

Supplementary Information for: 'A 'Sting' on Grubbs' Catalyst: An Insight into Hydride Migration Between Boron and Transition Metal.'

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Experimental Data

General Remarks

All procedures were carried out under an inert atmosphere using standard Schlenk line techniques unless mentioned otherwise. Chemicals were obtained from Sigma Aldrich and Fisher Scientific. All solvents were purified using an Anhydrous Engineering solvent system. NMR spectra were recorded on a JEOL ECP 300 Spectrometer (^{11}B , ^{31}P), a JEOL ECP 400 Spectrometer (^1H , ^{13}C), a JEOL delta 270 Spectrometer (^1H , ^{13}C) and on a JEOL delta 400 Spectrometer (^1H , ^{13}C) at ambient temperature in deuterated solvent. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are referenced chemical shifts relative to high frequency of residual solvent and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are referenced relative to high frequency of 85 % H_3PO_4 . Mass spectra were recorded on an Applied Biosystems QStar XL (ESI, LC-MS) and on a VG Quattro (ESI, LC-MS). Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol. $\text{Na}[\text{Bm}]$ was prepared by a literature method (reference S1).

$[\text{RuCl}\{\text{HB}(\text{CH}_2\text{Ph})(\text{mt})_2\}(\text{PCy}_3)]$ (**5**)

To a well-stirred solution of $[\text{Ru}(\text{=CHPh})\text{Cl}_2(\text{PCy}_3)_2]$ (150.0 mg, 0.183 mmol) in anhydrous THF (100 mL) was added $\text{Na}[\text{Bm}]$ (53.0 mg, 0.201 mmol) and the reaction mixture was stirred for 2.5 h at ambient temperature under an inert N_2 atmosphere. An orange precipitate was isolated by filtration and dried under vacuum. The solid was recrystallised from $\text{CH}_2\text{Cl}_2/\text{hexane}$ to provide an analytical pure sample of **5** (63.4 mg, 0.084 mmol, 46 %).

NMR (DMF-d_7) δ [ppm]; $^{31}\text{P}\{^1\text{H}\}$; 75.3 (s, $\text{Ru}(\text{PCy}_3)$, h.h.w. 14 Hz). $^{11}\text{B}\{^1\text{H}\}$ 15.3 (s, h.h.w. 85 Hz). ^1H and ^{13}C assignments were made by using the following correlation techniques: COSY, DEPT135, HMQC and HMBC. ^1H NMR; -15.3 (br, Ru-H), 1.04 – 1.16 (m, 9H, PCy_3), 1.26 – 1.45 (m, 6H, PCy_3), 1.48 – 1.63 (m, 12H, PCy_3), 1.88 – 1.98 (m, 5H, $\text{PCy}_3/\text{CH}_2\text{Ph}$), 2.33 – 2.42 (m, 3H, PCy_3), 3.39 (s, 6H, NCH_3), 6.76 – 6.82 (m, 1H, Ph-H (para)), 6.87 (d, $^3J_{\text{HH}} = 2.0$ Hz, 2H, Ph-H (ortho)), 6.88 (s, 2H, Ph-H (meta)), 7.21 (d, $^3J_{\text{HH}} = 2.4$ Hz, 2H, BNCHCHNMe), 7.69 (d, $^3J_{\text{HH}} = 2.0$ Hz, 2H, BNCHCHNMe). $^1\text{H}\{^{11}\text{B}\}$ NMR (CD_2Cl_2) -15.1 (d, $^2J_{\text{HP}} = 28.0$ Hz, 1H, RuH). $^{13}\text{C}\{^1\text{H}\}$ NMR 26.7 (s, PCy_3), 27.7 (d, $J_{\text{HP}} = 10.6$ Hz, PCy_3), 28.8 (br s, CH_2Ph), 33.0 (s, NCH_3), 37.2 (br d, $J_{\text{HP}} = 16.7$ Hz, PCy_3), 117.6 (s, BNCHCHNMe), 122.5 (s, BNCHCHNMe), 123.7 (s, Ph-C (para)), 126.8 (s, Ph-C (meta)), 129.4 (s, Ph-C (ortho)), 139.2 (s, Ph-C (quaternary)), 165.9 (s, $\text{N}(\text{CS})\text{N}$). MS-(ESI) $^+$ $m/z = 711$ $[\text{M}]^+$. IR (powder film) 2205w (RuHB), 1599m, 1555m, 1492s, 1472s, 1447s, 1394s, 1207s. Elemental analysis calculated for $\text{C}_{33}\text{H}_{51}\text{BCIN}_4\text{PRuS}_2$. CH_2Cl_2 C: 49.13, H: 6.43, N: 6.74, found C: 49.93; H: 6.55; N: 6.74.

$\text{Na}[\text{D}_2\text{B}(\text{mt})_2]$ (**6**)

A Schlenk flask was charged with $\text{Na}[\text{BD}_4]$ (0.24 g, 5.7 mmol), 1-methyl-1H-imidazole-2-thiol (1.30 g, 11.4 mmol) and THF (100 mL). The mixture was heated to reflux with stirring for 7 h during which time evolution of hydrogen gas (HD) was observed. The mixture was allowed to cool and was filtered to remove any NaBD_4 and tri-substituted compound. All volatiles were removed under reduced pressure and the resulting residue was washed with dichloromethane (2×15 mL) to remove any unreacted 1-methyl-1H-imidazole-2-thiol to provide the product as a white solid (1.18 g, 4.47 mmol, 78 %).

NMR (DMSO-d_6) $^{11}\text{B}\{^1\text{H}\}$ -10.4 (br s, hhw = 350 Hz); ^1H 3.40 (s, 6H, $2 \times \text{NCH}_3$), 6.71 (d, 2H, $2 \times \text{NCHCHN}$, $^3J_{\text{HH}} = 2.0$ Hz), (d, 2H, $2 \times \text{NCHCHN}$, $^3J_{\text{HH}} = 2.0$ Hz). $^{13}\text{C}\{^1\text{H}\}$ 33.9 (s, NCH_3), 115.6 (s, NCHCHN), 123.8 (s, NCHCHN), 163.2 (C=S). IR 1800w, 1738w (B-D),^[S2] other bands include 1660w, 1622w, 1554w, 1454s, 1407s, 1374s, 1296m, 1187s, 880s. MS ESI $^+$ 610 [$3 \times \{\text{D}_2\text{B}(\text{mt})_2\} - \text{mt}$] 100%, 551 ($2\text{M} + \text{Na}$) $^+$ 70%, 287 ($\text{M} + \text{Na}$) $^+$ 20%. ESI 241 ($\text{M} - \text{Na}^+$) 100 %. Elemental analysis calculated for $\text{C}_8\text{H}_{10}\text{D}_2\text{BN}_4\text{S}_2\text{Na} \cdot \frac{1}{4}\text{H}_2\text{O}$ C: 35.77, N: 20.85; found C: 35.64; N: 20.56.

$[\text{RuCl}\{\text{BD}(\text{CHDPh})(\text{mt})_2\}(\text{PCy}_3)]$ (**5-d**₂)

To a well-stirred solution of $[\text{Ru}(=\text{CHPh})\text{Cl}_2(\text{PCy}_3)_2]$ (100.0 mg, 0.122 mmol) in anhydrous THF (75 mL) was added $\text{Na}[\text{Bm-d}_2]$ (32.0 mg, 0.121 mmol) and the reaction mixture was stirred for 3 h at ambient temperature under an inert N_2 atmosphere. After this time the solvent volume was reduced to 15 mL and an orange solid was isolated by filtration. The solid was recrystallised from CH_2Cl_2 /hexane to provide an analytical pure sample of **5-d**₂ (48.0 mg, 0.063 mmol, 52 %).

$^2\text{D}\{^1\text{H}\}$ (CH_2Cl_2 , referenced to CD_2Cl_2) 1.53 (br, 1D, CHDPh), -15.2 (br, 1D, Ru-D). $^{11}\text{B}\{^1\text{H}\}$ 15.1 (s). MS-ESI⁺ 713 ($\text{M}-\text{Cl}$)⁺ 15%, 609 [$\text{M}-\text{Cl}-(\text{BCHDPh})$]⁺ 100%. IR (powder film) 1600m, 1555m, 1472s, 1448s, 1395s, 1206s. Elemental analysis calculated for $\text{C}_{33}\text{H}_{49}\text{D}_2\text{BCIN}_4\text{PRuS}_2 \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ C: 51.90, N: 7.28, found C: 52.02; N: 6.70.

DFT Calculations

To confirm the X-ray structure and obtain further insight, DFT calculations on **5** (with and without solvation fields) and its isomers **5'**, **5i** and **5ii** (with and without the agostic $\text{Ru}\dots\text{H}_{27\text{A}}$ interaction in the starting geometry), were carried out (see Table S1 and Figure S2). DFT calculations were performed using the Jaguar 6.0 program suite.^[S3] Starting geometries were taken from the X-ray crystal structure of **5**, and atom position changes made using the Maestro 5.0 program.^[S4] All geometry optimisations were performed using the B3PW91 functional^[S4,S5] with basis sets of 6-31G* quality for the ligand atoms and LACV3P for ruthenium. Geometry optimisation of **5** was also carried out in two different solvent continuums, using the solvation model built into the Jaguar 6.0 suite.^[S3] Dielectric constants of 2.023 and 38.3 with probe radii of 2.78 and 2.48 were used, simulating both a non-polar solvent (cyclohexane) and a polar solvent (DMF) respectively.

Table S1. Structural data from X-Ray crystal determination and calculated optimised geometries of complex **5** and isomers.

	Ru-B	Ru-P	Ru-Cl	Ru-H ₁₀₀	Ru-H _{27A}	B-H ₁₀₀	P-Ru-B	B-Ru-H ₁₀₀
X-ray ^a	2.12	2.28	2.50	1.66	2.02	1.50	121.53	44.7
5 ^b	2.14	2.27	2.45	1.62	2.074	1.48	128.7	45.4
5 ^c (C_6H_{12})	2.14	2.28	2.47	1.62	2.076	1.53	128.5	45.4
5 ^c (DMF)	2.15	2.29	2.50	1.61	2.078	1.56	129.4	46.4
5i ^d	2.11	2.32	2.43	1.59	2.177	3.558	84.2	146.8
5ii ^d	2.12	2.47	2.46	1.62	1.902	3.325	84.1	125.0

Bond length (Å) and angles (°) for complex **5**. a) from X-ray analysis; b) DFT structure without solvent field; c) DFT structure with solvent field; d) Isomers of **5** with H₁₀₀ and Cl in the two different *cis* positions.

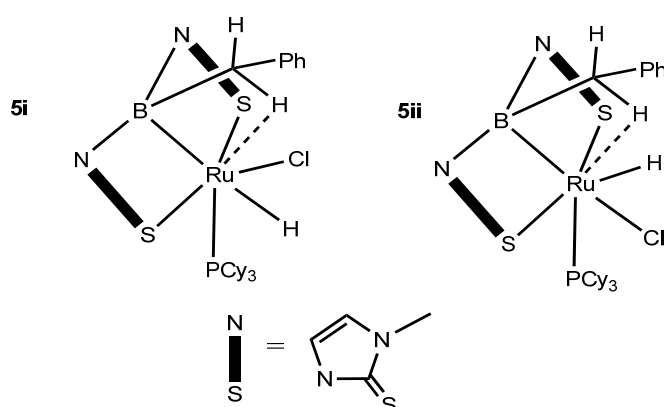


Figure S1. The different isomers of complex **5** studied by DFT calculations: **5i**, **5ii**.

Of the isomers calculated, **5** was the most stable, being approximately 10 kcal mol⁻¹ lower in energy than the others. The optimised geometry of **5** is close to that of the X-ray determined structure. The only major variation between the structures is a 7° difference in the P-Ru-B angle. Despite the fact that X-ray parameters for hydrogen atoms are inherently imprecise and likely to be inaccurate (not reflecting internuclear distances) it is worthy of note that the Ru-H and B-H distances are in good agreement. The observed (and computed) geometry of complex **5**

implies that it is in a situation along the reaction coordinate for cleavage of the B-H bond and formation of B-Ru and Ru-H bonds.

Optimisation initiated from structure **5'** converges to **5**. This behaviour is consistent with the geometry in the crystal being the lowest energy for this complex. Structures **5i** and **5ii** (with and without agostic Ru...H_{27A} interactions in the starting geometry) optimized to geometries with an agostic interaction (see Table S1). Insignificant variations of geometry result from variation in solvent field applied (see Table S1). The values of Ru-B and Ru-H₁₀₀ are similar in **5** and its isomers **5i** and **5ii** consistent with relatively little change in bond order for these interactions.

The Cambridge Structural Database (CSD)^[S7] contains a number of 3-centre-2-electron Ru-H-B moieties providing interesting context for the geometry of complex **5**. Relevant structures include adducts of (carba)borane cages, BH₄ or pyrazolylborate ligands. Of the most closely similar complexes (Ru-H-BN₂), the average Ru-H, B-H and Ru-B distances were 1.885 Å, 1.232 Å and 2.766 Å respectively. None of these complexes contained bonding geometries for complex **5**.

References

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