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Chemistry of Diruthenium and Dirhodium Analogues of Pentaborane(9): Synthesis and Characterization of Metal N,S-Heterocyclic Carbene and B-Agostic Complexes

Dipak Kumar Roy, Bijan Mondal, R. S. Anju, and Sundargopal Ghosh^{*,[a]}

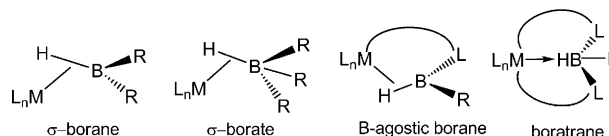
Abstract: Building upon our earlier results on the synthesis of electron-precise transition-metal–boron complexes, we continue to investigate the reactivity of pentaborane(9) and tetraborane(10) analogues of ruthenium and rhodium towards thiazolyl and oxazolyl ligands. Thus, mild thermolysis of *nido*-[(Cp**RuH*)₂B₃H₇] (1) with 2-mercaptobenzothiazole (2-mbtz) and 2-mercaptobenzoxazole (2-mboz) led to the isolation of Cp*-based (Cp* = η⁵-C₅Me₅) borate complexes **5a,b** [Cp**RuBH*₃L] (**5a**: L = C₇H₄NS₂; **5b**: L = C₇H₄NOS) and agostic complexes **7a,b** [Cp**RuBH*₂(L)₂], (**7a**: L = C₇H₄NS₂; **7b**: L = C₇H₄NOS). In a similar fashion, a rhodium analogue of penta-

borane(9), *nido*-[(Cp**Rh*)₂B₃H₇] (2) yielded rhodaboratrane [Cp**RhBH*(L)₂], **10** (L = C₇H₄NS₂). Interestingly, when the reaction was performed with an excess of 2-mbtz, it led to the formation of the first structurally characterized N,S-heterocyclic rhodium-carbene complex [(Cp**Rh*)(L)₂(1-benzothiazol-2-ylidene)] (**11**) (L = C₇H₄NS₂). Furthermore, to evaluate the scope of this new route, we extended this chemistry towards the diruthenium analogue of tetraborane(10), *arachno*-[(Cp**RuCO*)₂B₂H₆] (**3**), in which the metal center possesses different ancillary ligands.

Introduction

The combination of boron and transition metals has put forward a huge range of compounds that exhibit remarkable structural varieties. Among the compounds featuring a direct M–B bond, 1) transition metal borides are major, with more than 130 different structural types;^[1–5] 2) metallaboranes^[6–10] and heteroboranes,^[11–15] in which the framework is stabilized by 3c–2e bond, are continuously growing; 3) another known class is transition-metal complexes with boron-containing ligands derived from conjugated boron heterocycles.^[16] In addition to these well-established classes of boron–transition-metal compounds, recent advancement established a fourth class, that is, the transition-metal–boron complexes composed of electron-precise 2c–2e bonds.^[17–21] Such compounds can be termed as borane, boryl, boratrane, bridging, and terminal borylene complexes.^[17–21] Among the various new types recognized, the electron-precise transition-metal agostic and σ-borane complexes shown below have been a subject of regular importance.^[17,18]

Since its inception in 1996,^[23] σ-borane metal complexes caught the attention of various groups due to their role in a wide variety of catalytic transformations. For example, Hartwig et al. made the most representative examples of σ-borane



complexes in which the B–H bond of a neutral borane coordinated to a transition metal center.^[23–25] They were followed by the groups of Weller^[18b] and Shimoi.^[22b,26] Subsequently, Sabo-Etienne et al. isolated an agostic-ruthenium complex by coordinating a potentially hemilabile boron-containing ligand to the ruthenium center.^[18a,27] Furthermore, the first authentication of metallaboratrane [(Ru(CO)(PPh₃){B(mt)₃}] (M → B) (mt = methimazolyl) was achieved by Hill et al. in 1999.^[20a,28]

Increasing numbers of multimetallic boron complexes containing a single boron atom as a ligand^[29,30] stimulated us to design an efficient route to sigma and agostic complexes that does not require the use of any preformed boron-containing ligands. Herein, we present the chemistry of the metal analogues of pentaborane(9) and tetraborane(10) with thiazolyl ligands. The results demonstrate the influence of the transition metals and the significance of a broad variation of the ancillary ligands in product formation. The preliminary results of this work have been communicated earlier.^[31]

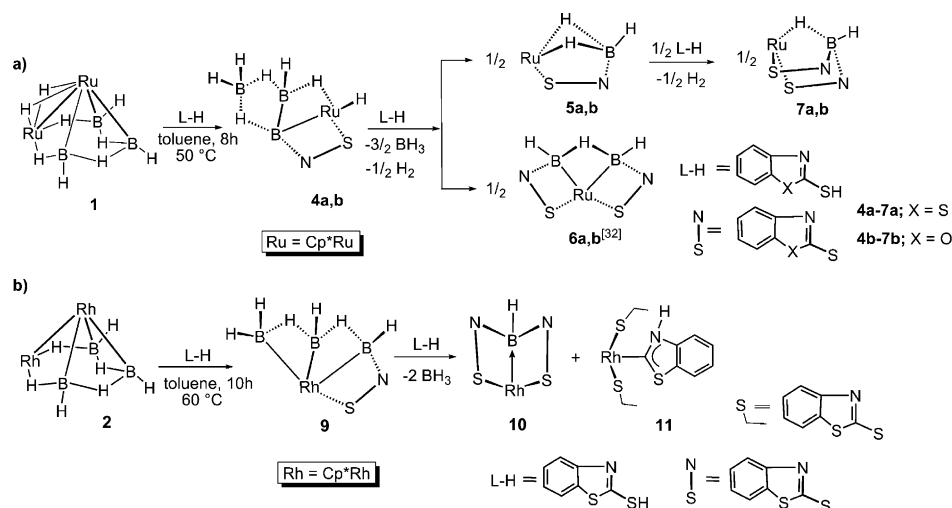
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Supporting information for this article is available on the WWW under
<http://dx.doi.org/10.1002/chem.201405218>.

Results and Discussion

Synthesis and characterization of borane complexes

As shown in Scheme 1a, the reaction of *nido*-[[Cp*RuH]₂B₃H₇], **1** with one equiv of 2-mercaptobenzothiazole (2-mbtz) or 2-



Scheme 1. Synthesis of various electron-precise boron-transition metal (Ru, Rh) complexes and Rh-N,S heterocyclic carbene complex.

mercaptobenzoxazole (2-mboz) yielded sensitive intermediates [Cp*RuB₃H₇L] **4a,b** (**4a**: L = C₇H₄NS₂; **4b**: L = C₇H₄NOS), which have been isolated by thin-layer chromatography. ¹¹B NMR spectroscopic analyses of **4a,b** show three chemical shifts with equal intensities. The ¹H NMR spectrum reveals the presence of one kind of Cp* protons along with three kinds of upfield chemical shifts at δ = −2.42, −4.03, −7.70 (**4a**) and −1.83, −3.73, and −7.11 ppm (**4b**). The identities of **4a,b** have been confirmed from the spectroscopic studies and a solid-state X-ray structure analysis of their Rh analogue (Scheme 1b, compound **9**, see below), which possesses a butterfly geometry, similar to those observed in tetraborane(10) and its analogues.^[33] The exact positions of the hydrogens have been located based on the results from ¹¹B{¹H}/¹H{¹¹B} HSQC experiments and ¹¹B{¹H}/¹¹B{¹H} correlation spectra.

Intermediates **4a** or **4b** on further reaction with 2-mbtz or 2-mboz yielded bis(sigma)borate complexes **5a,b** along with diborane(6) analogues of ruthenium [Cp*RuB₂H₃(L)₂], **6a,b**^[31] (**5a**, **6a**: L = C₇H₄NS₂ and **5b**, **6b**: L = C₇H₄NOS). Compounds **5a,b** displayed a single ¹¹B chemical shift at δ = 8.4 and 11.1 ppm, whereas the ¹H NMR spectrum shows the upfield signals for Ru–H–B at δ = −8.42 and −8.40 ppm, respectively. The solid-state X-ray structure of **5a,b**, shown in Figure 1a,b, is consistent with the spectroscopic results that reveal the presence of one 2-mbtz and 2-mboz ligand, respectively. Depending on the resonance forms, compounds **5a,b** may be regarded as a bis(sigma) imine-borane with an anionic thiolate arm (S[−]) or a bis(sigma)borate complex with a neutral thione (C=S) arm. The C–S lengths in **5a** and **5b** (1.671(5) and 1.662(5) Å,

respectively) are shorter than thiophene and more like a C=S bond. It seemed more appropriate to describe the compounds **5a** and **5b** as bis(sigma)borate complexes.

On the other hand, based on the X-ray structure analysis and computational study, compounds **6a,b** may be considered as diborane(6) derivatives,^[31] in which the [Cp*Ru] fragment replaces the bridging hydrogen atom. Thus, it is formally bonded to the B₂H₅ system through a three-center B–Ru–B bond. Note that, although the first metalladiborane(6) analogue was structurally characterized by Shore et al. in 1989,^[33] only a handful of them are recognized.^[34b] The B–B bond length of 1.773(11) Å and the B–Ru–B bond angle of 47.53(11)° in **6a** are in excellent agreement with the analogous values of complex [(η^5 -C₅H₅)Fe(CO)₂(η^2 -B₂H₅)].^[34]

Interestingly, treatment of either **5a** or **5b** with one more equiv of 2-mbtz or 2-mboz led to the isolation of agostic complexes [Cp*RuBH₂(L)₂], (**7a,b**) (**7a**: L = C₇H₄NS₂; **7b**: L = C₇H₄NOS). The ¹¹B NMR spectroscopic studies show the presence of a single boron atom at δ = −5.8 and −11.8 ppm, respectively, and the ¹H NMR spectra shows distinct signals for the Ru–H–B proton. The solid-state X-ray structures, shown in Figure 1c,d, confirm that the single

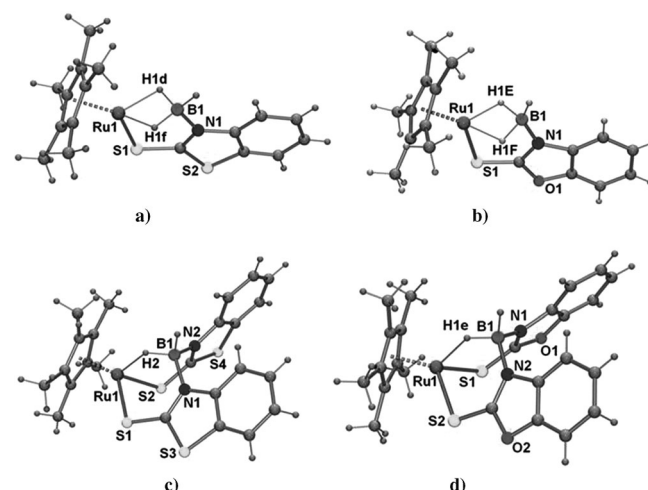
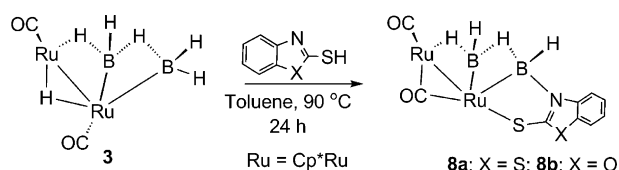


Figure 1. Structures and labeling diagrams of **5a,b** and **7a,b**: Selected bond lengths [Å]: a) Compound **5a**: Ru1–B1 2.216(6), B1–N1 1.514(7), Ru1–S1 2.3154 (16), S1–C17 1.671(5); b) Compound **5b**: Ru1–B1 2.236(6), B1–N1 1.513(7), Ru1–S1 2.359(12), Ru1–H1e 1.69(5), Ru1–H1f 1.73(5), B1–H1e 1.191(18), B1–H1f 1.187(8), B1–H1d 1.150(18), C11–S1 1.662(5); c) Compound **7a**: Ru1–H2 1.830(3), B1–N1 1.563(3), Ru1–B1 2.753(1), Ru1–S1 2.336(7), B1–H2 1.160(3), S1–C1 1.675(3); d) Compound **7b**: Ru1–H2 1.89(3), B1–N1 1.546(5), Ru1–S1 2.3833(11), B1–H2 1.156(18), Ru1–B1 2.836(5), Ru1–S2 2.371(6), C11–S1 1.643(4), C18–S2 1.644(9).

boron atom is linked to the ruthenium center through the B–H–M bridge. Thus, based on the experimental findings and computational study,^[32] compounds **7a,b** can best be described as agostic-ruthenium complexes with an “end-on” coordination.^[18a,22b]

Reactivity of *arachno*-[(Cp**RuCO*)₂B₂H₆] (**3**) towards thia-/ox-azolyl ligands

To examine the scope of our new method, we extended this chemistry towards a different metallaborane precursor in which the metal center possesses different ancillary ligands. As a result, we performed the reaction of diruthenium analogue of tetraborane(10),^[29] *arachno*-**3** with 2- mbtz and 2- mboz ligands (Scheme 2). To our surprise, the ¹¹B NMR spectra of both



Scheme 2. Synthesis of tetraborane(10) analogues **8a** and **8b**.

the products obtained from these reaction mixtures reveal the presence of two types of boron environments in the downfield region. Thin-layer chromatographic work up allowed us to isolate yellow solids in good yields. The IR spectra show the presence of both terminal and bridging CO groups. Based on the spectroscopic data, mass spectrometry, and the X-ray diffraction analysis, they have been established as [(Cp**RuCO*)₂B₂H₃L], **8a,b** (**8a**: L = C₇H₄NS₂; **8b**: L = C₇H₄NSO).

The molecular structure of **8a**, shown in Figure 2, shows that the core geometry and the basic structural features are very similar to *arachno*-**3** and **9**. The Ru–B bond length of 2.155 Å in **8a** is significantly shorter compared with that of

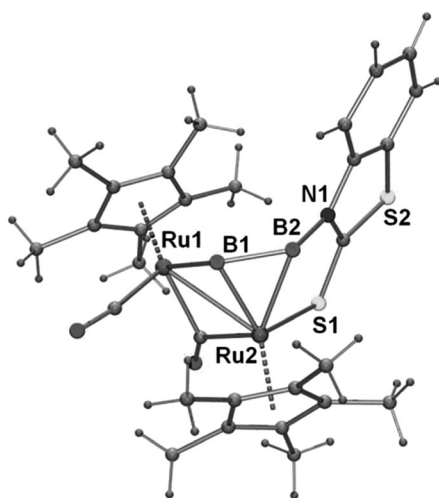


Figure 2. Molecular structures and labeling diagram of **8a**: Selected bond lengths [Å]: B1–B2 1.740(3), B1–Ru2 2.130(2), B1–Ru1 2.155(19), B2–N1 1.540(3), S1–Ru1 2.383(5), Ru1–Ru2 2.813(2).

arachno-**3** (2.250(3) Å). The dihedral angle between the planes B2–Ru1–B1 and Ru1–B1–Ru2, of 129.2° is higher than that observed in *arachno*-B₄H₁₀ (117.48° by electron diffraction and microwave spectroscopy).^[34a] Although the X-ray quality crystals of **8b** have not been obtained, the identity is inferred by comparing the spectral data to **8a**.

The presence of coordinated 2-mbtz or 2-mboz ligand in **8a** and **8b** led us to utilize them as possible precursors for the synthesis of metal borane σ-complexes. However, they failed to react with additional equivalents of ligand even under more forcing conditions to generate the agostic complexes. Comparison of the structures of **8a** and the intermediates **4a,b** and **9** (see below) possessing the same core geometry but differing the transition metal and ancillary ligands defines the change in reactivity pattern of the metallaborane clusters.

Treatment of *nido*-2 with the thiazolyl ligand

Having an entry to the isoelectronic and isostructural precursor of *nido*-**1**, that is, *nido*-[(Cp**Rh*)₂B₃H₇] (**2**), we explored the reaction of *nido*-**2** with 2-mbtz and 2-mboz ligands. Unlike *nido*-**1**, the reaction occurs in a more straightforward way to generate the intermediate [(Cp**Rh*)₂B₃H₆L] (**9**; L = C₇H₄NS₂). The ¹¹B NMR spectrum of **9** shows the appearance of three resonances at δ = 15.6, 2.8, and 0.8 ppm, whereas the ¹H NMR spectrum shows the presence of one type of Cp* protons along with up-field peaks associated to B–H–B protons. The solid-state X-ray structure of **9**, shown in Figure 3a, possesses butterfly geome-

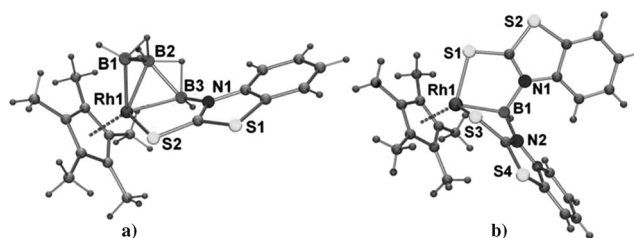


Figure 3. Molecular structures and labeling diagram of **9** and **10**. Selected bond lengths [Å]: a) **9**: Rh1–B1 2.1765(19), B1–B2 1.801(3), B2–B3 1.820(3), Rh1–S3 2.3403(4). b) Compound **10**: Molecular structures and labeling diagram of **10**: Selected bond lengths [Å]: Rh1–B1: 2.139(10), B1–N1 1.607(11), Rh1–S1 2.306(2), S1–C11 1.687(9).

try similar to that observed in tetraborane(10). In addition, the core geometry of **9** can be correlated to [(Cp**IrH*)₂B₃H₇]^[35] by replacing the Cp**Ir* moiety by isolobal Cp**Rh* fragment and the Ir–H and B–H protons by one 2-mbtz ligand. Compound **9**, upon reaction with one molecule of 2-mbtz, yielded [Cp**RhBH*(L)₂], **10** (L = C₇H₄NS₂) (Scheme 1b; see above). The ¹¹B NMR spectrum of **10** signifies a chemical shift at δ = 10.2 ppm and the ¹H NMR spectrum reveals the presence of a single Cp* along with the terminal B–H proton.

The molecular structure of **10** shows the presence of a direct metal–boron bond, which is further supported by two benzothiazolyl bridges (Figure 3b). The Rh–B distance of 2.139(10) Å is longer than the typical range seen in rhodium-boryl complexes (1.96–2.05 Å) and similar to the distance

found in first reported rhodaboratrane complex (2.132(6) Å).^[28b] The geometry at boron is distorted tetrahedral, whereas the rhodium center is in a distorted octahedral arrangement with a pendent Cp* ligand. The natural bond orbital (NBO) analysis of compound **10** shows a strong covalent Rh–B interaction (see the Supporting Information, Figure S1) with Wiberg Bond Index (WBI) value of 0.67 (2.172 Å) and an area of charge concentration was observed along the Rh–B bond only. Based on the presence of Cp* ligand on the metal center and terminal B–H atom, to the best of our knowledge, compound **10** is the first example of a neutral metallaboratrane, in which the {B(2-mbz)₂} fragment adopts a bicyclo[3.3.0] cage at the Rh center.

Interestingly, when we performed the reaction of **9** with excess 2-mbtz ligand, we isolated a highly polar compound **11** in moderate yield. The ¹¹B NMR spectrum shows no ¹¹B chemical shift, whereas the ¹³C NMR spectrum reveals a downfield signal at $\delta = 180.2$ ppm, which falls in the range of transition metal–NHC complexes.^[36] The ¹H NMR spectrum of **11** shows well-resolved signals for the benzimidazolin-2-ylidene and benzothiazole ligands along with a characteristic downfield resonance at $\delta = 17.71$ ppm for the SCNH proton. The ¹H and ¹³C NMR chemical shifts corroborated well with the DFT calculated values (¹³C: $\delta_{\text{DFT}} = 190$ ppm and ¹H: $\delta_{\text{DFT}} = 16.4$ ppm). The identity of compound **11** was finally ascertained to be rhodium NSHC complex [(Cp*Rh)(L₂)(1-BzThzylid)] by the X-ray diffraction analysis.

Since the first appearance of crystalline N-heterocyclic carbene (NHC),^[37] the chemistry of these complexes and their transition-metal compounds have gained a rapid popularity for their application in catalysis.^[38–41] Compared with diaminocarbenes with an N-heterocyclic ring, less attention has been paid to N,X-heterocyclic carbenes (X = O, S, P), because the free ligands are unstable and undergo an easy proton-catalyzed chemical equilibrium with their dimers.^[42,43] Figure 4 shows that the Rh atom is bonded to one Cp* ligand, two 2-mbtz ligands through sulfur atoms and the carbon atom of the benzothiazolin-2-ylidene in a slightly distorted octahedral fashion. The Rh–C8 separation (1.995(3) Å) falls in the shortest range observed for these types of complexes.^[37b] A series of N,S-heterocyclic complexes with different transition metals is listed in Table 1, which corroborates the M–C distance and ¹³C chemical

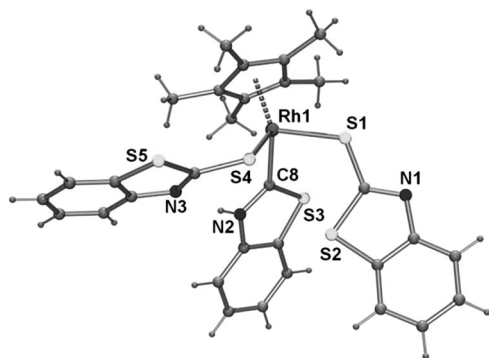


Figure 4. Molecular structures and labeling diagram of **11**: Selected bond lengths [Å]: Rh1–C8: 1.9950(3), Rh1–S1 2.3765(10), C8–S3 1.715(4), C8–N2 1.320(5), C15–N3 1.298(5), C15–S4 1.725(4).

shift of carbene carbon of **11**.^[44–48] The average Rh–S bond length in **11** is 2.389 Å, which is longer than that observed in rhodaboratrane^[31] **10** (2.324 Å).

The major disparity between benzimidazolin-2-ylidene and benzothiazolin-2-ylidene ligands is the distortion of the geometry of the heterocycles of the latter owing to the long S–C distances. Thus, the distortion in the heterocycle ring and the lack of a third substituent at the sulfur atom leads to a small Rh–C8–S3 (122.2°) compared with the Rh–C8–N2 (127.7°) angle in **11**.

To shed light into the structure and the bonding nature of **11**, density functional theory (DFT) calculations were conducted. The optimized structure closely resembles the observed one experimentally (Figure S6). The NBO analysis on **11** shows a strong Rh–C bond having Wiberg Bond Index (WBI) of 0.75 (1.900 Å) (for LMOs, see the Supporting Information, Figure S2).

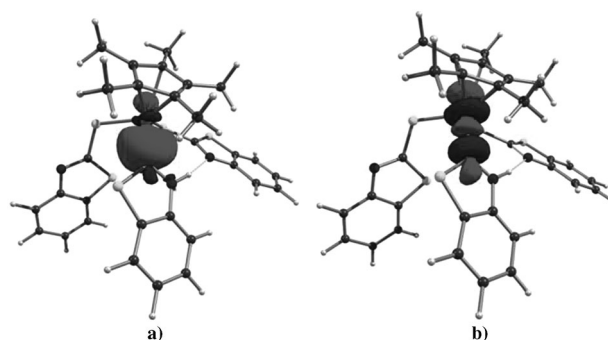
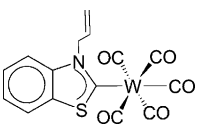
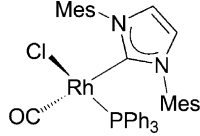
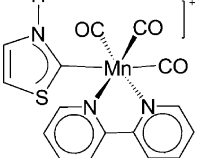
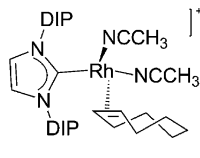
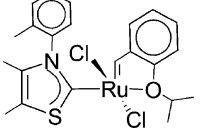
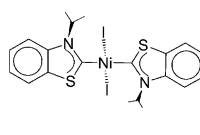
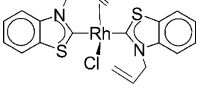
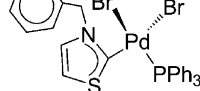
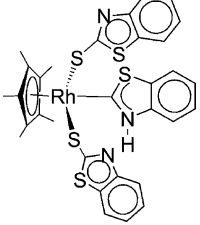
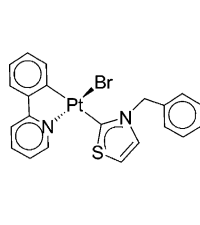
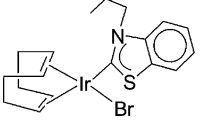
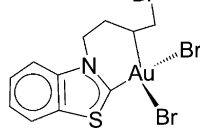


Figure 5. a) and b) showing Rh–C bonding and anti-bonding interactions, respectively, as obtained from the NBO analysis of **11**.

Compound **11** can be described as a Fischer-type carbene, in which the M–C bond is further stabilized by delocalizing hetero atom (N2 and S3) lone pair electrons to Rh–C bond. A similar situation also arose from NBO second-order perturbation energy analysis (see the Supporting Information, Figure S3). The charge decomposition analysis (CDA) study^[49] for donation and back-donation of electrons in **11** reveals that the total number of electrons transferred from transition-metal fragment to ylidene fragment is 0.02 e. However, the extended charge decomposition analysis^[50] establishes that a net of 0.23 e has been gained by the metal fragment that increases the electrophilicity of the carbene center.

Another remarkable feature of **11** is the presence of a highly deshielded ¹H chemical shift for N–H proton at $\delta = 17.71$ ppm. Such a downfield chemical shift may be due to the presence of strong hydrogen bonding with partially covalent character.^[51] The crystal packing diagram (the Supporting Information, Figure S4) shows that the molecule possesses an intramolecular hydrogen bonding between N2 and N3 atoms (2.809 Å). The bond angle (170.35°) is also consistent with the significant hydrogen-bonding trend reported for other compounds.^[51] In addition, the NBO analysis shows a strong delocalization (31.83 kcal mol^{−1}) from filled LP of N3 into the $\sigma^*(\text{N2–H})$ orbital, which is in agreement with the observed enhanced hydrogen bonding.

Table 1. Structural data and ^{13}C NMR chemical shifts of various N,S-heterocyclic complexes of transition metals.

Metal-NHC complexes	$d(\text{M}-\text{C})$ [Å] ^[a]	^{13}C NMR ^[b]	Metal-NHC complexes	$d(\text{M}-\text{C})$ [Å] ^[a]	^{13}C NMR ^[b]
	2.231	224.3		2.032	183.3
18 e; octahedra ^[44a]			16 e; sq. planar ^[45b]		
	2.024	225.5		1.998	175.1
18 e; octahedra ^[45]			16 e; sq. planar ^[46b]		
	1.947	287.5		1.896	221.8
16 e; sq. pyramid ^[46]			16 e; sq. planar ^[47a]		
	—[c]	224.3		1.980	208.4
16 e; sq. planar ^[44a]			16 e; sq. planar ^[47b]		
	1.995	180.1		1.939	197.5
18 e; octahedra ^[this work]			16 e; sq. planar ^[48a]		
	1.981	218.9		1.939	186.8
18 e; sq. planar ^[44b]			16 e; sq. planar ^[48b]		

[a] Metal-to-carbene carbon distance. [b] ^{13}C NMR chemical shift of the carbene carbon. [c] Structural data not available.

Conclusion

In this article, we have described the synthesis of a series of electron-precise boron–transition-metal compounds. The synthetic route used in this work for various transition-metal–boron complexes showed that they are now accessible without the use of preformed boron-containing ligands. In addition, we have demonstrated that the transition metals and a broad variation of the ancillary ligands play an important role in the formation of these complexes. In addition, we report the first structurally characterized Rh-NSHC complex. Investigations to evaluate the possibility of such unusual bonding situations are well illustrated by theoretical findings.

Experimental Section

General procedures and instrumentation

All syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques. Solvents were dried by common methods and distilled under Ar before use. Compounds **1**,^[52] **2**,^[52] and **3**^[29] were prepared according to literature methods, whereas other chemicals were obtained commercially and used as received. The external reference for the ^{11}B NMR spectra, $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$, was synthesized using a literature method.^[53] Thin-layer chromatography was carried out on 250 mm diameter aluminum-supported silica gel TLC plates. NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ , ppm, CDCl_3 , 7.26), whereas a sealed tube containing $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ in $[\text{D}_6]\text{benzene}$ (δ_{B} , ppm,

–30.07) was used as an external reference for ^{11}B NMR spectroscopy. Infrared spectra were recorded on a Nicolet iS10 spectrometer. Microanalyses for C, H, and N were performed on Perkin Elmer Instruments series II model 2400. Mass spectra were recorded either on Bruker MicroTOF-II mass spectrometer in ESI ionization mode or on Bruker Ultraflextreme using 2,5-dihydroxybenzoic acid as a matrix and a ground steel target plate in MALDI ionization mode.

Synthesis of 4a,b–7a,b from nido-1: In a flame-dried Schlenk tube, compound **1** (0.13 g, 0.25 mmol) was added to toluene (10 mL), followed by the addition of 2-mercaptobenzothiazole (0.21 g, 1.25 mmol). The mixture was heated at 50 °C for 8 h. The solvent was evaporated in vacuo and the residue was extracted into hexane and passed through Celite. After removal of solvent from filtrate, the residue was subjected to chromatographic workup using silica-gel TLC plates. Elution with hexane/ CH_2Cl_2 (90:10 v/v) yielded red **4a** (0.025 g, 23%), red **5a** (0.041 g, 28%), yellow **6a** (0.037 g, 35%), and yellow **7a** (0.015 g, 10%). Similarly, *nido-1* (0.13 g, 0.25 mmol) on thermolysis with 2-mercaptobenzothiazole (0.21 g, 1.25 mmol) yielded red **4b** (0.028 g, 26%), red **5b** (0.031 g, 22%), yellow **6b** (0.030 g, 30%), and yellow **7b** (0.007 g, 5%).

Note that, although the compounds **4a,b–7a,b** were produced from the reaction of *nido-1* with 2-mbtz or 2-mboz in a single run, they have been isolated in a stepwise manner as shown in Scheme 1 (see above).

Compound 4a: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 7.65–7.22 (m, 4H, Ph), 4.30 (s, 2H, BH_i), 3.90 (s, 1H, BH_i), 1.86 (s, 15H, Cp^*), –2.42 (br, 1H, B–H–B), –4.03 (br, 1H, B–H–B), –7.70 (br, 1H, Ru–H–B), –14.91 ppm (s, 1H, Ru–H); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 146.8 (C=N), 139.3 (CS), 128.1, 125.2, 123.9, 117.3, 112.9 (C=C), 99.3 (C_5Me_5), 9.8 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 30.5 (br, 1B), –1.6 (br, 1B), –14.3 ppm (br, 1B); IR (hexane): $\tilde{\nu}$ = 2439, 2402 cm^{-1} (w) (BH_i); MS (ESI $^+$): m/z calcd for $^{12}\text{C}_{17}\text{H}_{26}^{11}\text{B}_3^{15}\text{N}_1^{32}\text{S}_2^{101}\text{Ru}$: 443; found: 442.01.

Compound 5a: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 8.01–7.35 (m, 4H, Ph), 5.9 (br 1H, BH_i), 1.99 (s, 15H, Cp^*), –8.42 ppm (br, 2H, Ru–H–B); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 150.1 (C=N), 139.4 (CS), 129.9, 126.1, 124.8, 116.7 (Ph), 101.2 (C_5Me_5), 10.7 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 8.4 ppm (br, 1B); IR (hexane): $\tilde{\nu}$ = 2390 cm^{-1} (w) (BH_i); MS (ESI $^+$): m/z calcd for $^{12}\text{C}_{17}\text{H}_{22}^{11}\text{B}_1^{15}\text{N}_1^{32}\text{S}_2^{101}\text{Ru}$: 416; found: 416.5836; elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{22}\text{BN}_2\text{S}_2\text{Ru}$: C, 49.02; H, 5.33; N, 3.36; found: C, 50.45; H, 5.17; N, 3.01.

Compound 6a: ^1H NMR (400 MHz, CDCl_3 , 22 °C): 7.75–7.40 (m, 8H, Ph), 5.18 (br, 2H, BH_i), 1.94 (br, 1H, B–H–B), 1.60 ppm (s, 15H, Cp^*); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 149.7 (C=N), 139.1 (CS), 129.4, 126.9, 124.0, 116.1 (Ph), 101.8 (C_5Me_5), 9.7 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 12.3 (br, 2B); IR (hexane): $\tilde{\nu}$ = 2437 cm^{-1} (w) (BH_i); MS (MALDI): m/z calcd for $\text{C}_{24}\text{H}_{27}\text{B}_2\text{N}_2\text{RuS}_4$ (isotope envelope): 594 [$\text{M}+\text{H}$] $^+$; found: 594; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{26}\text{B}_2\text{N}_2\text{S}_4\text{Ru}$: C, 48.55; H, 4.42; N, 4.72; found: C, 48.01; H, 4.97; N, 4.99.

Compound 7a: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 8.21–7.23 (m, 8H, Ph), 6.31 (br, 1H, BH_i), 1.75 (s, 15H, Cp^*), –8.82 ppm (br, 1H, Ru–H–B); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 149.9 (C=N), 139.6 (CS), 130.5, 127.3, 124.9, 116.8 (Ph), 101.1 (C_5Me_5), 10.9 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = –5.8 ppm (br, 1B); IR (hexane): $\tilde{\nu}$ = 2461 cm^{-1} (w) (BH_i); MS (MALDI): m/z calcd for $\text{C}_{24}\text{H}_{25}\text{BN}_2\text{S}_4\text{Ru}$ (isotope envelope): 581 [M] $^+$; found: 581; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{25}\text{BN}_2\text{S}_4\text{Ru}$: C, 49.56; H, 4.34; N, 4.82; found: C, 50.25; H, 4.07; N, 4.18.

Compound 4b: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 7.95–7.14 (m, 4H, Ph), 4.8 (br, 2H, BH_i), 4.1 (br, 1H, BH_i), 1.89 (s, 15H, Cp^*), –1.83 (br, 1H, B–H–B), –3.73 (br, 1H, B–H–B), –7.11 (br, 1H, Ru–H–B), –14.01 ppm (s, 1H, Ru–H); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 149.8 (C=N), 143.3 (CO), 132.1, 127.1, 126.3, 120.3, 117.3 (C=C), 101.3 (C_5Me_5), 10.3 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 33.8 (br, 1B), 1.5 (br, 1B), –11.9 ppm (br, 1B); IR (hexane): $\tilde{\nu}$ = 2449, 2416 cm^{-1} (w) (BH_i); MS (ESI $^+$): m/z calcd for $^{12}\text{C}_{17}\text{H}_{25}^{11}\text{B}_3^{14}\text{N}^{16}\text{O}^{101}\text{Ru}^{32}\text{S}$: 425; found: 424.923.

Compound 5b: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 8.01–7.35 (m, 4H, Ph), 5.9 (br, 1H, BH_i), 1.99 (s, 15H, Cp^*), –8.40 ppm (br, 2H, Ru–H–B); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 150.1 (C=N), 146.4 (CO), 129.9, 126.1, 124.8, 116.7 (Ph), 101.2 (C_5Me_5), 10.7 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 11.1 ppm (br, 1B); IR (hexane): $\tilde{\nu}$ = 2390 cm^{-1} (w) (BH_i); MS (ESI $^+$): m/z calcd for $^{12}\text{C}_{17}\text{H}_{22}^{11}\text{B}_1^{14}\text{N}^{16}\text{O}^{101}\text{Ru}^{32}\text{S}$: 400; found: 399.987.

Compound 6b: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 7.91–7.33 (m, 8H, Ph), 5.58 (br, 2H, BH_i), 2.03 (br, 1H, B–H–B), 1.60 ppm (s, 15H, Cp^*); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 151.2 (C=N), 148.3 (CO), 131.7, 128.1, 126.3, 118.4 (Ph), 102.3 (C_5Me_5), 10.3 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 15.7 ppm (br, 2B); IR (hexane): $\tilde{\nu}$ = 2451 cm^{-1} (w) (BH_i); MS (ESI $^+$): MS (MALDI): m/z calcd for $\text{C}_{24}\text{H}_{27}\text{B}_2\text{N}_2\text{O}_2\text{RuS}_2$ (isotope envelope): 562; found: 562 [$\text{M}+\text{H}$] $^+$.

Compound 7b: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 8.17–7.13 (m, 8H, Ph), 6.51 (br, 1H, BH_i), 1.78 (s, 15H, Cp^*), –8.23 ppm (br, 1H, Ru–H–B); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 151.6 (C=N), 147.6 (CO), 132.3, 129.1, 125.8, 117.6 (Ph), 102.6 (C_5Me_5), 10.9 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = –11.8 ppm (br, 1B); IR (hexane): $\tilde{\nu}$ = 2468 cm^{-1} (w) (BH_i); MS (MALDI): m/z calcd for $\text{C}_{24}\text{H}_{26}\text{BN}_2\text{O}_2\text{RuS}_2$ (isotope envelope): 550 [$\text{M}+\text{H}$] $^+$; found: 550.

Synthesis of 9–11 from nido-2: In a flame-dried Schlenk tube, compound **2** (0.13 g, 0.25 mmol) was added to toluene (10 mL) followed by the addition of 2-mercaptobenzothiazole (0.32 g, 2.0 mmol). The mixture was heated at 60 °C for 10 h. The solvent was evaporated in vacuo and the residue was extracted into hexane/ CH_2Cl_2 mixture and passed through Celite. After removal of solvent from filtrate, the residue was subjected to chromatographic workup using silica-gel TLC plates. Elution with hexane/ CH_2Cl_2 (60:40 v/v) yielded yellow **9** (0.021 g, 19%) and yellow **10** (0.022 g, 15%). When eluting with hexane/ CH_2Cl_2 (10:90 v/v), we isolated red **11** in 24% (0.045 g) yield.

Although compounds **9–11** have been isolated from the same reaction, note that boratrane **10** and the Rh–N,S–HC complex **11** can be synthesized from intermediate **9** by using a stoichiometric amount of the 2-mbtz ligand.

Compound 9: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 7.95–7.29 (m, 4H, Ph), 4.11 (s, 2H, BH_i), 3.71 (s, 1H, BH_i), 1.71 (s, 15H, Cp^*), –1.56 (br, 1H, B–H–B), –4.33 ppm (br, 1H, B–H–B); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 143.2 (C=N), 135.8 (CS), 126.7, 124.8, 121.3, 114.3 (C=C), 101.1 (C_5Me_5), 9.4 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 15.6 (br, 1B), 2.8 (br, 1B), 0.8 ppm (br, 1B); IR (hexane): $\tilde{\nu}$ = 2441, 2410 cm^{-1} (w) (BH_i).

Compound 10: ^1H NMR (400 MHz, CDCl_3 , 22 °C): 7.82–7.15 (m, 8H, Ph), 6.32 (br, 1H, BH_i), 1.66 ppm (s, 15H, Cp^*); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 149.2 (C=N), 138.9 (CS), 129.1, 126.2, 123.7, 115.4 (Ph), 99.9 (C_5Me_5), 10.2 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 10.2 ppm (br, 1B); IR (hexane): $\tilde{\nu}$ = 2416 cm^{-1} (w) (BH_i); MS (MALDI): m/z calcd for $\text{C}_{24}\text{H}_{25}\text{BN}_2\text{S}_4\text{Rh}$ (isotope envelope): 583; found: 583 [$\text{M}+\text{H}$] $^+$; elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{BN}_2\text{S}_4\text{Rh}$: C, 49.49; H, 4.16; N, 4.81; found: C, 49.07; H, 4.38; N, 4.57.

Compound 11: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 17.71 (br, N–H), 7.76–7.15 (m, 12H, Ph), 1.66 ppm (s, 15H, Cp*); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 180.1 (Rh=C), 143.2, 148.4 (C=N), 138.9, 133.2 (CS), 130.0, 129.2, 127.7, 126.4, 123.7, 120.3, 118.6, 115.4 (Ph), 100.3 (C_5Me_5), 9.8 ppm (C_5Me_5); IR (hexane): $\tilde{\nu}$ = 3528 cm^{-1} (N–H); MS (MALDI): m/z calcd for $\text{C}_{31}\text{H}_{28}\text{N}_3\text{S}_5\text{Rh}$ (isotope envelope): 723 $[\text{M}]^+$; found: 723.

Synthesis of 8a,b from arachno-3: Compound **3** (0.1 g, 0.33 mmol) was dissolved in toluene (15 mL) in a flame-dried Schlenk tube. 2-Mercaptobenzothiazole (0.26 g, 1.56 mmol) was added into that solution and the solution was heated up to 90 °C for 24 h. After removal of solvent from filtrate, the residue was subjected to chromatographic workup using silica-gel TLC plates. Elution with hexane/ CH_2Cl_2 (80:20 v/v) yielded yellow **8a** (0.13 g, 19%). Similarly, compound **3** (0.50 g, 0.89 mmol) on thermolysis with 2-mercaptobenzoxazole (0.12 g, 0.89 mmol) yielded yellow **8b** (0.10 g, 15%).

Compound 8a: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 7.79–7.23 (m, 4H, Ph), 4.31 (br, 1H, BH_t), 3.02 (br, 1H, BH_t), 1.85 (s, 15H, Cp*), 1.81 (s, 15H, Cp*), 0.96 ppm (br, 1H, B–H–B); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 189.2 (CO), 180.4 (CO), 144.4 (C=N), 132.1 (CS), 131.5, 128.2, 123.4, 119.2 (Ph), 101.5 (C_5Me_5), 99.5 (C_5Me_5), 11.9 (C_5Me_5), 9.2 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 65 (br, 1B), 11 ppm (br 1B); IR (hexane): $\tilde{\nu}$ = 2461, 2455 (w) (BH_t), 1891 (CO), 1780 cm^{-1} (CO); MS (MALDI): m/z calcd for $\text{C}_{29}\text{H}_{41}\text{B}_2\text{NO}_2\text{S}_2\text{Ru}_2$ (isotope envelope): 723 $[\text{M}]^+$; found: 722; elemental analysis calcd (%) for $\text{C}_{29}\text{H}_{41}\text{B}_2\text{NO}_2\text{S}_2\text{Ru}_2$: C, 48.14; H, 5.71; N, 1.93; found: C, 48.20; H, 5.33; N, 1.61.

Compound 8b: ^1H NMR (400 MHz, CDCl_3 , 22 °C): δ = 7.88–7.20 m, 4H, Ph), 5.01 (br, 1H, BH_t), 4.92 (br, 1H, BH_t), 1.89 (s, 15H, Cp*), 1.79 (s, 15H, Cp*), 1.01 ppm (br, 1H, B–H–B); ^{13}C NMR (100 MHz, CDCl_3 , 22 °C): δ = 191.2 (CO), 183.2 (CO), 149.7 (C=N), 138.5 (CS), 128.5, 127.2, 124.6, 120.2 (Ph), 107.5 (C_5Me_5), 100.3 (C_5Me_5), 13.9 (C_5Me_5), 10.3 ppm (C_5Me_5); ^{11}B NMR (128 MHz, CDCl_3 , 22 °C): δ = 72 (br, 1B), 18 ppm (br 1B); IR (hexane): $\tilde{\nu}$ = 2461, 2455 (w) (BH_t), 1893 (CO), 1799 cm^{-1} (CO); MS (MALDI): m/z calcd for $\text{C}_{29}\text{H}_{41}\text{B}_2\text{NO}_3\text{SRu}_2$ (isotope envelope): 707 $[\text{M}]^+$; found: 706; elemental analysis calcd (%) for $\text{C}_{29}\text{H}_{41}\text{B}_2\text{NO}_3\text{SRu}_2$: C, 49.23; H, 5.84; N, 1.97; found: C, 49.99; H, 5.01; N, 1.89.

X-ray Structure determination

The crystal data for **5a,b**, **7a,b**, **8a,b**, **9**, **10**, and **11** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated $\text{MoK}\alpha$ (λ = 0.71073 Å) radiation at 296 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97.^[54] The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 5a: CCDC: 953206, $\text{C}_{17}\text{H}_{22}\text{BNRuS}_2$, M_r = 416.36, Triclinic space group $P\bar{1}$, a = 10.3252(4), b = 13.3442(5), c = 13.9633(5) Å, α = 71.995(2), β = 89.204(2), γ = 89.593(2)°, V = 1829.49(12) Å³, Z = 4, ρ_{calcd} = 1.512 g cm^{-3} , μ = 1.080 mm^{-1} , $F(000)$ = 848, R_1 = 0.0467, wR_2 = 0.1060, 6403 independent reflections [$2\theta \leq 50^\circ$] and 487 parameters.

Crystal data for 7a: CCDC: 953208, $\text{C}_{24}\text{H}_{25}\text{BN}_2\text{RuS}_4$, M_r = 581.58, Monoclinic space group $P2_1/c$, a = 8.9171(3), b = 17.1451(6), c = 16.1582(5) Å, β = 91.932(2)°, V = 2468.93(14) Å³, Z = 4, ρ_{calcd} = 1.565 g cm^{-3} , μ = 0.989 mm^{-1} , $F(000)$ = 1184, R_1 = 0.0272, wR_2 = 0.0718, 4834 independent reflections [$2\theta \leq 52^\circ$] and 302 parameters.

Crystal data for 5b: CCDC: 955867, $\text{C}_{17}\text{H}_{22}\text{BNORuS}$, M_r = 400.30, Triclinic space group $P\bar{1}$, a = 8.9711(5), b = 9.1884(5), c = 11.3176(6) Å,

α = 74.283(3), β = 86.680(3), γ = 76.751(3)°, V = 874.12(8) Å³, Z = 2, ρ_{calcd} = 1.521 g cm^{-3} , μ = 1.016 mm^{-1} , $F(000)$ = 408, R_1 = 0.0444, wR_2 = 0.1146, 3050 independent reflections [$2\theta \leq 50^\circ$] and 214 parameters.

Crystal data for 7b: CCDC: 955866, $\text{C}_{24}\text{H}_{25}\text{BN}_2\text{O}_2\text{RuS}_2$, M_r = 549.46, Monoclinic space group $P2_1/n$, a = 8.6715(2), b = 8.5233(3), c = 32.6532(10) Å, β = 90.377(2)°, V = 2413.34(13) Å³, Z = 4, ρ_{calcd} = 1.512 g cm^{-3} , μ = 0.846 mm^{-1} , $F(000)$ = 1120, R_1 = 0.0406, wR_2 = 0.0919, 4314 independent reflections [$2\theta \leq 50.34^\circ$] and 357 parameters.

Crystal data for 8a: CCDC: 1022996, $\text{C}_{29}\text{H}_{34}\text{B}_2\text{NO}_2\text{Ru}_2\text{S}_2$, M_r = 716.45, Monoclinic space group $P2_1/c$, a = 17.554(2), b = 14.6518(19), c = 23.737(3) Å, β = 94.480(5)°, V = 6086.4(14) Å³, Z = 8, ρ_{calcd} = 1.564 g cm^{-3} , μ = 1.156 mm^{-1} , $F(000)$ = 2888, R_1 = 0.0688, wR_2 = 0.1607, 5892 independent reflections [$2\theta \leq 40.98^\circ$] and 725 parameters.

Crystal data for 9: CCDC: 953207, $\text{C}_{17}\text{H}_{25}\text{B}_3\text{NRhS}_2$, M_r = 442.84, Monoclinic space group $P2_1/c$, a = 8.6402(2), b = 14.9215(2), c = 15.7116(3) Å, β = 105.908(2)°, V = 1948.04(7) Å³, Z = 4, ρ_{calcd} = 1.510 g cm^{-3} , μ = 1.089 mm^{-1} , $F(000)$ = 904, R_1 = 0.0207, wR_2 = 0.0418, 3840 independent reflections [$2\theta \leq 50^\circ$] and 246 parameters.

Crystal data for 10: CCDC: 953205, $\text{C}_{24}\text{H}_{24}\text{BN}_2\text{RhS}_4$, M_r = 582.41, Monoclinic space group $P2_1/c$, a = 8.3734(13), b = 17.471(3), c = 16.649(2) Å, β = 90.444(6)°, V = 2435.5(6) Å³, Z = 4, ρ_{calcd} = 1.588 g cm^{-3} , μ = 1.060 mm^{-1} , $F(000)$ = 1184, R_1 = 0.0571, wR_2 = 0.1508, 4051 independent reflections [$2\theta \leq 50^\circ$] and 299 parameters.

Crystal data for 11: CCDC: 1022995, $\text{C}_{32}\text{H}_{30}\text{Cl}_2\text{N}_3\text{S}_5\text{Rh}$, M_r = 790.70, Triclinic space group $P\bar{1}$, a = 12.1748(4), b = 12.4579(4), c = 13.5612(3) Å, α = 103.781(2), β = 100.220(2), γ = 117.848(2)°, V = 1663.49(8) Å³, Z = 2, ρ_{calcd} = 1.579 g cm^{-3} , μ = 1.016 mm^{-1} , $F(000)$ = 804, R_1 = 0.0395, wR_2 = 0.1041, 8464 independent reflections [$2\theta \leq 57.58^\circ$] and 418 parameters.

Computational Details

All quantum-chemical calculations were performed by using the Gaussian 09, Revision C.01^[55] suite of programs. The charge decomposition analysis was carried out by using Multiwfn V. 3.1.^[56] Geometry optimizations have been performed at the DFT level of theory by using the B3LYP^[57] functional in combination with SDD basis set for Rh atom and all electron double zeta 6-31g* basis sets for the rest of the atoms without any symmetry constraints. Vibrational analysis was carried out for all structures, and the absence of any imaginary frequency confirmed that all structures represent minima on the potential energy hypersurface. The $\delta(^1\text{H})$ and $\delta(^{13}\text{C})$ chemical shifts were calculated at the aforementioned level. Computation of the NMR shielding tensors employed gauge-including atomic orbitals (GIAOs)^[58] using the implementation of Schreckenbach, Wolff, Ziegler, and co-workers.^[59,60] The chemical shifts were referenced to TMS. NBO^[31] analysis has also been done as implemented in Gaussian.

Acknowledgements

This work was supported by the Department of Science and Technology, New Delhi, India (Project No. SR/SI/IC-13/2011). IIT Madras is gratefully acknowledged for computational facilities. D.K.R. thanks the Council of Scientific and Industrial Research (CSIR), India, and A.R.S. is grateful to University Grants Commis-

sion for a Research Fellowship. B.M. thanks IIT Madras for research fellowship.

Keywords: agostic interactions · borane · carbene · rhodium · transition metals

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Received: September 10, 2014

Published online on December 23, 2014