### SUPPLEMENTARY INFORMATION

## Chemistry of ruthenium $\sigma$ -borane complex, [Cp\*RuCO( $\mu$ -H)BH<sub>2</sub>L] (Cp\* = $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; L = C<sub>7</sub>H<sub>4</sub>NS<sub>2</sub>) with terminal and internal alkynes: Structural characterization of vinyl hydroborate and vinyl complexes of ruthenium.

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# I Supplementary data

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Bond lengths	2a		2b		3a		3b	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
d(Ru-B)	2.35	2.37	2.31	2.33	-	-	-	-
d(Ru-H <sub>b</sub> )	1.64	1.69	1.62	1.67	-	-	-	-
$d(B-H_t)$	1.11	1.20	-	-	-	-	-	-
d(B-N)	1.56	1.56	1.56	1.56	-	-	-	-
<i>d</i> (B-C)	1.54	1.55	1.55	1.56	-	-	-	-
d(Ru-S)	2.37	2.39	2.37	2.40	2.36	2.39	2.36	2.37
d(Ru-C)	2.24	2.26	2.24	2.25	2.07	2.08	2.07	2.07
<i>d</i> (C-C)	1.39	1.40	1.42	1.42	1.33	1.35	1.33	1.35
d(N-C)	1.33	1.34	1.34	1.34	1.34	1.35	1.34	1.35

Table S1. Experimental and DFT calculated bond lengths (Å) of 2-3(a-b)

**Table S2**. Experimental and DFT calculated <sup>11</sup>B, <sup>1</sup>H NMR chemical shifts ( $\delta$ , ppm) and IR values of **2-3(a-b)** 

Compound		<sup>11</sup> B NMR		<sup>1</sup> H NMR			IR Valu	ies	
		Exp.	Cal.		Exp.	Cal.		Exp.	Cal.
2a	В	-10.8	-10.7	Ru- <u>H</u> -B	-10.49	-7.41	B-H <sub>t</sub>	2362	2554
2b	В	-2.7	4.9	Ru- <u>H</u> -B	-10.62	-6.69	С=О	1719	1752
<b>3</b> a	-	-	-	-	-	-	C=0	1946	1727
3b	-	-	-	-	-	-	C=O	1922	1750

Compound	НОМО	LUMO	ΔΕ
2a	-5.12	-1.36	3.76
2b	-5.69	-1.75	3.94
3a	-5.29	-1.85	3.44
3b	-5.54	-1.92	3.62

**Table S3**. DFT calculated energies of the HOMO and LUMO (eV) and HOMO-LUMO gaps ( $\Delta E = E_{LUMO}-E_{HOMO}$ , eV) for compounds **2-3(a-b**)

Table S4. Selected Wiberg Bond Indices (WBI) for 2-3(a-b)

Compound	Ru-B	Ru-H <sub>b</sub>	B-H <sub>b</sub>	Ru-C	Ru-S	B-C	B-N
2a	0.27	0.37	0.46	0.47	0.74	0.96	0.66
2b	0.27	0.36	0.47	0.46	0.73	0.87	0.64
3a	-	-	-	0.75	0.73	-	-
3b	-	-	-	0.73	0.74	-	-

Entry	Proposed reactions	Products	$\Delta H$ (Kcal/mol)
1	1 + HC≡CMgBr	2a	-0.37
2	$1 + MeO_2CC \equiv CCO_2Me$	2b	-7.99
3	$1 + MeO_2CC \equiv CCO_2Me$	2c	-33.57
4	$1 + PhC \equiv CH$	3a	-19.11
5	$1 + PhC \equiv CH$	31	-3.31
6	31	3a	-19.11
7	$1 + MeO_2CC \equiv CH$	3b	-19.08
8	$1 + MeO_2CC \equiv CH$	4a	-3.31
9	4a	3b	-15.76
10	$1 + MeO_2CC \equiv CH$	4b	-3.45
11	4b	3b	-15.63

Table S5. Calculated heat of reaction

3I = Hypothetical Phenyl substutated vinyl hydroborate complex





HOMO-14

HOMO-1



Fig. S1. Frontier molecular orbitals of compound 2b



**Fig. S2.** NBO analysis of **2a**. (a, b) show B-H bonding and anti-bonding interactions; (c, d) show C-C bonding and anti-bonding interactions with Ru.



E = -1512.95464543 a.u

Fig. S3. Optimized geometry of compound 2a

Cartesian coordinates for the calculated structure of 2a (in Å)

Center Number	Atomic Number	Atomic Type	Coor X	dinates (Angsti Y	coms) Z
1	5	0	-0.234284	-1.283260	-0.256949
2	6	0	3.404950	0.568518	-1.417028
3	6	0	3.738391	1.027058	-0.094388
4	6	0	3.963248	-0.108320	0.731749
5	6	0	3.768804	-1.285273	-0.066616
6	6	0	3.429284	-0.865021	-1.385694
7	6	0	-1.129898	1.092587	0.028986
8	6	0	-3.573954	0.592904	-0.054113

9	6	0	-4.961989	0.474421	-0.083223
10	1	0	-5.596695	1.351272	-0.008670
11	6	0	-5.513788	-0.800573	-0.209596
12	1	0	-6.592484	-0.917084	-0.234492
13	6	0	-4.685758	-1.927892	-0.299354
14	1	0	-5.130467	-2.913681	-0.392457
15	6	0	-3.297272	-1.809518	-0.269299
16	1	0	-2.659454	-2.681760	-0.336331
17	6	0	-2.735645	-0.533381	-0.152333
18	6	0	0.606782	-1.642644	1.003860
19	1	0	1.127514	-2.600354	1.036104
20	6	0	0.932149	-0.701254	1.993525
21	1	0	1.640398	-0.965172	2.776513
22	1	0	0.260974	0.110372	2.251368
23	7	0	-1.373565	-0.220470	-0.109481
24	44	0	1.834098	-0.133990	-0.010555
25	16	0	-2.603664	2.046673	0.107640
26	16	0	0.411133	1.794470	0.106627
27	1	0	-0.556657	-2.168671	-1.001043
28	1	0	0.663127	-0.642084	-1.132036
29	1	0	3.217512	1.189356	-2.280998
30	1	0	3.807792	2.059229	0.220832
31	1	0	4.225839	-0.086838	1.779840
32	1	0	3.868673	-2.307672	0.269938
33	1	0	3.218678	-1.519710	-2.220149



#### E = -2428.37154025 a.u

## Fig. S4. Optimized geometry of compound 2b

Cartesian coordinates for	r the calculated structure of <b>2b</b> (in Å)

Center	Atomic	Atomic	linates (Angstroms)		
Number	Number	Туре	Х	Y	Z
1	44	0	1.045510	5.731678	8.440139
2	16	0	3.065406	6.505479	9.499601
3	17	0	2.564960	2.871703	6.463677
4	16	0	5.589122	5.017005	10.194465
5	6	0	0.476015	7.238373	6.875223
6	6	0	0.279673	7.852076	8.146097
7	6	0	-0.696488	7.106730	8.869225
8	6	0	-1.117974	6.018146	8.033984

9	6	0	-0.396379	6.095610	6.804413
10	5	0	2.321686	3.813966	8.052232
11	1	0	2.230341	5.077857	7.456239
12	7	0	3.640015	3.929037	8.885928
13	6	0	4.011845	5.096932	9.442030
14	6	0	4.550467	2.884246	9.130567
15	6	0	5.704099	3.308093	9.813687
16	6	0	6.727664	2.422955	10.147578
17	1	0	7.612736	2.768409	10.671356
18	6	0	6.573143	1.081206	9.804945
19	1	0	7.353638	0.370493	10.056723
20	6	0	5.410720	0.644090	9.155231
21	1	0	5.294114	-0.407377	8.913478
22	6	0	4.392134	1.530797	8.813726
23	1	0	3.498270	1.180126	8.316417
24	6	0	0.994571	3.597523	8.851409
25	6	0	-0.035769	2.607862	8.389474
26	8	0	-0.769435	2.977071	7.328243
27	6	0	-1.671333	1.974150	6.828042
28	1	0	-1.116648	1.084097	6.521086
29	1	0	-2.168533	2.431110	5.971704
30	1	0	-2.398011	1.701532	7.597292
31	8	0	-0.113636	1.516683	8.906563
32	6	0	0.890599	4.234707	10.116329
33	6	0	-0.376718	4.208199	10.885420
34	8	0	-1.485040	3.983204	10.442020
35	8	0	-0.151446	4.474375	12.191106

36	6	0	-1.306682	4.456092	13.041323
37	1	0	-2.029671	5.213296	12.725161
38	1	0	-0.935291	4.675890	14.042632
39	1	0	-1.784912	3.473535	13.014322
40	1	0	1.768639	4.378935	10.733617
41	1	0	-0.488026	5.411688	5.974068
42	1	0	-1.829271	5.255297	8.311415
43	1	0	-1.057672	7.326041	9.863486
44	1	0	0.816646	8.714948	8.517604
45	1	0	1.153697	7.577199	6.104701



E = -1830.65567512 a.u

Fig. S5. Optimized geometry of compound 3a

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	Х	Y	Z
			1 (71)71	1 10 40 27	0.1007.00
1	6	0	-1.6/12/1	-1.194027	2.138/69
2	6	0	-2.722380	-1.822991	1.410514
3	6	0	-2.260838	-3.112790	0.977086
4	6	0	-0.924561	-3.257083	1.429647
5	6	0	-0.546769	-2.084323	2.151015
6	6	0	-1.981651	-0.952217	-1.514171
7	6	0	0.074247	0.363125	-0.103757
8	6	0	1.929352	-0.997197	-0.853327
9	6	0	3.844366	0.451486	-0.196892
10	6	0	5.033784	1.094271	0.140907
11	1	0	5.986668	0.718934	-0.217526
12	6	0	4.968593	2.216339	0.964764
13	1	0	5.881331	2.733778	1.241402
14	6	0	3.733110	2.663433	1.451336
15	1	0	3.695541	3.521342	2.114997
16	6	0	2.542526	2.028241	1.103261
17	1	0	1.597026	2.376162	1.496720
18	6	0	2.594788	0.921628	0.247239
19	6	0	-0.240753	1.676824	-0.232554
20	1	0	0.578316	2.361623	-0.445406
21	6	0	-1.527490	2.382859	-0.194171
22	6	0	-1.528825	3.738441	-0.586346

Cartesian coordinates for the calculated structure of 3a (in Å)

23	1	0	-0.596403	4.192148	-0.913583
24	6	0	-2.692171	4.504319	-0.572491
25	1	0	-2.656046	5.543188	-0.887958
26	6	0	-3.898138	3.938483	-0.154212
27	1	0	-4.808640	4.529877	-0.139961
28	6	0	-3.916864	2.599994	0.245818
29	1	0	-4.848112	2.146342	0.574019
30	6	0	-2.753437	1.834031	0.226249
31	1	0	-2.789088	0.798290	0.532066
32	7	0	1.528234	0.113758	-0.198972
33	8	0	-2.637248	-0.694565	-2.429707
34	44	0	-0.998089	-1.423898	-0.006816
35	16	0	0.851326	-2.211878	-1.314929
36	16	0	3.653924	-1.036058	-1.112688
37	1	0	-0.282270	-4.103982	1.228514
38	1	0	-2.829206	-3.840586	0.416269
39	1	0	-3.710549	-1.417213	1.243493
40	1	0	-1.719362	-0.224216	2.612964
41	1	0	0.399328	-1.914039	2.644133



E = -1827.48116572 a.u

## Fig. S6. Optimized geometry of compound 3b

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Cartesian	coordinates	for the	calculated	structure	of <b>3b</b> (	(in Å	).
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Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	Х	Y	Z
1	6	0	2.297948	-0.121562	1.746078
2	8	0	2.703946	0.185077	2.784315
3	6	0	2.358597	-0.438548	-2.170145
4	6	0	1.862721	-1.751656	-1.987586
5	6	0	2.708473	-2.420054	-1.029347
6	6	0	3.717509	-1.504602	-0.634062
7	6	0	3.491615	-0.258713	-1.317994
8	6	0	0.525393	1.043248	-0.063137
9	6	0	1.261794	2.329568	-0.245514
10	8	0	1.898937	2.637888	-1.231715
11	8	0	1.159978	3.134316	0.836030

12	6	0	1.902387	4.363357	0.776811
13	1	0	2.967900	4.159069	0.642895
14	1	0	1.724099	4.856350	1.732956
15	1	0	1.551474	4.985961	-0.050606
16	6	0	-0.809203	1.184511	-0.041160
17	1	0	-1.275918	2.159537	-0.103820
18	7	0	-1.793702	0.158060	0.084717
19	6	0	-1.565650	-1.103813	0.530828
20	6	0	-3.151843	0.437279	-0.181354
21	6	0	-3.689043	1.618136	-0.703456
22	1	0	-3.058146	2.452900	-0.980210
23	6	0	-5.069416	1.700514	-0.885055
24	1	0	-5.492542	2.613743	-1.290591
25	6	0	-5.910434	0.629357	-0.560899
26	1	0	-6.981651	0.715920	-0.709989
27	6	0	-5.377614	-0.555586	-0.054794
28	1	0	-6.018700	-1.396115	0.189082
29	6	0	-3.998583	-0.638855	0.125447
30	44	0	1.735351	-0.642838	0.051553
31	16	0	-0.109485	-1.853865	0.922937
32	16	0	-3.064693	-2.004972	0.696856
33	1	0	4.515953	-1.705572	0.066983
34	1	0	2.603614	-3.441303	-0.691212
35	1	0	1.000227	-2.181116	-2.477622
36	1	0	1.925400	0.332128	-2.791085
37	1	0	4.094796	0.634621	-1.251846

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