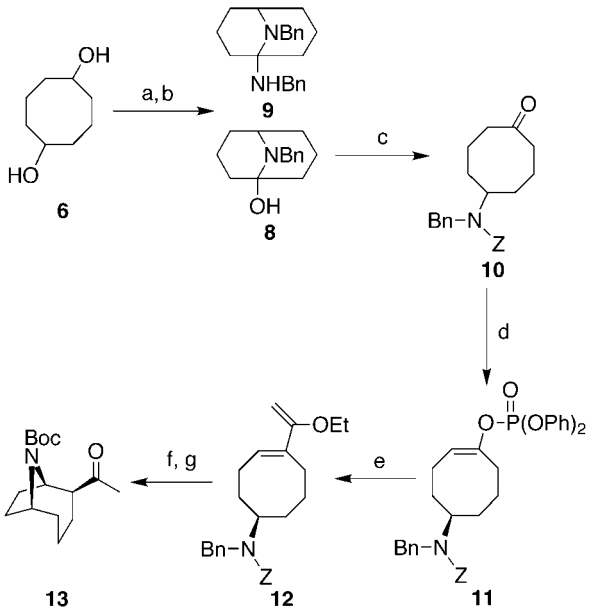

Scheme 2. Formal total synthesis of (+)-anatoxin-a (**1**). See reference [10] for abbreviations. a) PDC, CH_2Cl_2, 100%; b) 1. aq $PhCH_2NH_2$ (40%), *p*-TsOH (30 mol%), △; 2. H_2SO_4 (10%), 81% over two steps; c) $PhCH_2OCOCl$, $Sc(OTf)_3$ (5 mol%), iPr_2NEt, MeCN, 95%; d) (*R*,*R*)-**7**·HCl, *n*BuLi (2 equiv), $(PhO)_2POCl$, THF, −100 °C, 89%, 89% *ee*; e) $[Pd(PPh_3)_4]$, CH_2=CH(OEt)$SnBu_3$, LiCl, THF, △, 84%; f) 45% HBr in AcOH, 95%; g) Pd/C, H_2, MeOH, $(tBuCO)_2O$, 89%.

quenching of the reaction mixture with diphenyl chlorophosphate gave the enol phosphate **11** with high enantioselectivity (89% *ee*).[13]

Completion of the formal synthesis was achieved by a Stille reaction of enol phosphate[14] **11** with CH_2=CH(OEt)$SnBu_3$ in the presence of $[Pd(PPh_3)_4]$ and LiCl in THF, followed by a novel cascade reaction. This sequence entailed unmasking the enone moiety with concomitant nitrogen deprotection and intramolecular conjugate addition to give the required bridged azabicycle.[15] Changing the protecting group from benzyl to *tert*-butoxycarbonyl gave ketone **13**, which was identical, by ^1H and ^{13}C NMR, and IR spectroscopy and MS, to that reported by the group of Rapoport.[4] The $[\alpha]_D^{22}$ value we obtained (+47.2, $c = 0.8$ in CH_2Cl_2) is consistent with the production of the natural enantiomer ($[\alpha]_D^{22} = +51.9$, $c = 0.795$ in CH_2Cl_2).[4] Ketone **13** has been converted into (+)-anatoxin-a (**1**) by Rapoport et al. in three steps.

In conclusion, this paper describes one of the most concise and efficient routes (34% overall yield, including the final literature steps) to enantiomerically enriched (+)-anatoxin-a. Key steps in our synthesis include a highly enantioselective desymmetrization of an eight-membered ring ketone, and a novel cascade reaction to set up the 9-azabicyclo[4.2.1]nonane skeleton. Such desymmetrization reactions of medium and perhaps large ring ketones could find wide applications in synthesis.

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2,2′-*commo*-Bis[2-ruthena-*nido*-1-(η^5-pentamethylcyclopentadienyl)ruthenahexaborane(12)]: An Unusual Ruthenaborane Related to Ruthenocene and Exhibiting a Linear Triruthenium Fragment**

Xinjian Lei, Maoyu Shang, and Thomas P. Fehlner*

The intimate connection between metallaborane chemistry and organometallic chemistry is expressed in the existence of isoelectronic pairs of compounds, for example, $[(CO)_4FeB_2H_5]^-$[1, 2] versus $[(CO)_4Fe(\eta^2\text{-}C_2H_4)]$ and $[(\eta^5\text{-}C_5H_5)CoB_4H_8]$[3] versus $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4H_4)]$.[4–8] One of the fascinating aspects of these inorganic analogues of organo-

[*] Prof. T. P. Fehlner, Dr. X. Lei, Dr. M. Shang
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, IN 46556 (USA)
Fax: (+1) 219-631-6652
E-mail: fehlner.1@nd.edu

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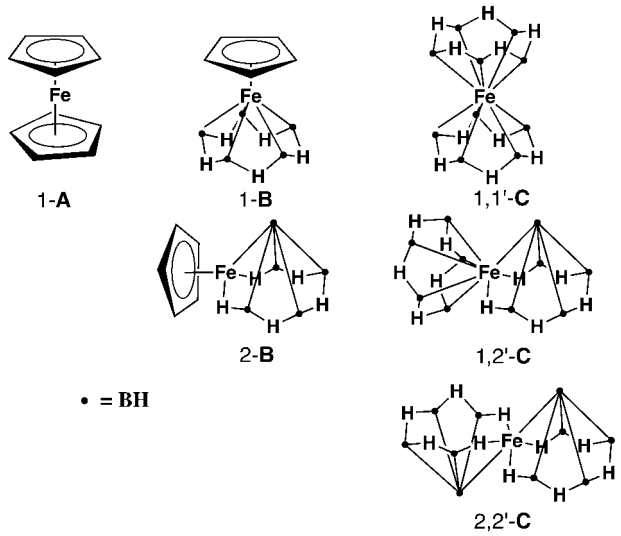
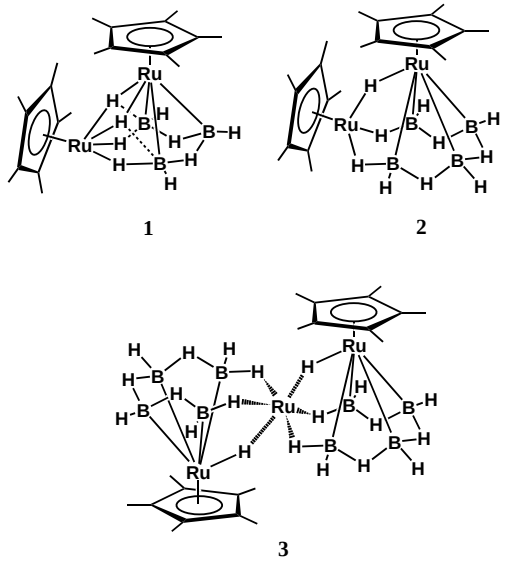
metallic compounds is the greater structural diversity displayed; for example, both [1-(η^5-C_5H_5)CoB_4H_8] and [2-(η^5-C_5H_5)CoB_4H_8] are known.[3, 9] Realizing these connections, one can begin with a known metallocene, such as ferrocene, and generate an array of ferraborane analogues as shown in Scheme 1. Indeed, this is not a purely theoretical exercise as



Scheme 1. Connection between ferrocene and ferraborane analogues.

chemical, spectroscopic, and calculational studies have appeared describing 1-**B**, 2-**B**, and 2,2′-**C**.[10–13] The last compound is formally similar to $B_5H_{10}BeB_5H_{10}$, which is the only metal derivative of this type to have been characterized by a solid-state structure.[14]

Although metallaboranes often have been found as trace products in complex reactions, for example [1,2-{Fe(CO)$_3$}$_2$$B_3H_7$],[15] their existence created synthetic goals. Thus, a method for the production of dimetallapentaboranes in excellent yields was subsequently developed.[16] We[17] and others[18] have recently described the synthesis of *nido*-[1,2-{Cp*Ru}$_2$$B_3H_9$] (**1**, Cp* = η^5-C_5Me_5) from the reaction of monoboranes with [{Cp*$RuCl_2$}$_2$]. Further, **1** cleanly adds a monoborane fragment to produce *nido*-[1,2-(Cp*Ru)$_2$(μ-H)B_4H_9] (**2**), which can be viewed as a metal analogue of either 1-**B** or 2-**B** (Scheme 1) depending on which Cp*RuH fragment is transformed into the isolobal BH fragment.[17] At the same time, the continuing characterization of unexpected coproducts creates the next generation of synthetic goals. In this vein, we now report *commo*-[{1-(Cp*Ru)(μ-H)B_4H_9}$_2$Ru] (**3**), which is an unusual ruthenaborane analogue of both $B_5H_{10}FeB_5H_{10}$[12] and $B_5H_{10}BeB_5H_{10}$.[14]



A solid-state structure determination of **3** (Figure 1) shows two dimetallahexaborane cages fused in a transoid fashion with one basal ruthenium atom common to both core skeletons.[19] A consequence of the intercage connection is

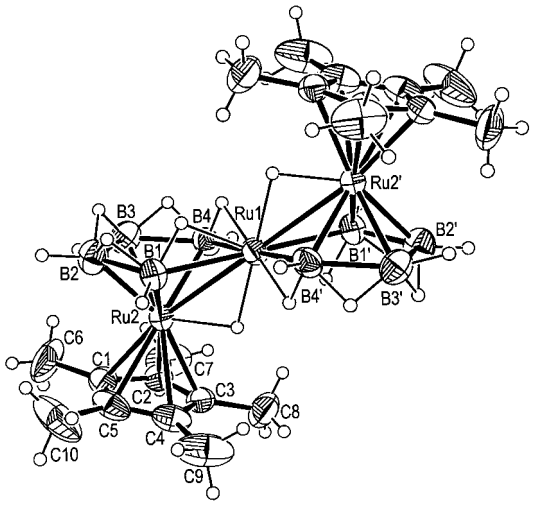


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Ru1–B4 2.320(17), Ru1–B1 2.325(16), Ru1–Ru2 2.7930(10), Ru2–B2 2.121(18), Ru2–B3 2.132(19), Ru2–B1 2.143(18), Ru2–B4 2.150(15); Ru2-Ru1-Ru2′ 180.00(4).

that the three metal atoms form a linear array. The outer Ru atoms, which occupy the 1-positions of the individual pentagonal pyramids, are η^5-coordinated to C_5Me_5 ligands. The inner Ru atom, which simultaneously occupies the 2-positions of both pentagonal pyramids, has six nearest neighbor hydrogen atoms in a distorted octahedral geometry. In total, there are six skeletal hydrogen atoms per pentagonal pyramid, five of which occupy the open pentagonal face with the sixth bridging a Ru–Ru edge. Consequently, each of the fused clusters resembles the structure of **2**, and there is a close correspondence between most of the structural parameters of **3** and those of **2**. However, the hydrogen-bridged Ru–Ru distance in **3** is significantly shorter than that in **2** (2.7930(10) vs. 2.8527(4) Å), reflecting the significantly different environment of the unique Ru atom.

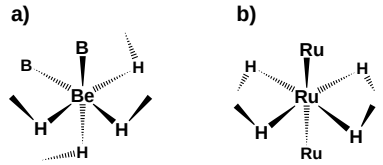
The spectroscopic data of **3** are fully in accord with the solid-state structure, and no evidence of fluxional behavior is observed. The ^{11}B NMR chemical shifts as well as the ^{1}H shifts (assigned by ^{1}H{^{11}B} selective decoupling) of the terminal and B-H-B bridging hydrogen atoms correspond closely to those of the comparable atoms of **2**. However, the ^{1}H resonance of the hydrogen atoms that bridge B1 or B4 and the central ruthenium atom is shifted by 3.3 ppm to higher field, whereas

that of the Ru-H-Ru bridging hydrogen atoms is shifted by 2.9 ppm to lower field, thereby inverting their relative positions in the spectrum compared to **2**. These differences also reflect the distinctly different electronic environment of the unique metal center of **3** relative to **2**.

Counting electrons in **3** becomes transparent once one realizes that the basal Ru atom in **2** receives five electrons from its Cp* ligand as well as five from the {(Cp*Ru)-(μ-H)B_4H_9} fragment. Thus, replacement of the basal Cp* ligand of **2** with a {(Cp*Ru)(μ-H)B_4H_9} fragment retains the 18-electron count on the central Ru atom of **3**. Alternatively, **3** is analogous to $B_5H_{10}BeB_5H_{10}$ in that the two-electron Be atom is mimicked by the unique Ru atom of **3**, which can be thought to possess two valence electrons and six nonbonding electrons (the t_{2g} set). Finally, in terms of counting cluster valence electrons (cve),[20] the formal disproportionation in Equation (1) based on the cage condensation principle is self-evident.

$$\underset{2\times 48\ \text{cve}}{2\{(Cp^*Ru)(\mu\text{-}H)B_4H_9\}RuCp^*} \rightarrow \underset{18\ \text{cve}}{Cp^*RuCp^*} + \underset{78\ \text{cve}}{\{(Cp^*Ru)(\mu\text{-}H)B_4H_9\}_2Ru} \quad (1)$$

Although analogous to $B_5H_{10}BeB_5H_{10}$, the structure of **3** differs as illustrated in Scheme 2. The dihedral angle between the two basal planes of the two boron cages of the



Scheme 2. Comparison of the nearest neighbor environments of a) $B_5H_{10}BeB_5H_{10}$[14] and b) **3**.

beryllaborane is 66°, placing the apical boron fragments in a *gauche* orientation (a) in terms of the six-coordinate Be center. However, in **3** the basal planes are coplanar, leading to a transoid arrangement of the fused pentagonal pyramids (b) and a linear array of metal atoms. Hence, compound **3** offers an alternative strategy for the formation of linear multinuclear metal complexes. Indeed **3** (d(Ru–Ru) = 2.7930(10) Å) can be compared with $[Ru_3(dpa)_4Cl_2]$ (dpa = bis(2-pyridyl)amido anion), containing a linear multiply bonded Ru_3 moiety (d(Ru–Ru) = 2.2537(5) Å).[21] However, the Ru-Ru-Ru interaction in **3** is qualitatively different in that it is best described as a Ru^{II} ion coordinated to two ruthenaborane ligands as indicated above. On the other hand, as **3** constitutes an isomeric form of a sandwich complex, it suggests the accessibility of variants of multidecker sandwich compounds[22–29] with linear chains of metal atoms.

The pathway for the formation of **3** is unknown; however, note that **1** contains a {Cp*Ru(μ-H)$_4$} fragment with a Ru center nearly the same as those in [{Cp*Ru(μ-H)$_2$}$_2$].[30] In the presence of chlorinated solvents, the latter generates coordinatively unsaturated species, ultimately leading to [Cp*Ru(arene)]$^+$ complexes. Thus, it is possible that **1** is similarly activated by loss of a one-electron Cp*Ru metal fragment in the presence of the radical generator $[Co_2(CO)_8]$. Research to establish the origin of **3** continues.

Experimental Section

3: All the preparative work was carried out under an Ar atmosphere. $[Co_2(CO)_8]$ (0.19 g, 0.57 mmol) in hexane (20 mL) was added dropwise to a solution of **1** (0.29 g, 0.57 mmol) in hexane (20 mL). The reaction mixture was stirred for 15 h at room temperature. The products are [1-(Cp*Ru)-2-{Cp*Ru(CO)}-3-{Co(CO)$_2$}(μ_3-CO)B_3H_6], [1-{Cp*RuH(CO)}B_3H_7], [Co_4-(CO)$_{12}$], [{Cp*Ru(CO)$_2$}$_2$], and small amounts of **3**.[17] Column chromatography (room temperature, hexane) gave a dark brown band which contained [1-{Cp*RuH(CO)}B_3H_7], [$Co_4(CO)_{12}$], and **3**, with the other products eluting in subsequent fractions.[17] Repeated fractional crystallization at −40°C removed nearly all of the [$Co_4(CO)_{12}$] (according to IR spectroscopy). The supernatant was then concentrated and kept at −40 °C for several days, after which needlelike crystals of **3** mixed with some black crystals of [$Co_4(CO)_{12}$] appeared on the bottom of the flask. The black crystals were removed by washing with hexane, and 12 mg of orange needles of **3** remained (≈8% yield based on available boron in **1**). MS (EI): m/z: 684 (isotopic pattern for 3 Ru and 8 B atoms); calcd for a weighted average of isotopomers lying within the instrument resolution: 684.1787, found: 684.1751; ^{11}B NMR (hexane, 22 °C): δ = 4.7 (d, ^1J(B,H) = 130 Hz, 4 B), 19.3 (d, ^1J(B,H) = 120 Hz, 4 B); in the {^{1}H}^{11}B NMR spectrum these two signals appear as singlets; ^{1}H NMR: ([D$_6$]benzene, 22 °C): δ = 3.72 (partially collapsed quartet (pcq), 4 H, BH$_t$), 2.83 (overlapping pcq, 4 H, BH$_t$), 1.72 (s, 30 H, $C_5(CH_3)_5$), −2.88 (br, 6 H, B-H-B), −10.64 (s, 2 H, Ru-H-Ru), −16.66 (br, 4 H, B-H-Ru).

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have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-112935. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Liquid Crystals Based on Hypervalent Sulfur Fluorides: Pentafluorosulfuranyl as Polar Terminal Group**

Peer Kirsch,* Matthias Bremer, Michael Heckmeier, and Kazuaki Tarumi

Recently, active matrix liquid crystal displays (AM-LCD or thin film transistor LCD, TFT-LCD) have been evolving rapidly towards becoming the major technology for flat panel diplays.[1] To save costs in the mass production of display panels, there is a strong tendency to reduce the driving voltage of active matrix LCD. On the materials side, the consequence of this trend is the demand for liquid crystals with a higher dielectric anisotropy ($\Delta\varepsilon$) in order to obtain an electrooptical response.[2, 3]

[*] Dr. P. Kirsch, Dr. M. Bremer, Dr. M. Heckmeier, Dr. K. Tarumi
Merck KGaA, Liquid Crystals Division
D-64271 Darmstadt (Germany)
Fax: (+49) 6151-72-2593
E-mail: peer.kirsch@merck.de

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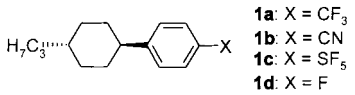
In designing liquid crystals the most efficient way to increase $\Delta\varepsilon$ is by using a polar terminal group with the maximum possible dipole moment. The current limit for AMD-compatible materials is achieved with the trifluoromethyl group (e.g. **1a**: $\Delta\varepsilon = 8.6$). Unfortunately, the much



more polar and nematogenic materials based on a terminal cyano group (e.g. **1b**, PCH-3: $\Delta\varepsilon = 21.1$) cannot be used for active matrix diplays. The cyano group tends to solvate ubiquituous ionic impurities[4] resulting in a low voltage holding ratio[5] and observable flicker and contrast loss in the display panel.

To further increase the dielectric anisotropy ($\Delta\varepsilon$) of the materials, a polar ring such as 1,3-dioxane or 1,3-dithiane can be introduced. Fluorine substituents in *ortho*-position to the terminal group also result in an increase of $\Delta\varepsilon$, but at the cost of a drop of the clearing points by 30–40 K per lateral fluorine atom.[6, 7] For polar two-ring materials in particular this latter option leads to unacceptably low clearing points.

Following and anticipating the technological trend to lower driving voltage, we concentrated on the identification and evaluation of a new, more polar terminal group that is compatible with active matrix technology and does not require lateral fluorination to obtain an acceptably high dielectric anisotropy ($\Delta\varepsilon$). Our interest was especially focused on two-ring materials with low rotational viscosity (γ_1).[3] Other prerequisites for practical display applications are high chemical and photochemical stability of the liquid crystalline materials.

A most interesting candidate as a highly polar head group for liquid crystals is the pentafluorosulfuranyl group.[8] This functional group is known to be even more stable than trifluoromethyl against hydrolytic agents, also at elevated temperatures. In addition, the dipole moment μ of 3.44 D of pentafluorosulfuranylbenzene[9] (compared to 2.60 D for benzotrifluoride) indicates that liquid crystals with very high dielectric anisotropy can be obtained. A semiempirical calculation[10] (PM3) on 4-(propylcyclohexyl)pentafluorosulfuranylbenzene (**1c**) gave a $\Delta\varepsilon_{PM3}$ value of 22.2, exceeding even that of the cyano-based based PCH-3.

The chemistry of pentafluorosulfuranylbenzene derivatives was first studied thoroughly at the beginning of the 1960s by W. A. Sheppard,[9] and its use for liquid crystals was the subject of a preliminary investigation in our group at the end of the 1980s.[11] These studies were impeded by the inconvenient synthesis of pentafluorosulfuranylbenzene derivatives, which was based on a two-step reaction of aromatic disulfides with silver difluoride in the severely ozone-depleting solvent 1,1,2-trichloro-1,2,2-trifluoroethane ("Freon 113"). The recent introduction of the direct fluorination of deactivated aromatic disulfides made the precursor **2** commercially available in kilogram quantities.[12] This finally enabled us to develop a suitable synthesis, systematically screen pentafluorosulfuranyl-derived liquid crystals, and compare them with conventional cyano- and fluoro-based materials.

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