**Chemistry of ruthenium σ -borane complex,
[Cp $\star$ RuCO(μ -H)BH₂L] (Cp $\star$ = η^5 -C₅Me₅;
L = C₇H₄NS₂) with terminal and internal alkynes:
Structural characterization of vinyl hydroborate and
vinyl complexes of ruthenium**

K. Saha, B. Joseph, R. Borthakur, R. Ramalakshmi, Thierry Roisnel, S.
Ghosh

► To cite this version:

K. Saha, B. Joseph, R. Borthakur, R. Ramalakshmi, Thierry Roisnel, et al.. Chemistry of ruthenium σ -borane complex, [Cp $\star$ RuCO(μ -H)BH₂L] (Cp $\star$ = η^5 -C₅Me₅; L = C₇H₄NS₂) with terminal and internal alkynes: Structural characterization of vinyl hydroborate and vinyl complexes of ruthenium. Polyhedron, 2017, 125, pp.246-252. 10.1016/j.poly.2017.01.003 . hal-01515169

HAL Id: hal-01515169

<https://hal-univ-rennes1.archives-ouvertes.fr/hal-01515169>

Submitted on 4 Jul 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chemistry of ruthenium σ -borane complex, $[\text{Cp}^*\text{RuCO}(\mu\text{-H})\text{BH}_2\text{L}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{L} = \text{C}_7\text{H}_4\text{NS}_2$) with terminal and internal alkynes: Structural characterization of vinyl hydroborate and vinyl complexes of ruthenium.

Koushik Saha^a, Benson Joseph^a, Rosmita Borthakur^a, Rongala Ramalakshmi^a, Thierry Roisnel^b and Sundargopal Ghosh^{a,*}

Abstract: The chemistry of ruthenium-borane complex, $[\text{Cp}^*\text{RuCO}(\mu\text{-H})\text{BH}_2\text{L}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{L} = \text{C}_7\text{H}_4\text{NS}_2$), **1** with various alkynes has been explored. Photolysis of **1** with alkynyl-Grignard, $[\text{HC}\equiv\text{CMgBr}]$ in toluene led to the isolation of vinyl hydroborate complex $[\text{Cp}^*\text{Ru}(\mu\text{-H})\text{BH}\{\text{HC}=\text{CH}_2\}\text{L}]$, **2a** as a sole product. Compound **2a** can be viewed as a ruthenium-borate complex with an ethylene moiety. Further, the chemistry of **1** with various internal and terminal alkynes has been performed in photolytic conditions. Photolysis of **1** with $[\text{RC}\equiv\text{CR}]$ ($\text{R} = \text{CO}_2\text{Me}$) yielded vinyl hydroborate complex $[\text{Cp}^*\text{Ru}(\mu\text{-H})\text{BCl}\{\text{RC}=\text{CR}\}\text{L}]$, **2b**. Terminal alkynes $[\text{HC}\equiv\text{CR}]$ ($\text{R} = \text{Ph}$ or CO_2Me) under the same reaction conditions led to the isolation of metal vinyl complexes $[\text{Cp}^*\text{Ru}(\text{CO})(\text{C}_2\text{HR})(\text{L})]$, **3a** and **3b** (**3a**: $\text{R} = \text{Ph}$; **3b**: $\text{R} = \text{CO}_2\text{Me}$). In addition, DFT calculations were carried out to analyze the bonding and electronic structures of these new compounds.

Keywords: ruthenium, alkyne, vinyl, hydroboration, borane.

^aDepartment of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India.

^bInstitut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, F-35042 Rennes Cedex, France.

*Corresponding Author. Phone: (+91) 44 2257 4230; Fax: (+91) 44 2257 4202.

E-mail address: sghosh@iitm.ac.in

1. Introduction

Transition-metal complexes of boron,[1-3] have attracted considerable interest over the last few decades. A wide variety of coordination modes of these complexes have been structurally characterized and theoretically examined [4] that led to the progress of new subclasses such as sigma, agostic, boryl, borylene, boratrane and more [1–18]. Hill, Parkin, Bourissou, Sabo-Etienne, Braunschweig, Weller, Aldridge, and others have synthesized a number of such novel complexes by substitution and addition reactions of boron containing ligands at an electronically unsaturated metal centre [19–34]. Transition-metal-boryl, borylene, σ -borane and agostic complexes have been extensively used in hydroboration reactions to generate organoboron

compounds such as vinylboranes [5-6, 35–40]. For example, the titanocene bis(borane) complex has been used as a catalyst for the hydroboration of vinylarenes [35-38]. Marder, Wright and others have used boryl complexes of Ru as effective catalyst for hydroboration of alkynes [40-41]. Our group has shown the use of a trimetallic triply-bridged borylene complex, $[(\mu_3\text{-BH})(\text{Cp}^*\text{RuCO})_2(\mu\text{-CO})\text{Fe}(\text{CO})_3]$ to generate vinylborylene complexes through hydroboration of alkynes [42]. Further, we have described the hydroboration of terminal alkynes using a ruthenium–borate complex that yielded vinylborane complexes [43-44].

Hydroboration has been a fascinating area of research since its discovery in 1956 by H. C. Brown [45-48]. Addition of a boron-hydrogen bond across an unsaturated moiety is one of the most studied reactions in organic synthesis [48-51]. The substitution of a carbon atom for an electron deficient boron atom in an extended organic π -system generates entirely new families of ligands with better ligating properties towards transition metals. For example, monoanionic “boratabenzene” and dianionic “borole” ligands obtained by substitution in the benzene ring and $[\text{C}_5\text{H}_5]^-$ ligand respectively, show unique ligating properties. Recently, we have reported the Rh- and Ru-vinyl hydroborate complexes from the reaction of Rh–N,S-heterocyclic carbene complex $[(\text{Cp}^*\text{Rh})(\text{L}_2)(1\text{-benzothiazol-2-ylidene})]$ ($\text{L} = \text{C}_7\text{H}_4\text{NS}_2$) with $\text{BH}_3\cdot\text{THF}$ and reaction of ruthenium borate/borane complexes with various alkynes respectively [44,52]. Such types of complexes of iron and chromium have been synthesized earlier by Schmid and Braunschweig [53-54]. Based on these observations, herein, in this article, we explored the reactivity of ruthenium σ -borane complex towards terminal and internal alkynes that led to the isolation of some interesting ruthenium vinyl hydroborate and vinyl complexes.

2. Experimental details

2.1. General procedures and instrumentation

All the syntheses were carried out under argon atmosphere using standard Schlenk and glovebox techniques. Solvents were dried by using common methods and distilled under Ar before use. Compound $[\text{Cp}^*\text{RuCO}(\mu\text{-H})\text{BH}_2\text{L}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{L} = \text{C}_7\text{H}_4\text{NS}_2$), **1** was prepared according to a reported method, [55] whereas other chemicals ($[\text{Cp}^*\text{RuCl}_2]_2$, $[\text{LiBH}_4\cdot\text{THF}]$, 2-mercaptobenzothiazole, phenylacetylene, methyl propiolate, ethynylmagnesium bromide and dimethyl acetylenedicarboxylate) were obtained commercially and used as received. The external reference for the ^{11}B NMR, $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ was synthesized according to a reported method [56]. Thin-layer chromatography was conducted on 250 mm diameter aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded with 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference

(δ , ppm, [D₆] benzene, 7.16 ppm, CDCl₃, 7.26 ppm), whereas a sealed tube containing [Bu₄N(B₃H₈)] in [D₆] benzene (δ_B , ppm, -30.07) was used as an external reference to obtain ¹¹B NMR spectra. The IR spectra were recorded with a Nicolet iS10 spectrometer. The photoreactions described in this report were conducted in a Luzchem LZC-4V photoreactor, with irradiation at 254–350 nm. Mass spectra were recorded with a Bruker MicroTOF-II mass spectrometer in ESI ionization mode.

2.2. Synthesis of **2a**

In a flame-dried Schlenk tube, yellow solution of **1** (0.100 g, 0.225 mmol) and ethynylmagnesium bromide (1 equiv) in toluene (15 mL) were irradiated for 5 h. The volatile components were removed under vacuum and the remaining residue was passed through Celite. After removal of solvent, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (30:70 v/v) mixture yielded yellow **2a** (0.089 g, 89.4%).

Compound **2a** ESI-MS m/z calcd for C₁₉H₂₄BNS₂Ru ([M+H]⁺) 444.0; found 444.3; ¹¹B NMR (22 °C, 160 MHz, CDCl₃): δ = -10.8 ppm (br, 1B); ¹H NMR (22 °C, 500 MHz, CDCl₃): δ = 7.16–7.76 (m, 4H; Ph), 3.45, 2.26 (d, 2H; CH₂), 3.07 (br, 1H; BH_t), 2.82 (t, 1H; CH), 1.79 (s, 15H; Cp*), -10.49 ppm (br, 1H; Ru-H-B); ¹³C NMR (22 °C, 125 MHz, CDCl₃): δ = 182.4 (C=S), 144.1 (CN), 130.5 (CS), 126.5–116.1 (s, Ph), 90.4 (s, C₅Me₅), 62.8 (s, CH₂), 31.7 (s, BCH), 10.2 ppm (s, C₅(CH₃)₅); IR (hexane): ν_{max} = 2962, 2915 (C=CH), 2362 (BH_t), 1743 cm⁻¹ (BH_b).

2.3. Synthesis of **2b** and **2c**

In a flame-dried Schlenk tube, yellow solution of **1** (0.100 g, 0.225 mmol) and dimethyl acetylenedicarboxylate (1 equiv) in toluene (15 mL) were irradiated for 5 h. The volatile components were removed under vacuum and the remaining residue was passed through Celite. After removal of solvent, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (20:80 v/v) mixture yielded yellow **2b** (0.05 g, 37.5%) and **2c** (0.07 g, 55.64%).

Note that compound **2c** was reported earlier [30].

Compound **2b** ESI-MS m/z calcd for C₂₃H₂₇BNO₄S₂ClRu ([M+H]⁺) 594.0; found 594.1; ¹¹B NMR (22 °C, 160 MHz, CDCl₃): δ = -2.7 ppm (br, 1B); ¹H NMR (22 °C, 500 MHz, CDCl₃): δ = 7.36–8.16 (m, 4H; Ph), 6.12 (s, 1H; CH), 3.78, 3.62 (s, 6H; OCH₃), 1.77 (s, 15H; Cp*), -10.62 ppm (br, 1H; Ru-H-B); ¹³C NMR (22 °C, 125 MHz, CDCl₃): δ = 190.2 (C=S), 172.8, 172.5

(CO₂Me), 143.8 (CN), 136.5 (CS), 132.5–118.6 (s, Ph), 97.2 (s, C₅Me₅), 59.4, 35.6 (s, C-CO₂Me), 53.4, 49.9 (OCH₃), 9.4 ppm (s, C₅(CH₃)₅); IR (hexane): $\bar{\nu}$ = 2920 (C=CH), 1731 (BH_b), 1719 cm⁻¹ (CO).

2.4. Synthesis of **3a**

In a flame-dried Schlenk tube, yellow solution of **1** (0.100 g, 0.225 mmol) and phenylacetylene (1 equiv) in THF (15 mL) were irradiated for 6 h. The volatile components were removed under vacuum and the remaining residue was passed through Celite. After removal of solvent, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (70:30 v/v) mixture yielded yellow **3a** (0.048g, 40.1%).

Compound **3a** ESI-MS m/z calcd for C₂₆H₂₅NOS₂Ru ([M+H]⁺) 534.0; found 534.0; ¹H NMR (22 °C, 500 MHz, CDCl₃): δ = 7.32–7.97 (m, 9H; Ph), 3.27 (s, 1H; CH), 1.73 ppm (s, 15H; Cp*); ¹³C NMR (22 °C, 125 MHz, CDCl₃): δ = 201.2 (CO), 192.2 (C=S), 141.9 (CN), 133.4 (CS), 133.2–123.1 (s, Ph), 94.9 (s, C₅Me₅), 68.4, 31.2 (s, C=C), 9.9 ppm (s, C₅(CH₃)₅); IR (hexane): $\bar{\nu}$ = 2925 (C=CH), 1946 cm⁻¹ (CO).

2.5. Synthesis of **3b**, **4a** and **4b**

In a flame-dried Schlenk tube, the yellow solution of **1** (0.100 g, 0.225 mmol) and methyl propiolate (1 equiv) in toluene (15 mL) were irradiated for 6 h. The volatile components were removed under vacuum and the remaining residue was passed through Celite. After removal of solvent, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (60:40 v/v) mixture yielded orange **3b** (0.067 g, 57.8%), yellow **4a** (0.031 g, 27.5%) and yellow **4b** (0.019 g, 16.9%).

Note that compounds **4a** and **4b** were reported earlier [30].

Compound **3b** ESI-MS m/z calcd for C₂₂H₂₃NO₃S₂Ru ([M+H]⁺) 516.0; found 516.0; ¹H NMR (22 °C, 500 MHz, CDCl₃): δ = 7.34–7.54 (m, 4H; Ph), 3.92 (s, 1H; CH), 3.89 (s, 3H; OCH₃), 1.72 ppm (s, 15H; Cp*); ¹³C NMR (22 °C, 125 MHz, CDCl₃): δ = 211.2 (CO), 180.6 (C=S), 177.5 (CO₂Me), 149.1 (CN), 141.8 (CS), 127.3–121.2 (s, Ph), 95.0 (s, C₅Me₅), 32.3, 24.8 (s, C=C), 31.6 (OCH₃), 9.5 ppm (s, C₅(CH₃)₅); IR (hexane): $\bar{\nu}$ = 2957 (C=CH), 1922 cm⁻¹ (CO).

2.6. Computational details

All molecular geometries (Cp analogues) have been optimized without symmetry constraints by using GAUSSIAN 09 series of programs [57] by employing the hybrid functional B3LYP [58-60] with combination of SDD [61] basis set on Ru and 6-31+G(2d,p) basis set for rest of the

atoms. The X-ray coordinates were used as a starting geometry to complete geometry optimizations. The optimized geometries are in minima energy in the potential energy hypersurface diagram without any imaginary frequencies. We calculated ^1H and ^{11}B NMR shielding tensors employed at the B3LYP/GIAO [62-64] level of theory. TMS (SiMe_4) was used as internal standard (B3LYP H shielding constant 31.6 ppm) for the ^1H NMR chemical shift calculations. The ^{11}B NMR chemical shifts were calculated relative to B_2H_6 (B3LYP B shielding constant 93.8 ppm) and converted to the usual $\text{F}_3\text{B.OEt}_2$ scale using the experimental $\delta(^{11}\text{B})$ value of B_2H_6 , 16.6 ppm [65]. Bonding analysis was carried out using the natural bond orbital (NBO) method [66-67]. Wiberg bond indexes (WBI) [68] of some of selected bonds were obtained on natural bond orbital (NBO) analysis.

2.7. X-ray structure determination

The crystal data for compounds **2a** and **3a** were collected and integrated with a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo-K α ($\lambda = 0.71073$) radiation at 296 K. The crystal data for compounds **2b** and **3b** were collected and integrated with a D8 VENTURE Bruker AXS diffractometer, with multilayer monochromated Mo-K α ($\lambda = 0.71073$) radiation at 150 K. The structures were solved by heavy atom methods using SHELXS-97 or SHELXT-2015 and were refined by using SHELXL-2014 [69-71]. In compound **2a**, hydrogen atoms (H1X and H2X) on B3 are located from difference electron density Fourier maps and refined freely. All the other hydrogens were put at calculated positions as a riding model with respect to B3. In compound **2b**, the hydrogen atom (H26) on C26 is located from difference electron density Fourier maps and refined freely. All the other hydrogens were put at calculated positions as a riding model with respect to C26. In compound **3a**, all the hydrogen atoms were put at calculated positions as a riding model with respect to their parent atoms. In compound **3b**, all the hydrogens were put at calculated positions as a riding model with respect to their parent atoms.

Crystal data for **2a**: CCDC: 1494547; $\text{C}_{19}\text{H}_{24}\text{BNRuS}_2$; $M_r = 442.39$; monoclinic; space group $P2_1/n$; $a = 8.8306(4) \text{ \AA}$, $b = 14.7102(5) \text{ \AA}$, $c = 15.6008(7) \text{ \AA}$, $\beta = 106.2612(17)^\circ$; $V = 1945.47(14) \text{ \AA}^3$; $Z = 4$; $\rho_{\text{calcd}} = 1.510 \text{ g.cm}^{-3}$; $\mu = 1.021 \text{ mm}^{-1}$; $F(000) = 904$; $R_1 = 0.0255$; $wR_2 = 0.0519$; 3443 independent reflections [$2\theta \leq 50^\circ$] and 230 parameters.

Crystal data for **2b**: CCDC: 1494545; $\text{C}_{23}\text{H}_{27}\text{BCINO}_4\text{RuS}_2$; $M_r = 592.90$; monoclinic; space group $P2_1/n$; $a = 10.9339(9) \text{ \AA}$, $b = 16.1200(14) \text{ \AA}$, $c = 14.6615(11) \text{ \AA}$, $\beta = 103.359(3)^\circ$; $V = 2514.2(4) \text{ \AA}^3$; $Z = 4$; $\rho_{\text{calcd}} = 1.566 \text{ g.cm}^{-3}$; $\mu = 0.926 \text{ mm}^{-1}$; $F(000) = 1208$; $R_1 = 0.0293$; $wR_2 = 0.0620$; 5736 independent reflections [$2\theta \leq 50.48^\circ$] and 312 parameters.

Crystal data for **3a**: CCDC: 1436709; $C_{26}H_{25}NORuS_2$; $M_r = 532.66$; monoclinic; space group $P2_1/c$; $a = 20.3667(10)$ Å, $b = 7.8438(4)$ Å, $c = 15.8425(8)$ Å, $\beta = 111.096(2)^\circ$; $V = 2361.2(2)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.498$ g.cm⁻³; $\mu = 0.859$ mm⁻¹; $F(000) = 1088$; $R_1 = 0.0348$; $wR_2 = 0.0706$; 4159 independent reflections [$2\theta \leq 50^\circ$] and 285 parameters.

Crystal data for **3b**: CCDC: 1494546; $C_{22}H_{23}NO_3RuS_2$; $M_r = 514.60$; monoclinic; space group $P2_1/n$; $a = 8.4056(9)$ Å, $b = 26.740(3)$ Å, $c = 10.2660(11)$ Å, $\beta = 111.585(3)^\circ$; $V = 2145.6(4)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.593$ g.cm⁻³; $\mu = 0.949$ mm⁻¹; $F(000) = 1048$; $R_1 = 0.0246$; $wR_2 = 0.0559$; 4907 independent reflections [$2\theta \leq 50.48^\circ$] and 268 parameters.

3. Results and discussion

3.1. Reactivity of **1** towards alkynyl-Grignard, $[HC\equiv CMgBr]$ and $[RC\equiv CR]$ ($R = CO_2Me$)

As shown in Scheme 1a, photolysis of **1** with alkynyl-Grignard $[HC\equiv CMgBr]$ in toluene led to the isolation of vinyl hydroborate complex $[Cp^*Ru(\mu-H)BH\{HC=CH_2\}L]$, **2a** ($L = C_7H_4NS_2$). Interestingly, when the reaction was performed with $[RC\equiv CR]$ ($R = CO_2Me$), it yielded different types of vinyl hydroborate complexes $[Cp^*Ru(\mu-H)BX\{RC=CHR\}L]$, **2b-c** ($R = CO_2Me$, $L = C_7H_4NS_2$; **2b**: $X = Cl$; **2c**: $X = H$) (Scheme 1b). Although produced in a mixture, these compounds could be separated by careful thin layer chromatographic (TLC) techniques. All the compounds were reasonably air stable and can be handled in air for extended periods in the pure crystalline state. The compounds were isolated in moderate to good yields and characterized by IR, NMR spectroscopy, mass spectrometry and X-ray diffraction studies.

Scheme 1a-b. Reactivity of **1** with alkynyl-Grignard and internal alkyne

Compounds **2a** and **2b** were isolated as moderately stable yellow solids in 89 and 37% yields respectively. Both the compounds exhibit a single ^{11}B chemical shift at -10.8 and -2.7 ppm respectively. The ^1H NMR spectrum of **2a** shows the chemical shifts for the olefinic protons at δ = 3.45, 2.82 and 2.26 ppm and the BH_t was observed at δ = 3.07 ppm. On the otherhand, ^1H NMR spectrum of **2b** shows chemical shift for olefinic protons at δ = 6.12 ppm, whereas no chemical shift was observed in the region 3-4 ppm corresponding to BH_t proton. Both **2a** and **2b** showed an upfield chemical shift at δ = -10.49 and -10.62 ppm which may be assigned to Ru-H-B protons. Furthermore, both ^1H and ^{13}C NMR spectra show peaks confirming the presence of Cp^* and 2-mbzt (2-mbzt = 2-mercaptobenzothiazole) ligands.

The solid-state X-ray structures of **2a** and **2b**, shown in Fig. 1, show that they are vinyl hydroborate complexes of ruthenium [44]. These structures further reveal that **2a** and **2b** are formed by the hydroboration of ethynylmagnesium bromide and dimethylacetylenedicarboxylate respectively by the borate unit in **1**. The geometry of both **2a** and **2b** around ruthenium center can be considered as pseudo-octahedral with a pentamethylcyclopentadienyl ligand. The Ru and ethylenic carbon bond lengths as well as Ru-B bond distances are well within the reported values [72-77]. Terminal olefinic carbon in both **2a** and **2b** approach the ruthenium more closely. The C=C bond distances (1.391(4) Å for **2a** and 1.421(2) Å for **2b**) are consistent with a double bond distance, similar to the cationic olefin complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{H}_2\text{C}=\text{CH}^t\text{Bu}]^+$, (1.393(9) Å) [79]. On the otherhand the B-C bond distances of 1.541(4) Å and 1.557(3) Å in **2a** and **2b** respectively, are match well in the B-C single bonds range of 1.50–1.64 Å and are found to be unperturbed by the close Ru-H-B association [52].

To shed some light on the possible pathway for the formation of **2a**, photolysis of **1** with ethynylmagnesium bromide was monitored by ^1H NMR spectroscopy. The ^1H NMR spectra of the solution at different intervals showed the traces of acetylene. This might have generated from the hydrolysis of ethynylmagnesium bromide along with the formation of $\text{Mg}(\text{OH})\text{Br}$ (aq). The extra hydrogen in **2a** might have come from the solvent during the photolysis.

Significant feature of complexes **2a** and **2b** is the $\eta^2\text{-CC}$ interaction towards the ruthenium accompanied by an agostic interaction. Vinyl hydroborate complex **2b** on the otherhand, can be compared to the $[\text{Cp}^*\text{Ru}(\mu\text{-H})\text{BH}\{\text{R}^1\text{C}=\text{CHR}^2\}(\text{L})]$ ($\text{R}^1=\text{R}^2=\text{CO}_2\text{Me}$; $\text{L}=\text{C}_7\text{H}_4\text{NS}_2$) [44] isolated under similar reaction conditions, where the only difference is the replacement of the terminal B-H by a chlorine atom. We believe that the source of chlorine in molecule **2b** is from CH_2Cl_2 . This might have occurred while we were extracting the main reaction mixture with CH_2Cl_2 solvent. In fact, when the reaction mixture was extracted in non-chlorinated solvent (toluene), we didn't see a trace of **2b**.

Fig. 1. X-ray structures of **2a** (H1X, H2X are located and all other hydrogens are in calculated positions; thermal ellipsoids are set at 15% probability) and **2b** (H26 is located and all other hydrogens are in calculated position; thermal ellipsoids are set at 50% probability). Selected bond lengths (Å) and bond angles (°): **a)** B3-C18 1.541(4), B3-N1 1.568(3), B3-Ru1 2.352(3), B3-H2X 1.11(2), B3-H1X 1.38(2), C18-C19 1.391(4), C18-Ru1 2.175(2), C19-Ru1 2.241(2), Ru1-S3 2.3712(6), Ru1-H1X 1.65(2), C11-S3 1.685(2); C19-C18-B3 121.4(2), C18-Ru1-C19 36.68(9), C18-Ru1-B3 39.56(9), C11-S3-Ru1 101.68(7); **b)** B11-N12 1.562(2), B11-Cl2 1.843(2), B11-Ru1 2.311(2), B11-H11 1.286(15), S1-Ru1 2.3711(5), Ru1-H11 1.62(2), C21-B11 1.557(3), C21-Ru1 2.1690(18), C21-C26 1.421(2), C26-Ru1 2.2444(18); C26-C21-B11 115.83(16), C21-Ru1-B11 40.52(7), C26-Ru1-B11 67.28(7), C21-Ru1-C26 37.52(6).

In order to gain some insight into the electronic interactions of compounds **2a**, **2b** and **2c**, density functional theory (DFT) calculations were undertaken on the level of B3LYP functional using SDD/6-31+G(2d,p) basis set. The experimental bond parameters of **2a**, **2b** and **2c** are well reproduced by theoretical calculations (Table S1). The calculated IR, ^1H and ^{11}B NMR values of **2a** and **2b** are fairly consistent with those experimental observed values (Table S2). The energy gap between HOMO and LUMO of **2b** and **2c** (~3.94 eV) is larger by 0.2 eV than **2a** that shows the thermodynamic stability of **2b** and **2c** over **2a** (Table S3). This may be due to the presence of ester group in compounds **2b** and **2c**. The molecular orbitals (HOMO and HOMO-1) of **2a** mainly show the bonding interactions between Ru and $\pi(\text{C-C})$ of olefin and Ru-H-B. The LUMO+1 shows the corresponding *anti*-bonding interactions (Fig.2). The molecular orbital interactions of **2b** are observed to be same as **2a** (Fig. S1). In addition, natural bonding orbital (NBO) analysis of **2a** suggests that significant delocalization occurs from $\sigma(\text{B-H})$ as well as from $\pi(\text{C-C})$ to vacant Ru center by stabilizing interaction of 4.89 and 73.11 kcal/mol respectively (Fig. S2). Further, the Wiberg bond indices of (WBI) of Ru-B, Ru-S, B-H_b and B-N bonds, given in Table S4, illustrate strong bonding interactions among them.

Fig. 2. Molecular orbital involved in bonding and *anti*-bonding interactions with Ru-H-B and Ru-C=C in **2a**.

3.2. Reactivity of **1** towards terminal alkynes [$\text{HC}\equiv\text{CR}$] ($\text{R} = \text{Ph}$ and CO_2Me)

As shown in Scheme 2, photolysis of **1** with [$\text{HC}\equiv\text{CR}$] ($\text{R} = \text{Ph}$ or CO_2Me) in toluene followed by evaporation of solvent and chromatographic workup using TLC, led to the isolation of new compounds **3a** and **3b** as $[\text{Cp}^*\text{Ru}(\text{CO})(\text{C}_2\text{HR})(\text{L})]$, (**3a**: $\text{R} = \text{Ph}$; **3b**: $\text{R} = \text{CO}_2\text{Me}$, $\text{L} = \text{C}_7\text{H}_4\text{NS}_2$) along with our earlier reported vinyl hydroborate complexes **4a** and **4b** $[\text{Cp}^*\text{Ru}(\mu\text{-H})\text{BH}\{\text{R}^1\text{C}=\text{CHR}^2\}(\text{L})]$ (**4a**: $\text{R}^1 = \text{CO}_2\text{Me}$, $\text{R}^2 = \text{H}$; **4b**: $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CO}_2\text{Me}$) [44]. All the compounds were isolated in moderate to good yields and characterized by IR, NMR spectroscopy, mass spectrometry and X-ray diffraction studies.

Scheme 2. Reactivity of **1** with terminal alkynes

Both compounds **3a** and **3b** did not show any chemical shift in the ^{11}B NMR spectra that confirm the absence of boron in the compounds, ^1H NMR spectra of **3a** and **3b** on the other hand showed the presence of 2-mbzt and alkene signals along with the Cp^* chemical shifts. The identities of compounds **3a** and **3b** were finally ascertained by X-ray crystallographic analysis (Fig. 3).

Fig. 3. X-ray structures of **3a** (all the hydrogens are in calculated position; thermal ellipsoids are set at 30% probability) and **3b** (all the hydrogens are in calculated position; thermal ellipsoids are set at 40% probability). Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$): **a**) C12-Ru1 2.076(3), C12-C20 1.336(4), C12-N1 1.497(3), Ru1-S1 2.3621(7); N1-C12-Ru1 110.62(17); **b**) C21-Ru1 2.0766(16), C21-C26 1.335(2), C26-N27 1.431(2), N27-C28 1.357(2), C28-S1 1.6806(18), C28-S2 1.7406(17), Ru1-S1 2.3435(5); Ru1-C21-C26 133.24(12), C21-C26-N27 126.99(14), C28-S1-Ru1 112.76(6).

Compounds **3a** and **3b** were found to be η^1 -bound vinyl complexes of ruthenium. Compound **3a** forms a five membered metallaheterocycle containing ruthenium, carbon, nitrogen and sulfur atoms. The ruthenium centre coordinated to Cp^* , CO and the vinyl carbon in η^1 -fashion. Thus, the geometry around the metal becomes pseudo-octahedral. The C12-C20 (Fig. 3a) distance in **3a** is 1.336(4) $\text{\AA}$ which is consistent with a double bond, similar to those observed in other transition metal η^1 -vinyl complexes (Table 1). Compound **3a** can be compared to the Rh vinyl complex $[\text{Cp}^*\text{RhBr}(\text{C}_2\text{H}_2)\text{L}]$ ($\text{L} = \text{C}_7\text{H}_4\text{NS}_2$) [79]. Similarly the C21-C26 bond distance of 1.335(2) $\text{\AA}$ in **3b** (Fig. 3b) is also consistent with a double bond, similar to those observed in other transition metal η^1 -vinyl complexes (Table 1). Metal-alkenyl complexes are well recognized species among the classical organometallic compounds and play a vital role in many synthetic and catalytic reactions [80-81]. Complexes **3a** and **3b** are an additional entry to this class of compounds, although it possesses a unique structural type with metallaheterocycles.

Table 1Comparison of various structural parameters of η^1 -vinyl complexes

Compounds	M- η^1 C distance(Å)	C=C distance (Å)
[Cp*RhBr(C ₂ H ₂)(C ₇ H ₄ NS ₂)] [79]	2.027(8)	1.316(11)
[Ru(CO)(HC=CC ₃ H ₈)Cl(C ₅ N ₂ H ₈)(PPh ₃) ₂] [81]	2.05	1.32
[Ru(CO) ₂ (HC=CHSiMe ₂ OEt)Cl(PPh ₃) ₂] [82]	2.109	1.345
[Ru(CO)(CO ₂ Me)(HC=CHPh)(PPh ₃) ₂] [83]	2.030	1.294
[Ru(CO)(O ₂ CH)(HC=CHPh)(PPh ₃) ₂] [84]	2.036	1.35
[Cp*Ru(CO)(C ₂ HPh)(L)] 3a [this work]	2.076(3)	1.336(4)
[Cp*Ru(CO)(C ₂ HCO ₂ Me)(L)] 3b [this work]	2.0766(16)	1.335(2)

It is interesting to observe that while the reaction of compound **1** with phenylacetylene gave exclusively **3a**, methyl propiolate on the other hand gave **3b** along with vinyl hydroborate complexes, **4a** and **4b** (Scheme 2). Thus, to understand the pathway for the formation of these complexes, we carried out DFT calculations on these molecules. The computed energy values, provided in Table S5, demonstrate the formation of products **2a**, **2b** and **2c**, **3a** and **3b**, **4a** and **4b**. In case of dimethyl acetylenedicarboxylate the formation of **2c** is more favourable than **2b**. In case of phenylacetylene the formation of **3a** (-19.11 kcal/mol) is more favourable over the vinyl hydroborate complex **3I** (hypothetical phenyl substituted vinyl hydroborate complex) (-3.31 kcal/mol). It goes through the unstable intermediate **3I** which eventually converts to **3a**. Similarly, **3b** (-19.08 kcal/mol) was found to be more stable compared to **4a** (-3.31 kcal/mol) and **4b** (-3.45 kcal/mol). However, the presence of ester group might have made **4a** and **4b** relatively stable compared to **3I** to exist in the solid state. Thus, from the theoretical calculations we can predict that the hydroborate complexes may be the intermediate in the formation of the vinyl complexes.

4. Conclusions

In conclusion, we have described the utility of a ruthenium σ -borane complex **1** towards the hydroboration of alkynes to generate ruthenium vinyl hydroborate and vinyl complexes. Reaction of **1** with alkynyl-Grignard, led to the isolation of vinyl hydroborate complex with an ethylene moiety which is a rare example of this type. Terminal alkynes on the otherhand led to the isolation of metal vinyl complexes containing five and six membered metallaheterocycle. DFT calculations further support the pathway for the formation of these new complexes. Reactivity of **1** with other alkynyl derivatives is underway to make different hydroborate derivatives.

Acknowledgments

This work is supported by the Council of Scientific and Industrial Research (CSIR; No. 01(2837)/15/EMR-II) New Delhi, India. IIT Madras is gratefully acknowledged for computational facilities. K.S. is thankful to the Council of Scientific and Industrial Research (CSIR), India for Research Fellowship. B.J. and R.R. are grateful to the University Grants Commission (UGC) for research fellowships and R.B. thanks IIT Madras for research fellowship.

Appendix A. Supplementary data

CCDC 1494547 (**2a**), 1494545 (**2b**), 1436709 (**3a**) and 1494546 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org>.

References

- [1] C.E. Housecroft, T.P. Fehlner, in: F.G.A. Stone, R. West (Eds.), *Advances in Organometallic Chemistry*, Academic Press, New York, Vol. 21, 1981, pp. 57–112.
- [2] C.E. Housecroft, *Boranes and Metallaboranes*, Wiley, New York, 1990.
- [3] R. Thompson, in: R.J. Brotherton, H. Steinberg (Eds.), *Progress in Boron Chemistry*, Pergamon, Oxford, 1970, pp. 173–230.
- [4] G. Frenking, N. Fröhlich, *Chem. Rev.* 100 (2000) 717–774.
- [5] H. Braunschweig, M. Colling, *Coord. Chem. Rev.* 223 (2001) 1–51.
- [6] H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem. Int. Ed.* 45 (2006) 5254–5274.
- [7] S. Ghosh, X. Lei, C.L. Cahill, T.P. Fehlner, *Angew. Chem. Int. Ed.* 39 (2000) 2900–2902.
- [8] D.K. Roy, S.K. Bose, R.S. Anju, V. Ramkumar, S. Ghosh, *Inorg. Chem.* 51 (2012) 10715–10722.
- [9] S. Ghosh, A.M. Beatty, T.P. Fehlner, *Collect. Czech. Chem. Commun.* 67 (2002) 808–812.
- [10] K. Geetharani, S.K. Bose, S. Sahoo, B. Varghese, S.M. Mobin, S. Ghosh, *Inorg. Chem.* 50 (2011) 5824–5832.
- [11] K. Geetharani, S.K. Bose, G. Pramanik, T.K. Saha, V. Ramkumar, S. Ghosh, *Eur. J. Inorg. Chem.* (2009) 1483–1487.

- [12] S. Ghosh, B.C. Noll, T.P. Fehlner, Dalton Trans. (2008) 371–378.
- [13] S.K. Bose, K. Geetharani, B. Varghese, S. Ghosh, Inorg. Chem. 49 (2010) 6375–6377.
- [14] S.K. Bose, K. Geetharani, S. Sahoo, K.H.K. Reddy, B. Varghese, E.D. Jemmis, S. Ghosh, Inorg. Chem. 50 (2011) 9414–9422.
- [15] S. Sahoo, K.H.K. Reddy, R.S. Dhayal, S.M. Mobin, V. Ramkumar, E.D. Jemmis, S. Ghosh, Inorg. Chem. 48 (2009) 6509–6516.
- [16] S.K. Bose, K. Geetharani, B. Varghese, S. Ghosh, Inorg. Chem. 50 (2011) 2445–2449.
- [17] R.S. Dhayal, S. Sahoo, K.H.K. Reddy, S.M. Mobin, E.D. Jemmis, S. Ghosh, Inorg. Chem. 49 (2010) 900–904.
- [18] K. Geetharani, B.S. Krishnamoorthy, S. Kahlal, S.M. Mobin, J.-F. Halet, S. Ghosh, Inorg. Chem. 51 (2012) 10176–10184.
- [19] A.F. Hill, G.R. Owen, A.J.P. White, D.J. Williams, Angew. Chem. Int. Ed. 38 (1999) 2759–2761.
- [20] V.K. Landry, J.G. Melnick, D. Buccella, K. Pang, J.C. Ulichny, G. Parkin, Inorg. Chem. 45 (2006) 2588–2597.
- [21] Y. Gloaguen, G. Alcaraz, A.-F. Pécharman, E. Clot, L. Vendier, S. Sabo-Etienne, Angew. Chem. Int. Ed. 48 (2009) 2964–2968.
- [22] H. Braunschweig, R.D. Dewhurst, Angew. Chem. Int. Ed. 48 (2009) 1893–1895.
- [23] R. Dallanegra, A.B. Chaplin, A.S. Weller, Angew. Chem. Int. Ed. 48 (2009) 6875–6878.
- [24] C.Y. Tang, N. Phillips, J.I. Bates, A.L. Thompson, M.J. Gutmann, S. Aldridge, Chem. Commun. 48 (2012) 8096–8098.
- [25] J.F. Hartwig, K.S. Cook, M. Hapke, C.D. Incarvito, Y. Fan, C.E. Webster, M.B. Hall, J. Am. Chem. Soc. 127 (2005) 2538–2552.
- [26] D.K. Roy, S.K. Bose, R.S. Anju, B. Mondal, V. Ramkumar, S. Ghosh, Angew. Chem. Int. Ed. 52 (2013) 3222–3226.
- [27] S.K. Bose, K. Geetharani, V. Ramkumar, S.M. Mobin, S. Ghosh, Chem. Eur. J. 15 (2009) 13483–13490.
- [28] S. Ghosh, A.M. Beatty, T.P. Fehlner, J. Am. Chem. Soc. 123 (2001) 9188–9189.
- [29] S. Ghosh, X. Lei, M. Shang, T.P. Fehlner, Inorg. Chem. 39 (2000) 5373–5382.
- [30] M. Sircoglou, S. Bontemps, M. Mercy, K. Miqueu, S. Ladeira, N. Saffon, L. Maron, G. Bouhadir, D. Bourissou, Inorg. Chem. 49 (2010) 3983–3990.

- [31] K. Geetharani, S. Tussupbayev, J. Borowka, M.C. Holthausen, S. Ghosh, *Chem. Eur. J.* 18 (2012) 8482–8489.
- [32] S.K. Bose, K. Geetharani, S. Ghosh, *Chem. Commun.* 47 (2011) 11996–11998.
- [33] D.K. Roy, B. Mondal, P. Shankhari, R.S. Anju, K. Geetharani, S.M. Mobin, S. Ghosh, *Inorg. Chem.* 52 (2013) 6705–6712.
- [34] R.S. Anju, D.K. Roy, B. Mondal, K. Yuvaraj, C. Arivazhagan, K. Saha, B. Varghese, S. Ghosh, *Angew. Chem. Int. Ed.* 53 (2014) 2873–2877.
- [35] A.A. Oluyadi, S. Ma, C.N. Muhoro, *Organometallics* 32 (2013) 70–78.
- [36] S.G. Thangavelu, K.E. Hocker, S.R. Cooke, C.N. Muhoro, *J. Organomet. Chem.* 693 (2008) 562–566.
- [37] J.F. Hartwig, C.N. Muhoro, *Organometallics* 19 (2000) 30–38.
- [38] D.J.H. Emslie, B.E. Cowie, K.B. Kolpin, *Dalton Trans.* 41 (2012) 1101–1117.
- [39] H. Braunschweig, R.D. Dewhurst, V.H. Gessner, *Chem. Soc. Rev.* 42 (2013) 3197–3208.
- [40] R.T. Baker, J.C. Calabrese, S.A. Westcott, T.B. Marder, *J. Am. Chem. Soc.* 117 (1995) 8777–8784.
- [41] G.R. Clark, G.J. Irvine, W.R. Roper, L.J. Wright, *Organometallics* 16 (1997) 5499–5505.
- [42] S.K. Bose, D.K. Roy, P. Shankhari, K. Yuvaraj, B. Mondal, A. Sikder, S. Ghosh, *Chem. Eur. J.* 19 (2013) 2337–2343.
- [43] R.S. Anju, B. Mondal, K. Saha, S. Panja, B. Varghese, S. Ghosh, *Chem. Eur. J.* 21 (2015) 11393–11400.
- [44] K. Saha, B. Joseph, R. Ramalakshmi, R.S. Anju, B. Varghese, S. Ghosh, *Chem. Eur. J.* 22 (2016) 7871–7878.
- [45] H.C. Brown, B.C.S. Rao, *J. Am. Chem. Soc.* 78 (1956) 5694–5695.
- [46] H. Brown, B.C. Rao, *J. Org. Chem.* 22 (1957) 1136–1137.
- [47] R. Köster, *Justus Liebigs Ann. Chem.* 618 (1958) 31–43.
- [48] D.S. Matteson, in: F.R. Hartley (Ed.), *The Metal-Carbon Bond*, Wiley, Chichester, Vol. 4, 1987, pp. 307–409.
- [49] M. Davidson, A.K. Hughes, T.B. Marder, K. Wade, *Contemporary Boron Chemistry*, RSC, Cambridge, 2000, pp. 371–472.
- [50] C.C. Chong, R. Kinjo, *ACS Catal.* 5 (2015) 3238–3259.
- [51] A. Suzuki, *Angew. Chem. Int. Ed.* 50 (2011) 6722–6737.

- [52] D.K. Roy, A. De, S. Panda, B. Varghese, S. Ghosh, *Chem. Eur. J.* 21 (2015) 13732–13738.
- [53] G. Schmid, F. Alraun, R. Boese, *Chem. Ber.* 124 (1991) 2255–2258.
- [54] H. Braunschweig, R.D. Dewhurst, T. Herbst, K. Radacki, *Angew. Chem. Int. Ed.* 47 (2008) 5978–5980.
- [55] R. Ramalakshmi, K. Saha, D.K. Roy, B. Varghese, A.K. Phukan, S. Ghosh, *Chem. Eur. J.* 21 (2015) 17191–17195.
- [56] G.E. Ryschkewitsch, K.C. Nainan, in: G.W. Parshall (Ed.), *Inorganic Syntheses*, Wiley, Hoboken, Vol. 15, 1974, pp. 113–114.
- [57] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Gaussian 09, Revision B.01, Wallingford CT, (2010).
- [58] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648–5652.
- [59] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785–789.
- [60] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098–3100.
- [61] M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* 86 (1987) 866–872.
- [62] F. London, *J. Phys. Radium.* 8 (1937) 397–409.
- [63] R. Ditchfield, *Mol. Phys.* 27 (1974) 789–807.
- [64] K. Wolinski, J.F. Hinton, P. Pulay, *J. Am. Chem. Soc.* 112 (1990) 8251–8260.
- [65] T.P. Onak, H.L. Landesman, R. Williams, I. Shapiro, *J. Phys. Chem.* 63 (1959) 1533–1535.
- [66] F.C. Weinhold, R. Landis, *Valency and bonding: A natural bond orbital donor-acceptor perspective*, Cambridge University Press, Cambridge, U.K., (2005).
- [67] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 88 (1988) 899–926.
- [68] K. Wiberg, *Tetrahedron* 24 (1968) 1083–1096.

- [69] G.M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997.
- [70] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.
- [71] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343–350.
- [72] X. Lei, M. Shang, T.P. Fehner, J. Am. Chem. Soc. 121 (1999) 1275–1287.
- [73] S. Ghosh, B.C. Noll, T.P. Fehner, Angew. Chem. Int. Ed. 44 (2005) 6568–6571.
- [74] R.S. Anju, K. Saha, B. Mondal, V. Dorcet, T. Roisnel, J.-F. Halet, S. Ghosh, Inorg. Chem. 53 (2014) 10527–10535.
- [75] R.S. Anju, K. Saha, B. Mondal, T. Roisnel, J.-F. Halet, S. Ghosh, Dalton Trans. 44 (2015) 11306–11313.
- [76] R.S. Anju, D.K. Roy, K. Geetharani, B. Mondal, B. Varghese, S. Ghosh, Dalton Trans. 42 (2013) 12828–12831.
- [77] K. Yuvaraj, D.K. Roy, K. Geetharani, B. Mondal, V.P. Anju, P. Shankhari, V. Ramkumar, S. Ghosh, Organometallics 32 (2013) 2705–2712.
- [78] D.L. Coombs, S. Aldridge, A. Rossin, C. Jones, D.J. Willock, Organometallics 23 (2004) 2911–2926.
- [79] D.K. Roy, K. Yuvaraj, R. Jagan, S. Ghosh, J. Organomet. Chem. 811 (2016) 8–13.
- [80] M.L.H. Green, M.J. Smith, J. Chem. Soc. A (1971) 3220–3223.
- [81] M.R. Torres, A. Santos, A. Perales, J. Ros, J. Organomet. Chem. 353 (1988) 221–228.
- [82] S.M. Maddock, C.E.F. Rickard, W.R. Roper, L.J. Wright, Organometallics 15 (1996) 1793–1803.
- [83] M.R. Torres, H. Loumrhari, J. Ros, A. Perales, J. Organomet. Chem. 385 (1990) 379–386.
- [84] H. Loumrhari, L. Matas, J. Ros, M.R. Torres, A. Perales J. Organomet. Chem. 403 (1991) 373–381.

Chemistry of ruthenium σ -borane complex, $[\text{Cp}^*\text{RuCO}(\mu\text{-H})\text{BH}_2\text{L}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{L} = \text{C}_7\text{H}_4\text{NS}_2$) with terminal and internal alkynes: Structural characterization of vinyl hydroborate and vinyl complexes of ruthenium.

Koushik Saha^a, Benson Joseph^a, Rosmita Borthakur^a, Rongala Ramalakshmi^a, Thierry Roisnel^b and Sundargopal Ghosh^{a,*}

Reaction of ruthenium σ -borane complex $[\text{Cp}^*\text{RuCO}(\mu\text{-H})\text{BH}_2\text{L}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{L} = \text{C}_7\text{H}_4\text{NS}_2$) with alkynes form ruthenium vinyl hydroborate and vinyl complexes.