Communications

A Novel Dinuclear Ruthenium(I)/Ruthenium(III) Half-Sandwich Complex Containing Two Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dithiolate Ligands and Its Reactivity with Alkynes[†]

De-Hong Wu, Cheng Ji, Yi-Zhi Li, and Hong Yan*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering,
The Joint Laboratory of Metal Chemistry, Nanjing University-Jin Chuan Group Ltd.,
Nanjing University, Nanjing 210093, China

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*Summary: [(p-cymene)RuCl$_2$]$_2$ reacts with 1,2-dicarba-closo-dodecaborane-1,2-dithiolate in the presence of excess sulfur to generate the first dinuclear complex, (p-cymene)Ru(μ-S$_2$)Ru(S$_2$C$_2$B$_{10}$H$_{10}$)$_2$ (**1**). Treatment of **1** with alkynes affords the addition complexes (p-cymene)Ru(μ-S$_2$)Ru(S$_2$C$_2$B$_{10}$H$_{10}$)$_2$(R$_1$C═CR$_2$) (R$_1$ = H (CO$_2$Me), R$_2$ = CO$_2$Me (H), **2a** (**2b**); R$_1$ = C$_6$H$_5$, R$_2$ = H, **3b**; R$_1$ = R$_2$ = CO$_2$Me, **4**).*

During the past decade considerable attention has been devoted to metal complexes with *o*-carboranedichalcogenolate ligands, due to their unique molecular structures.[1] Mononuclear 16e half-sandwich complexes of Co, Rh, Ir, Ru, and Os have been described that contain a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand, $[E_2C_2(B_{10}H_{10})]^{2-}$ (E = S, Se).[2−5] These sterically congested, mononuclear coordination compounds can be stored conveniently and used for further transformations in a controlled way under various conditions.[6] For instance, insertion of alkynes into metal−chalcogen bonds leading to B−H bond activation, the formation of metal−boron bonding, and functionalization of the carborane cage in positions B(3)/B(6) was observed.[5] As a continuation of this interesting chemistry, in the present communication we describe a novel unsaturated dinuclear ruthenium complex containing two $[S_2C_2(B_{10}H_{10})]^{2-}$ units and report its reactivity toward alkynes.

The reaction of [(*p*-cymene)RuCl$_2$]$_2$ with Li$_2$[S$_2$C$_2$(B$_{10}$H$_{10}$)] led to the mononuclear 16e (*p*-cymene)Ru[S$_2$C$_2$(B$_{10}$H$_{10}$)].[5f] However, in the presence of an excess of sulfur the above reaction solely generates a dinuclear complex, **1** (Scheme 1).[7]

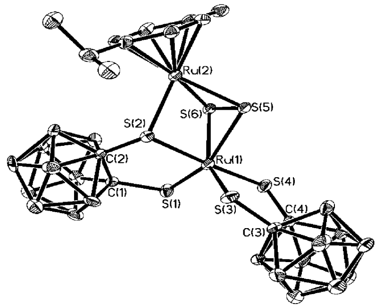

Figure 1. Molecular structure of **1** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): C(1)−C(2) = 1.661(6), C(1)−S(1) = 1.804(4), C(2)−S(2) = 1.826(5), C(3)−C(4) = 1.647(7), C(3)−S(3) = 1.786(5), C(4)−S(4) = 1.787(5), Ru(1)−S(1) = 2.1997(15), Ru(1)−S(3) = 2.1919(14), Ru(1)−S(4) = 2.3769(13), Ru(1)−S(5) = 2.3819(13), Ru(1)−S(2) = 2.3846(12), Ru(1)−S(6) = 2.4085(12), S(5)−S(6) = 2.0358(17), Ru(1)···Ru(2) = 3.414; S(1)−Ru(1)−S(3) = 117.30(6), S(1)−Ru(1)−S(4) = 85.22(5).

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* To whom correspondence should be addressed. E-mail: hyan1965@nju.edu.cn. Fax: (+86)-25- 83314502.

[†] Dedicated to Professor Thomas P. Fehlner on the occasion of his 70th birthday.

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(7) Synthesis of **1**: *o*-carborane (58 mg, 0.4 mmol) was dissolved in diethyl ether (15 mL) and lithiated by the addition of a 2.0 M cyclohexane solution of *n*-butyllithium (0.6 mL, 1.2 mmol). The addition of sulfur (43 mg, 1.34 mmol) led to a slightly yellow suspension, and then a solution of [(*p*-cymene)RuCl$_2$]$_2$ (123 mg, 0.2 mmol) in THF (40 mL) was added at ambient temperature. The color of the resultant mixture gradually changed from orange to green. After 10 h the solvents were removed under reduced pressure and the residue was chromatographed on silica. Elution with petroleum ether/CH$_2$Cl$_2$ (1:2) gave a green compound of **1**. Suitable single crystals for X-ray analysis were obtained from petroleum ether/CH$_2$Cl$_2$ in 2 weeks. **1**: yield 105 mg (65%); mp 205 °C dec. Anal. Calcd for C$_{14}$H$_{34}$B$_{20}$Ru$_2$S$_6$: C, 20.68; H, 4.21. Found: C, 20.80; H, 4.13. ESI-MS (*m*/*z*): calcd for C$_{14}$H$_{34}$B$_{20}$Ru$_2$S$_6$, 813.11; found, 814.10 ([M + H]$^+$, 100%). ^{1}H NMR (CDCl$_3$): δ 1.28 (d, J = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 1.39 (d, J = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 2.32 (s, 3H, CH$_3$), 2.73 (sept. J = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 5.23 (d, J = 6.0 Hz, 1H, C$_6$H$_4$), 5.32 (d, J = 6.0 Hz, 1H, C$_6$H$_4$), 6.12 (d, J = 6.0 Hz, 2H, C$_6$H$_4$). ^{13}C NMR (CDCl$_3$): δ 18.87 (C$_6$H$_4$−*C*H$_3$), 22.78, 23.39 (CH(*C*H$_3$)$_2$), 31.58 (*C*H(Me)$_2$), 81.95, 83.52, 84.38, 85.55 (CH in *p*-cymene), 86.43, 88.08, 102.23, 104.81, 108.95, 111.82 (*o*-carborane and quaternary C in *p*-cymene). ^{11}B{^{1}H} NMR (CDCl$_3$): δ −8.1, −7.2, −6.4, −5.5, −4.5 (1:1:1:3:4). IR (KBr, cm^{-1}): ν 2587 (ν_{B-H}). Crystal data: C$_{14}$H$_{34}$B$_{20}$Ru$_2$S$_6$, monoclinic, space group $P2_1/c$, a = 13.053(3) Å, b = 10.024(2) Å, c = 25.586(5) Å, β = 98.120(3)°, V = 3314.3(12)) Å^3, Z = 4, T = 153(2) K, μ = 1.302 mm^{-1}, 6513 reflections observed, 4778 independent reflections, R1($I > 2\sigma(I)$) = 0.0477, wR2($I > 2\sigma(I)$) = 0.0924, GOF = 1.042.

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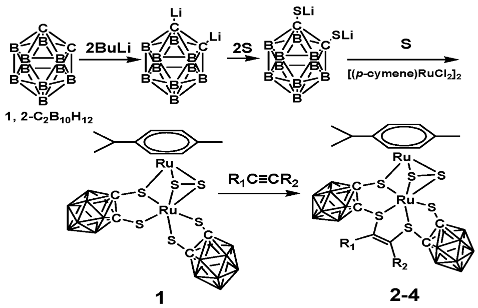
Scheme 1



2a	2b	3b	4
R_1 = H R_2 = CO_2Me	CO_2Me H	C_6H_5 H	CO_2Me CO_2Me

Its solid-state structure (Figure 1) shows that a bridging S−S bond is present instead of the two bridging Cl atoms in [(*p*-cymene)$RuCl_2$]$_2$. The *p*-cymene fragment at Ru(1) is replaced by sulfur atoms of two $[S_2C_2(B_{10}H_{10})]^{2-}$ ligands that donate six electrons. As a result, Ru(1) is bonded to six sulfur atoms in a distorted-octahedral arrangement. Only two examples of complexes with a RuS_6 core have been reported, which contain 2-aminoethanethiolate and 1,2-dicyanoethylenedithiolate, respectively.[8] In **1** the S(1)−Ru(1)−S(3) angle of 117° heavily deviates from 90° and introduces considerable strain to the structure. Note that in **1** Ru(1) is electronically unsaturated (16e) with a charge of +3 and Ru(2) bearing a *p*-cymene unit is electronically saturated (18e) with a charge of +1, in contrast to Ru(II)/Ru(II) in the starting material [(*p*-cymene)$RuCl_2$]$_2$.

Compound **1** shows reactivity with alkynes. The reaction with $HC{\equiv}CCO_2Me$ affords **2a** and **2b** in an approximate ratio of 1:1 (Scheme 1). Both spectroscopic data and solid-state structures confirm two isomers arising from the regio- and stereoselective addition of the alkyne.[9] In **2a** (Figure 2) the alkyne addition takes place selectively at S(1) and S(3) sites from two individual $[S_2C_2(B_{10}H_{10})]^{2-}$ fragments to generate a five-membered RuSCCS ring. As a result, the S(1)−Ru(1)−S(3) angle changes from 117° in **1** to 87°, thus reducing the strain that is present in **1**. On the other hand, the generation of **2a** leads to coordinative S(1)→Ru(1) (2.2519 Å) and S(3)→Ru(1) (2.2612 Å) bonds which are longer than the corresponding covalent bonds (2.1997, 2.1919 Å) in **1**. Moreover, the alkyne addition leads to a change of the Ru(1) atom from a 16e center to a 18e one, accompanied by a change of the charge from +3 to +1. The C(5)−C(6) bond (1.312 Å) is typical of a double bond. Analogous addition of alkynes has not been reported previously.

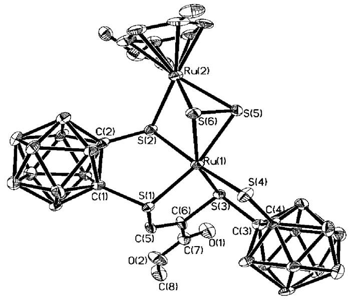


Figure 2. Molecular structure of **2a** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2519(16), Ru(1)−S(2) = 2.3920(16), Ru(1)−S(3) = 2.2612(15), Ru(1)−S(4) = 2.3651(17), Ru(1)−S(5) = 2.3870(16), Ru(1)−S(6) = 2.4211(15), S(5)−S(6) = 2.043(2), C(5)−S(1) = 1.802(6), C(6)−S(3) = 1.772(6), C(5)−C(6) = 1.312(9), C(1)−C(2) = 1.681(9), C(3)−C(4) = 1.655(8), Ru(1)···Ru(2) = 3.422; S(1)−Ru(1)−S(3) = 86.87(5), S(1)−Ru(1)−S(4) = 93.56(6).

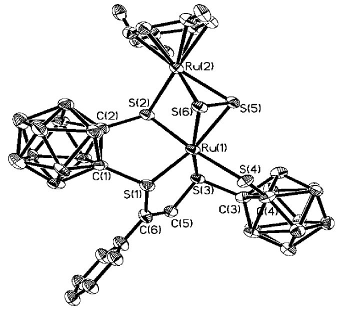


Figure 3. Molecular structure of **3b** (30% probability displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2394(19), Ru(1)−S(2) = 2.3742(19), Ru(1)−S(3) = 2.2692(18), Ru(1)−S(4) = 2.3818(19), Ru(1)−S(5) = 2.3901(17), Ru(1)−S(6) = 2.4062(18), S(5)−S(6) = 2.030(2), C(6)−S(1) = 1.789(7), C(5)−S(3) = 1.734(7), C(5)−C(6) = 1.394(10), C(1)−C(2) = 1.643(9), C(3)−C(4) = 1.659(10), Ru(1)···Ru(2) = 3.419; S(1)−Ru(1)−S(3) = 87.35(6), S(1)−Ru(1)−S(4) = 91.41(6).

Upon heating of **2a**, a mixture of **2a** and **2b** in a ratio of approximately 1:1 is observed. The same is observed for **2b**. This demonstrates that the two species interconvert. Another fact is that the reaction of **1** with methyl propiolate at ambient temperature also leads to a mixture of **2a** and **2b** in a ratio of 1:1. These observations suggest that the energy barrier between **2a** and **2b** is low and the size of the CO_2Me group does not significantly affect the regioselectivity of the alkyne addition. However, in the case of $HC{\equiv}CPh$, only one species, **3b**, is produced,[10] and the solid-state structure (Figure 3) demonstrates that the terminal carbon atom is added to S(3) rather than S(1). Heating **3b** does not generate its isomer, consistent with the greater steric effect of the phenyl group.

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(9) Synthesis of **2a** and **2b**: methyl propiolate (0.08 mL, 1 mmol) was added to **1** (81 mg, 0.1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 16 h at ambient temperature. After removal of the solvent the residue was chromatographed to give **2a** (petroleum ether/CH_2Cl_2 (1:2)) and **2b** (petroleum ether/CH_2Cl_2 (1:5)). **2a**: yield 36 mg (40%); mp 230 °C dec. Anal. Calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_6$: C, 24.09; H, 4.27. Found: C, 24.28; H, 4.35. MALDI-TOF MS (*m/z*): calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_6$, 897.130; found, 898.224 ($[M + H]^+$, 75%). ^1H NMR ($CDCl_3$): δ 1.21 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.35 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.19 (s, 3H, CH_3), 2.68 (sept. J = 7.0 Hz, 1H, $CH(CH_3)_2$), 3.99 (s, 3H, OCH_3), 5.04 (d, J = 6.0 Hz, 1H, C_6H_4), 5.08 (d, J = 6.0 Hz, 1H, C_6H_4), 6.12 (d, J = 6.0 Hz, 1H, C_6H_4), 6.14 (d, J = 6.0 Hz, 1H, C_6H_4), 8.21 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$): δ 18.87 ($C_6H_4{-}CH_3$), 22.97, 23.39 ($CH(CH_3)_2$), 31.78 ($CH(Me)_2$), 54.71 (OCH_3), 80.58, 81.81, 82.51, 85.73 (CH in *p*-cymene), 90.31, 93.56, 94.28, 99.68, 100.16, 107.78 (*o*-carborane and quaternary C in *p*-cymene), 142.64 (*C*=CH), 149.14 (H*C*=C), 162.42 (C=O). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −6.9, −4.3, −2.0 (4:2:4). IR (KBr, cm^{-1}): ν 2581 (ν_{B-H}). Crystal data: $C_{18}H_{38}B_{20}O_2Ru_2S_6$, triclinic, space group $P1$, a = 12.0780(16) Å, b = 13.0508(18) Å, c = 13.4696(19) Å, α = 106.665(2)°, β = 97.858(2)°, γ = 108.704(2)°, V = 1864.4(4) $Å^3$, Z = 2, T = 298(2) K, μ = 1.169 mm^{-1}, 7160 reflections observed, 5155 independent reflections, R1($I > 2\sigma(I)$) = 0.0634, wR2($I > 2\sigma(I)$) = 0.1409, GOF = 1.039. **2b**: yield 33 mg (39%); mp 232 °C dec. Anal. Calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_6$: C, 24.09; H, 4.27. Found: C, 23.88; H, 4.32. MALDI-TOF MS (*m/z*): calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_6$, 897.130; found, 898.224 ($[M + H]^+$, 75%). ^1H NMR ($CDCl_3$): δ 1.24 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.37 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.24 (s, 3H, CH_3), 2.71 (sept. J = 7.0 Hz, 1H, $CH(CH_3)_2$), 3.95 (s, 3H, OCH_3), 5.07 (d, J = 6.0 Hz, 1H, C_6H_4), 5.13 (d, J = 6.0 Hz, 1H, C_6H_4), 6.12 (d, J = 6.0 Hz, 1H, C_6H_4), 6.14 (d, J = 6.0 Hz, 1H, C_6H_4), 8.29 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$): δ 18.61 ($C_6H_4{-}CH_3$), 22.68, 23.07 ($CH(CH_3)_2$), 31.45 ($CH(Me)_2$), 54.10 (OCH_3), 80.23, 81.15, 82.14, 84.98 (CH in *p*-cymene), 89.84, 90.18, 97.45, 99.09, 103.52, 107.26 (*o*-carborane and quaternary C in *p*-cymene), 144.32 (*C*=CH), 150.73 (H*C*=C), 161.69 (C=O). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −6.8, −4.5, −2.3 (4:2:4). IR (KBr, cm^{-1}): ν 2579 (ν_{B-H}).

The internal alkyne $MeO_2CC\equiv CCO_2Me$ reacts with **1** to afford **4**, on the basis of spectroscopic data.[11] $PhC\equiv CPh$ does not react with **1**. Again, this shows alkyne addition has steric requirements.

In summary, a novel dinuclear Ru(I)/Ru(III) complex (**1**) containing one bridging S−S bond and two $[S_2C_2(B_{10}H_{10})]^{2-}$ units has been synthesized through the reaction of $[(p\text{-cymene})RuCl_2]_2$ with $Li_2[S_2C_2(B_{10}H_{10})]$ and excess sulfur. It is the 16e Ru(III) center in a distorted octahedron that determines its reactivity. The alkyne addition at two of the six sulfur atoms gives rise to the more stable products **2**−**4** due to reduced strain and the formation of a 18e Ru(I) center. The steric factor of alkynes is important to successful additions. A detailed investigation on the reaction chemistry of **1** is under way.

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Supporting Information Available: Text giving detailed synthesis details and characterization data for compounds **1**−**4** and CIF files giving X-ray crystallographic data for the structure determinations of compounds **1**, **2a**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Synthesis of **3b**: phenylacetylene (0.1 mL, 1 mmol) was added to **1** (81 mg, 0.1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 18 h at ambient temperature. After removal of the solvent the residue was chromatographed to give **3b** (petroleum ether/CH_2Cl_2 (1:4)). **3b**: yield 73 mg (80%); mp 238 °C dec. Anal. Calcd for $C_{22}H_{40}B_{20}Ru_2S_6$: C, 28.87; H, 4.40. Found: C, 28.69; H, 4.29. MALDI-TOF MS (*m*/*z*): calcd for $C_{22}H_{40}B_{20}Ru_2S_6$, 915.156; found, 916.218 ($[M + H]^+$, 85%). ^1H NMR ($CDCl_3$): δ 1.24 (d, $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 1.37 (d, $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 2.23 (s, 3H, CH_3), 2.71 (sept, $J = 7.0$ Hz, 1H, $CH(CH_3)_2$), 5.05 (d, $J = 6.0$ Hz, 1H, C_6H_4), 5.12 (d, $J = 6.0$ Hz, 1H, C_6H_4), 6.13 (d, $J = 6.0$ Hz, 1H, C_6H_4), 6.15 (d, $J = 6.0$ Hz, 1H, C_6H_4), 7.18 (s, 1H, $HC{=}C$), 7.49 (m, 3H, Ph), 7.64 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 18.51 ($C_6H_4{-}CH_3$), 22.58, 22.99 ($CH(CH_3)_2$), 31.38 ($CH(CH_3)_2$), 80.11, 81.04, 82.09, 85.25 (CH in *p*-cymene), 90.74, 91.13, 92.48, 92.97, 99.43, 106.99 (*o*-carborane and quaternary C in *p*-cymene), 127.93, 129.55, 131.03 (phenyl group), 132.80 ($HC{=}C$), 133.88 ($C{=}CH$), 151.57 (quaternary C in phenyl group). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −6.8, −4.4, −2.2 (4:2:4). IR (KBr, cm^{-1}): ν 2581 (ν_{B-H}). Crystal data: $C_{22}H_{40}B_{20}Ru_2S_6$, triclinic, space group $P\bar{1}$, $a = 11.722(5)$ Å, $b = 13.909(5)$ Å, $c = 13.911(5)$ Å, $\alpha = 117.938(4)°$, $\beta = 98.632(5)°$, $\gamma = 90.543(6)°$, $V = 1972.6(13)$ Å^3, $Z = 2$, $T = 298(2)$ K, $\mu = 1.103$ mm^{-1}, 7557 reflections observed, 5000 independent reflections, $R1(I > 2\sigma(I)) = 0.0639$, $wR2(I > 2\sigma(I)) = 0.1366$, GOF = 1.000.

(11) Synthesis of **4:** dimethyl acetylenedicarboxylate (0.1 mL, 1 mmol) was added to **1** (81 mg, 0.1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 18 h at ambient temperature. After removal of the solvent the residue was chromatographed to give **4** (petroleum ether/CH_2Cl_2 (1:2)). **4**: yield 74 mg (78%); mp 236 °C dec. Anal. Calcd for $C_{20}H_{40}B_{20}O_4Ru_2S_6$: C, 25.14; H, 4.22. Found: C, 24.91; H, 4.34. MALDI-TOF MS (*m*/*z*): calcd for $C_{20}H_{40}B_{20}O_4Ru_2S_6$, 955.136; found, 956.478 ($[M + H]^+$, 45%). ^1H NMR ($CDCl_3$): δ 1.23 (d, $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 1.36 (d, $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 2.22 (s, 3H, CH_3), 2.70 (sept, $J = 7.0$ Hz, 1H, $CH(CH_3)_2$), 3.92 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 5.06 (d, $J = 6.0$ Hz, 1H, C_6H_4), 5.11 (d, $J = 6.0$ Hz, 1H, C_6H_4), 6.14 (d, $J = 6.0$ Hz, 1H, C_6H_4), 6.15 (d, $J = 6.0$ Hz, 1H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 18.49 ($C_6H_4{-}CH_3$), 22.59, 23.00 ($CH(CH_3)_2$), 31.42 ($CH(Me)_2$), 54.16, 54.31 (OCH_3), 80.36, 81.46, 82.29, 85.55 (CH in *p*-cymene), 91.06, 91.64, 92.11, 99.87, 101.67, 107.52 (*o*-carborane and quaternary C in *p*-cymene), 144.89, 148.64 ($C{=}C$), 163.39, 163.97 ($C{=}O$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −6.6, −4.1, −2.0 (4:2:4). IR (KBr, cm^{-1}): ν 2579 (ν_{B-H}).