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Synthesis and Coordination Chemistry of 3a,7a-Azaborindenyl, a New Isoelectronic Analogue of the Indenyl Ligand

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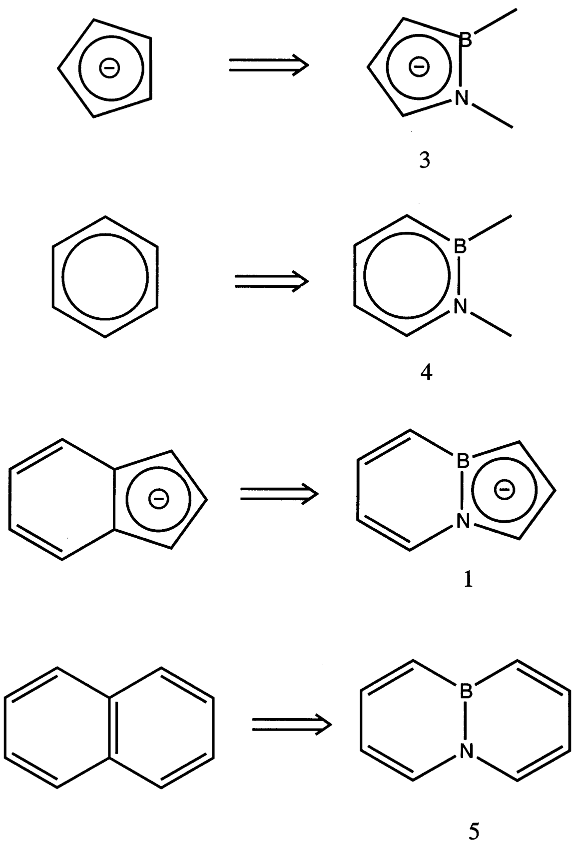
*Summary: The fused-ring diheteroaromatic 3a,7a-azaborindenyl anion (**1**) has been prepared by a synthesis using the Grubbs ring-closing metathesis. **1** has been converted to the Cp^*ZrCl_2 complex **2**, which closely resembles the corresponding (Ind)Cp^*ZrCl_2.*

The cyclopentadienyl (Cp) group is surely the most widely used ligand in organometallic chemistry, while the indenyl (Ind) group is a particularly important type of Cp ligand.[1] Group 4 metal Cp derivatives are important homogeneous catalysts for the polymerization of olefins, and in this class Ind derivatives are among the most active and stereoselective catalysts.[2] Since 1996 we have been interested in the modification of Ziegler−Natta catalysts by the substitution of boron-based heterocycles for Cp.[3,4] In this communication we report on the synthesis of the new indenyl surrogate 3a,7a-azaborindenyl (**1**) and on its conversion to the indenyl-like zirconium complex **2**.

Scheme 1



The replacement of an adjacent pair of carbon atoms of Cp by boron and nitrogen leads to the isoelectronic 1,2-azaborolyl (**3**; Scheme 1), which has been used as an electron-rich[5,6] surrogate for Cp in a variety of transition-metal complexes.[7,8] In a similar manner the replacment of two carbon atoms of benzene by boron and nitrogen transforms it into the isoelectronic 1,2-dihydro-1,2-azaborine (**4**),[9,10] which has been shown to have arene-like properties.[11] Ring fusion of **3** and **4** at the BN positions leads to 3a,7a-azaborindenyl (**1**), which is isoelectronic with indenyl. To the best of our knowledge, **1** has not previously been mentioned in the chemical literature. However it is obviously closely related to 4a,8a-azaboranaphthalene (**5**)[12] and similar B,N-aromatics[13] which were prepared by Dewar and co-workers in the 1960s.

We have previously shown that **3** and **4** could be prepared via syntheses using ring-closing metathesis (RCM) on appropriate vinyl or allyl aminoboranes.[8] These syntheses have now been extended to the preparation of ring-fused **1**,[14] as illustrated in Scheme 2.

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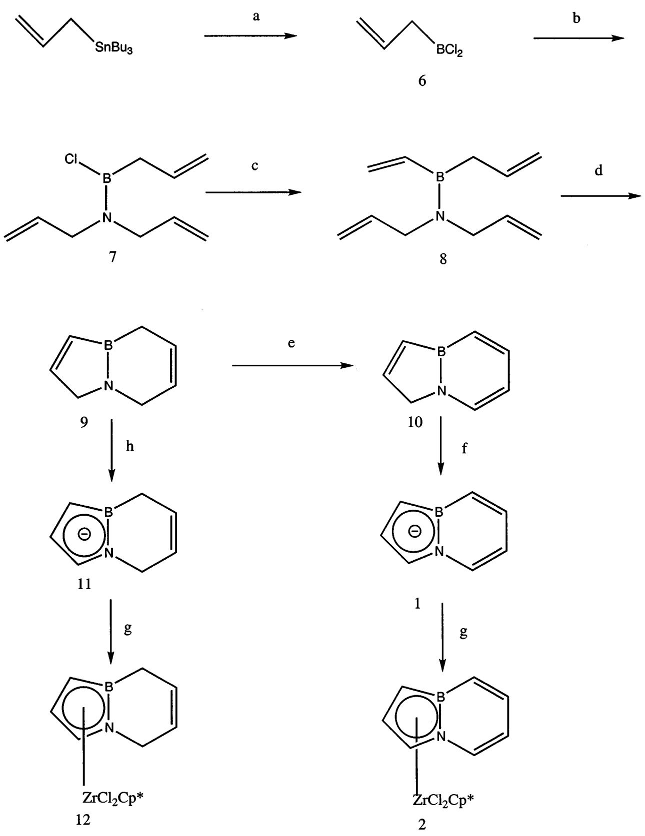
Allyltributyltin reacts with BCl_3 in pentane at −78 °C to afford allylboron dichloride (**6**), which is not isolated.[15]

Scheme 2[a]



[a] Legend: (a) BCl_3; (b) $(C_3H_5)_2NH$; (c) C_2H_3MgBr; (d) $(Cy_2P)_2(PhCH)RuCl_2$; (e) DDQ; (f) $KN(SiMe_3)_2$; (g) CP^*ZrCl_3; (h) LDA.

In situ addition of diallylamine at −78 °C followed by triethylamine gives adduct **7** in 95% yield.[14a] The reaction of **7** with vinylmagnesium bromide affords **8** in 84% yield.[14b] Both **7** and **8** display ^1H and ^{13}C NMR spectra which show that the *N*-allyl groups are nonequivalent. This is an expected consequence of slow rotation about the B−N bond on the NMR time scale.[16] The treatment of **8** with 5 mol % of Grubbs catalyst ($(Cy_3P)_2(PhCH)RuCl_2$) in refluxing CH_2Cl_2 for 24 h gives a 59% yield of **9**,[14c] which is formed by two RCM sequences.[17,18] Dehydrogenation of **9** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in pentane affords a 30% yield of the azaborindene **10** as a pale yellow liquid which has a strong indene-like odor.[14d]

The sequential reaction of **10** with $KN(SiMe_3)_2$ and Cp^*ZrCl_3 in toluene affords a 60% yield of yellow crystals of **2**.[14e] The molecular structure of **2** is illustrated in Figure 1, and selected bond distances are collected in Table 1.[19] The structure closely resembles

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(14) Experimental procedures and characterization of new compounds are as follows. (a) Allyl(diallylamino)boron chloride (**7**): a solution of allyltributyltin (62.2 g, 0.19 mol)23 in 50 mL of hexane was added dropwise to a solution of BCl_3 (24.8 g, 0.21 mol) in 120 mL of hexane at −78 °C. After the reaction mixture was stirred at −78 °C for 1 h, it was warmed to 25 °C for 2 h followed by recooling to −78 °C. Then diallylamine (23.5 mL, 0.19 mol) was added dropwise, followed by triethylamine (26.7 mL, 0.19 mol). The mixture was stirred for 12 h while it was slowly warmed to 25 °C. The solvent was removed under reduced pressure, and the product (33.1 g, 95%) was obtained by distillation (bp 38 °C at 0.1 Torr). HRMS: m/z calcd for $C_9H_{15}{}^{11}B^{35}ClN$ 183.0986, found 183.0984. ^1H NMR (C_6D_6, 300 MHz): δ 1.90 (d, J = 7.1 Hz, 2H, CH_2B), 3.32 (d, J = 5.2 Hz, 2H, CH_2N), 3.65 (d, J = 5.5 Hz, 2H, CH_2N'), 4.8−5.0 (m, 6H, 3Vi *H*), 5.3 (m, 1H, Vi *H*), 5.5 (m, 1H, Vi *H*), 5.9 (m, 1H, Vi *H*). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 38.1. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 50.5, 51.3, 115.0, 116.0, 116.2, 134.9, 135.0 (one allyl and one vinyl C not observed). (b) Allyl(diallylamino)vinylborane (**8**): a solution of vinylmagnesium bromide, which had been prepared from vinyl bromide (23.5 g, 0.22 mol) and magnesium (5.3 g, 0.2 mol) in 250 mL of THF, was added to a solution of **3** (33.1 g, 0.18 mol) in 100 mL of THF at −78 °C. The reaction mixture was stirred for 10 h and warmed slowly to 25 °C. The solvent was removed under reduced pressure, and the residue was extracted with pentane. The solvent was removed from the extracts, and the product (26.5 g, 84%) was distilled (bp 36 °C at 0.1 Torr). HRMS: m/z calcd for $C_{11}H_{18}{}^{11}BN$ 175.1532, found 175.1529. ^1H NMR (C_6D_6, 400 MHz): δ 1.94 (d, J = 7.3 Hz, 2H, BCH_2), 3.48 (broad s, 4H, $2NCH_2$), 4.88 (m, 6H, Vi CH_2), 5.46 (m, 2H, Vi *H*), 5.8−6.0 (m, 3H, Vi *H*), 6.26 (dd, J = 19.6, 13.7 Hz, 1H, BC*H*). ^{11}B NMR (C_6D_6, 115 MHz): δ 39.7. ^{13}C NMR (CH_2D_2, 125.7 MHz): δ 24 (broad), 51, 51.4, 113.3, 115.2, 115.5, 131.4, 135.1, 136.5, 137.6, 139 (broad). Anal. Calcd for $C_{11}H_{18}BN$: C, 75.44; H, 10.38; N, 8.00. Found: C, 75.38; H, 10.29; N, 8.02. (c) 4,7-Dihydro-4a,7a-azaborindene (**9**): a solution of **8** (26.5 g, 0.15 mol) in 50 mL of CH_2Cl_2 was added to a solution of $(Cy_3P)_2(PhCH)RuCl_2$ (6.23 g, 75 mmol) in 150 mL of CH_2Cl_2, and the resulting mixture was heated to reflux for 24 h. The solvent was removed under reduced pressure, and the residue was distilled to obtain the product (10.6 g, 59%; bp 27 °C at 0.1 Torr). HRMS: m/z calcd for $C_7H_{10}{}^{11}BN$ 119.0906, found 119.0906. ^1H NMR (C_6D_6, 400 MHz): δ 1.68 (broad, s, 2H, CH_2B), 3.19 (d, J = 3 Hz, 2H, CH_2N), 3.46 (m, 2H, CH_2N'), 5.50 (d, m, J = 10.3 Hz, 1H, Vi *H*), 5.84 (d, m, J = 10.3 Hz, 1H, Vi *H*), 6.22 (d, J = 7.7 Hz, 1H, Vi *H*), 6.78 (d, J = 8.1 Hz, 1H, Vi *H*). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 37.7. ^{13}C NMR (C_6D_6, 100.5 MHz): δ 13.0 (broad), 45.6, 60.0, 124.8, 125.8, 133 (broad), 148. (d) 3a,7a-Azaborindene (**10**): a solution of **9** (4.5 g, 37.8 mol) in 25 mL of pentane was added to a suspension of DDQ (10.4 g, 45.6 mol) in 50 mL of pentane. The mixture was stirred at 25 °C for 10 h, after which the solid was removed by filtration. The filtrate was distilled, affording product (1.3 g, 30%; bp 26 °C at 0.1 Torr). HRMS: m/z calcd for $C_7H_{10}{}^{11}BN$ 117.0750, found 117.0752. ^1H NMR (C_6D_6, 400 MHz): δ 3.52 (broad, s, 2H, CH_2N), 6.11 (t, J = 6.3 Hz, 1H, C(5)*H*), 6.52 (m, 2H, C(1)*H*C(2)*H*), 6.94(d, J = 6.3, 1H, C(4)*H*), 7.06 (d, J = 11.1 Hz, 1H, BC*H*), 7.61(dd, J = 11.1, 6.3 Hz, 1H, C(6)*H*). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 34.2. ^{13}C NMR (C_6D_6, 100.5 MHz): δ 58.8, 109.5, 124 (broad), 133.6 (broad), 135.3, 143.2, 144.2. Anal. Calcd for $C_7H_{10}BN$: C, 71.87; H, 6.91; N, 11.98. Found: C, 71.77; H, 7.04; N, 11.85. (e) (3a,7a-Azaborindenyl)(pentamethylcyclopentadienyl)zirconium dichloride (**2**): a 0.5 M solution of $KN(SiMe_3)_2$ (6.80 mL, 3.40 mmol) in toluene was added dropwise to a solution of **12** in 10 mL of toluene at −78 °C. The mixture was stirred for 6 h and slowly warmed to 0 °C. The solution was filtered, and the solid was washed successively with 3 × 5 mL of toluene and 3 × 10 mL of pentane. Ethyl ether (15 mL) was added to the solid, and the resulting suspension was added to a solution of Cp^*ZrCl_3 (1.12 g, 3.36 mmol) in 10 mL of ether at −50 °C. The resulting orange suspension was stirred for 10 h and warmed slowly to 25 °C. After removal of the volatiles under vacuum, the product was extracted with ether. The extracts were slowly concentrated by partial removal of solvent, and the resulting solution was stored at −20 °C until yellow crystals (0.71 g, 51%) were obtained. The structure was confirmed by X-ray crystallography. ^1H NMR (CD_2Cl_2, 400 MHz): δ 2.00 (s, 15H, Cp*Me*), 4.85 (dd, J = 5.1, 1.8 Hz, 1H, C(1)*H*), 6.27 (dd, J = 5.3, 2.4 Hz, 1H, C(2)*H*), 6.58 (td, J = 6.6, 1.1 Hz, 1H, C(5)*H*), 6.82 (t, J = 2.4 Hz, 1H, C(3)*H*), 7.15 (d, J = 11.7 Hz, 1H, C(7)*H*), 7.36 (dd, J = 11.7, 6.4 Hz, 1H, C(6)*H*), 7.64 (dd, J = 6.0, 1.0 Hz, 1H, C(4)*H*). ^{11}B NMR (CD_2Cl_2, 115.5 MHz): δ 23.8. ^{13}C NMR (CD_2Cl_2, 100.5 MHz): δ 12.6, 115.4, 115.8, 121.5, 125.0, 129.6, 136.9; C(3), C(4) not observed. Anal. Calcd for $C_{17}H_{22}$ BCl_2NZr: C, 49.40; H, 5.38; N, 3.37. Found: C, 49.03; H, 5.53; N, 3.23. (f) (4,7-Dihydro-3a,7a-azaborindenyl)(pentamethylcyclopentadienyl)zirconium dichloride (**12**): in a manner similar to that for the preparation of **2**, **9** (0.30 g, 2.56 mmol) was converted to **11** with LDA in ether, which on treatment with Cp^*ZrCl_3 (0.85 g, 2.56 mmol) gave **12** (0.63 g, 60%). The structure was confirmed by X-ray crystallography. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.70 (dm, J = 20 Hz, 1H, C(7)*H*), 2.00 (dm, J = 20 Hz, 1H, C(7)*H′*), 2.00 (s, 15H, Cp*Me*), 4.04 (dm, J = 17.9 Hz, 1H, C(4)*H*), 4.14 (dd, J = 4.9, 2.4 Hz, 1H, C(1)*H*), 4.62 (dm, J = 17.9 Hz, 1H, C(4)*H′*), 5.54 (dm, J = 10.6 Hz, 1H, Vi *H*), 5.82 (dd, J = 5.1, 2.5 Hz, 1H, C(2)*H*), 5.89 (dm, J = 10.6 Hz, 1H, Vi *H*), 6.32 (t, J = 2.5 Hz, 1H, C(3)*H*). ^{11}B NMR ($CDCl_3$, 115.5 MHz): δ 32.3. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 12.7, 13.0 (broad), 45.9, 93.0 (broad), 117.3, 121.6, 122.7, 124.0, 126.9. Anal. Calcd for $C_{17}H_{24}BCl_2NZr$: C, 49.16; H, 5.84; N, 3.37. Found: C, 48.80; H, 6.12; N, 3.21.

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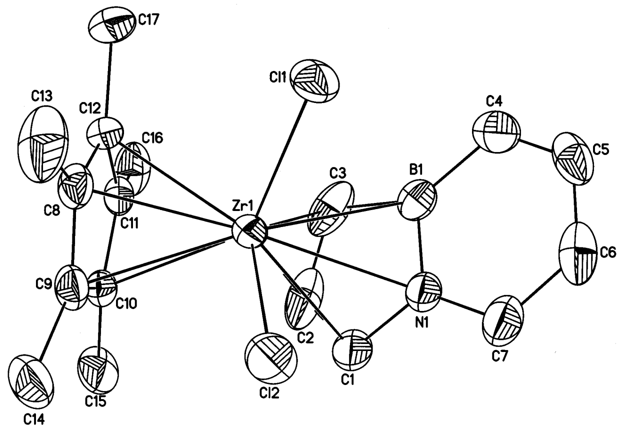

Figure 1. Molecular structure of **2** (ORTEP).

Table 1. Selected Bond Lengths (Å) for 2 and 12

bond	**2**[a]	**12**[a]
B−Zr	2.713(2)	2.690(2)
N−Zr	2.6118(15)	2.5560(10)
C(1)−Zr	2.501(2)	2.481(2)
C(2)−Zr	2.472(2)	2.458(2)
C(3)−Zr	2.469(2)	2.466(2)
C(Cp*)−Zr	2.435−2.583	2.442−2.582
B−N	1.458(3)	1.449(3)
B−C(3)	1.511(3)	1.508(3)
C(2)−C(3)	1.405(4)	1.410(4)
C(1)−C(2)	1.366(4)	1.376(4)
C(1)−C(N)	1.402(2)	1.394(3)
B−C(4)	1.506(4)	1.555(3)
C(4)−C(5)	1.353(3)	1.496(3)
C(5)−C(6)	1.411(3)	1.315(3)
C(6)−C(7)	1.344(3)	1.492(3)
C(7)−N	1.394(2)	1.467(2)

[a] The labeling schemes are the same for **2** and **12**.

thatof Cp*(Ind)ZrCl$_2$.[20] The C$_3$BN portion of the azaborindenyl unit is η^5-bound to Zr, while the carbocyclic portion of the C$_4$BN ring is not coordinated. The C$_3$BN ring is completely planar but is unsymmetrically bound to Zr. The C(1)C(2)C(3) unit is closer to Zr (2.47−2.50 Å) than are the bridgehead B (2.713 Å) and N (2.612 Å). Similar slip distortions of the metal away from boron are a common feature of π-coordinated boron heterocycles.[21] On the other hand, Cp*(Ind)ZrCl$_2$ shows a similar distortion in which the bridgehead carbon atoms are less strongly coordinated than those of the three-carbon bridge.[20] The indenyl distortion must be a consequence of unsymmetrical electron delocalization caused by the benzo fusion.[22]

To gain insight into the coordination in **2**, we have prepared the corresponding complex of dihydroazaborindenyl (**11**). Thus, **9** reacts with LDA in ether to afford **11**, which on treatment with Cp*ZrCl$_3$ in toluene gives a 55% yield of **12** as yellow crystals.[14f] The molecular structure of **12**[23] is very similar to that of **2**. Selected bond distances of **12** are compared with those of **2** in Table 1. The major difference in coordination is that the N atom is 0.056 Å closer and the B atom is 0.023 Å closer to Zr in **12** than in **2**. Thus, the more unsymmetrical coordination in **2** must be due in part to the perturbation of the electron delocalization caused by the fused aromatic C$_4$BN ring.

In summary, we have developed a synthesis of the 3a,7a-azaborindenyl ligand. This ligand is isoelectronic and isostructural with indenyl but is likely to be more electron rich.[5,6] Hence, differences between the chemistry of azaborindenyl and indenyl metal complexes are likely consequences of electronic rather than structural differences. Future work will focus on the use of azaborindenyl as a surrogate for indenyl in significant organometallic catalysts.

Acknowledgment. This work was supported by the National Science Foundation and The Dow Chemical Co.

Supporting Information Available: Tables of crystallographic data for **2** and **12** and the ^{1}H NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Crystal data for **2**: C$_{17}$H$_{22}$BCl$_2$NZr, monoclinic, $P2_1/c$, a = 15.5538(18) Å, b = 8.4495(10) Å, c = 14.666(2) Å, β = 112.151(2)°, V = 1785.2(4) Å^3, Z = 4, D_c = 1.538 g cm^{-3}, T = 158(2) K, λ(Mo Kα) = 0.710 73 Å. Data were collected on a Siemens SMART CCD instrument. Final R indices ($I > 2\sigma(I)$): R1 = 0.0253, wR2 = 0.0619. R indices (all data): R1 = 0.0288, wR2 = 0.0638.

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(23) Crystal data for **12**: C$_{17}$H$_{24}$BCl$_2$NZr, monoclinic, $P2_1/c$, a = 15.635(3) Å, b = 8.5006(15) Å, c = 14.714(3) Å, β = 111.497(3)°, V = 1819.6 Å^3, Z = 4, D_c = 1.516 g cm^{-3}, T = 158(2) K, λ(Mo Kα) = 0.710 73 Å. Data were collected on a Siemens SMART CCD instrument. Final R indices ($I > 2\sigma(I)$): R1 = 0.0287, wR2 = 0.0703. R indices (all data): R1 = 0.0334, wR2 = 0.0723.