(dt, ^3J(P,H) = 13.6 Hz, ^3J(H,H) = 7.5 Hz, 9H; $ClRhP(CH_2CH_3)_3$); $^{13}C\{^1H\}$ NMR: $\delta = 0.11$ (ddt, ^1J(Rh,C) = 21.2 Hz, ^2J(P (unique),C) = 8.2 Hz, ^2J(P(mutually *trans*),C) = 5.5 Hz, $RhCH_3$). **12**: $^{31}P\{^1H\}$ NMR: $\delta = 45.8$ (d, ^1J(Rh,P) = 123 Hz, 2P); ^1H NMR: $\delta = 8.09$ (m, 2H; COPh), 7.05 (m, 3H; COPh), 2.23 (m, 6H; $PCH(CH_3)_2$), 1.06 (dvt, J = 6.9 Hz, 18H; $PCH(CH_3)_2$), 0.99 (dvt, J = 7.0 Hz, 18H; $PCH(CH_3)_2$), −20.92 (dt, ^2J(Rh,H) = 44.5 Hz, ^3J(P,H) = 10 Hz, 1H; RhH); IR (film): $\tilde{\nu} = 1650\,cm^{-1}$ (C=O).

[13] I. El-Idrissi, O. Eisenstein, Y. Jean, *New. J. Chem.* **1990**, *14*, 671.

[14] Complex **6** was prepared from **2** and a small excess of MeCHO in benzene at room temperature.

[15] a) Coordinatively saturated acylrhodium–hydride complexes undergo decarbonylation via unsaturated intermediates.[8, 9a] b) The coordinatively unsaturated $[(Et_3P)_2Rh(Cl)(MeCO)(H)]$ complex cannot be observed at room temperature. It undergoes immediate decarbonylation, evolving methane.

[16] However, **4** rapidly decomposes upon heating at 55 °C for 1 hour. A similar reactivity was observed in the case of six-coordinate acylrhodium–hydride complexes.[9a]

[17] Selected references: a) R. F. Heck, *J. Am. Chem. Soc.* **1964**, *86*, 2796; b) D. N. Lawson, J. A. Osborn, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1733; c) S. Franks, F. R. Hartley, J. R. Chipperfield, *Inorg. Chem.* **1981**, *20*, 3238; d) D. Forster, *Adv. Organomet. Chem.* **1979**, *17*, 255; e) A. Haynes, B. E. Mann, G. E. Morris, P. M. Maitlis, *J. Am. Chem. Soc.* **1993**, *115*, 4093; f) P. M. Maitlis, A. Haynes, G. J. Sunley, M. J. Howard, *J. Chem. Soc. Dalton Trans.* **1996**, 2187, and references therein; g) T. R. Griffin, D. B. Cook, A. Haynes, J. M. Pearson, D. Monti, G. E. Morris, *J. Am. Chem. Soc.* **1996**, *118*, 3029; h) J. Rankin, A. C. Benyei, A. D. Poole, D. J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.* **1999**, 3771; i) L. Gonsalvi, H. Adams, G. L. Sunley, E. Ditzel, A. Haynes, *J. Am. Chem. Soc.* **1999**, *121*, 11233; j) for a recent review on MeI addition to Rh^I complexes, see: P. R. Sharp in *Comprehensive Organometallic Chemistry II, Vol. 8* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, J. D. Atwood), Pergamon, **1995**, pp. 190–200, and references therein.

[18] The formation of **8** and **10** in the reaction of MeI with **2** and **3**, respectively, is accompanied by side products (20–40 % depending on the temperature and on the amount of MeI added). Presumably, diiodide complexes are formed as was reported.[19a] In the case of the reaction of **2** or **11** with MeI (see also Table 1), we observed the formation of *trans*-$[(iPr_3P)_2Rh(I)_2Me]$ (**9**) as a by-product.

[19] a) H. L. M. van Gaal, J. M. J. Verlaak, T. Posno, *Inorg. Chem. Acta* **1977**, *23*, 43; b) R. A. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1981**, 126.

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[22] G. Aullon, S. Alvarez, *Inorg. Chem.* **1996**, *35*, 3137, and references therein.

[23] a) Complex **2** was found to be monomeric in benzene: D. Schneider, H. Werner, *Angew. Chem.* **1991**, *103*, 710; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 700. b) We have observed that complex **1** reacts with $[\{(cyclooctene)_2RhCl\}_2]$ in benzene to give monophosphane complexes, indicating the dissociation of iPr_3P.

[24] In contrast to compound **3**, $[(Me_3P)_3RhCl]$ is reported to react with an excess of MeCHO and PhCHO to give acyl hydride complexes.[8, 9a] The reason for the higher reactivity of $[(Me_3P)_3RhCl]$ over $[(Et_3P)_3RhCl]$ with aldehydes is not clear. It may be due to an associative phosphane displacement, preceded by coordination of the aldehyde, which is easier with a lower bulk at the metal center.

[25] Since complexes **2** and **11** show different selectivities in the reaction with a mixture of MeI and aldehyde, different intermediates are likely to be involved; hence we propose the dissociation of phosphane rather than that of N_2 from **11**. Nitrogen does not readily dissociate from **11**: D. L. Thorn, T. H. Tulip, J. A. Ibers, *J. Chem. Soc. Dalton Trans.* **1979**, 2022.

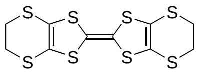
[26] Electron-donating ligands coordinated to Rh^I centers facilitate the oxidative addition of MeI, see for example: a) S. S. Basson, J. G. Leipoldt, A. Roodt, J. A. Venter, T. J. Van Der Walt, *Inorg. Chem. Acta* **1986**, *119*, 35; b) G. J. Van Zyl, G. J. Lampbrecht, J. G. Leipoldt, T. W. Swaddle, *Inorg. Chem. Acta* **1986**, *143*, 223; c) see also ref. [17c] and [17i], and references therein.

[27] A similar tendency is observed with the dimer $[\{(Et_3P)_2Rh(Cl)\}_2]$, which unlike the monomer **3**, reacts slowly with aldehydes at room temperature, giving predominantly carbonyl complexes.[15b]

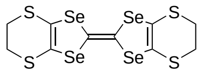
Quasi One-Dimensional Organic Superconductor MDT-TSF · AuI_2 with $T_c = 4.5$ K at Ambient Pressure**

Kazuo Takimiya,* Yoshiro Kataoka, Yoshio Aso,
Tetsuo Otsubo,* Hiroshi Fukuoka, and Shoji Yamanaka

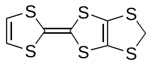
Although the first organic superconductors were prepared from radical-cation salts (Bechgaard salts) based on tetramethyltetraselenafulvalene (TMTSF) under extremely cryogenic conditions ($T_c < 1.4$ K), higher T_c superconductors were developed from heterocycle-fused tetrathiafulvalenes (TTFs), represented by bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).[1] Whereas the Bechgaard salts have quasi one-dimen-



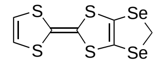
BEDT-TTF



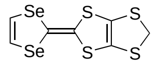
BETS



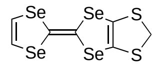
MDT-TTF



MDS-TTF



MDT-STF



MDT-TSF **1**

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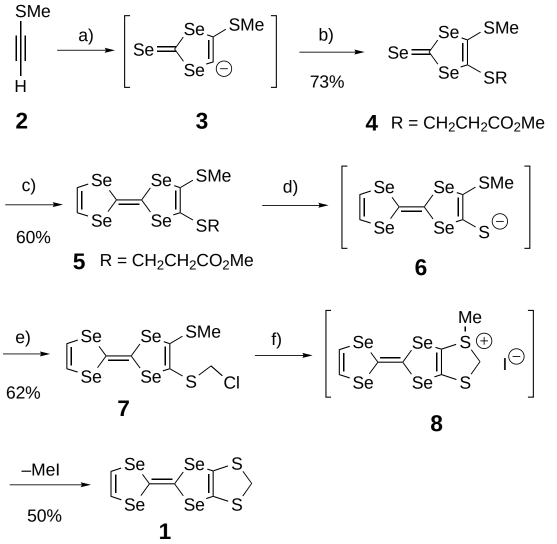
sional electronic structures, the subsequent superconductors are characterized by unique quasi two-dimensional electronic structures due to multisulfur atomic interactions. The most typical is the κ-type salts, such as (BEDT-TTF)$_2$[Cu{N(CN)$_2$}X] salts with T_c values higher than 10 K,[2] which no longer have donor-stacked structures. In this regard, it may be worthy to note that methylenedithiotetrathiafulvalene (MDT-TTF), which does not include as many sulfur atoms as BEDT-TTF, can form a κ-type superconducting AuI$_2$ salt with a relatively high T_c of 4.1–4.3 K.[3] Since replacement of some or all sulfur atoms in such multisulfur-based donors by selenium atoms provides novel electron donors with different electronic structures, in particular strengthening its metallic character due to strong nonbonding selenium interactions,[4] we are interested in the selenium variants of MDT-TTF. From this series, the methylenediseleno-TTF (MDS-TTF)[5] and methylenedithio-diselenadithiafulvalene (MDT-STF)[6] have been already synthesized but no superconducting salts from them have been so far reported. The discovery of novel λ-type superconductors with a high T_c (9.7 K) based on bis(ethylenedithio)tetraselenafulvalene (BETS) as a selenium variant of BEDT-TTF[7] suggests the most intriguing selenium variant of MDT-TTF might be methylenedithiotetraselenafulvalene (MDT-TSF, **1**), which still remains unknown apparently due to the lack of an appropriate synthetic method. We now would like to present the efficient synthesis of **1** and the superconducting behavior of its AuI$_2$ salt.

For the synthesis of **1**, we have adopted a synthetic strategy of the initial formation of the TSF skeleton followed by the construction of the outer 1,3-dithiole ring, as shown in Scheme 1. This route involves a combination of very effective synthetic techniques recently developed by our group, namely, one-pot formation of 1,3-diselenole-2-selone from a terminal alkyne,[8] a trialkyl phosphite-mediated coupling reaction to the TSF derivative, and finally heterocycle formation by transalkylation on a chalcogen atom.[9] In addition, we have taken advantage of a deprotection/realkylation protocol of a novel, protected TSF–thiolate building block **5**.[10] For the first step, methylthioacetylene (**2**)[11] was successively treated with nBuLi, selenium powder, and carbon diselenide, to generate in situ the vinyl anion intermediate (**3**), which was then quenched with 3-thiocyanatopropionic acid methyl ester[12] to give a 1,3-diselenole-2-selone derivative (**4**) in 73 % yield. Cross-coupling of **4** with unsubstituted 1,3-diselenole-2-selone gave the desired asymmetrical TSF derivative **5** in 60 % yield. Treatment of **5** with cesium hydroxide monohydrate in DMF generated the reactive TSF monothiolate (**6**), which was alkylated in situ with chloroiodomethane to give **7** in 62 % yield. Formation of the outer 1,3-dithiolene ring was achieved by an initial halogen exchange to the corresponding iodide followed by spontaneous transalkylation into **1** via the sulfonium salt **8**.



Scheme 1. Synthesis of MDT-TSF (**1**). a) BuLi, Se, CSe$_2$, THF; b) NCS(CH$_2$)$_2$CO$_2$Me; c) 1,3-diselenole-2-selone, P(OMe)$_3$, C$_6$H$_6$; d) CsOH · H$_2$O; e) ClCH$_2$I; f) NaI, 2-butanone.

Orange platelike crystals of **1** were obtained by recrystallization from chlorobenzene and subjected to an X-ray crystallographic analysis. The molecule has a slightly bent structure and forms a face-to-face dimer with a center of symmetry arranged orthogonally to the neighboring dimers. Cyclic voltammetry of **1** showed two reversible redox waves at 0.52 and 0.75 V versus a Ag/AgCl reference electrode in benzonitrile. Both the first and second half-wave oxidation potentials are nearly the same as those of the parent TSF ($E_{1/2}$ = 0.49 and 0.78 V).

Electrocrystallization of **1** in chlorobenzene containing tetrabutylammonium diiodoaurate as a supporting electrolyte gave needle-shaped crystals in a few days. Its electrical conductivity is very high (2000 S cm^{-1}, an average of 8 samples) at room temperature. Resistivity as a function of temperature monotonously decreases down to low temperature and abruptly drops at 4.5 K, which is characteristic of the onset of a superconducting transition (Figure 1). Magnetic susceptibility with a SQUID susceptometer also reveals its superconductivity (Figure 2). The diamagnetic shielding at 2 K shows 80 % of the perfect diamagnetism, to indicate that the salt is a bulk superconductor. In both zero-field cooled (ZFC) and field cooled (FC) measurements, the susceptibility starts to decrease at 4.2 K, which is slightly lower than that of the conductivity measurement.

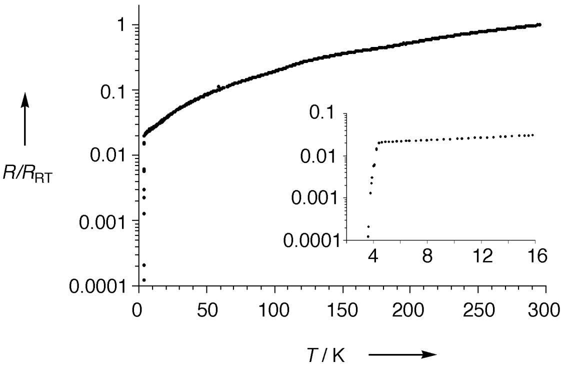


Figure 1. Temperature dependence of conductivity of $\mathbf{1}_2 \cdot$ AuI$_2$. Inset: the domain 2–16 K, expanded.

An X-ray crystal structure analysis revealed an interesting structural feature of the salt:[13] The MDT-TSF donor, unlike the neutral one, is completely planar and uniformly stacked

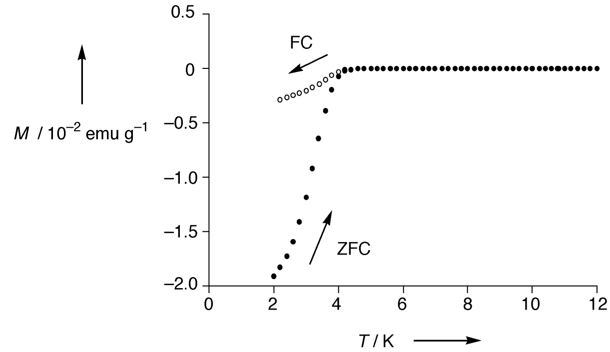


Figure 2. Temperature dependence of the magnetic susceptibility of $\mathbf{1}_2\cdot\text{AuI}_2$.

along the *a*-axis (Figure 3a). In the anion layer, the position and population of AuI_2^- units are not precisely determined, presumably due to the disorder or different periodicity of the anions from the donor arrangement. The ratio of the donor to anion is determined as approximately 2:1 on the basis of an elemental analysis.[14] In the donor sheets, there are many nonbonded Se–Se contacts, not only in the intrastacking direction but also interstacking direction (Figure 3b). These nonbonded Se–Se interactions are presumably responsible for its unexpected stacking structure that is quite different from the *κ*-type of the related superconducting $(\text{MDT-TTF})_2\cdot\text{AuI}_2$ salt. A calculation using the extended-Hückel tight-binding approximation[15] indicated that the overlap integrals between intrastacks are about five times as large as that between the interstacks. This means that the $(\text{MDT-TSF})_2\cdot\text{AuI}_2$ salt is essentially a quasi one-dimensional superconductor, which is reminiscent of the Bechgaard salts.[1]

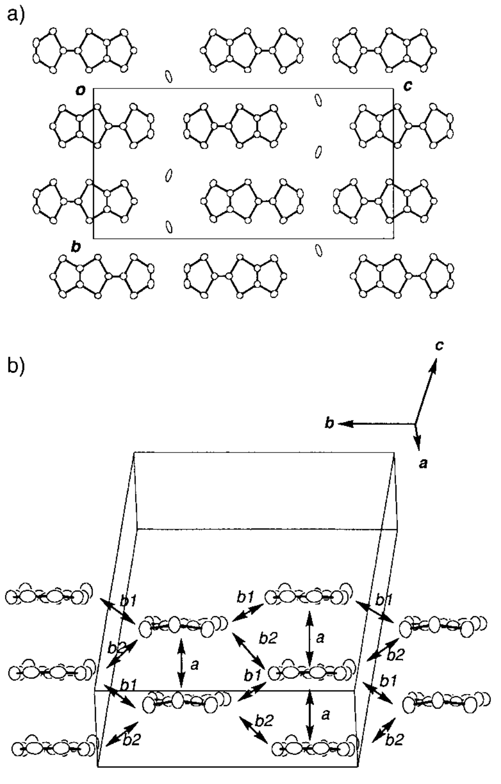


Figure 3. a) Crystal structure of $\mathbf{1}_2\cdot\text{AuI}_2$ viewed along *a*-axis direction and b) a side view of the donor sheet. Calculated overlap integrals are $a = -18.89\times10^{-3}$, $b1 = 3.64\times10^{-3}$, and $b2 = 0.4\times10^{-3}$.

In summary, we have succeeded in the synthesis of a new electron donor MDT-TSF and its superconducting radical cation salt $(\text{MDT-TSF})_2\cdot\text{AuI}_2$. Unexpectedly, the salt, in spite of relatively high T_c, has a quasi one-dimensional stacking structure. In addition, it is noteworthy that the room temperature conductivity of $(\text{MDT-TSF})_2\cdot\text{AuI}_2$ is extraordinary high ($2000\ \text{S cm}^{-1}$) among organic superconductors. These results clearly demonstrate the unique electronic structure of MDT-TSF, which allows enhanced nonbonded Se–Se interactions.

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[13] X-ray crystal structure analyses were made on a Rigaku AFC7R four-circle diffractometer ($\text{Mo}_{K\alpha}$ radiation $\lambda = 0.71069$ Å, graphite monochromator, $T = 296$ K, $\omega - 2\theta$ scan, $2\theta_{\max} = 55.0°$). The structure for $\mathbf{1}_2\cdot\text{AuI}_2$ was solved with a direct method and refined by a full-matrix least-squares fit on $|F|$. All calculations were performed using the crystallographic software package teXsan (Molecular Structure Corporation, **1985**, **1992**). Crystal data for $\mathbf{1}_2\cdot\text{AuI}_2$: $\text{C}_{14}\text{H}_8\text{S}_4\text{Se}_8\text{AuI}_2$, $M = 1386.91$, black needles ($0.65\times0.03\times0.02$ mm), orthorhombic, space group *Pnma* (No. 62), $a = 4.016(6)$, $b = 12.513(3)$, $c = 25.424(3)$ Å, $V = 1277(1)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 3.605\ \text{g cm}^{-3}$, $\mu = 199.27\ \text{cm}^{-1}$, $R = 0.039$,

$wR = 0.051$, 1534 measured reflections, 946 observed reflections ($I > 3.0\sigma(I)$), 83 refined parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-146823. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[14] Elemental analysis of $\mathbf{1}_2\cdot AuI_2$ [%]: calcd for $C_{14}H_8S_4Se_8AuI_2$: C 12.12, H 0.58; found: C 12.63, H 0.84.

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Synthesis of $[(Cp^*Re)_2B_nH_n]$ $n = 8-10$: Metal Boride Particles That Stretch the Cluster Structure Paradigms**

Sundargopal Ghosh, Maoyu Shang, Yaping Li, and Thomas P. Fehlner*

Metal borides are substances of considerable interest because of their physical, chemical, and electrical properties.[1–4] Their simple stoichiometries belie complex extended structures and consequently, metal borides are rarely treated in basic inorganic texts. Yet, it was from metal borides that a solution to the molecular borane cluster structure problem arose, for example, CaB_6 formulated as a Zintl phase $[Ca^{2+}][B_6^{2-}]$ with a three-dimensional network of octahedral B_6 cages[5] comparable with discrete $[B_6H_6^{2-}]$ ions.[6] At the other end of the compositional scale, metal clusters with interstitial boron atoms have been identified which have the local bonding environment of boron in metal-rich borides.[7] However, the borides of intermediate compositions, for example, CrB_4[8], find no models in the molecular world. To date there has been no need to invoke a comparison as nearly all known metallaboranes contain late transition metal fragments and follow the same structural paradigm as the boranes.[9, 10] Indeed it is a measure of the success of the cluster-electron counting rules and the isolobal analogy that boranes, metallaboranes, and metal clusters are linked in such a simple, conceptually pleasing, fashion.[11–14]

Recently we discovered a few unusual compounds that do not fit the mold of the borane paradigm.[15] Compared with compounds containing later transition metal fragments, these compounds exhibit structures characterized by high metal-coordination number, cross-cluster bonds, and unexpected stability for low valent Group 6 and 7 metal compounds. In trying to understand the cause of this behavior we adopted an approach which has been usefully applied to borides of intermediate stoichiometries.[16] Burdett and co-workers have pointed out that information on electronic structure is revealed by the change in structure with metal type at constant stoichiometry.[17, 18] Specifically, for MB_2 and MB_4 borides (where M = metal) they demonstrated a correlation between the occupation of orbitals of MM and MB antibonding character and observed structure variation. In going from late to early transition metals, the metal-atom coordination number increases and the extent of MM and MB bonding increases. For $[(Cp^*WH)_2B_7H_7]$, $[(Cp^*Re)_2B_7H_7]$, and $[(Cp^*W)_3HB_8H_8]$, we argued that in moving from late to earlier transition metals the geometric deviations from the cluster shapes of borane chemistry reflect a similar transition from electronic structures characteristic of boranes to those characteristic of borides.

An unconventional view based on three compounds constitutes an interesting curiosity rather than a useful idea. In further support we can now offer the characterization of a homologous series of metallaboranes that begins with $[(Cp^*Re)_2B_7H_7]$. These compounds establish a new set of cluster geometries remarkably different from the canonical deltahedra of the $[B_nH_n]^{2-}$ boranes that underpin the cluster-electron counting rules.[19, 20] The oblate cluster shapes, high metal-coordination numbers, and cross-cluster bonds featured support the idea that variation in the transition metal can drive a change from borane- to boride-like bonding.

Subsequent to the isolation of $[(Cp^*Re)_2B_7H_7]$ from the reaction of $[Cp^*ReCl_4]$ and monoboranes,[15] we found that it is formed in a more straightforward manner from the reaction of $[(Cp^*ReH_2)_2B_4H_4]$ with BH_3THF.[21] Further development of this reaction permits the compounds $[(Cp^*Re)_2B_nH_n]$, $n = 8-10$, to be isolated and characterized. Although produced in a mixture, they are insensitive to air and moisture and can be separated by thin layer chromatography (TLC) on the laboratory bench. Reactions of pure $[(Cp^*Re)_2B_nH_n]$, $n = 7-10$, with BH_3THF demonstrate sequential cluster build up. So far all efforts to produce a compound with $n > 10$ have failed.

The molecular structures of the new compounds in the solid state,[22] are shown in Figures 1–3. $[(Cp^*Re)_2B_8H_8]$ possesses a C_2 axis bisecting the B1-B2 and B5-B6 edges (See also Figure 4). Three ^{11}B resonances in the intensity ratio 2:4:2 are observed by solution NMR spectroscopy in the temperature range −90 to 22 °C suggesting accidental overlap of two signals or a low-barrier fluxional process in solution. The complex $[(Cp^*Re)_2B_9H_9]$ possesses a plane of symmetry passing through the Re atoms and B5 consistent with the ^{11}B resonances (2:2:2:2:1) in solution NMR spectroscopy. The complex $[(Cp^*Re)_2B_{10}H_{10}]$ possesses a C_2 axis bisecting the B2-B3 and B7-B8 edges consistent with the observed ^{11}B resonances (2:2:2:2:2). The wide range of boron chemical shifts and some uncharacteristically upfield terminal BH resonance signals constitutes the NMR signature of this

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