

A Novel B-H→Ru Agostic Bond. Crystal Structure of [RuCl{7,8-μ-S(CH₂CH₂)S-C₂B₉H₁₀}(PPh₃)₂].Me₂CO

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The complex [RuCl{7,8-μ-S(CH₂CH₂)S-C₂B₉H₁₀}(PPh₃)₂].Me₂CO **1** contains octahedral ruthenium(II), the sixth coordination site being occupied by an agostic B-H→Ru in the first example of B(3)-H→Ru coordination in the solid state; solution NMR studies show the presence of B(3)-Ru-H bonding.

Three general modes of bonding the *nido*-ion [7,8-C₂B₉H₁₂]⁻ to transition metal ions have been reported: η⁵-coordination to the open pentagonal C₂B₃ face¹ as in *closo*-[Ru(PPh₃)₂H₂C₂B₉H₁₁];² *exo-nido*-coordination as in *exo-nido*-[Rh(PPh₃)₂{7,8-μ-(CH₂)₃-7,8-C₂B₉H₁₀}];³ a mixed mode composed of η⁵-coordination and one Rh-H-B bridge as in [Rh(PPh₃)₂C₂B₉H₁₁]₂.⁴

Besides these three types of M-C₂B₉ interaction, a rarer M-B σ-bond is also known: e.g. the B(10)-Ru σ-bond in [N(PPh₃)₂][RuW(μ-CC₆H₄Me-4)(μ-σ,η⁵-C₂B₉H₈Me₂)(CO)₃(η-C₅H₅)].⁵ All B-H→M or B-M bonds found in the literature for derivatives of [7,8-C₂B₉H₁₂]⁻ involve one boron atom of the open face. When *exo-nido*-coordination takes place, there are two B-H→M interactions: with a boron atom of the open face and the second with a boron atom of the second layer.⁶ However, in no case has a B(3)-H→M interaction been found [B(3) is connected to both carbaborane carbon atoms].

During our investigations on the coordination chemistry of macrocyclic derivatives of *exo*-dithiocarbaborane compounds,⁷⁻¹¹ we have observed a dependence between the ω angle and the exocluster chain length¹² (Fig. 1), the shorter the exocluster chain, the smaller being the ω angle [defined as the angle subtended by lines drawn from the midpoint of the S...S vector to the atom M and to the midpoint of the C(carb)...C(carb) vector respectively]. This led us to think that the use of short exocluster chains such as in [7,8-μ-S(CH₂CH₂)S-C₂B₉H₁₀]⁻ could lead to a B(3)-H→M interaction, the first example of this type of interaction involving B(3). We detected a B(3)-Rh σ-interaction in [Me₄N][RhCl{7,8-μ-S(CH₂CH₂)S-C₂B₉H₁₀}]{μ-7,8-μ-S(CH₂CH₂)S-C₂B₉H₉}],¹³ but have not hitherto been able to observe, in the solid state, an agostic B(3)-H→M bond. Here we report on such a bond, which proves that the interactions between the macrocycle and the carbaborane allow the otherwise unlikely formation of rare B(3)-M and B(3)-H→M interactions.

To a deoxygenated ethanol solution (30 cm³) containing [Me₄N][7,8-μ-S(CH₂CH₂)S-C₂B₉H₁₀] (98 mg, 0.329 mmol) was added [RuCl₂(PPh₃)₃] (315 mg, 0.328 mmol), and the mixture refluxed for 1 h under N₂. The warm mixture was filtered and the orange solid obtained washed with ethanol (20 cm³, warm) and diethyl ether (10 cm³) to yield an analytically

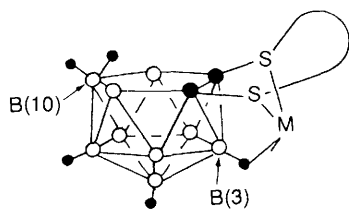


Fig. 1

pure solid [RuCl{7,8-μ-S(CH₂CH₂)S-C₂B₉H₁₀}(PPh₃)₂] **1** (yield 200 mg, 65%).[†]

The ¹¹B{¹H} NMR spectrum displays five signals with intensities 2 : 2 : 2 : 2 : 1,[†] and is similar to that of the free ligand (2 : 1 : 2 : 2 : 1 : 1)¹³ but for the fact that the first intensity 1 absorption, attributed to B(3) in the free ligand, has been displaced to higher field in the complex (by ca. 19 ppm). In [Me₄N][RhCl{7,8-μ-S(CH₂CH₂)S-C₂B₉H₁₀}]{σ-7,8-μ-S(CH₂CH₂)S-C₂B₉H₉} we found an upfield shift of 25 ppm for the B(3) resonance, suggesting a direct σ B-Ru bond. A downfield shift in the range 5–20 ppm would be expected for a three-centre two-electron B-H→M interaction.¹⁴ The ¹H NMR spectrum shows a resonance at δ -17.4 attributable to Ru-H, and supporting a B-Ru-H interaction.

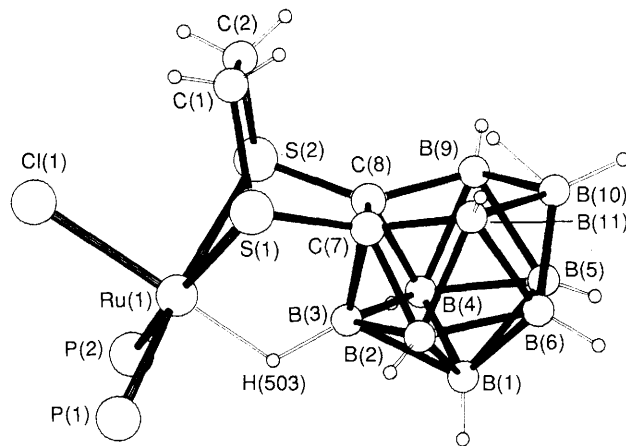


Fig. 2 Molecular structure of **1** with atom labelling. The phenyl groups and all hydrogen atoms, except H(503), have been omitted for clarity. Selected intramolecular distances (Å) and angles (°) are as follows: Ru(1)-S(1) 2.431(1), Ru(1)-S(2) 2.432(1), Ru(1)-P(1) 2.361(1), Ru(1)-P(2) 2.372(1), Ru(1)-Cl(1) 2.410(1), Ru(1)-H(503) 1.63(4), B(3)-H(503) 1.21(4), Cl(1)-Ru(1)-S(1) 90.80(5), Cl(1)-Ru(1)-S(2) 90.42(5), Cl(1)-Ru(1)-P(1) 92.67(5), Cl(1)-Ru(1)-P(2) 94.10(5), Cl(1)-Ru(1)-H(503) 176(1), S(1)-Ru(1)-S(2) 76.32(4), S(1)-Ru(1)-P(1) 93.32(5), S(1)-Ru(1)-P(2) 166.03(4), S(1)-Ru(1)-H(503) 87(1), S(2)-Ru(1)-P(1) 169.24(4), S(2)-Ru(1)-P(2) 90.55(5), S(2)-Ru(1)-H(503) 92(1), P(1)-Ru(1)-P(2) 99.50(5), P(1)-Ru(1)-H(503) 84(1), P(2)-Ru(1)-H(503) 88(1).

[†] Data for [RuCl{7,8-μ-S(CH₂CH₂)S-C₂B₉H₁₀}(PPh₃)₂] **1**: FTIR (KBr) ν(B-H) 2547 and 2530 cm⁻¹; ¹H NMR (CDCl₃): δ 7.37–7.16 (m, 30H), 3.34 (d, J 8.3 Hz, 2H), 2.77 (d, J 8.3 Hz, 2H), -2.4 (br, 1H) and -17.4 (br, 1H); ¹¹B{¹H} NMR (CHCl₃, external BF₃·Et₂O as reference, upfield shifts are negative): δ -5.7 (2B), -16.5 (2B), -19.0 (2B), -29.9 (2B) and -36.3 (1B) (Found: C, 53.8; H, 5.0; S, 7.0. C₄₀H₄₄B₉ClP₂RuS₂ requires C, 54.3; H, 5.0; S, 7.25%).

The molecular structure of the complex in the solid state was determined by X-ray crystallography.‡ In contrast with the ^{11}B and ^1H NMR spectra, this study clearly established the presence of a new type of $\text{B}(3)\text{-H}\rightarrow\text{Ru}$ bond. The molecular structure of **1** consists of a $\text{Ru}^{\text{II}}\text{Cl}$ moiety attached to the ligand $7,8\text{-}\mu\text{-S}(\text{CH}_2\text{CH}_2)\text{S-C}_2\text{B}_9\text{H}_{10}$ via the sulfur atoms, and to two PPh_3 ligands. The carbaborane ligand is further coordinated to the Ru atom via a $\text{B-H}\rightarrow\text{Ru}$ agostic bond ($\omega = 110^\circ$, equal to the angle found in $[\text{Me}_4\text{N}][\text{RhCl}\{7,8\text{-}\mu\text{-S}(\text{CH}_2\text{CH}_2)\text{S-C}_2\text{B}_9\text{H}_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-S}(\text{CH}_2\text{CH}_2)\text{S-C}_2\text{B}_9\text{H}_9\}]$). This $\text{B}(3)\text{-Ru}$ [$\text{B}(3)\text{-H}\rightarrow\text{Ru}$] distance is longer than the $\text{Ru-B}(10)$ distance in $[\text{N}(\text{PPh}_3)_2][\text{RuW}(\mu\text{-CC}_6\text{H}_4\text{Me-}4)(\mu\text{-}\sigma,\eta^5\text{-C}_2\text{B}_9\text{H}_8\text{Me}_2)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^5$ and the $\text{B}(3)\text{-Rh}$ distance in $[\text{Me}_4\text{N}][\text{RhCl}\{7,8\text{-}\mu\text{-S}(\text{CH}_2\text{CH}_2)\text{S-C}_2\text{B}_9\text{H}_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-S}(\text{CH}_2\text{CH}_2)\text{S-C}_2\text{B}_9\text{H}_9\}]$ (2.41 Å vs. 2.15 and 2.12 Å, respectively), but close to the $\text{B}(10)\text{-Ru}$ [$\text{B}(10)\text{-H}\rightarrow\text{Ru}$] distance in $[\text{RuW}(\mu\text{-CC}_6\text{H}_4\text{Me-}4)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (2.41 Å in **1** vs. 2.40 Å).⁵

In conclusion, a $\text{B}(3)\text{-H}\rightarrow\text{Ru}$ agostic bond has been observed for the first time in the solid state, which evolves to a $\text{B}(3)\text{-Ru-H}$ bond in solution, as shown by NMR studies.

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‡ Crystal data: orange crystal (0.05 × 0.16 × 0.25 mm), grown from acetone by slow evaporation. Triclinic, $P\bar{1}$ (No. 2), $Z = 2$; $a = 11.814(4)$, $b = 11.855(3)$, $c = 16.810(3)$ Å; $\alpha = 105.16(2)$, $\beta = 94.91(2)$, $\gamma = 92.44(2)^\circ$; $V = 2259(1)$ Å³; $Z = 2$; $D_c = 1.386$ g cm⁻³. Data were collected at 23°C [7132 reflections with $I > 2\sigma(I)$] on a Rigaku 5S diffractometer using Mo-K α radiation ($\lambda = 0.71069$ Å); $2\theta_{\text{max}} = 55^\circ$. The structure was solved by direct methods and refined to $R = 0.047$ and $R_w = 0.050$ using the TEXSAN-TEXRAY system (Single Crystal Structure Analysis Software, Version 5.0, Molecular Structure Corporation, The Woodlands, Texas, 1989). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.