11}B-NMR (THF-d_8): $\delta = 55.41$.

3.3. *(1-Indenyl)diisopropylborane (1d)*

BCl^iPr_2 [16] (21.20 g, 0.16 mol) was added dropwise to a stirred suspension of lithium indenide (LiInd) (18.32 g, 0.15 mol) in hexane (300 ml) at −78°C. A color change from white to light yellow was taken to indicate the equivalence point. After the suspension had warmed to ambient temperature, the lithium chloride formed was filtered off and washed with several portions of hexane. After removal of the solvent, the residue was warmed under vacuum (10^{-6} bar) and **1d** was collected by condensation (29.23 g, 92%) as a yellowish liquid.

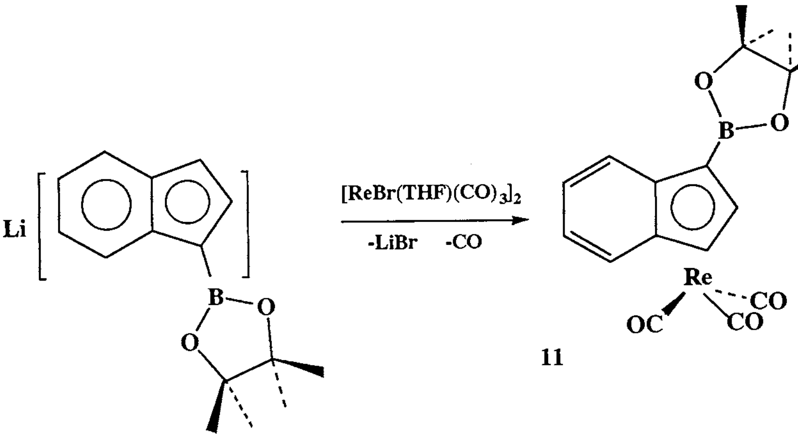
MS (EI, 70 eV): m/z $(I_{rel}) = 212$ (53, M$^+$), 115 (45, $C_9H_7^+$).

^{1}H-NMR ($CDCl_3$): $\delta = 0.75$ (m, 2Me + 2Me), 1.04 (m, 2H), 4.17 (s, 1H), 6.30 (dm, 1H, $^3J = 5.5$ Hz), 6.97 (dm, 1H), 7.16 (tm, 1H), 7.18 (dm, 1H), 7.05 (tm, 1H), 7.41 (dm, 1H). ^{13}C-NMR ($CDCl_3$): $\delta = 17.87$ (Me), 20.39 (*C*HMe2), 52.13 (*C*B), 133.45, 132.43, C_6H_4: 123.49, 124.00, 124.01, 125.31, 146.15, 146.87. ^{11}B-NMR ($CDCl_3$): $\delta = 87$.

3.4. *(3-Indenyl)diisopropylborane (2d)*

Triethylamine (0.45 g, 4.45 mmol) was added to a stirred solution of compound **1d** (1.02 g, 4.78 mmol) in hexane (20 ml) at r.t. After 1 h, the solvent was removed in a vacuum to leave a yellowish liquid with 95% of **2d**, but traces of **1d** still remained.

^{1}H-NMR ($CDCl_3$): $\delta = 1.02$ (m, 2Me + 2Me), 1.85 (m, 2H), 3.39 (m, 2H), 6.38 (m, 1H), 7.11–7.23 (m, 3H), 7.41 (dm, 1H). ^{13}C-NMR ($CDCl_3$): $\delta = 17.18$ (Me), 23.91 ($CHMe_2$), 40.32, 122.11, 123.26, 123.90, 125.73, 135.40, 143.76, 147. 89, 150.53 (*C*B). ^{11}B-NMR ($CDCl_3$): $\delta = 54$.



Scheme 3.

3.5. Lithium [1-(diisopropylboryl)indenide] (4d)

Compound **1d** (2.80 g, 12.20 mmol) in THF (20 ml) was added dropwise to a stirred solution of LiTMP (1.81 g, 12.20 mmol) in THF (80 ml) at −78°C within 5 min. After the solution had warmed to ambient temperature, hexane was added, the upper layer was taken off and the residue was dried a long time in a vacuum to leave **4d** as a light brown, slightly sticky powder, highly sensitive to air and humidity. $LiN(SiMe_3)_2$ [17] and LiInd can also be used as base but deborylation occurs with LDA.

^{11}B-NMR (THF-d_8): $\delta = 51.44$.

3.6. 2-[1-(Trimethylsilyl)inden-3-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

Me_3SiCl (0.21 g, 1.96 mmol) was added to a stirred suspension of $Li[C_9H_6B(O_2C_2Me_4)]$ (0.46 g, 1.86 mmol) in hexane (50 ml) at r.t. After 8 h, the light yellow suspension was heated under reflux for 4 h. After the orange mixture had cooled down, the lithium chloride formed was filtered off and carefully washed with several portions of hexane. The solvent was then removed in a vacuum to leave **5** (0.60 g, 60%) as a yellowish powder.

MS (EI, 70eV): m/z (I_{rel}) = 314 (40, M^+), 299 (13, M^+-Me), 214 (81, $C_9H_6BO_2SiMe_2^+$), 183 (15, M^+-3Me).

^1H-NMR ($CDCl_3$): $\delta = 0.04$ (s, 3Me), 1.44 (s, 4Me), 3.71 (d, 1H), 7.24 (dt, 1H), 7.34 (dt, 1H), 7.45 (d, 1H), 7.51 (dd, 1H), 8.02 (dd, 1H). ^{13}C-NMR ($CDCl_3$): $\delta = -1.99$, 25.76, 49.81, 84.05, 123.52, 124.08, 124.78, 125.98, 132.55, 146.97, 147.79, 152.02. ^{11}B-NMR ($CDCl_3$): $\delta = 29.41$.

Table 3
^1H-NMR data of complexes **8**, **9**, **10** and **11** (C_6D_6)

8	**9**	**10**	**11**	Assignment
7.55	8.12	7.35(2)	8.08	$C\mathit{H}(7)$
7.36	7.28	6.85(6)	6.91	$C\mathit{H}(4)$
7.06, 6.98	7.00(2)		6.69, 6.59	$C\mathit{H}(5,6)$
4.45	4.48	5.18	5.67	$C\mathit{H}(2,3)$[a]
3.96	4.34	4.81	5.10	$C\mathit{H}(2,3)$[a]
2.90				$N(C\mathit{H}_3)_2$
	1.25, 1.26	1.25, 1.26	1.15, 1.16	$O_2C_2(C\mathit{H}_3)_4$
1.57	1.65			$C_5(C\mathit{H}_3)_5$

[a] These assignments are tentative and possibly should be reversed.

3.7. [1-{Bis(dimethylamino)boryl}indenyl](pentamethylcyclopentadienyl)iron (8)

$[Cp^*Fe(MeCN)_3]PF_6$ [18] (2.02 g, 4.41 mmol) in MeCN (20 ml) was added dropwise to a stirred solution of $Li[C_9H_6B(NMe_2)_2]$ (0.97 g, 4.41 mmol) in THF (40 ml) at r.t. After 1 h, the solvent was removed in a vacuum. Hexane was then added. The solid formed was filtered off and carefully washed with several portions of hexane. The solvent was then removed in a vacuum to leave **8** (1.64 g, 92%) as a purple powder.

MS (EI, 70 eV): m/z (I_{rel}) = 404 (8, M^+), 326 (51, $FeCp_2^{*+}$), 116 (22, $C_9H_8^+$).

^{11}B-NMR (C_6D_6): $\delta = 34.08$.

3.8. (Pentamethylcyclopentadienyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)indenyl]iron (9)

$[Cp^*Fe(MeCN)_3]PF_6$ [18] (0.48 g, 1.05 mmol) in MeCN (15 ml) was added dropwise to a stirred solution of $Li[C_9H_6B(O_2C_2Me_4)]$ (0.26g, 1.05 mmol) in THF (40 ml) at r.t. After 1 h, the solvent was removed in a vacuum. Hexane was then added. The solid formed was filtered off and carefully washed with several portions of hexane. The solvent was then removed in a vacuum to leave **9** (0.41 g, 90%) as a red powder; m.p. 142°C. Crystallization from hexane at −30°C gives small red crystals, not suitable for a X-ray structure.

Table 4
^{13}C-NMR data of complexes **8**, **9**, **10** and **11** (C_6D_6)

8	**9**	**10**	**11**	Assignment
Not observed	Not observed	Not observed	Not observed	$C(1)$
70.26, 85.01	69.87, 81.96	67.26, 75.91	76.11, 96.86	$C(2,3)$
91.87, 93.62	93.32, 94.26	91.13, 92.15	109.88, 113.06	$C(3a,7a)$
122.01, 122.89, 128.03, 130.76	122.69, 123.79, 126.71, 130.10	122.81, 123.54, 124.73, 128.39	123.70, 125.69, 126.58, 126.75	$C(4,5,6,7)$
77.13	77.66			$C_5(CH_3)_5$
10.48	10.00		$C_5(CH_3)_5$	
			193.14	CO
42.18				$N(CH_3)_2$
	25.52, 25.59	25.19, 25.34	24.51, 24.55	$O_2C_2(CH_3)_4$
	82.85	83.25	83.89	$O_2C_2(CH_3)_4$

MS (EI, 70 eV): m/z (I_{rel}) = 432 (100, M$^+$), 326 (11, $FeCp_2^{*+}$), 115 (7, $C_9H_7^+$). Anal. Found: C, 69.18; H, 7.77. $C_{25}H_{33}BFeO_2$ calc.: C, 69.48; H, 7.70.

^{11}B-NMR (C_6D_6): $\delta = 33.78$.

3.9. *Bis[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-indenyl]iron* (**10**)

A suspension of $FeBr_2$(DME) (0.90 g, 3.23 mmol) in THF (30 ml) was added dropwise to a stirred solution of $Li[C_9H_6B(O_2C_2Me_4)]$ (1.60 g, 6.46 mmol) in THF (80 ml) at −78°C. After 15 h, the solvent was removed and toluene was added. The lithium bromide formed was filtered off and carefully washed with several portions of toluene. The solvent was then removed in a vacuum to leave the isomer mixture **10** (ratio 4/1, from ^{1}H-NMR spectrum) as a brown powder. After two crystallizations from toluene at −80°C, the major isomer was obtained as purple needles; m.p. 186°C.

MS (EI, 70 eV): m/z (I_{rel}) = 538 (4, M$^+$), 412 [100, MH$^+$-$B(O_2C_2Me_4)$], 115 (20, $C_9H_7^+$). Anal. Found: C, 66.86; H, 6.66. $C_{30}H_{36}B_2FeO_4$ calc.: C, 66.97, H, 6.74.

^{11}B-NMR (C_6D_6): $\delta = 34.21$.

3.10. *[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-(tricarbonyl)rhenium* (**11**)

$[ReBr(THF)(CO)_3]_2$ [19] (1.05 g, 1.25 mmol) in THF (15 ml) was added dropwise to a stirred solution of $Li[C_9H_6B(O_2C_2Me_4)]$ (0.59 g, 2.38 mmol) in THF (35 ml) at r.t. After 15 min, the solvent was removed in a vacuum. Hexane was then added. The lithium bromide formed was filtered off and carefully washed with several portions of hexane. By removing the solvent, small colorless crystals of **11** were obtained (0.38 g, 60%); m.p. 158.5°C.

MS (EI, 70 eV): m/z (I_{rel}) = 512 (100, M$^+$), 386 [66, $C_9H_6Re(CO)_3^+$], 300 (70, $C_9H_5Re^+$), 115 (27, $C_9H_7^+$). Anal. Found: C, 41.98; H, 3.55. $C_{18}H_{18}BO_5Re$ calc: C, 42.28; H, 3.55.

^{11}B-NMR (C_6D_6): $\delta = 30.80$.

IR (in hexane): 1936, 1943, 2029 cm^{-1}.

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