

Electronic Supplementary Information

Experimental and theoretical studies on the (co)cyclotrimerization of alkynes (and ethylene) in a TpRh compound.

Giovanni Bottari,^a Juan José Moreno,^a Verónica Salazar,^b Jesús Campos,^a Kurt Mereiter,^c Nuria Rendón,^a Jesús Emmanuel Cerón,^b Joaquín López-Serrano,^{*a} Margarita Paneque,^{*a} and Laura L. Santos,^{*a}

^a Instituto de Investigaciones Químicas, Departamento de Química Inorgánica, and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla, Av. Américo Vespucio 49, Isla de la Cartuja, 41092 Sevilla, Spain.

^b Área Académica de Químicas, Universidad Autónoma del Estado de Hidalgo, 42184 Mineral de la Reforma, Hidalgo, México.

^c Department of Chemistry, Vienna University of Technology, Getreidemarkt 9/164SC, A-1060 Vienna, Austria.

E-mail: laura@iiq.csic.es; joaquin.lopez@iiq.csic.es; paneque@iiq.csic.es

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1. X-ray structure determination for the Rh complexes **3**, **4**, **5**, **8**, and **9**.

Single crystals for X-ray diffraction studies of the five compounds reported herein were obtained by slow evaporation from hexane:diethyl ether (**3**, **4**, **5**), hexane:CH₂Cl₂ (**8**), or chloroform (**9**) solutions. Solid state compound **4** is an *n*-hexane hemisolvate of the respective Rh complex. Solid state compound **8** is a 1:1 cocrystal of the respective Rh complex and di-*tert*-butyl acetylenedicarboxylate (DTBAD), which was used in excess as an educt for the synthesis of the complex. Solid state compound of **9** is a CHCl₃ monosolvate. X-ray diffraction data were collected at *T* = 100 and 173 K (Bruker Kryoflex cooler) either on a Bruker Smart APEX CCD diffractometer using graphite-monochromatized Mo-K α radiation (λ = 0.71073 Å) from a sealed tube (**3**, **4**, **5** and **8**) or on a Bruker APEX-II CCD diffractometer using Mo-K α radiation generated by an Incoatec microfocus source (**9**) (Centro de Investigaciones, Tecnología e Innovación Universidad de Sevilla, CITIUS). Data collection was carried out by means of fine-sliced ω - and φ -scans covering mostly complete Ewald spheres with θ_{\max} = 30 - 30.6°. The frames were integrated with program *SAINT* and corrections for absorption and $\lambda/2$ effects were applied with program *SADABS*. After structure solution with program *SHELXS97* and direct methods, refinement on F^2 was carried out with the program *SHELXL97*. Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions, except those of the coordinated water molecule in **9**, and thereafter treated as riding using AFIX 137 instructions for CH₃ groups. Crystallographic data are compiled in Table S1. Structural diagrams of the complexes (Figs. S1 – S6) and Tables (Tab. S2 – S6) with selected geometric parameters are given below. Atomic parameters are provided in CIF-format as Supporting Information (**3** (11-811), **4** (12-831), **5** (13-864), **8** (14-790), **9** (15-jcm2812a)). CCDC-1411328 – 1411332 (for **3**, **4**, **5**, **8** and **9**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

As stated above, the solid state structure of **4** is a hemisolvate of the Rh-complex in general position and a centrosymmetric *n*-hexane molecule. The *n*-hexane molecule adopts the usual planar zig-zag carbon chain and is with its long direction oriented approximately parallel to the *a*-axis of the crystallographic unit-cell. All hexane molecules are located in the crystal lattice in infinite narrow channels, which extend parallel to *a* at $y=0, z=1/2$ and $y=1/2, z=0$ (Fig. S2b). The *n*-hexane molecule refined to an occupancy of

85(1)%. The chemical formula and quantities derived quantities reported in Table S1 are given for an idealized 100% occupancy.

The solid state structure of **8** is an unusual 1:1 cocrystal of the Rh-complex **8** with the reagent DTBAD (di-*tert*-butyl acetylenedicarboxylate), a solid at room temperature, which was used in excess for the synthesis of the Rh-complex. The DTBAD molecule in **8** shows a *gauche*-like conformation with the interplanar angle between its two COO groups measuring 77.5°. A projection of the entire crystal structure of **8** showing the arrangement of the DTBAD molecules between the Rh-complexes is presented in Fig. S4b.

The crystal structure of **9** consists of dimers bound through four H bonds between molecules crystallographically related by an inversion center (Fig. S6). The oxygen center (O5) of the coordinated water molecule acts as a donor to form two hydrogen bonds of intermediate strength (T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 8-76) with the oxygen atoms O2 and O3 as acceptors. The dimensions of these hydrogen bonds are: O5...O2 = 2.861(2) Å, O5...O3 = 2.631(2) Å, H5B...O2 = 2.07 Å, H5A...O3 = 1.87 Å (for O5-H = 0.84 Å), O5-H5B...O2 = 157°, O5-H5A...O3 = 150° (for H5A-O5-H5B = 104°). Thus, the hydrogen bond to the terminal carboxyl oxygen O3 is distinctly stronger than that to O2. Interestingly, also the terminal carboxyl oxygen O1 is involved in a pronounced hydrogen bond interaction, here with the C-H group of a CHCl₃ solvate molecule as the donor, C30...O1 = 3.005(2) Å, C30-H30 = 1.00 Å, H30...O1 = 2.04 Å, and C30-H30...O1 = 162° (Fig. S6).

Computer programs used:

Bruker programs: *SAINT*, version 6.36A and higher; *SADABS*, versions 2.05 and 2006; *SHELXTL*, version 2008/4 (Bruker AXS Inc., Madison, WI, 2009).

SHELXS97 and *SHELXL97*: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

Table S1. Crystal data and structure refinement for compounds **3**, **4** and **5**.

	3 (11-811)	4 (12-831)	5 (13-864)
formula	C ₂₅ H ₃₆ BN ₆ O ₄ Rh	C ₃₈ H ₅₇ BN ₆ O ₈ Rh [C ₃₅ H ₅₀ BN ₆ O ₈ Rh·½(C ₆ H ₁₄)]	C ₃₅ H ₅₀ BN ₆ O ₈ Rh
fw	598.32	839.62	796.53
cryst.size, mm	0.64 × 0.26 × 0.19	0.57 × 0.20 × 0.19	0.45 × 0.25 × 0.18
crystal system	triclinic	monoclinic	monoclinic
space group	<i>P</i> -1 (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> , Å	8.9717(5)	10.4464(4)	16.6055(9)
<i>b</i> , Å	8.9893(5)	15.8720(6)	17.9739(10)
<i>c</i> , Å	17.3228(9)	25.0317(10)	13.6837(7)
α , deg	84.085(2)	90	90
β , deg	86.363(2)	90.839(1)	107.888(1)
γ , deg	79.803(2)	90	90
<i>V</i> , Å ³	1366.23(13)	4149.9(3)	3886.7(4)
<i>T</i> , K	100	173	173
<i>Z</i>	2	4	4
ρ_{calc} , g cm ⁻³	1.454	1.344	1.361
μ , mm ⁻¹ (MoK α)	0.667	0.467	0.495
<i>F</i> (000)	620	1764	1664
absorption corrections	multi-scan, 0.89-1.00	multi-scan, 0.82–1.00	multi-scan, 0.81–1.00
θ range, deg	2.5 – 30.0	2.3 - 30.0	2.3 - 30.0
no. of rflns measd	20454	32468	34631
<i>R</i> _{int}	0.019	0.036	0.041
no. of rflns unique	7865	11999	11263
no. of rflns <i>I</i> > 2 σ (<i>I</i>)	7585	10080	9028
no. of params / restraints	347 / 1	488 / 0	460 / 0
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0278	0.0464	0.0361
<i>R</i> ₁ (all data)	0.0290	0.0593	0.0515
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0677	0.0930	0.0732
<i>wR</i> ₂ (all data)	0.0684	0.0977	0.0783
Diff.Fourier.peak s min/max, eÅ ⁻³	-0.34 / 1.27	-0.78 / 0.68	-0.39 / 0.50

Table S2. Crystal data and structure refinement for compounds **8** and **9**.

	8 (14-790)	9 (15-jcm2812a)
formula	C ₄₇ H ₆₈ BN ₆ O ₁₂ Rh [C ₃₅ H ₅₀ BN ₆ O ₈ Rh·C ₁₂ H ₁₈ O ₄]	C ₂₃ H ₃₄ BN ₆ O ₅ Rh·CHCl ₃
fw	1022.79	707.66
cryst.size, mm	0.56 × 0.41 × 0.18	0.22 × 0.13 × 0.07
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> -1 (no. 2)
<i>a</i> , Å	11.4052(7)	9.6206(3)
<i>b</i> , Å	25.7392(16)	12.6144(4)
<i>c</i> , Å	19.1013(14)	13.4975(4)
α , deg	90	80.049(1)°
β , deg	107.309(2)	73.487(1)°
γ , deg	90	77.493(1)°
<i>V</i> , Å ³	5353.5(6)	1522.33(8)
<i>T</i> , K	173	100
<i>Z</i>	4	2
ρ_{calc} , g cm ⁻³	1.269	1.544
μ , mm ⁻¹ (MoK α)	0.380	0.87
<i>F</i> (000)	2152	724
absorption corrections	multi-scan, 0.87-1.00	multi-scan, 0.83-0.94
θ range, deg	2.2 - 30.0	1.7 - 30.6
no. of rflns measd	89809	18580
<i>R</i> _{int}	0.046	0.019
no. of rflns unique	15529	9317
no. of rflns <i>I</i> > 2 σ (<i>I</i>)	12808	8570
no. of params / restraints	604 / 0	377 / 2
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0456	0.0267
<i>R</i> ₁ (all data)	0.0581	0.0302
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.1058	0.0656
<i>wR</i> ₂ (all data)	0.1125	0.0676
Diff.Fourier.peak s min/max, eÅ ⁻³	-1.00 / 1.49	-0.84 / 1.15

Crystal structure of **3**

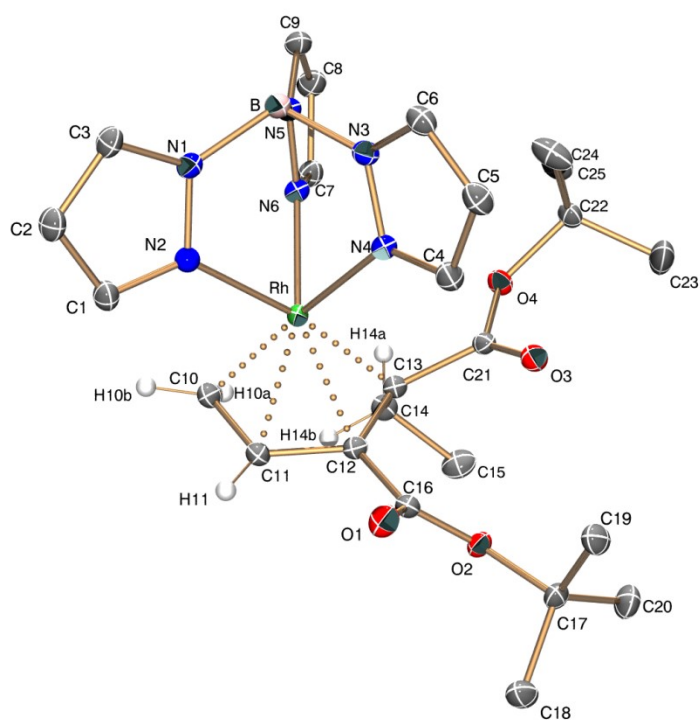


Figure S1: Structural diagram of the asymmetric unit of **3** showing 50% ellipsoids and the atom numbering. Most H-atoms omitted for clarity.

Table S3: Geometric data (Å, deg) of **3**.

Bond distances

Rh—C10	2.0819 (15)	C12—C13	1.460 (2)
Rh—N6	2.1007 (12)	C12—C16	1.507 (2)
Rh—C11	2.1094 (14)	C13—C21	1.503 (2)
Rh—C12	2.1103 (14)	C13—C14	1.529 (2)
Rh—N2	2.1210 (13)	C14—C15	1.532 (2)
Rh—C13	2.1287 (14)	C14—H14A	0.9900
Rh—N4	2.1817 (13)	C14—H14B	0.9900
B—N5	1.536 (2)	C15—H15A	0.9800
B—N3	1.541 (2)	C15—H15B	0.9800
B—N1	1.549 (2)	C15—H15C	0.9800
B—H0B	1.0000	C16—O1	1.2107 (18)
N1—C3	1.3514 (19)	C16—O2	1.3324 (17)

N1—N2	1.3641 (17)	O2—C17	1.4801 (17)
N2—C1	1.3357 (19)	C17—C18	1.516 (2)
C1—C2	1.401 (2)	C17—C20	1.521 (2)
C1—H1	0.9500	C17—C19	1.522 (2)
C2—C3	1.378 (2)	C18—H18A	0.9800
C2—H2	0.9500	C18—H18B	0.9800
C3—H3	0.9500	C18—H18C	0.9800
N3—C6	1.3491 (19)	C19—H19A	0.9800
N3—N4	1.3673 (17)	C19—H19B	0.9800
N4—C4	1.3325 (19)	C19—H19C	0.9800
C4—C5	1.399 (2)	C20—H20A	0.9800
C4—H4	0.9500	C20—H20B	0.9800
C5—C6	1.378 (2)	C20—H20C	0.9800
C5—H5	0.9500	C21—O3	1.2076 (18)
C6—H6	0.9500	C21—O4	1.3514 (17)
N5—C9	1.3484 (19)	O4—C22	1.4698 (17)
N5—N6	1.3586 (17)	C22—C23	1.517 (2)
N6—C7	1.3328 (19)	C22—C25	1.521 (2)
C7—C8	1.398 (2)	C22—C24	1.522 (2)
C7—H7	0.9500	C23—H23A	0.9800
C8—C9	1.382 (2)	C23—H23B	0.9800
C8—H8	0.9500	C23—H23C	0.9800
C9—H9	0.9500	C24—H24A	0.9800
C10—C11	1.448 (2)	C24—H24B	0.9800
C10—H10A	0.9600	C24—H24C	0.9800
C10—H10B	0.9599	C25—H25A	0.9800
C11—C12	1.423 (2)	C25—H25B	0.9800
C11—H11	0.9600 (1)	C25—H25C	0.9800

Bond angles

C10—Rh—N6	104.66 (5)	C10—C11—H11	120.9 (12)
C10—Rh—C11	40.41 (6)	Rh—C11—H11	124.8 (12)
N6—Rh—C11	143.80 (5)	C11—C12—C13	116.22 (13)
C10—Rh—C12	72.37 (6)	C11—C12—C16	117.73 (13)
N6—Rh—C12	141.20 (5)	C13—C12—C16	126.05 (13)
C11—Rh—C12	39.42 (5)	C11—C12—Rh	70.26 (8)

C10—Rh—N2	92.49 (5)	C13—C12—Rh	70.53 (8)
N6—Rh—N2	86.26 (5)	C16—C12—Rh	129.03 (10)
C11—Rh—N2	101.48 (5)	C12—C13—C21	117.72 (12)
C12—Rh—N2	132.01 (5)	C12—C13—C14	119.65 (12)
C10—Rh—C13	82.44 (6)	C21—C13—C14	113.10 (12)
N6—Rh—C13	101.11 (5)	C12—C13—Rh	69.17 (8)
C11—Rh—C13	70.57 (6)	C21—C13—Rh	104.78 (9)
C12—Rh—C13	40.29 (5)	C14—C13—Rh	125.40 (10)
N2—Rh—C13	171.89 (5)	C13—C14—C15	110.02 (13)
C10—Rh—N4	166.42 (5)	C13—C14—H14A	109.7
N6—Rh—N4	86.97 (5)	C15—C14—H14A	109.7
C11—Rh—N4	129.01 (5)	C13—C14—H14B	109.7
C12—Rh—N4	103.04 (5)	C15—C14—H14B	109.7
N2—Rh—N4	81.13 (5)	H14A—C14—H14B	108.2
C13—Rh—N4	102.46 (5)	C14—C15—H15A	109.5
N5—B—N3	109.23 (12)	C14—C15—H15B	109.5
N5—B—N1	108.75 (12)	H15A—C15—H15B	109.5
N3—B—N1	106.80 (12)	C14—C15—H15C	109.5
N5—B—H0B	110.7	H15A—C15—H15C	109.5
N3—B—H0B	110.7	H15B—C15—H15C	109.5
N1—B—H0B	110.7	O1—C16—O2	126.37 (13)
C3—N1—N2	109.41 (12)	O1—C16—C12	124.69 (13)
C3—N1—B	130.04 (13)	O2—C16—C12	108.80 (12)
N2—N1—B	120.25 (12)	C16—O2—C17	122.05 (12)
C1—N2—N1	106.73 (12)	O2—C17—C18	109.30 (12)
C1—N2—Rh	134.01 (10)	O2—C17—C20	101.98 (12)
N1—N2—Rh	119.26 (9)	C18—C17—C20	111.34 (13)
N2—C1—C2	110.54 (13)	O2—C17—C19	110.87 (12)
N2—C1—H1	124.7	C18—C17—C19	111.93 (13)
C2—C1—H1	124.7	C20—C17—C19	110.98 (13)
C3—C2—C1	104.48 (13)	C17—C18—H18A	109.5
C3—C2—H2	127.8	C17—C18—H18B	109.5
C1—C2—H2	127.8	H18A—C18—H18B	109.5
N1—C3—C2	108.84 (14)	C17—C18—H18C	109.5
N1—C3—H3	125.6	H18A—C18—H18C	109.5
C2—C3—H3	125.6	H18B—C18—H18C	109.5

C6—N3—N4	109.66 (12)	C17—C19—H19A	109.5
C6—N3—B	128.11 (13)	C17—C19—H19B	109.5
N4—N3—B	120.34 (12)	H19A—C19—H19B	109.5
C4—N4—N3	106.50 (12)	C17—C19—H19C	109.5
C4—N4—Rh	135.05 (10)	H19A—C19—H19C	109.5
N3—N4—Rh	117.76 (9)	H19B—C19—H19C	109.5
N4—C4—C5	110.59 (13)	C17—C20—H20A	109.5
N4—C4—H4	124.7	C17—C20—H20B	109.5
C5—C4—H4	124.7	H20A—C20—H20B	109.5
C6—C5—C4	104.75 (13)	C17—C20—H20C	109.5
C6—C5—H5	127.6	H20A—C20—H20C	109.5
C4—C5—H5	127.6	H20B—C20—H20C	109.5
N3—C6—C5	108.49 (13)	O3—C21—O4	124.44 (13)
N3—C6—H6	125.8	O3—C21—C13	126.59 (13)
C5—C6—H6	125.8	O4—C21—C13	108.93 (12)
C9—N5—N6	109.60 (12)	C21—O4—C22	121.39 (11)
C9—N5—B	131.20 (13)	O4—C22—C23	111.18 (13)
N6—N5—B	119.03 (12)	O4—C22—C25	102.16 (12)
C7—N6—N5	107.06 (12)	C23—C22—C25	110.67 (14)
C7—N6—Rh	131.47 (10)	O4—C22—C24	109.42 (12)
N5—N6—Rh	121.23 (9)	C23—C22—C24	112.92 (16)
N6—C7—C8	110.21 (14)	C25—C22—C24	109.96 (14)
N6—C7—H7	124.9	C22—C23—H23A	109.5
C8—C7—H7	124.9	C22—C23—H23B	109.5
C9—C8—C7	104.76 (13)	H23A—C23—H23B	109.5
C9—C8—H8	127.6	C22—C23—H23C	109.5
C7—C8—H8	127.6	H23A—C23—H23C	109.5
N5—C9—C8	108.37 (13)	H23B—C23—H23C	109.5
N5—C9—H9	125.8	C22—C24—H24A	109.5
C8—C9—H9	125.8	C22—C24—H24B	109.5
C11—C10—Rh	70.81 (8)	H24A—C24—H24B	109.5
C11—C10—H10A	122.1	C22—C24—H24C	109.5
Rh—C10—H10A	111.8	H24A—C24—H24C	109.5
C11—C10—H10B	116.2	H24B—C24—H24C	109.5
Rh—C10—H10B	115.2	C22—C25—H25A	109.5
H10A—C10—H10B	113.5	C22—C25—H25B	109.5

C12—C11—C10	119.10 (13)	H25A—C25—H25B	109.5
C12—C11—Rh	70.32 (8)	C22—C25—H25C	109.5
C10—C11—Rh	68.77 (8)	H25A—C25—H25C	109.5
C12—C11—H11	119.2 (12)	H25B—C25—H25C	109.5

Crystal structure of **4**

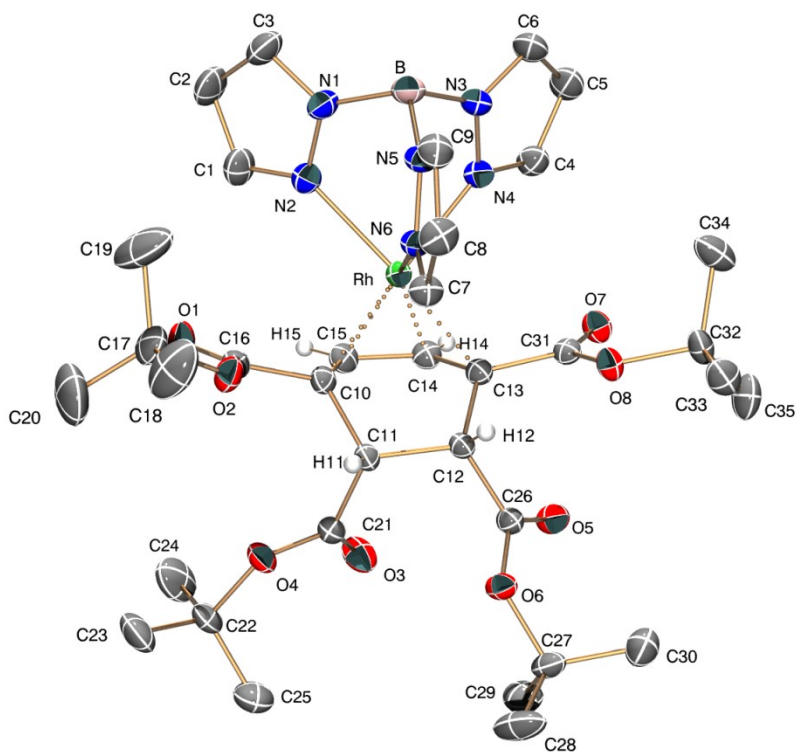


Figure S2a: Structural diagram of the asymmetric unit of **4** showing 50% ellipsoids and the atom numbering. Most H-atoms and the *n*-hexane solvent molecule were omitted for clarity.

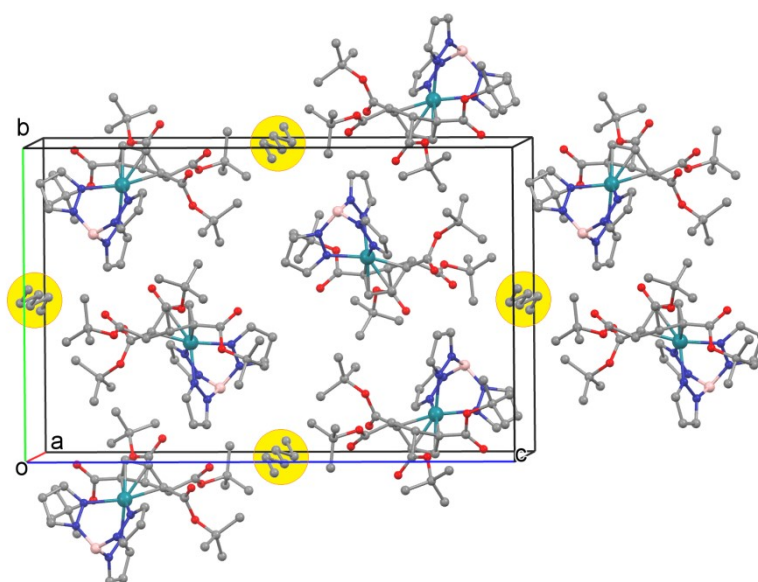


Figure S2b: Packing diagram of **4** viewed approximately down the *a*-axis showing the Rh-complexes and the highlighted *n*-hexane solvent molecules. H-atoms omitted for clarity.

Table S4: Geometric data (Å, deg) of **4**.

Bond distances

Rh—C15	2.102 (2)	C19—H19C	0.9800
Rh—C10	2.106 (2)	C20—H20A	0.9800
Rh—C13	2.106 (2)	C20—H20B	0.9800
Rh—N6	2.1069 (18)	C20—H20C	0.9800
Rh—C14	2.114 (2)	C21—O3	1.204 (3)
Rh—N4	2.1408 (19)	C21—O4	1.338 (3)
Rh—N2	2.1510 (19)	O4—C22	1.474 (3)
B—N5	1.532 (3)	C22—C24	1.512 (4)
B—N3	1.534 (3)	C22—C25	1.513 (4)
B—N1	1.549 (3)	C22—C23	1.513 (4)
B—H0B	1.0000	C23—H23A	0.9800
N1—C3	1.351 (3)	C23—H23B	0.9800
N1—N2	1.361 (3)	C23—H23C	0.9800
N2—C1	1.333 (3)	C24—H24A	0.9800
C1—C2	1.394 (4)	C24—H24B	0.9800
C1—H1	0.9500	C24—H24C	0.9800
C2—C3	1.373 (4)	C25—H25A	0.9800
C2—H2	0.9500	C25—H25B	0.9800
C3—H3	0.9500	C25—H25C	0.9800
N3—C6	1.353 (3)	C26—O5	1.201 (3)
N3—N4	1.367 (3)	C26—O6	1.343 (3)
N4—C4	1.336 (3)	O6—C27	1.485 (3)
C4—C5	1.392 (4)	C27—C29	1.514 (4)
C4—H4	0.9500	C27—C28	1.516 (4)
C5—C6	1.369 (4)	C27—C30	1.520 (4)
C5—H5	0.9500	C28—H28A	0.9800
C6—H6	0.9500	C28—H28B	0.9800
N5—C9	1.345 (3)	C28—H28C	0.9800
N5—N6	1.359 (2)	C29—H29A	0.9800
N6—C7	1.333 (3)	C29—H29B	0.9800
C7—C8	1.389 (3)	C29—H29C	0.9800
C7—H7	0.9500	C30—H30A	0.9800
C8—C9	1.376 (4)	C30—H30B	0.9800
C8—H8	0.9500	C30—H30C	0.9800

C9—H9	0.9500	C31—O7	1.203 (3)
C10—C15	1.443 (3)	C31—O8	1.357 (3)
C10—C16	1.497 (3)	O8—C32	1.474 (3)
C10—C11	1.538 (3)	C32—C33	1.514 (3)
C11—C21	1.521 (3)	C32—C35	1.517 (3)
C11—C12	1.541 (3)	C32—C34	1.518 (3)
C11—H11	1.0000	C33—H33A	0.9800
C12—C13	1.521 (3)	C33—H33B	0.9800
C12—C26	1.527 (3)	C33—H33C	0.9800
C12—H12	1.0000	C34—H34A	0.9800
C13—C14	1.447 (3)	C34—H34B	0.9800
C13—C31	1.489 (3)	C34—H34C	0.9800
C14—C15	1.409 (3)	C35—H35A	0.9800
C14—H14	0.9500	C35—H35B	0.9800
C15—H15	0.9500	C35—H35C	0.9800
C16—O1	1.205 (3)	C1S—C1S ⁱ	1.396 (13)
C16—O2	1.338 (3)	C1S—C2S	1.463 (9)
O2—C17	1.471 (3)	C1S—H1SA	0.9900
C17—C19	1.512 (4)	C1S—H1SB	0.9900
C17—C20	1.512 (4)	C2S—C3S	1.233 (9)
C17—C18	1.514 (4)	C2S—H2SA	0.9900
C18—H18A	0.9800	C2S—H2SB	0.9900
C18—H18B	0.9800	C3S—H3SA	0.9800
C18—H18C	0.9800	C3S—H3SB	0.9800
C19—H19A	0.9800	C3S—H3SC	0.9800
C19—H19B	0.9800		

Bond angles

C15—Rh—C10	40.12 (8)	C17—C18—H18B	109.5
C15—Rh—C13	69.39 (8)	H18A—C18—H18B	109.5
C10—Rh—C13	75.70 (8)	C17—C18—H18C	109.5
C15—Rh—N6	142.50 (8)	H18A—C18—H18C	109.5
C10—Rh—N6	102.40 (8)	H18B—C18—H18C	109.5
C13—Rh—N6	106.54 (8)	C17—C19—H19A	109.5
C15—Rh—C14	39.05 (9)	C17—C19—H19B	109.5
C10—Rh—C14	69.07 (9)	H19A—C19—H19B	109.5

C13—Rh—C14	40.10 (8)	C17—C19—H19C	109.5
N6—Rh—C14	146.20 (8)	H19A—C19—H19C	109.5
C15—Rh—N4	130.12 (8)	H19B—C19—H19C	109.5
C10—Rh—N4	169.93 (8)	C17—C20—H20A	109.5
C13—Rh—N4	99.02 (8)	C17—C20—H20B	109.5
N6—Rh—N4	87.27 (7)	H20A—C20—H20B	109.5
C14—Rh—N4	101.32 (8)	C17—C20—H20C	109.5
C15—Rh—N2	100.36 (8)	H20A—C20—H20C	109.5
C10—Rh—N2	100.72 (8)	H20B—C20—H20C	109.5
C13—Rh—N2	167.99 (8)	O3—C21—O4	126.0 (2)
N6—Rh—N2	85.38 (7)	O3—C21—C11	124.9 (2)
C14—Rh—N2	127.89 (8)	O4—C21—C11	109.04 (18)
N4—Rh—N2	82.68 (7)	C21—O4—C22	122.17 (19)
N5—B—N3	108.58 (19)	O4—C22—C24	109.1 (2)
N5—B—N1	109.3 (2)	O4—C22—C25	110.5 (2)
N3—B—N1	107.0 (2)	C24—C22—C25	111.9 (3)
N5—B—H0B	110.6	O4—C22—C23	102.1 (2)
N3—B—H0B	110.6	C24—C22—C23	112.0 (2)
N1—B—H0B	110.6	C25—C22—C23	110.8 (2)
C3—N1—N2	109.1 (2)	C22—C23—H23A	109.5
C3—N1—B	128.9 (2)	C22—C23—H23B	109.5
N2—N1—B	121.00 (18)	H23A—C23—H23B	109.5
C1—N2—N1	107.03 (19)	C22—C23—H23C	109.5
C1—N2—Rh	134.20 (17)	H23A—C23—H23C	109.5
N1—N2—Rh	117.86 (14)	H23B—C23—H23C	109.5
N2—C1—C2	110.3 (2)	C22—C24—H24A	109.5
N2—C1—H1	124.9	C22—C24—H24B	109.5
C2—C1—H1	124.9	H24A—C24—H24B	109.5
C3—C2—C1	104.8 (2)	C22—C24—H24C	109.5
C3—C2—H2	127.6	H24A—C24—H24C	109.5
C1—C2—H2	127.6	H24B—C24—H24C	109.5
N1—C3—C2	108.7 (2)	C22—C25—H25A	109.5
N1—C3—H3	125.6	C22—C25—H25B	109.5
C2—C3—H3	125.6	H25A—C25—H25B	109.5
C6—N3—N4	109.3 (2)	C22—C25—H25C	109.5
C6—N3—B	130.1 (2)	H25A—C25—H25C	109.5

N4—N3—B	120.05 (19)	H25B—C25—H25C	109.5
C4—N4—N3	106.26 (19)	O5—C26—O6	125.4 (2)
C4—N4—Rh	135.03 (16)	O5—C26—C12	124.4 (2)
N3—N4—Rh	118.68 (14)	O6—C26—C12	110.01 (18)
N4—C4—C5	110.8 (2)	C26—O6—C27	119.99 (17)
N4—C4—H4	124.6	O6—C27—C29	110.0 (2)
C5—C4—H4	124.6	O6—C27—C28	102.27 (18)
C6—C5—C4	104.9 (2)	C29—C27—C28	110.9 (2)
C6—C5—H5	127.6	O6—C27—C30	108.76 (19)
C4—C5—H5	127.6	C29—C27—C30	113.6 (2)
N3—C6—C5	108.7 (2)	C28—C27—C30	110.7 (2)
N3—C6—H6	125.6	C27—C28—H28A	109.5
C5—C6—H6	125.6	C27—C28—H28B	109.5
C9—N5—N6	109.81 (19)	H28A—C28—H28B	109.5
C9—N5—B	130.8 (2)	C27—C28—H28C	109.5
N6—N5—B	119.40 (18)	H28A—C28—H28C	109.5
C7—N6—N5	106.39 (18)	H28B—C28—H28C	109.5
C7—N6—Rh	133.22 (15)	C27—C29—H29A	109.5
N5—N6—Rh	120.38 (14)	C27—C29—H29B	109.5
N6—C7—C8	110.6 (2)	H29A—C29—H29B	109.5
N6—C7—H7	124.7	C27—C29—H29C	109.5
C8—C7—H7	124.7	H29A—C29—H29C	109.5
C9—C8—C7	104.8 (2)	H29B—C29—H29C	109.5
C9—C8—H8	127.6	C27—C30—H30A	109.5
C7—C8—H8	127.6	C27—C30—H30B	109.5
N5—C9—C8	108.3 (2)	H30A—C30—H30B	109.5
N5—C9—H9	125.8	C27—C30—H30C	109.5
C8—C9—H9	125.8	H30A—C30—H30C	109.5
C15—C10—C16	117.99 (19)	H30B—C30—H30C	109.5
C15—C10—C11	117.14 (18)	O7—C31—O8	124.6 (2)
C16—C10—C11	116.31 (19)	O7—C31—C13	126.2 (2)
C15—C10—Rh	69.77 (12)	O8—C31—C13	109.18 (18)
C16—C10—Rh	113.66 (14)	C31—O8—C32	121.84 (17)
C11—C10—Rh	113.23 (13)	O8—C32—C33	101.57 (18)
C21—C11—C10	106.01 (17)	O8—C32—C35	110.36 (19)
C21—C11—C12	114.43 (17)	C33—C32—C35	110.8 (2)

C10—C11—C12	108.52 (17)	O8—C32—C34	109.2 (2)
C21—C11—H11	109.2	C33—C32—C34	111.3 (2)
C10—C11—H11	109.2	C35—C32—C34	113.0 (2)
C12—C11—H11	109.2	C32—C33—H33A	109.5
C13—C12—C26	110.25 (17)	C32—C33—H33B	109.5
C13—C12—C11	110.86 (17)	H33A—C33—H33B	109.5
C26—C12—C11	116.59 (17)	C32—C33—H33C	109.5
C13—C12—H12	106.1	H33A—C33—H33C	109.5
C26—C12—H12	106.1	H33B—C33—H33C	109.5
C11—C12—H12	106.1	C32—C34—H34A	109.5
C14—C13—C31	116.92 (19)	C32—C34—H34B	109.5
C14—C13—C12	120.30 (19)	H34A—C34—H34B	109.5
C31—C13—C12	114.80 (18)	C32—C34—H34C	109.5
C14—C13—Rh	70.25 (12)	H34A—C34—H34C	109.5
C31—C13—Rh	117.09 (14)	H34B—C34—H34C	109.5
C12—C13—Rh	109.48 (14)	C32—C35—H35A	109.5
C15—C14—C13	114.0 (2)	C32—C35—H35B	109.5
C15—C14—Rh	69.99 (12)	H35A—C35—H35B	109.5
C13—C14—Rh	69.65 (12)	C32—C35—H35C	109.5
C15—C14—H14	123.0	H35A—C35—H35C	109.5
C13—C14—H14	123.0	H35B—C35—H35C	109.5
Rh—C14—H14	129.3	C1S ⁱ —C1S—C2S	107.5 (5)
C14—C15—C10	114.03 (19)	C1S ⁱ —C1S—H1SA	110.2
C14—C15—Rh	70.96 (12)	C2S—C1S—H1SA	110.2
C10—C15—Rh	70.11 (12)	C1S ⁱ —C1S—H1SB	110.2
C14—C15—H15	123.0	C2S—C1S—H1SB	110.2
C10—C15—H15	123.0	H1SA—C1S—H1SB	108.5
Rh—C15—H15	127.7	C3S—C2S—C1S	103.7 (6)
O1—C16—O2	125.6 (2)	C3S—C2S—H2SA	111.0
O1—C16—C10	124.3 (2)	C1S—C2S—H2SA	111.0
O2—C16—C10	109.98 (18)	C3S—C2S—H2SB	111.0
C16—O2—C17	122.65 (19)	C1S—C2S—H2SB	111.0
O2—C17—C19	108.5 (2)	H2SA—C2S—H2SB	109.0
O2—C17—C20	111.1 (2)	C2S—C3S—H3SA	109.5
C19—C17—C20	113.4 (3)	C2S—C3S—H3SB	109.5
O2—C17—C18	102.4 (2)	H3SA—C3S—H3SB	109.5

C19—C17—C18	110.6 (3)	C2S—C3S—H3SC	109.5
C20—C17—C18	110.4 (3)	H3SA—C3S—H3SC	109.5
C17—C18—H18A	109.5	H3SB—C3S—H3SC	109.5

Crystal structure of **5**

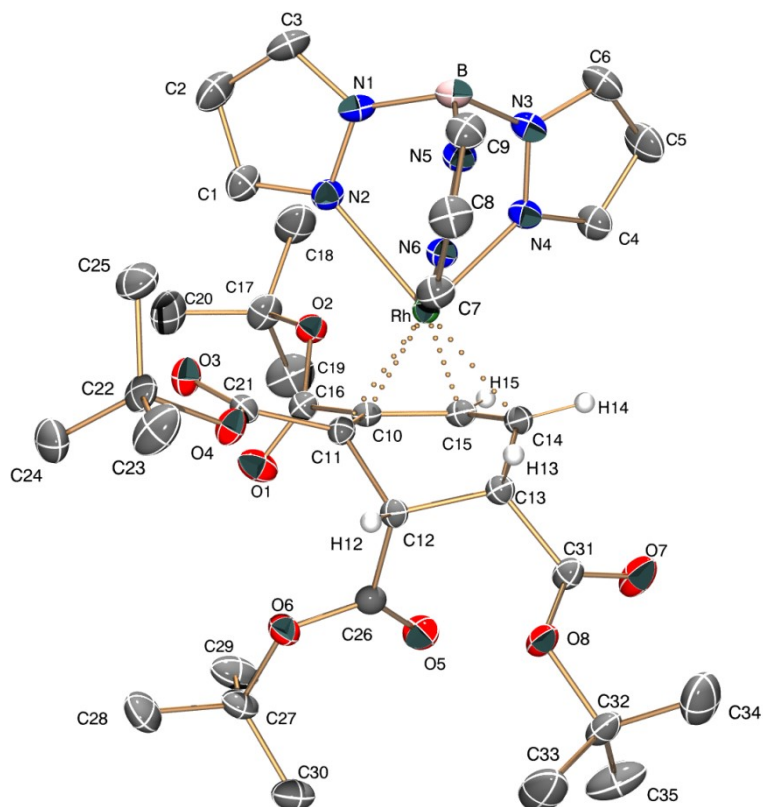


Figure S3: Structural diagram of the asymmetric unit of **5** showing 40% ellipsoids and the atom numbering. Most H-atoms omitted for clarity.

Table S5: Geometric data (Å, deg) of **5**.

Bond distances

Rh—C14	2.0881 (17)	C18—H18A	0.9800
Rh—C10	2.0891 (17)	C18—H18B	0.9800
Rh—C15	2.1036 (17)	C18—H18C	0.9800
Rh—N4	2.1072 (16)	C19—H19A	0.9800
Rh—C11	2.1330 (18)	C19—H19B	0.9800
Rh—N6	2.1376 (15)	C19—H19C	0.9800
Rh—N2	2.1972 (15)	C20—H20A	0.9800
B—N1	1.524 (3)	C20—H20B	0.9800
B—N5	1.538 (3)	C20—H20C	0.9800
B—N3	1.543 (3)	C21—O3	1.211 (2)
B—H0B	1.0000	C21—O4	1.350 (2)

N1—C3	1.347 (2)	O4—C22	1.473 (2)
N1—N2	1.372 (2)	C22—C24	1.509 (3)
N2—C1	1.332 (2)	C22—C23	1.518 (3)
C1—C2	1.386 (3)	C22—C25	1.523 (3)
C1—H1	0.9500	C23—H23A	0.9800
C2—C3	1.370 (3)	C23—H23B	0.9800
C2—H2	0.9500	C23—H23C	0.9800
C3—H3	0.9500	C24—H24A	0.9800
N3—C6	1.349 (3)	C24—H24B	0.9800
N3—N4	1.357 (2)	C24—H24C	0.9800
N4—C4	1.330 (2)	C25—H25A	0.9800
C4—C5	1.391 (3)	C25—H25B	0.9800
C4—H4	0.9500	C25—H25C	0.9800
C5—C6	1.366 (3)	C26—O5	1.207 (2)
C5—H5	0.9500	C26—O6	1.340 (2)
C6—H6	0.9500	O6—C27	1.485 (2)
N5—C9	1.349 (2)	C27—C29	1.513 (3)
N5—N6	1.360 (2)	C27—C28	1.518 (3)
N6—C7	1.337 (2)	C27—C30	1.520 (3)
C7—C8	1.394 (3)	C28—H28A	0.9800
C7—H7	0.9500	C28—H28B	0.9800
C8—C9	1.375 (3)	C28—H28C	0.9800
C8—H8	0.9500	C29—H29A	0.9800
C9—H9	0.9500	C29—H29B	0.9800
C10—C15	1.417 (3)	C29—H29C	0.9800
C10—C11	1.459 (2)	C30—H30A	0.9800
C10—C16	1.506 (2)	C30—H30B	0.9800
C11—C21	1.477 (2)	C30—H30C	0.9800
C11—C12	1.546 (2)	C31—O7	1.204 (2)
C12—C26	1.524 (2)	C31—O8	1.336 (2)
C12—C13	1.532 (2)	O8—C32	1.484 (2)
C12—H12	1.0000	C32—C33	1.506 (3)
C13—C14	1.515 (2)	C32—C35	1.507 (3)
C13—C31	1.523 (2)	C32—C34	1.509 (3)
C13—H13	1.0000	C33—H33A	0.9800
C14—C15	1.439 (2)	C33—H33B	0.9800

C14—H14	1.0000	C33—H33C	0.9800
C15—H15	1.0000	C34—H34A	0.9800
C16—O1	1.200 (2)	C34—H34B	0.9800
C16—O2	1.332 (2)	C34—H34C	0.9800
O2—C17	1.485 (2)	C35—H35A	0.9800
C17—C20	1.514 (3)	C35—H35B	0.9800
C17—C19	1.518 (3)	C35—H35C	0.9800
C17—C18	1.519 (3)		

Bond angles

C14—Rh—C10	70.52 (7)	O2—C16—C10	111.43 (15)
C14—Rh—C15	40.15 (7)	C16—O2—C17	120.77 (15)
C10—Rh—C15	39.51 (7)	O2—C17—C20	110.05 (16)
C14—Rh—N4	92.57 (7)	O2—C17—C19	109.96 (16)
C10—Rh—N4	128.07 (7)	C20—C17—C19	112.2 (2)
C15—Rh—N4	97.05 (7)	O2—C17—C18	101.67 (17)
C14—Rh—C11	75.82 (7)	C20—C17—C18	111.06 (18)
C10—Rh—C11	40.42 (6)	C19—C17—C18	111.40 (19)
C15—Rh—C11	68.78 (7)	C17—C18—H18A	109.5
N4—Rh—C11	165.77 (6)	C17—C18—H18B	109.5
C14—Rh—N6	106.77 (6)	H18A—C18—H18B	109.5
C10—Rh—N6	143.71 (6)	C17—C18—H18C	109.5
C15—Rh—N6	146.52 (6)	H18A—C18—H18C	109.5
N4—Rh—N6	87.77 (6)	H18B—C18—H18C	109.5
C11—Rh—N6	103.30 (6)	C17—C19—H19A	109.5
C14—Rh—N2	171.69 (6)	C17—C19—H19B	109.5
C10—Rh—N2	104.52 (6)	H19A—C19—H19B	109.5
C15—Rh—N2	132.09 (6)	C17—C19—H19C	109.5
N4—Rh—N2	85.36 (6)	H19A—C19—H19C	109.5
C11—Rh—N2	104.94 (6)	H19B—C19—H19C	109.5
N6—Rh—N2	81.22 (6)	C17—C20—H20A	109.5
N1—B—N5	107.56 (16)	C17—C20—H20B	109.5
N1—B—N3	109.70 (16)	H20A—C20—H20B	109.5
N5—B—N3	108.87 (16)	C17—C20—H20C	109.5
N1—B—H0B	110.2	H20A—C20—H20C	109.5
N5—B—H0B	110.2	H20B—C20—H20C	109.5

N3—B—H0B	110.2	O3—C21—O4	124.63 (17)
C3—N1—N2	109.37 (16)	O3—C21—C11	125.07 (17)
C3—N1—B	129.24 (17)	O4—C21—C11	110.23 (15)
N2—N1—B	121.28 (15)	C21—O4—C22	121.37 (14)
C1—N2—N1	106.16 (15)	O4—C22—C24	111.15 (16)
C1—N2—Rh	137.21 (13)	O4—C22—C23	101.96 (15)
N1—N2—Rh	116.63 (12)	C24—C22—C23	110.75 (18)
N2—C1—C2	110.75 (19)	O4—C22—C25	108.90 (16)
N2—C1—H1	124.6	C24—C22—C25	112.73 (18)
C2—C1—H1	124.6	C23—C22—C25	110.82 (17)
C3—C2—C1	105.21 (18)	C22—C23—H23A	109.5
C3—C2—H2	127.4	C22—C23—H23B	109.5
C1—C2—H2	127.4	H23A—C23—H23B	109.5
N1—C3—C2	108.50 (18)	C22—C23—H23C	109.5
N1—C3—H3	125.8	H23A—C23—H23C	109.5
C2—C3—H3	125.8	H23B—C23—H23C	109.5
C6—N3—N4	108.94 (16)	C22—C24—H24A	109.5
C6—N3—B	131.24 (17)	C22—C24—H24B	109.5
N4—N3—B	119.80 (16)	H24A—C24—H24B	109.5
C4—N4—N3	107.20 (16)	C22—C24—H24C	109.5
C4—N4—Rh	132.44 (13)	H24A—C24—H24C	109.5
N3—N4—Rh	120.00 (12)	H24B—C24—H24C	109.5
N4—C4—C5	110.00 (18)	C22—C25—H25A	109.5
N4—C4—H4	125.0	C22—C25—H25B	109.5
C5—C4—H4	125.0	H25A—C25—H25B	109.5
C6—C5—C4	105.09 (19)	C22—C25—H25C	109.5
C6—C5—H5	127.5	H25A—C25—H25C	109.5
C4—C5—H5	127.5	H25B—C25—H25C	109.5
N3—C6—C5	108.77 (18)	O5—C26—O6	125.99 (17)
N3—C6—H6	125.6	O5—C26—C12	124.81 (17)
C5—C6—H6	125.6	O6—C26—C12	109.17 (15)
C9—N5—N6	109.57 (15)	C26—O6—C27	121.46 (15)
C9—N5—B	130.88 (16)	O6—C27—C29	109.66 (16)
N6—N5—B	118.76 (14)	O6—C27—C28	102.03 (16)
C7—N6—N5	106.39 (14)	C29—C27—C28	110.96 (19)
C7—N6—Rh	133.52 (13)	O6—C27—C30	109.88 (16)

N5—N6—Rh	120.06 (11)	C29—C27—C30	112.87 (18)
N6—C7—C8	110.74 (17)	C28—C27—C30	110.91 (18)
N6—C7—H7	124.6	C27—C28—H28A	109.5
C8—C7—H7	124.6	C27—C28—H28B	109.5
C9—C8—C7	104.53 (17)	H28A—C28—H28B	109.5
C9—C8—H8	127.7	C27—C28—H28C	109.5
C7—C8—H8	127.7	H28A—C28—H28C	109.5
N5—C9—C8	108.76 (17)	H28B—C28—H28C	109.5
N5—C9—H9	125.6	C27—C29—H29A	109.5
C8—C9—H9	125.6	C27—C29—H29B	109.5
C15—C10—C11	112.60 (15)	H29A—C29—H29B	109.5
C15—C10—C16	120.84 (16)	C27—C29—H29C	109.5
C11—C10—C16	126.38 (16)	H29A—C29—H29C	109.5
C15—C10—Rh	70.80 (10)	H29B—C29—H29C	109.5
C11—C10—Rh	71.41 (10)	C27—C30—H30A	109.5
C16—C10—Rh	129.64 (12)	C27—C30—H30B	109.5
C10—C11—C21	118.51 (15)	H30A—C30—H30B	109.5
C10—C11—C12	115.80 (15)	C27—C30—H30C	109.5
C21—C11—C12	118.46 (15)	H30A—C30—H30C	109.5
C10—C11—Rh	68.17 (10)	H30B—C30—H30C	109.5
C21—C11—Rh	112.80 (12)	O7—C31—O8	125.44 (17)
C12—C11—Rh	112.40 (11)	O7—C31—C13	124.26 (17)
C26—C12—C13	113.18 (14)	O8—C31—C13	110.01 (15)
C26—C12—C11	106.98 (14)	C31—O8—C32	121.21 (14)
C13—C12—C11	108.30 (14)	O8—C32—C33	102.66 (15)
C26—C12—H12	109.4	O8—C32—C35	110.43 (16)
C13—C12—H12	109.4	C33—C32—C35	111.0 (2)
C11—C12—H12	109.4	O8—C32—C34	108.73 (17)
C14—C13—C31	113.75 (15)	C33—C32—C34	109.84 (19)
C14—C13—C12	109.63 (14)	C35—C32—C34	113.6 (2)
C31—C13—C12	116.46 (15)	C32—C33—H33A	109.5
C14—C13—H13	105.3	C32—C33—H33B	109.5
C31—C13—H13	105.3	H33A—C33—H33B	109.5
C12—C13—H13	105.3	C32—C33—H33C	109.5
C15—C14—C13	122.77 (16)	H33A—C33—H33C	109.5
C15—C14—Rh	70.51 (10)	H33B—C33—H33C	109.5

C13—C14—Rh	107.00 (11)	C32—C34—H34A	109.5
C15—C14—H14	115.7	C32—C34—H34B	109.5
C13—C14—H14	115.7	H34A—C34—H34B	109.5
Rh—C14—H14	115.7	C32—C34—H34C	109.5
C10—C15—C14	115.20 (16)	H34A—C34—H34C	109.5
C10—C15—Rh	69.69 (10)	H34B—C34—H34C	109.5
C14—C15—Rh	69.34 (10)	C32—C35—H35A	109.5
C10—C15—H15	122.0	C32—C35—H35B	109.5
C14—C15—H15	122.0	H35A—C35—H35B	109.5
Rh—C15—H15	122.0	C32—C35—H35C	109.5
O1—C16—O2	126.48 (17)	H35A—C35—H35C	109.5
O1—C16—C10	122.00 (16)	H35B—C35—H35C	109.5

Crystal structure of **8**

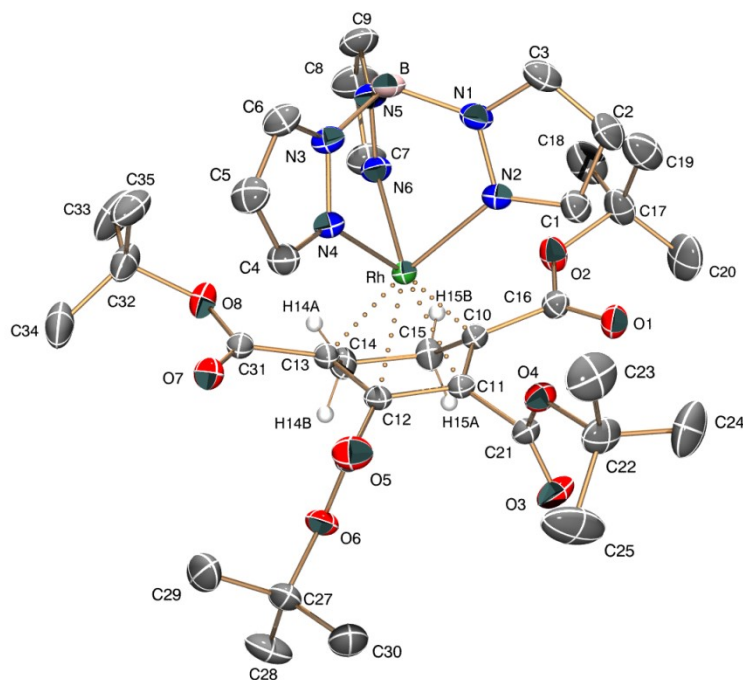


Figure S4a: Structural diagram of the asymmetric unit of **8** showing 50% ellipsoids and the atom numbering. Most H-atoms and the cocrystallized molecule of di-*tert*-butyl acetylenedicarboxylate (DTBAD) were omitted for clarity.

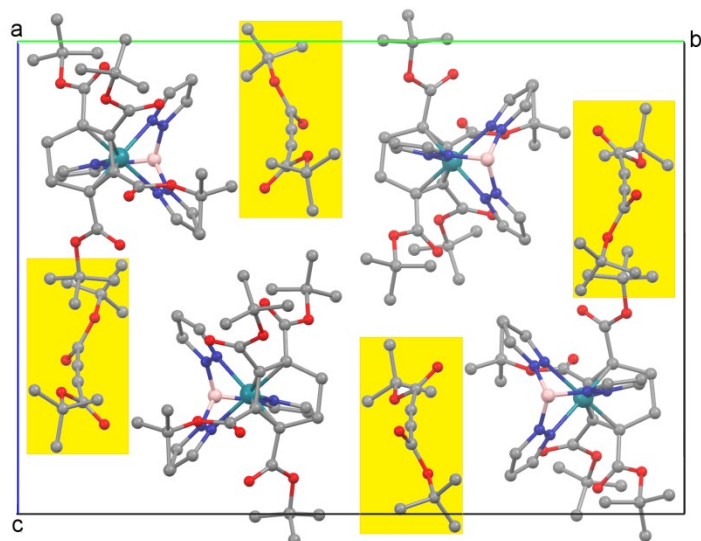


Figure S4b: Packing diagram of **8** in a view down the *a*-axis showing the disposition of the highlighted di-*tert*-butyl acetylenedicarboxylate (DTBAD) molecules between the Rh-complexes. H-atoms were omitted for clarity.

Table S6: Selected geometric data (Å, deg) of **8**.

Bond distances

Rh—C13	2.1035 (18)	C20—H20B	0.9800
Rh—C10	2.1126 (18)	C20—H20C	0.9800
Rh—C11	2.1159 (18)	C22—C24	1.499 (4)
Rh—N6	2.1163 (16)	C22—C25	1.509 (4)
Rh—C12	2.1170 (18)	C22—C23	1.512 (4)
Rh—N4	2.1341 (16)	C23—H23A	0.9800
Rh—N2	2.1661 (16)	C23—H23B	0.9800
O1—C16	1.210 (2)	C23—H23C	0.9800
O2—C16	1.337 (2)	C24—H24A	0.9800
O2—C17	1.470 (2)	C24—H24B	0.9800
O3—C21	1.204 (2)	C24—H24C	0.9800
O4—C21	1.325 (2)	C25—H25A	0.9800
O4—C22	1.492 (2)	C25—H25B	0.9800
O5—C26	1.192 (3)	C25—H25C	0.9800
O6—C26	1.337 (2)	C27—C29	1.518 (3)
O6—C27	1.479 (2)	C27—C30	1.520 (4)
O7—C31	1.206 (2)	C27—C28	1.524 (4)
O8—C31	1.343 (2)	C28—H28A	0.9800
O8—C32	1.481 (3)	C28—H28B	0.9800
N1—C3	1.344 (3)	C28—H28C	0.9800
N1—N2	1.365 (2)	C29—H29A	0.9800
N1—B	1.536 (3)	C29—H29B	0.9800
N2—C1	1.336 (3)	C29—H29C	0.9800
N3—C6	1.347 (3)	C30—H30A	0.9800
N3—N4	1.369 (2)	C30—H30B	0.9800
N3—B	1.537 (3)	C30—H30C	0.9800
N4—C4	1.331 (3)	C32—C33	1.513 (4)
N5—C9	1.347 (3)	C32—C35	1.513 (3)
N5—N6	1.355 (2)	C32—C34	1.522 (4)
N5—B	1.536 (3)	C33—H33A	0.9800
N6—C7	1.329 (3)	C33—H33B	0.9800
B—H0B	1.0000	C33—H33C	0.9800
C1—C2	1.397 (3)	C34—H34A	0.9800
C1—H1	0.9500	C34—H34B	0.9800

C2—C3	1.374 (3)	C34—H34C	0.9800
C2—H2	0.9500	C35—H35A	0.9800
C3—H3	0.9500	C35—H35B	0.9800
C4—C5	1.399 (3)	C35—H35C	0.9800
C4—H4	0.9500	O9—C38	1.203 (3)
C5—C6	1.375 (3)	O10—C38	1.316 (3)
C5—H5	0.9500	O10—C39	1.489 (3)
C6—H6	0.9500	O11—C43	1.195 (5)
C7—C8	1.395 (3)	O12—C43	1.324 (5)
C7—H7	0.9500	O12—C44	1.490 (4)
C8—C9	1.371 (4)	C36—C37	1.188 (4)
C8—H8	0.9500	C36—C38	1.462 (4)
C9—H9	0.9500	C37—C43	1.472 (4)
C10—C11	1.450 (3)	C39—C42	1.495 (5)
C10—C16	1.488 (3)	C39—C40	1.497 (4)
C10—C15	1.525 (3)	C39—C41	1.521 (5)
C11—C12	1.418 (3)	C40—H40A	0.9800
C11—C21	1.510 (3)	C40—H40B	0.9800
C12—C13	1.449 (3)	C40—H40C	0.9800
C12—C26	1.512 (3)	C41—H41A	0.9800
C13—C31	1.498 (3)	C41—H41B	0.9800
C13—C14	1.520 (3)	C41—H41C	0.9800
C14—C15	1.531 (3)	C42—H42A	0.9800
C14—H14A	0.9900	C42—H42B	0.9800
C14—H14B	0.9900	C42—H42C	0.9800
C15—H15A	0.9900	C44—C47	1.480 (5)
C15—H15B	0.9900	C44—C46	1.492 (8)
C17—C20	1.509 (4)	C44—C45	1.524 (9)
C17—C19	1.516 (4)	C45—H45A	0.9800
C17—C18	1.522 (3)	C45—H45B	0.9800
C18—H18A	0.9800	C45—H45C	0.9800
C18—H18B	0.9800	C46—H46A	0.9800
C18—H18C	0.9800	C46—H46B	0.9800
C19—H19A	0.9800	C46—H46C	0.9800
C19—H19B	0.9800	C47—H47A	0.9800
C19—H19C	0.9800	C47—H47B	0.9800

C20—H20A	0.9800	C47—H47C	0.9800
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Bond angles

C13—Rh—C10	75.49 (7)	O3—C21—O4	127.33 (18)
C13—Rh—C11	69.59 (7)	O3—C21—C11	120.66 (18)
C10—Rh—C11	40.10 (7)	O4—C21—C11	111.89 (15)
C13—Rh—N6	101.21 (7)	O4—C22—C24	109.3 (2)
C10—Rh—N6	102.38 (7)	O4—C22—C25	109.4 (2)
C11—Rh—N6	142.15 (7)	C24—C22—C25	114.5 (3)
C13—Rh—C12	40.15 (7)	O4—C22—C23	101.65 (18)
C10—Rh—C12	68.88 (7)	C24—C22—C23	110.7 (2)
C11—Rh—C12	39.15 (7)	C25—C22—C23	110.5 (2)
N6—Rh—C12	141.09 (7)	C22—C23—H23A	109.5
C13—Rh—N4	100.89 (7)	C22—C23—H23B	109.5
C10—Rh—N4	169.66 (7)	H23A—C23—H23B	109.5
C11—Rh—N4	129.59 (7)	C22—C23—H23C	109.5
N6—Rh—N4	87.78 (6)	H23A—C23—H23C	109.5
C12—Rh—N4	102.00 (7)	H23B—C23—H23C	109.5
C13—Rh—N2	173.08 (7)	C22—C24—H24A	109.5
C10—Rh—N2	100.51 (7)	C22—C24—H24B	109.5
C11—Rh—N2	103.68 (7)	H24A—C24—H24B	109.5
N6—Rh—N2	85.09 (6)	C22—C24—H24C	109.5
C12—Rh—N2	133.26 (7)	H24A—C24—H24C	109.5
N4—Rh—N2	82.07 (6)	H24B—C24—H24C	109.5
C16—O2—C17	122.39 (16)	C22—C25—H25A	109.5
C21—O4—C22	122.11 (16)	C22—C25—H25B	109.5
C26—O6—C27	121.57 (17)	H25A—C25—H25B	109.5
C31—O8—C32	121.34 (17)	C22—C25—H25C	109.5
C3—N1—N2	109.46 (18)	H25A—C25—H25C	109.5
C3—N1—B	129.07 (18)	H25B—C25—H25C	109.5
N2—N1—B	121.23 (16)	O5—C26—O6	127.16 (19)
C1—N2—N1	106.75 (16)	O5—C26—C12	127.39 (18)
C1—N2—Rh	135.97 (14)	O6—C26—C12	105.32 (17)
N1—N2—Rh	117.27 (12)	O6—C27—C29	108.80 (18)
C6—N3—N4	109.14 (17)	O6—C27—C30	109.86 (19)
C6—N3—B	128.92 (18)	C29—C27—C30	113.2 (2)

N4—N3—B	120.28 (16)	O6—C27—C28	101.7 (2)
C4—N4—N3	106.65 (16)	C29—C27—C28	112.0 (2)
C4—N4—Rh	134.35 (13)	C30—C27—C28	110.7 (2)
N3—N4—Rh	118.55 (12)	C27—C28—H28A	109.5
C9—N5—N6	109.83 (18)	C27—C28—H28B	109.5
C9—N5—B	130.92 (18)	H28A—C28—H28B	109.5
N6—N5—B	118.81 (16)	C27—C28—H28C	109.5
C7—N6—N5	106.66 (17)	H28A—C28—H28C	109.5
C7—N6—Rh	132.33 (15)	H28B—C28—H28C	109.5
N5—N6—Rh	120.86 (13)	C27—C29—H29A	109.5
N5—B—N1	107.81 (17)	C27—C29—H29B	109.5
N5—B—N3	110.22 (17)	H29A—C29—H29B	109.5
N1—B—N3	107.36 (16)	C27—C29—H29C	109.5
N5—B—H0B	110.5	H29A—C29—H29C	109.5
N1—B—H0B	110.5	H29B—C29—H29C	109.5
N3—B—H0B	110.5	C27—C30—H30A	109.5
N2—C1—C2	110.08 (19)	C27—C30—H30B	109.5
N2—C1—H1	125.0	H30A—C30—H30B	109.5
C2—C1—H1	125.0	C27—C30—H30C	109.5
C3—C2—C1	105.00 (19)	H30A—C30—H30C	109.5
C3—C2—H2	127.5	H30B—C30—H30C	109.5
C1—C2—H2	127.5	O7—C31—O8	125.00 (18)
N1—C3—C2	108.71 (19)	O7—C31—C13	124.48 (18)
N1—C3—H3	125.6	O8—C31—C13	110.51 (17)
C2—C3—H3	125.6	O8—C32—C33	101.80 (19)
N4—C4—C5	110.69 (18)	O8—C32—C35	109.24 (18)
N4—C4—H4	124.7	C33—C32—C35	111.1 (2)
C5—C4—H4	124.7	O8—C32—C34	111.01 (19)
C6—C5—C4	104.38 (19)	C33—C32—C34	111.7 (2)
C6—C5—H5	127.8	C35—C32—C34	111.5 (2)
C4—C5—H5	127.8	C32—C33—H33A	109.5
N3—C6—C5	109.13 (19)	C32—C33—H33B	109.5
N3—C6—H6	125.4	H33A—C33—H33B	109.5
C5—C6—H6	125.4	C32—C33—H33C	109.5
N6—C7—C8	110.3 (2)	H33A—C33—H33C	109.5
N6—C7—H7	124.8	H33B—C33—H33C	109.5

C8—C7—H7	124.8	C32—C34—H34A	109.5
C9—C8—C7	104.9 (2)	C32—C34—H34B	109.5
C9—C8—H8	127.5	H34A—C34—H34B	109.5
C7—C8—H8	127.5	C32—C34—H34C	109.5
N5—C9—C8	108.2 (2)	H34A—C34—H34C	109.5
N5—C9—H9	125.9	H34B—C34—H34C	109.5
C8—C9—H9	125.9	C32—C35—H35A	109.5
C11—C10—C16	117.35 (16)	C32—C35—H35B	109.5
C11—C10—C15	118.14 (16)	H35A—C35—H35B	109.5
C16—C10—C15	116.26 (16)	C32—C35—H35C	109.5
C11—C10—Rh	70.08 (10)	H35A—C35—H35C	109.5
C16—C10—Rh	114.45 (12)	H35B—C35—H35C	109.5
C15—C10—Rh	111.81 (12)	C38—O10—C39	120.6 (2)
C12—C11—C10	113.05 (16)	C43—O12—C44	122.1 (3)
C12—C11—C21	120.38 (17)	C37—C36—C38	172.8 (3)
C10—C11—C21	126.33 (17)	C36—C37—C43	176.5 (3)
C12—C11—Rh	70.47 (10)	O9—C38—O10	127.6 (3)
C10—C11—Rh	69.83 (10)	O9—C38—C36	121.0 (2)
C21—C11—Rh	132.48 (13)	O10—C38—C36	111.4 (2)
C11—C12—C13	114.24 (16)	O10—C39—C42	109.8 (3)
C11—C12—C26	120.98 (17)	O10—C39—C40	102.8 (2)
C13—C12—C26	124.48 (16)	C42—C39—C40	112.7 (3)
C11—C12—Rh	70.38 (10)	O10—C39—C41	108.8 (3)
C13—C12—Rh	69.42 (10)	C42—C39—C41	113.3 (3)
C26—C12—Rh	134.35 (13)	C40—C39—C41	108.9 (3)
C12—C13—C31	116.21 (16)	C39—C40—H40A	109.5
C12—C13—C14	118.75 (16)	C39—C40—H40B	109.5
C31—C13—C14	117.37 (16)	H40A—C40—H40B	109.5
C12—C13—Rh	70.43 (10)	C39—C40—H40C	109.5
C31—C13—Rh	112.97 (12)	H40A—C40—H40C	109.5
C14—C13—Rh	111.70 (12)	H40B—C40—H40C	109.5
C13—C14—C15	109.85 (15)	C39—C41—H41A	109.5
C13—C14—H14A	109.7	C39—C41—H41B	109.5
C15—C14—H14A	109.7	H41A—C41—H41B	109.5
C13—C14—H14B	109.7	C39—C41—H41C	109.5
C15—C14—H14B	109.7	H41A—C41—H41C	109.5

H14A—C14—H14B	108.2	H41B—C41—H41C	109.5
C10—C15—C14	110.47 (16)	C39—C42—H42A	109.5
C10—C15—H15A	109.6	C39—C42—H42B	109.5
C14—C15—H15A	109.6	H42A—C42—H42B	109.5
C10—C15—H15B	109.6	C39—C42—H42C	109.5
C14—C15—H15B	109.6	H42A—C42—H42C	109.5
H15A—C15—H15B	108.1	H42B—C42—H42C	109.5
O1—C16—O2	125.48 (18)	O11—C43—O12	128.8 (3)
O1—C16—C10	124.97 (18)	O11—C43—C37	122.1 (4)
O2—C16—C10	109.54 (16)	O12—C43—C37	109.0 (3)
O2—C17—C20	110.4 (2)	C47—C44—O12	110.0 (3)
O2—C17—C19	109.65 (19)	C47—C44—C46	111.5 (5)
C20—C17—C19	113.1 (2)	O12—C44—C46	109.4 (4)
O2—C17—C18	101.84 (18)	C47—C44—C45	110.7 (4)
C20—C17—C18	111.4 (2)	O12—C44—C45	101.3 (4)
C19—C17—C18	109.9 (2)	C46—C44—C45	113.5 (6)
C17—C18—H18A	109.5	C44—C45—H45A	109.5
C17—C18—H18B	109.5	C44—C45—H45B	109.5
H18A—C18—H18B	109.5	H45A—C45—H45B	109.5
C17—C18—H18C	109.5	C44—C45—H45C	109.5
H18A—C18—H18C	109.5	H45A—C45—H45C	109.5
H18B—C18—H18C	109.5	H45B—C45—H45C	109.5
C17—C19—H19A	109.5	C44—C46—H46A	109.5
C17—C19—H19B	109.5	C44—C46—H46B	109.5
H19A—C19—H19B	109.5	H46A—C46—H46B	109.5
C17—C19—H19C	109.5	C44—C46—H46C	109.5
H19A—C19—H19C	109.5	H46A—C46—H46C	109.5
H19B—C19—H19C	109.5	H46B—C46—H46C	109.5
C17—C20—H20A	109.5	C44—C47—H47A	109.5
C17—C20—H20B	109.5	C44—C47—H47B	109.5
H20A—C20—H20B	109.5	H47A—C47—H47B	109.5
C17—C20—H20C	109.5	C44—C47—H47C	109.5
H20A—C20—H20C	109.5	H47A—C47—H47C	109.5
H20B—C20—H20C	109.5	H47B—C47—H47C	109.5

Crystal structure of **9**

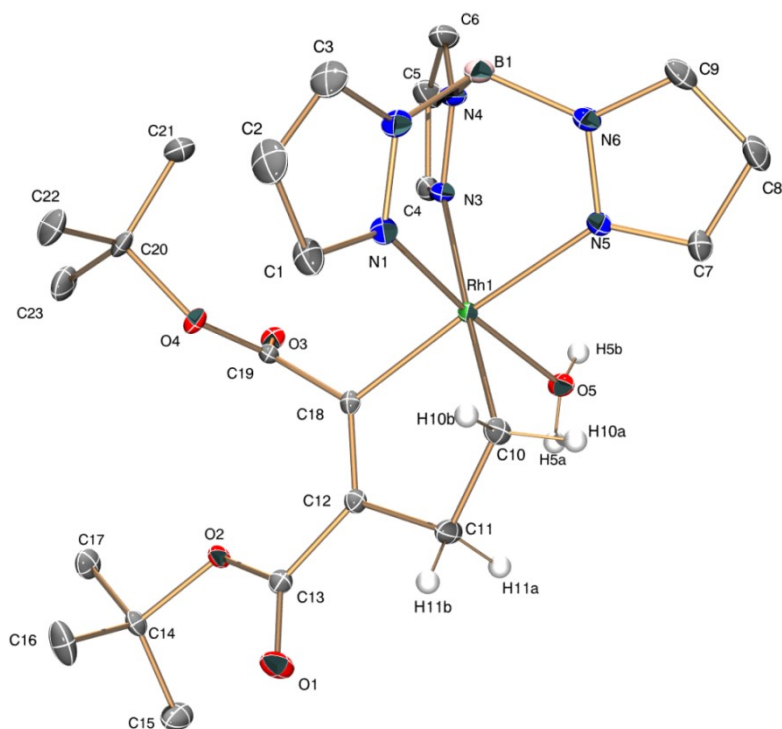


Figure S5: Structural diagram of the asymmetric unit of **9** showing 50% ellipsoids and the atom numbering. Most H-atoms and the CHCl_3 solvent molecule were omitted.

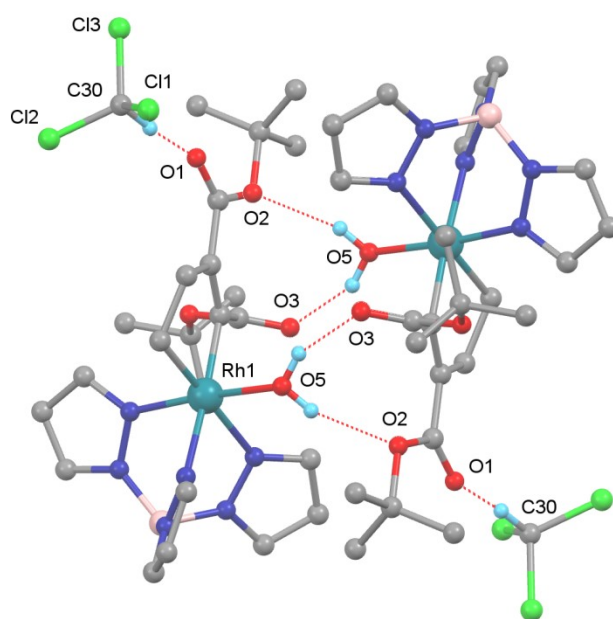
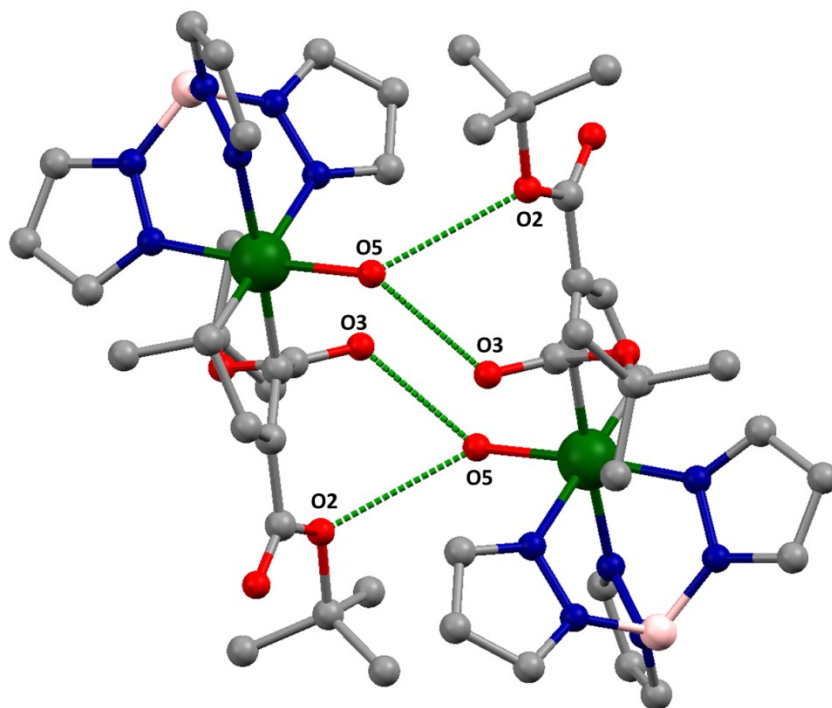


Figure S6: Structural diagram of the $O_{(\text{water})}\text{-H}\cdots\text{O}$ and $\text{C}_{(\text{CHCl}_3)}\text{-H}\cdots\text{O}$ hydrogen bonding pattern in the solid state structure of **9**. The two Rh complexes are related by inversion. They are cyclically linked by the four $\text{O-H}\cdots\text{O}$ bonds into a dimer. $\text{O5}\cdots\text{O2} = 2.861(2) \text{ \AA}$, $\text{O5}\cdots\text{O3} = 2.631(2) \text{ \AA}$, $\text{C30}\cdots\text{O1} = 3.005(2) \text{ \AA}$.

Table S7: Geometric data (Å, deg) of **9**.

Bond distances

Rh1—N1	1.9906 (13)	C8—H8	0.9500
Rh1—C18	2.0050 (14)	C9—H9	0.9500
Rh1—C10	2.0349 (15)	C10—C11	1.536 (2)
Rh1—O5	2.0788 (11)	C10—H10A	0.9900
Rh1—N5	2.1166 (12)	C10—H10B	0.9900
Rh1—N3	2.1906 (13)	C11—C12	1.511 (2)
N1—C1	1.331 (2)	C11—H11A	0.9900
N1—N2	1.3600 (18)	C11—H11B	0.9900
N2—C3	1.350 (2)	C12—C18	1.3507 (19)
N2—B1	1.543 (2)	C12—C13	1.4795 (19)
N3—C4	1.332 (2)	C14—C15	1.516 (2)
N3—N4	1.3605 (17)	C14—C17	1.517 (2)
N4—C6	1.346 (2)	C14—C16	1.517 (2)
N4—B1	1.536 (2)	C15—H15A	0.9800
N5—C7	1.3326 (19)	C15—H15B	0.9800
N5—N6	1.3583 (17)	C15—H15C	0.9800
N6—C9	1.347 (2)	C16—H16A	0.9800
N6—B1	1.540 (2)	C16—H16B	0.9800
O1—C13	1.2098 (18)	C16—H16C	0.9800
O2—C13	1.3514 (18)	C17—H17A	0.9800
O2—C14	1.4921 (17)	C17—H17B	0.9800
O3—C19	1.2197 (18)	C17—H17C	0.9800
O4—C19	1.3312 (17)	C18—C19	1.480 (2)
O4—C20	1.4870 (18)	C20—C23	1.517 (2)
O5—H5A	0.839 (9)	C20—C21	1.518 (2)
O5—H5B	0.835 (9)	C20—C22	1.520 (2)
B1—H1B	1.14 (2)	C21—H21A	0.9800
C1—C2	1.398 (2)	C21—H21B	0.9800
C1—H1	0.9500	C21—H21C	0.9800
C2—C3	1.372 (3)	C22—H22A	0.9800
C2—H2	0.9500	C22—H22B	0.9800
C3—H3	0.9500	C22—H22C	0.9800
C4—C5	1.399 (2)	C23—H23A	0.9800
C4—H4	0.9500	C23—H23B	0.9800

C5—C6	1.375 (2)	C23—H23C	0.9800
C5—H5	0.9500	C30—Cl2	1.745 (2)
C6—H6	0.9500	C30—Cl3	1.7527 (19)
C7—C8	1.395 (2)	C30—Cl1	1.759 (2)
C7—H7	0.9500	C30—H30	1.0000
C8—C9	1.378 (2)		

Bond angles

N1—Rh1—C18	92.65 (5)	Rh1—C10—H10B	109.7
N1—Rh1—C10	92.45 (6)	H10A—C10—H10B	108.2
C18—Rh1—C10	81.19 (6)	C12—C11—C10	108.32 (12)
N1—Rh1—O5	174.71 (5)	C12—C11—H11A	110.0
C18—Rh1—O5	92.59 (5)	C10—C11—H11A	110.0
C10—Rh1—O5	87.64 (5)	C12—C11—H11B	110.0
N1—Rh1—N5	87.63 (5)	C10—C11—H11B	110.0
C18—Rh1—N5	175.15 (5)	H11A—C11—H11B	108.4
C10—Rh1—N5	93.97 (5)	C18—C12—C13	127.07 (13)
O5—Rh1—N5	87.09 (5)	C18—C12—C11	115.95 (12)
N1—Rh1—N3	88.26 (5)	C13—C12—C11	116.93 (12)
C18—Rh1—N3	100.29 (5)	O1—C13—O2	122.83 (13)
C10—Rh1—N3	178.34 (5)	O1—C13—C12	123.16 (14)
O5—Rh1—N3	91.51 (5)	O2—C13—C12	114.00 (12)
N5—Rh1—N3	84.56 (5)	O2—C14—C15	110.13 (12)
C1—N1—N2	107.66 (13)	O2—C14—C17	102.55 (11)
C1—N1—Rh1	133.48 (11)	C15—C14—C17	110.38 (13)
N2—N1—Rh1	118.85 (10)	O2—C14—C16	110.16 (12)
C3—N2—N1	108.70 (14)	C15—C14—C16	112.80 (15)
C3—N2—B1	129.60 (14)	C17—C14—C16	110.34 (13)
N1—N2—B1	121.56 (12)	C14—C15—H15A	109.5
C4—N3—N4	106.70 (12)	C14—C15—H15B	109.5
C4—N3—Rh1	136.38 (10)	H15A—C15—H15B	109.5
N4—N3—Rh1	116.63 (10)	C14—C15—H15C	109.5
C6—N4—N3	109.68 (13)	H15A—C15—H15C	109.5
C6—N4—B1	130.77 (13)	H15B—C15—H15C	109.5
N3—N4—B1	119.43 (12)	C14—C16—H16A	109.5
C7—N5—N6	107.03 (12)	C14—C16—H16B	109.5

C7—N5—Rh1	134.66 (10)	H16A—C16—H16B	109.5
N6—N5—Rh1	118.26 (9)	C14—C16—H16C	109.5
C9—N6—N5	109.55 (13)	H16A—C16—H16C	109.5
C9—N6—B1	131.13 (13)	H16B—C16—H16C	109.5
N5—N6—B1	119.30 (12)	C14—C17—H17A	109.5
C13—O2—C14	120.27 (11)	C14—C17—H17B	109.5
C19—O4—C20	122.12 (12)	H17A—C17—H17B	109.5
Rh1—O5—H5A	126.3 (15)	C14—C17—H17C	109.5
Rh1—O5—H5B	117.5 (15)	H17A—C17—H17C	109.5
H5A—O5—H5B	104 (2)	H17B—C17—H17C	109.5
N4—B1—N6	108.25 (13)	C12—C18—C19	127.53 (13)
N4—B1—N2	109.07 (13)	C12—C18—Rh1	116.32 (10)
N6—B1—N2	107.62 (13)	C19—C18—Rh1	116.12 (10)
N4—B1—H1B	112.1 (12)	O3—C19—O4	124.70 (13)
N6—B1—H1B	109.9 (12)	O3—C19—C18	124.28 (13)
N2—B1—H1B	109.8 (12)	O4—C19—C18	110.69 (12)
N1—C1—C2	109.72 (16)	O4—C20—C23	111.24 (12)
N1—C1—H1	125.1	O4—C20—C21	108.83 (12)
C2—C1—H1	125.1	C23—C20—C21	112.76 (15)
C3—C2—C1	104.97 (15)	O4—C20—C22	101.67 (13)
C3—C2—H2	127.5	C23—C20—C22	110.72 (14)
C1—C2—H2	127.5	C21—C20—C22	111.08 (14)
N2—C3—C2	108.94 (15)	C20—C21—H21A	109.5
N2—C3—H3	125.5	C20—C21—H21B	109.5
C2—C3—H3	125.5	H21A—C21—H21B	109.5
N3—C4—C5	110.36 (14)	C20—C21—H21C	109.5
N3—C4—H4	124.8	H21A—C21—H21C	109.5
C5—C4—H4	124.8	H21B—C21—H21C	109.5
C6—C5—C4	104.67 (14)	C20—C22—H22A	109.5
C6—C5—H5	127.7	C20—C22—H22B	109.5
C4—C5—H5	127.7	H22A—C22—H22B	109.5
N4—C6—C5	108.59 (14)	C20—C22—H22C	109.5
N4—C6—H6	125.7	H22A—C22—H22C	109.5
C5—C6—H6	125.7	H22B—C22—H22C	109.5
N5—C7—C8	110.08 (14)	C20—C23—H23A	109.5
N5—C7—H7	125.0	C20—C23—H23B	109.5

C8—C7—H7	125.0	H23A—C23—H23B	109.5
C9—C8—C7	105.00 (14)	C20—C23—H23C	109.5
C9—C8—H8	127.5	H23A—C23—H23C	109.5
C7—C8—H8	127.5	H23B—C23—H23C	109.5
N6—C9—C8	108.34 (14)	Cl2—C30—Cl3	111.44 (11)
N6—C9—H9	125.8	Cl2—C30—Cl1	110.86 (10)
C8—C9—H9	125.8	Cl3—C30—Cl1	110.17 (10)
C11—C10—Rh1	109.77 (10)	Cl2—C30—H30	108.1
C11—C10—H10A	109.7	Cl3—C30—H30	108.1
Rh1—C10—H10A	109.7	Cl1—C30—H30	108.1
C11—C10—H10B	109.7		

2. COMPUTATIONAL DETAILS

2.1 Ligand exchange. Relaxed Potential Energy (PES) scans concerning ethylene release at $\kappa^2\text{-A}\cdot\text{C}_2\text{H}_2$ and $\kappa^2\text{-B}\cdot\text{C}_2\text{H}_4$.

Species $\kappa^2\text{-A}\cdot\text{C}_2\text{H}_2$ arises from the coordination of an alkyne molecule to $\kappa^2\text{-A}$, whereas the isomer $\kappa^2\text{-B}\cdot\text{C}_2\text{H}_4$ is formed by ethylene addition to $\kappa^2\text{-B}$. Since no cyclotrimerization product was detected experimentally for the acetylene system, we do not expect $\kappa^2\text{-B}$ to be an intermediate in the formation of **12**, as it would lead to the formation of **B**, then to **D** and, under an acetylene atmosphere, to $\text{D}\cdot\text{C}_2\text{H}_2$ and, finally, to the benzene adduct $\text{TpRh}(\text{C}_6\text{H}_6)$. Therefore, although the profile for $\kappa^2\text{-B}\cdot\text{C}_2\text{H}_4$ is attached for the sake of comparison, we will focus on ethylene loss from isomer $\kappa^2\text{-A}\cdot\text{C}_2\text{H}_2$. Unfortunately, and despite many attempts, we were unable to locate transition states associated with these processes. Nevertheless, relaxed potential energy scans of the $\text{Rh-C}_{\text{ethylene}}$ bond distance allowed us to obtain valuable information (in the scans, the Rh-C=C angle was frozen to ensure a reasonable detachment).

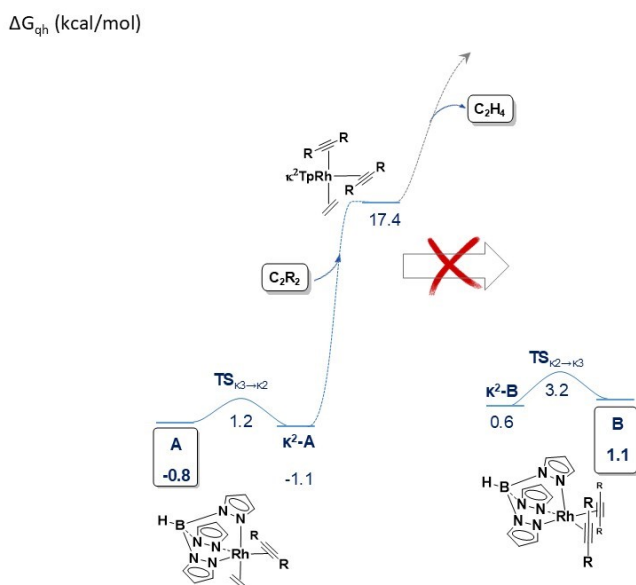


Figure S7. Associative ligand exchange from **A** via κ^2 intermediates. While acetylene extrusion from the high energy intermediate is almost barrier-less, ethene dissociation renders the overall formation of **B** more difficult than *via* associative exchange. Figures S7a to S7e illustrate the relaxed potential energy scans for ethene and acetylene dissociation leading to the above conclusion.

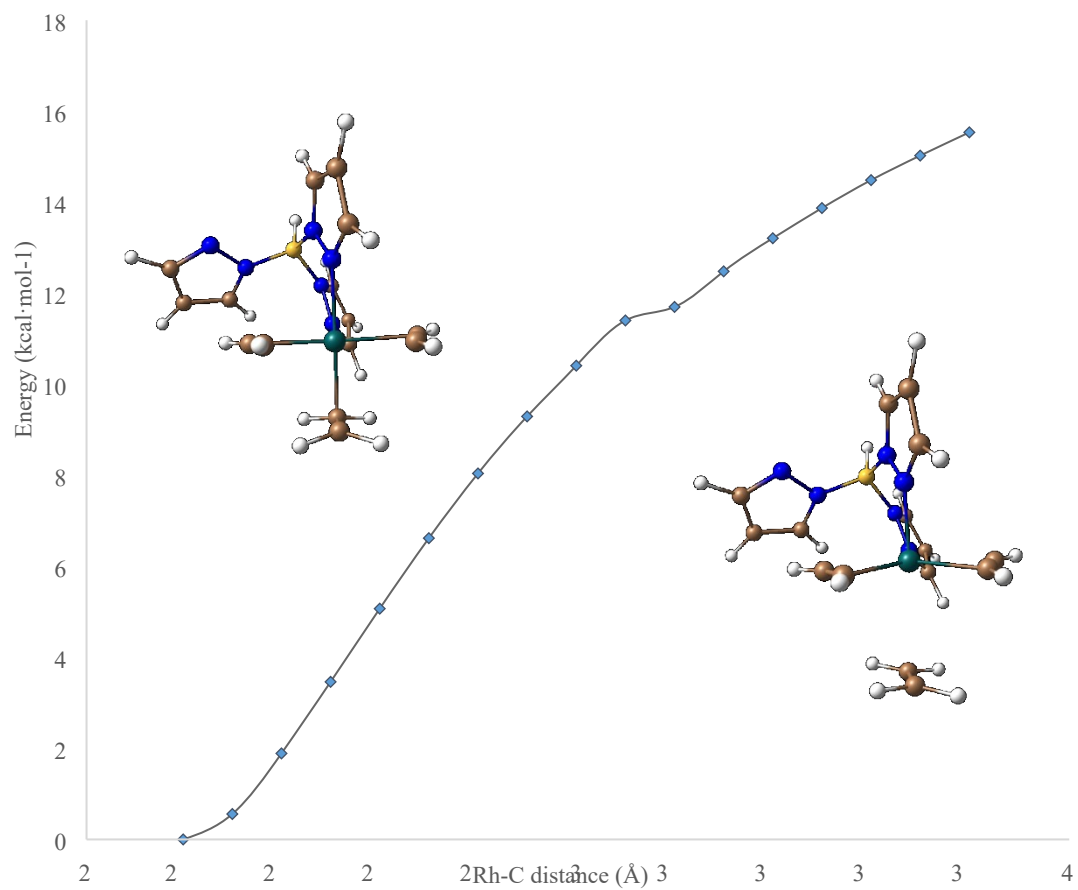


Figure S7a. Relaxed potential energy scan of the Rh-C_{ethylene} bond distance of isomer κ^2 -**A**·C₂H₂.

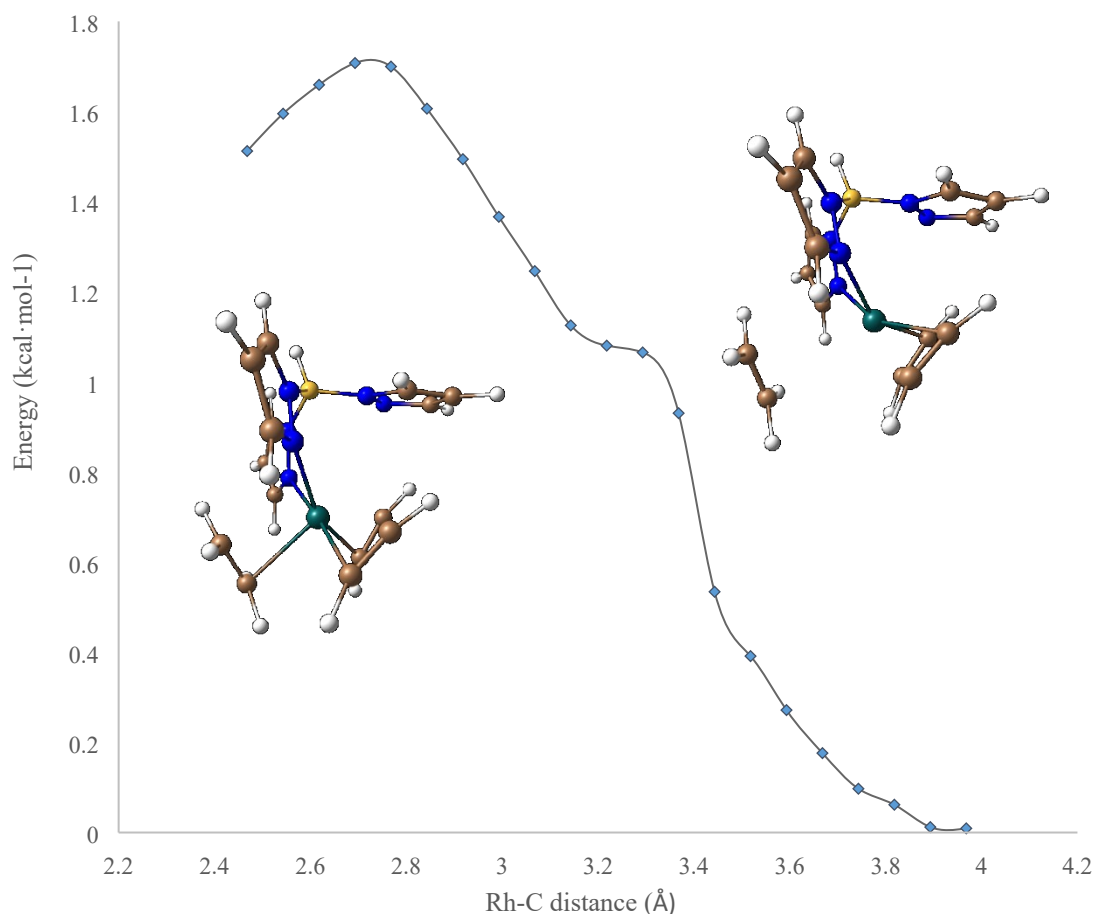


Figure S7b. Relaxed potential energy scan of the Rh-C_{ethylene} bond distance of isomer κ^2 -**B**·C₂H₄.

For isomer κ^2 -**A**·C₂H₂, ethylene loss requires a considerable barrier. In addition, it does not afford square planar κ^2 -**A**, then a subsequent isomerization should take place. The energies associated with these processes are higher than those calculated for carbon-carbon coupling at **A**, something that is in agreement with the absence of cyclotrimerization products in the reactions of **1** with acetylene. On the contrary, ethylene dissociation from isomer κ^2 -**B**·C₂H₄ has a very low energy barrier.

It is also worth mentioning that dissociation of either acetylene ligand from κ^2 -**A**·C₂H₂ to afford κ^2 -**A** has a lower energy barrier than that found for dissociation of ethylene.

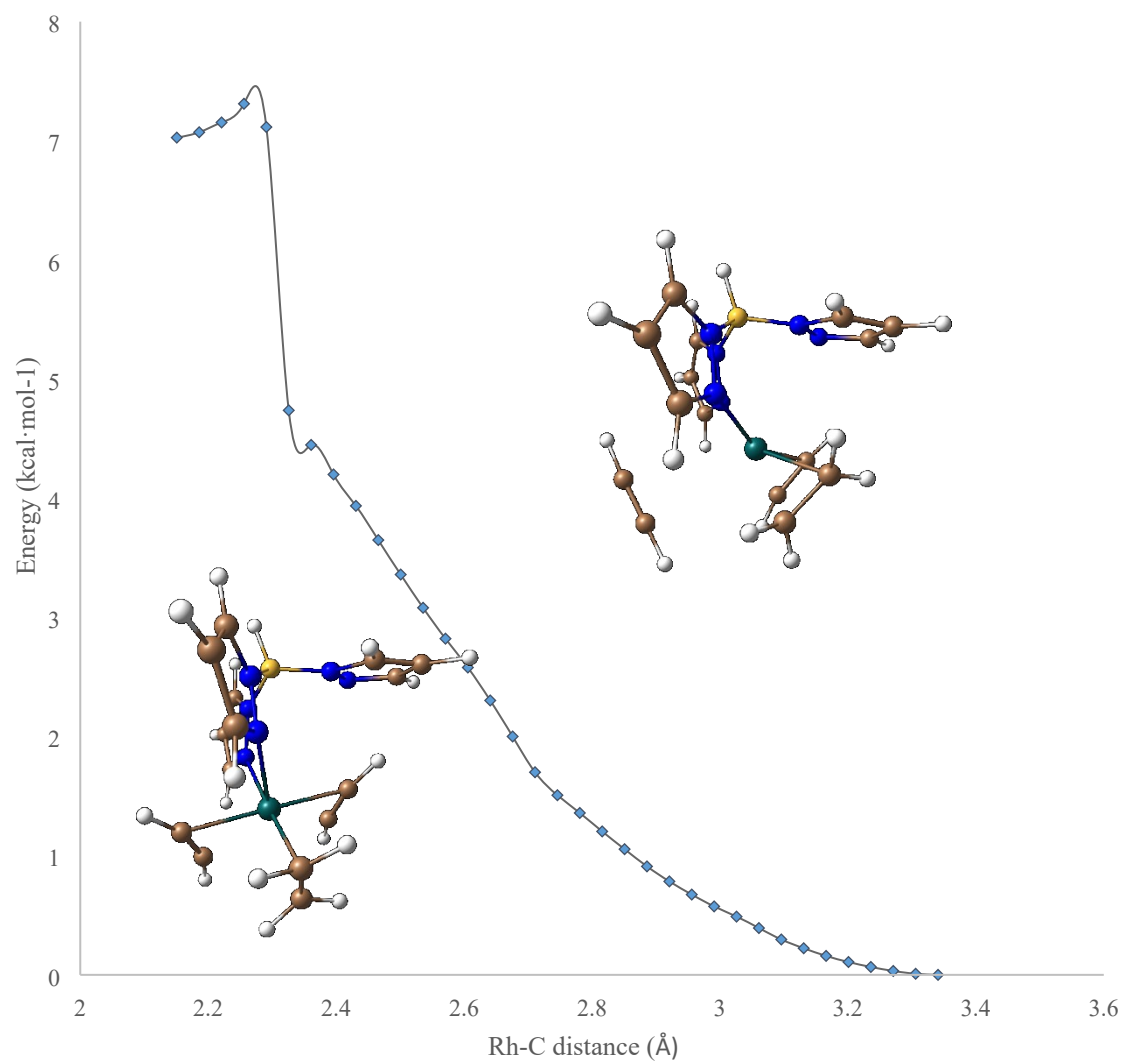


Figure S7c. Relaxed potential energy scan of the Rh-C_{acetylene1} bond distance of isomer $\kappa^2\text{-A}\cdot\text{C}_2\text{H}_2$.

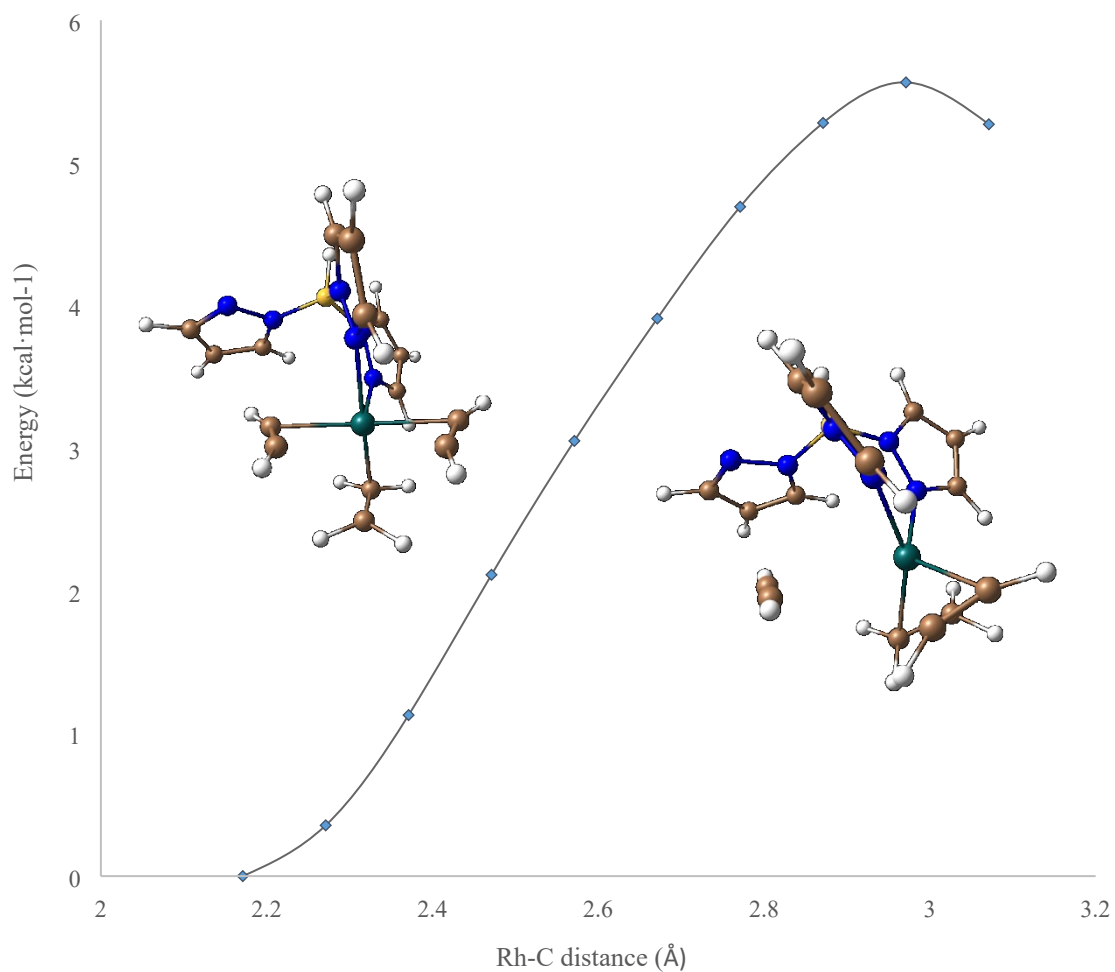


Figure S7d. Relaxed potential energy scan of the Rh-C_{acetylene2} bond distance of isomer $\kappa^2\text{-A}\cdot\text{C}_2\text{H}_2$.

An analogous situation occurs in the DMAD system in which the dissociation of ethylene from $\kappa^2\text{-A}'\cdot\text{DMAD}$ is associated with a barrier that is higher than the one found for ethylene loss from **A'** to afford [TpRh(DMAD)].

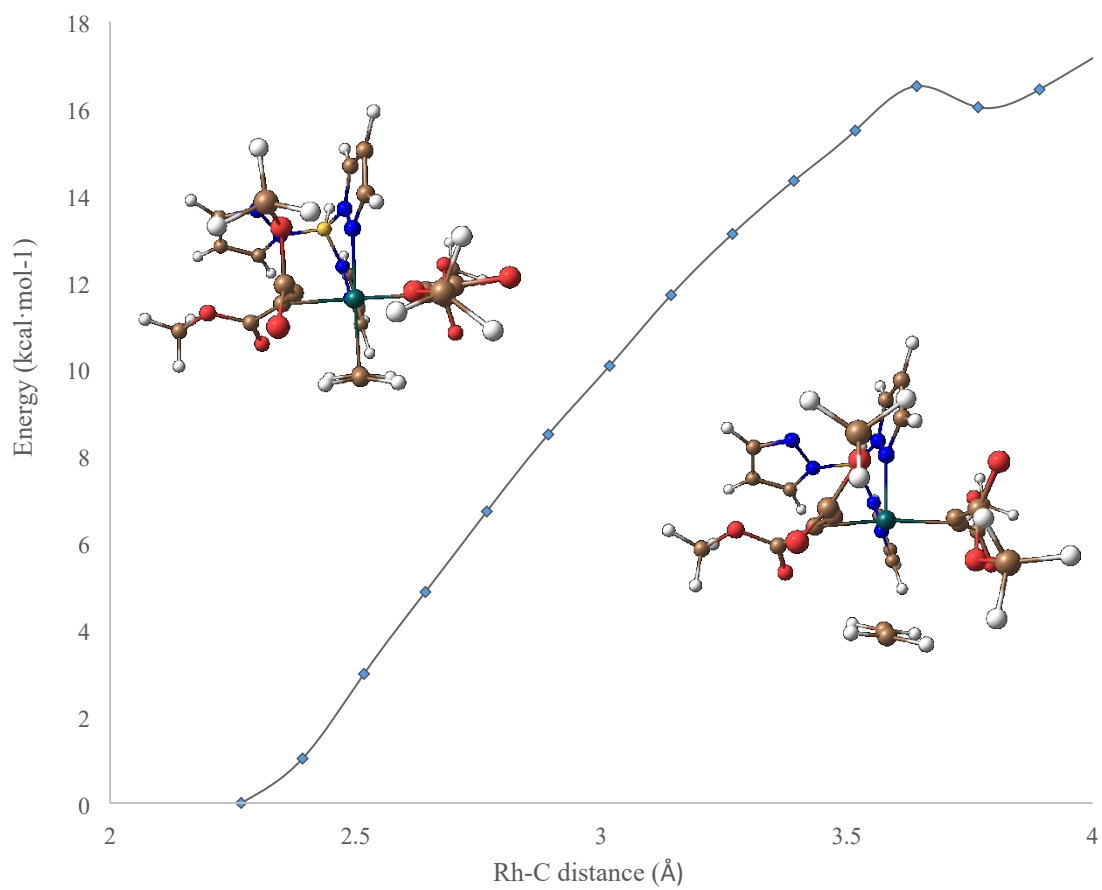


Figure S7e. Relaxed potential energy scan of the Rh-C_{ethylene} bond distance of κ^2 -A¹-DMAD.

2.2 Carbon-carbon coupling occurring at κ^2 -Tp species.

C-C coupling at κ^2 -Tp to afford rhodacycles is unlikely since the energy barriers associated with these processes are higher than those found for C-C coupling at **A** and **A'**.

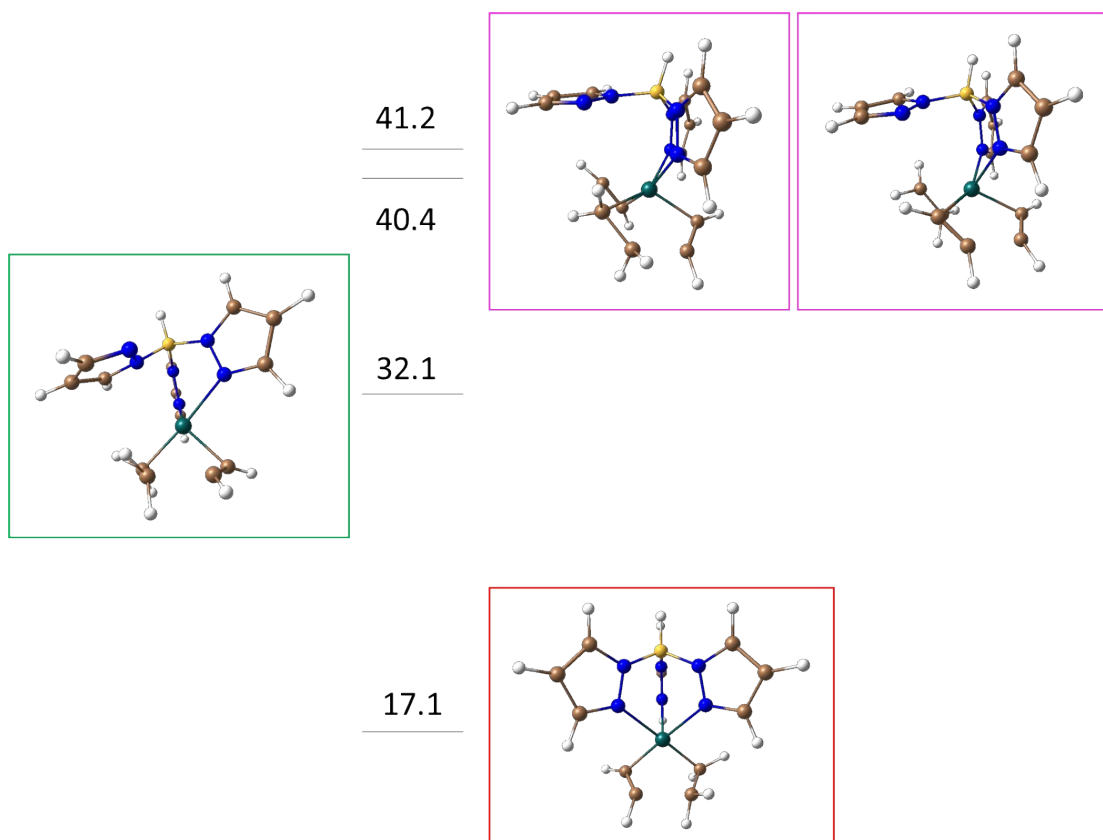


Figure S8. $\Delta G_{\text{q}h}^{\ddagger}$ ($\text{kcal}\cdot\text{mol}^{-1}$) corresponding to carbon-carbon coupling taking place at **A**, κ^2 -**A** and κ^2 -**A**· C_2H_2 , relative to **1**.

2.3 Electronic structure of intermediates on the way of formation of **12**.

The connectivity of the atoms of intermediate **G** was followed during its evolution to afford the reaction product **12** along the intrinsic reaction coordinate connecting the two species by means of localized orbital analysis. The position of the centroids of the localized orbitals (purple dots in the figures below) was used to follow the changes in the connectivity.

These results were obtained following the Pipek-Mezey (Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916) criterion and the procedure described by Vidossich and Lledós (Vidossich, P.; Lledós, A. *Dalton Trans.* **2014**, *43*, 11145). A typical input file for the generation of the formatted checkpoint file is also attached.

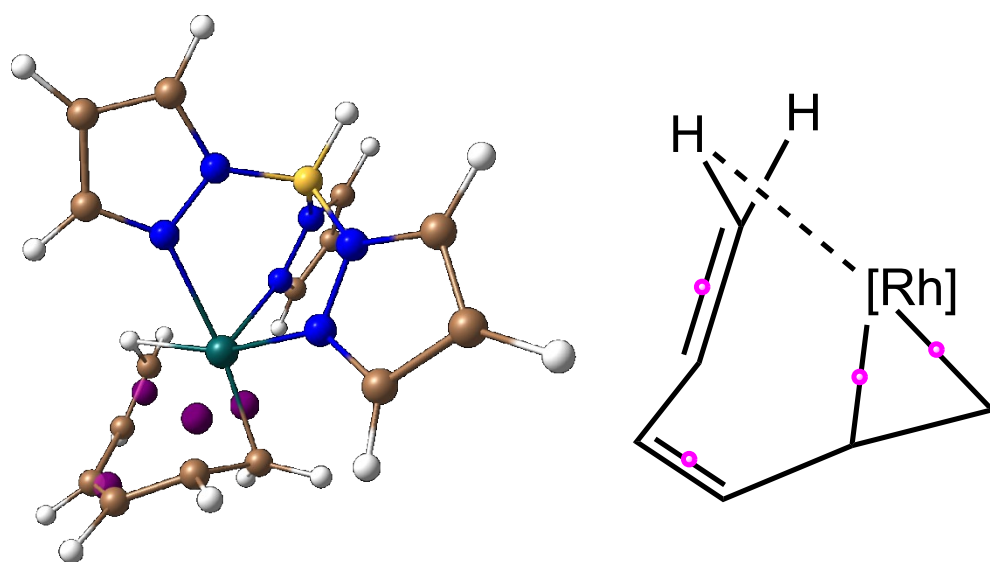


Figure S9a. Localized molecular orbital study of intermediate **G**. Purple dots represent the centroids of 2 C-Rh and 2 C-C σ and π bonds. According to this distribution, a metallacyclopropane formulation is proposed.

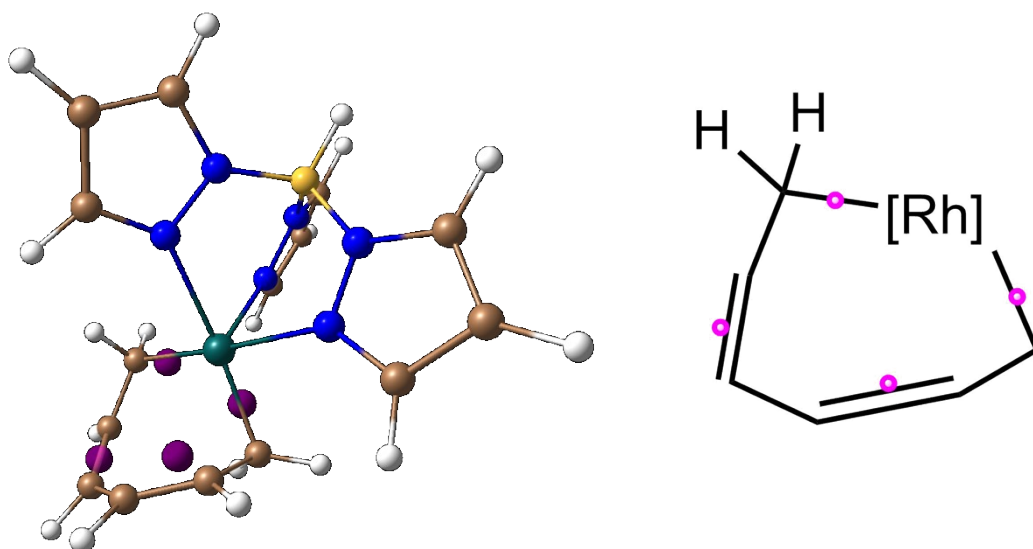


Figure S9b. Localized molecular orbital study compound **12**. Purple dots represent the centroids of 2 C-Rh and 2 C-C σ and π bonds. Their disposition agrees with the expected Rh-alkyl and Rh-allyl formulation.

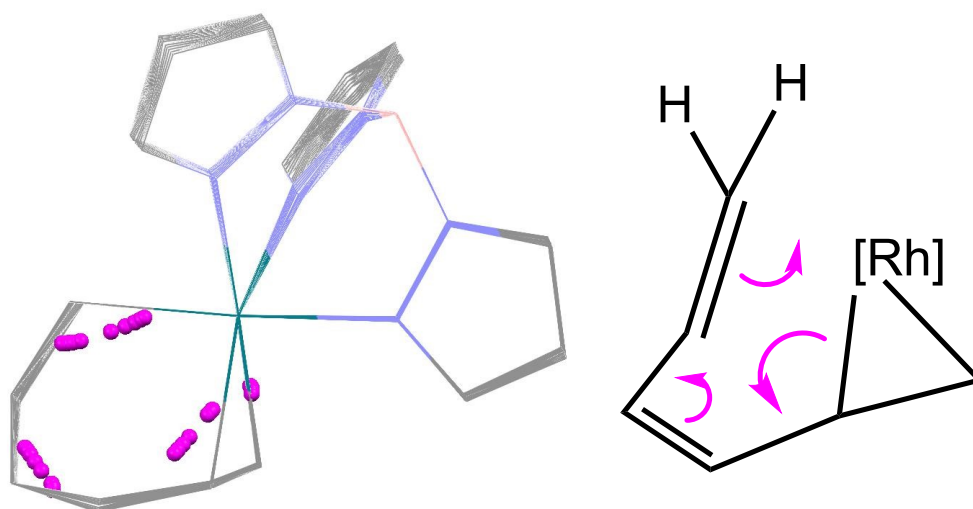


Figure S9c. Representation of the evolution of the centroids of selected localized molecular orbitals along the intrinsic reaction coordinate for the transformation of **G** into **12** evincing a synchronous electron reorganization.

Typical Gaussian input for orbital localization using the Pipek-Mezey scheme

```
%mem=8192MB
%chk=rh_allyl.chk
#p wb97xd/genecp symmetry=none nosymm

Rh_allyl

0 1
coords

Rh 0
SDD
****
C H N B 0
6-31G(d,p)
****

Rh 0
SDD

--Link1--
%mem=8192MB
%chk=rh_allyl.chk
#p IOp(4/9=20212) guess=(read,only,local,save,nosymm)
geom=allcheck pop=full wb97xd/genecp symmetry=none nosymm

Rh 0
SDD
****
C H N B 0
6-31G(d,p)
****

Rh 0
SDD
```

2.4 Alternative initial step in the formation of 12.

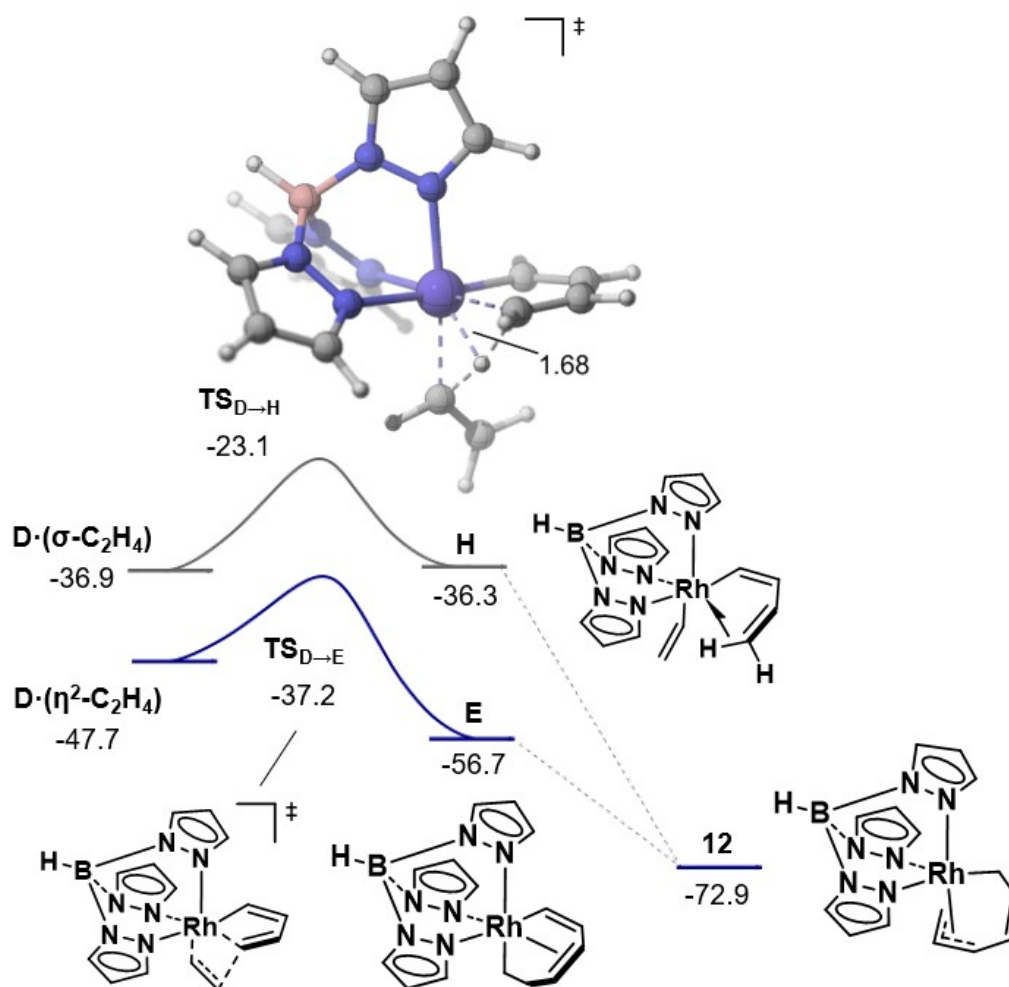
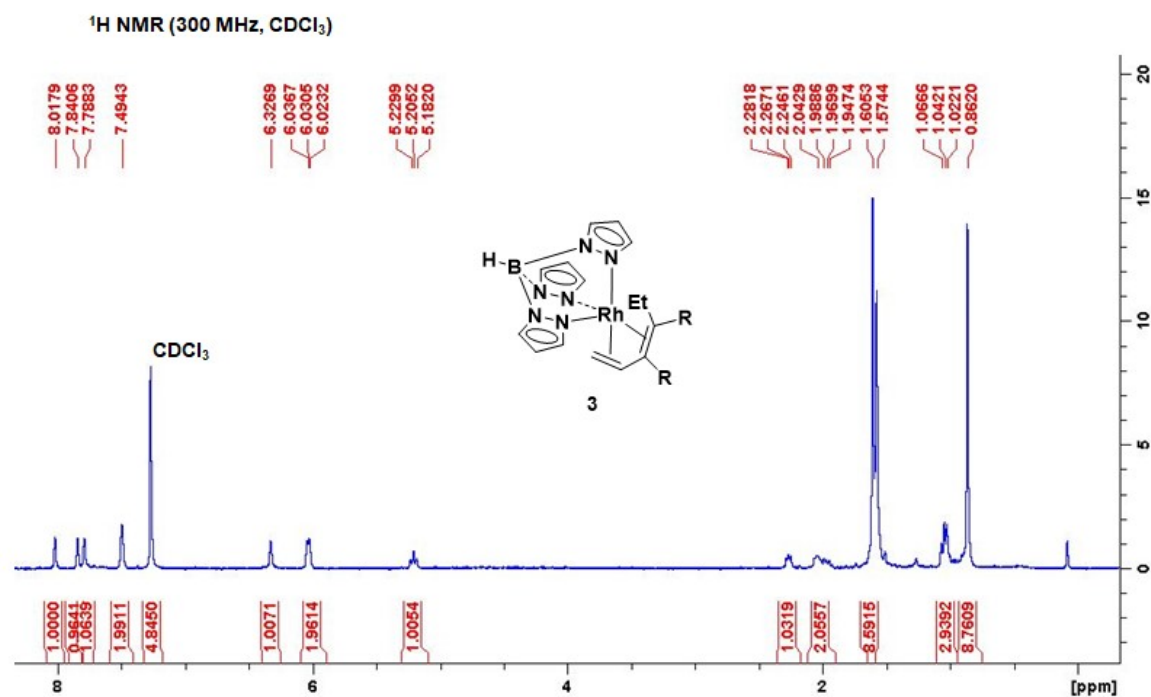


Figure S10. Energy profile (ΔG_{qh} in $\text{kcal}\cdot\text{mol}^{-1}$) for hydrogen migration from coordinated ethylene to the rhodacyclopentadiene of $D\text{-C}_2\text{H}_4$ as an alternative initial step to **12**. $D\text{-}\sigma\text{-C}_2\text{H}_4$ features an interaction between the metal and $\sigma\text{-C-H}$ electron density of the alkene. The overall energy barrier for this transformation from $D\cdot\eta^2\text{-C}_2\text{H}_4$ is $24.6\text{ kcal}\cdot\text{mol}^{-1}$. All energies are relative to $\mathbf{1} + 2\text{C}_2\text{H}_2 - \text{C}_2\text{H}_4$.

3. NMR spectra for complexes 3-5, 8-19.



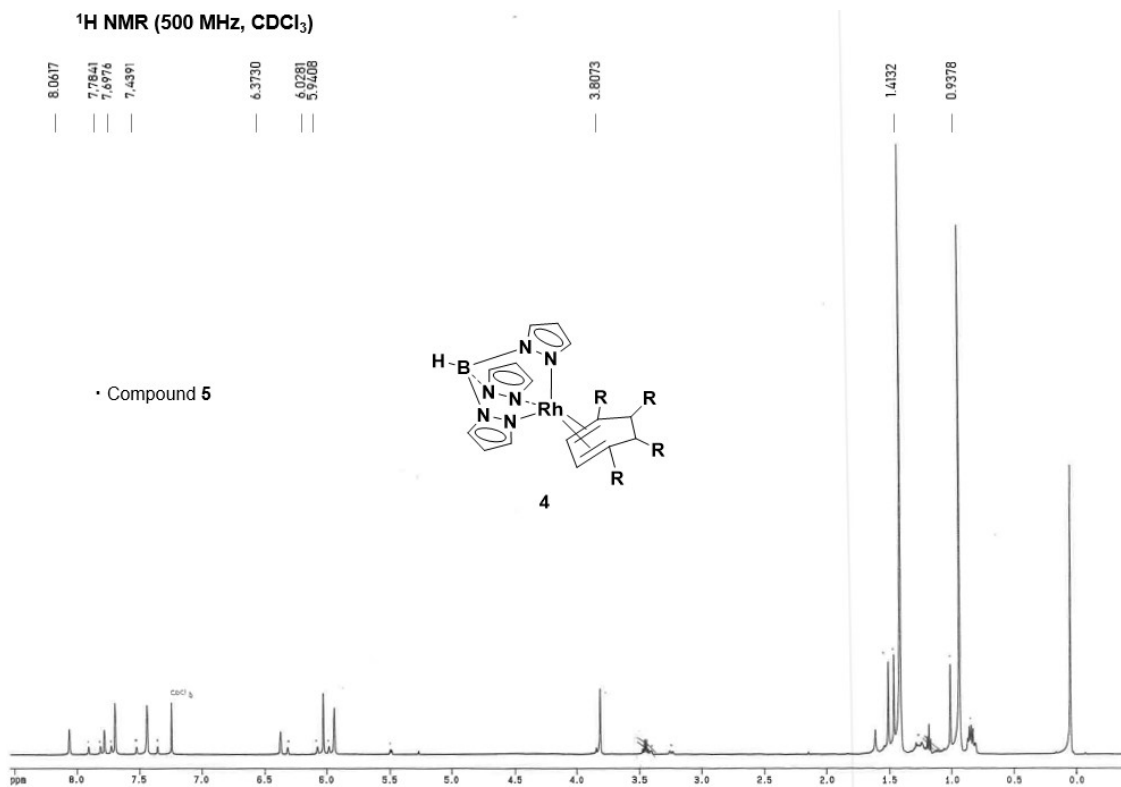


Figure S13. ¹H NMR spectrum of compound 4 (R = CO₂^tBu).

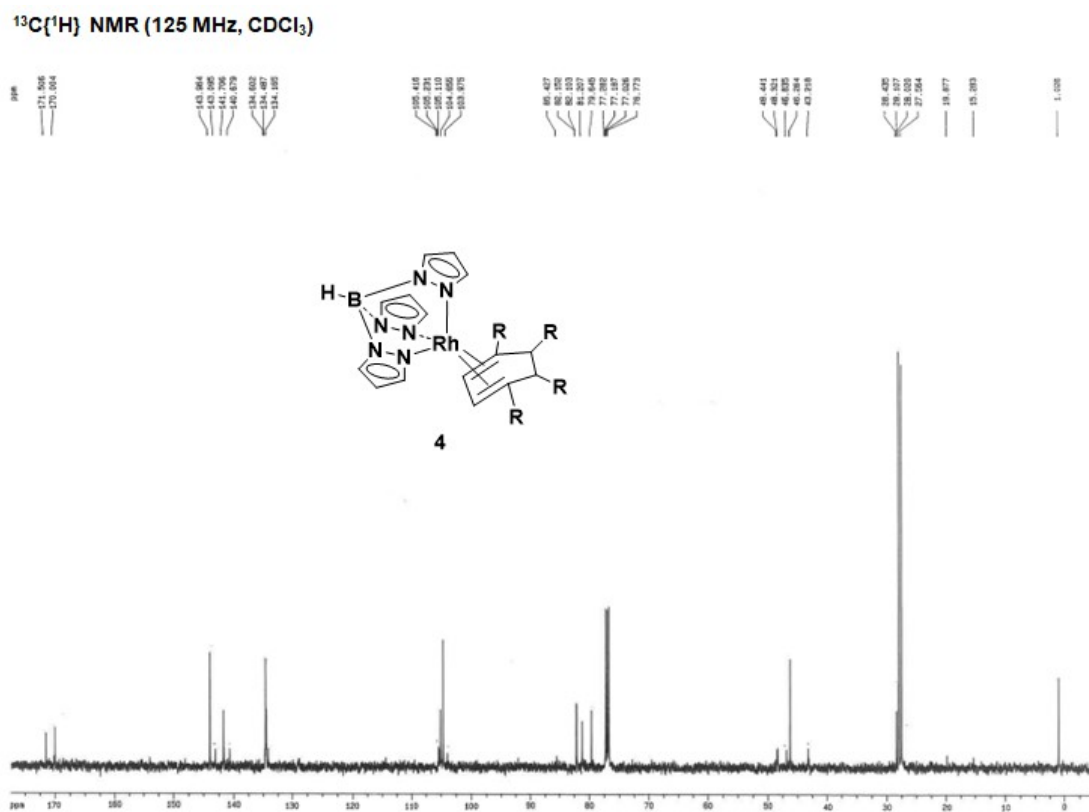


Figure S14. ¹³C{¹H} NMR spectrum of compound 4 (R = CO₂^tBu).

Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **5** ($\text{R} = \text{CO}_2^t\text{Bu}$).

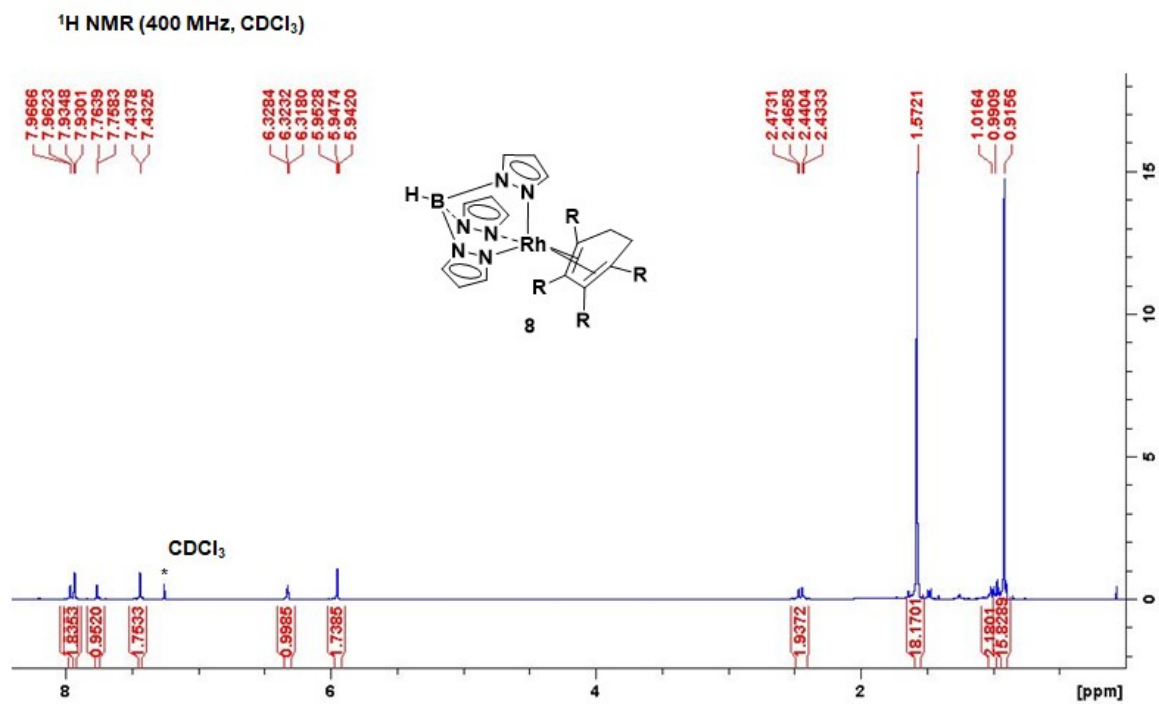


Figure S17. ^1H NMR spectrum of compound **8** ($\text{R} = \text{CO}_2^t\text{Bu}$).

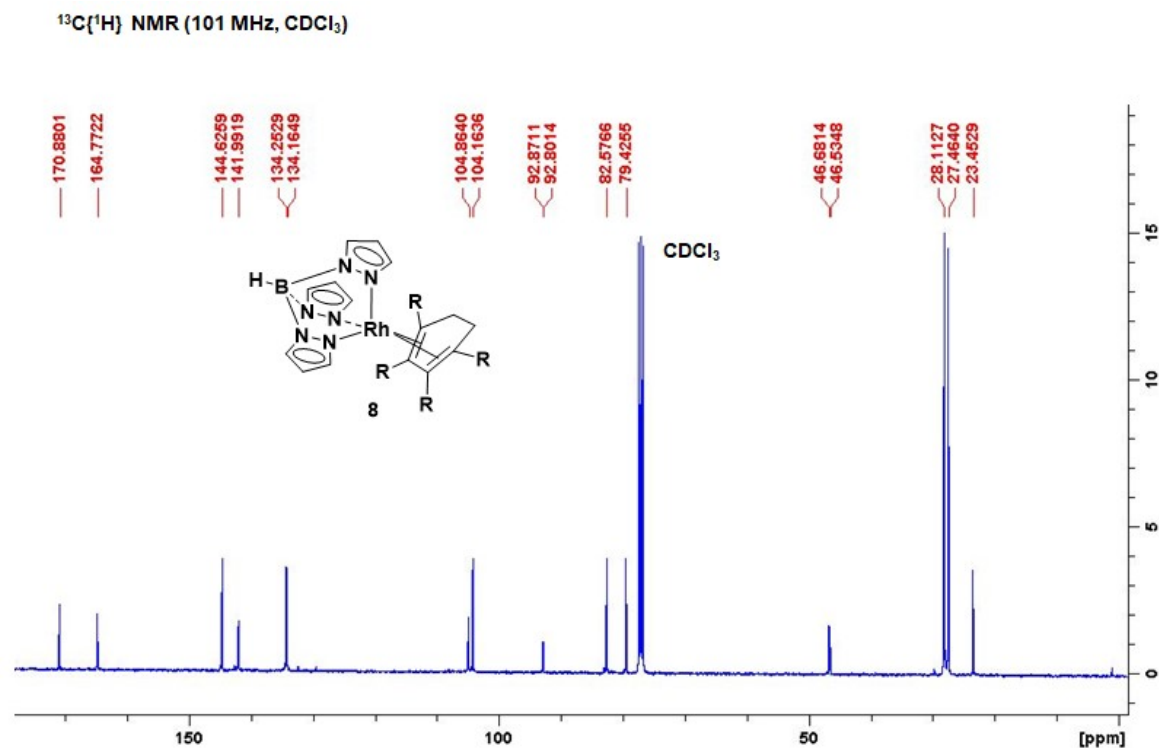


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **8** ($\text{R} = \text{CO}_2^t\text{Bu}$).

¹H NMR (400 MHz, CDCl₃)

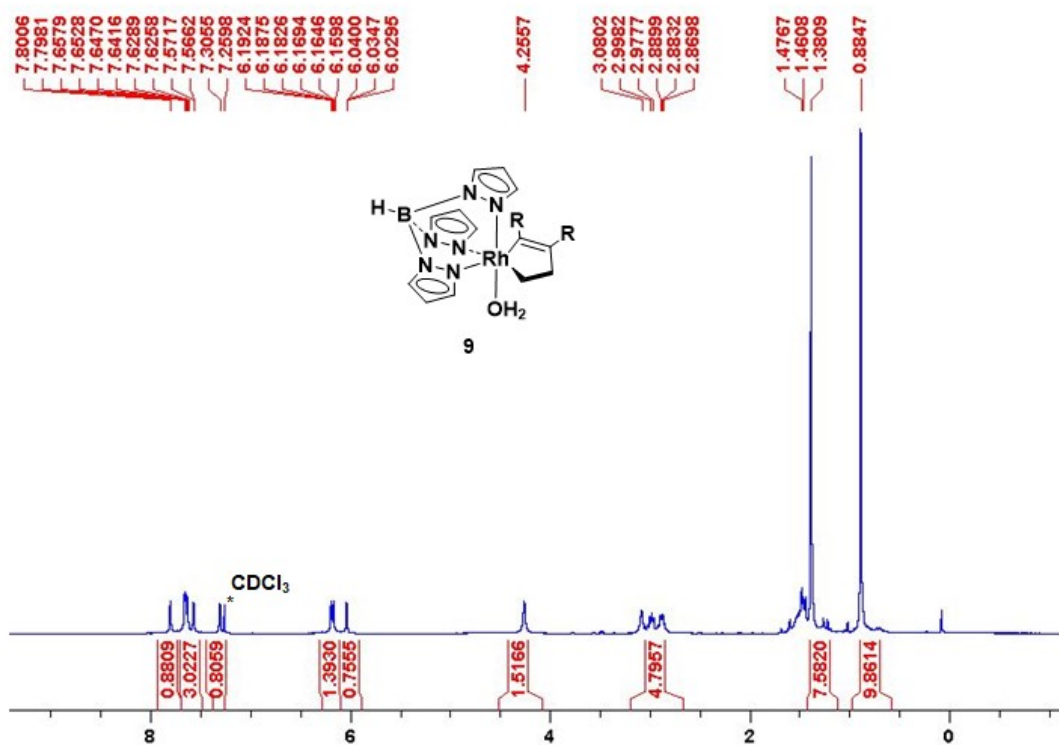


Figure S19. ¹H NMR spectrum of compound 9 (R = CO₂^tBu).

¹³C{¹H} NMR (101 MHz, CDCl₃)

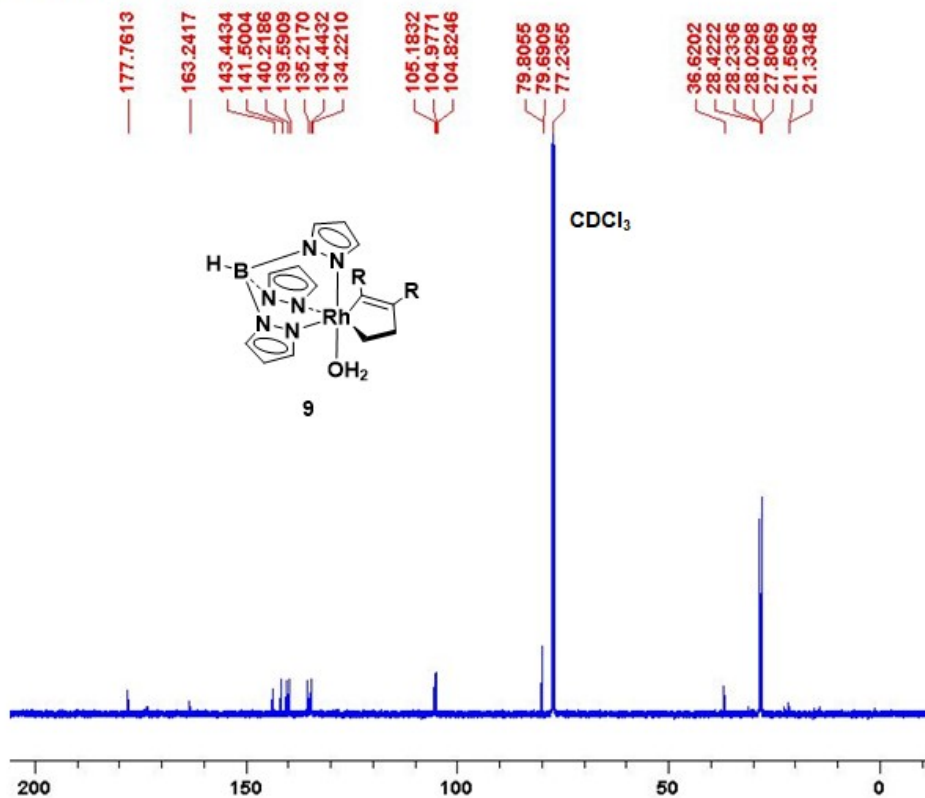


Figure S20. ¹³C{¹H} NMR spectrum of compound 9 (R = CO₂^tBu).

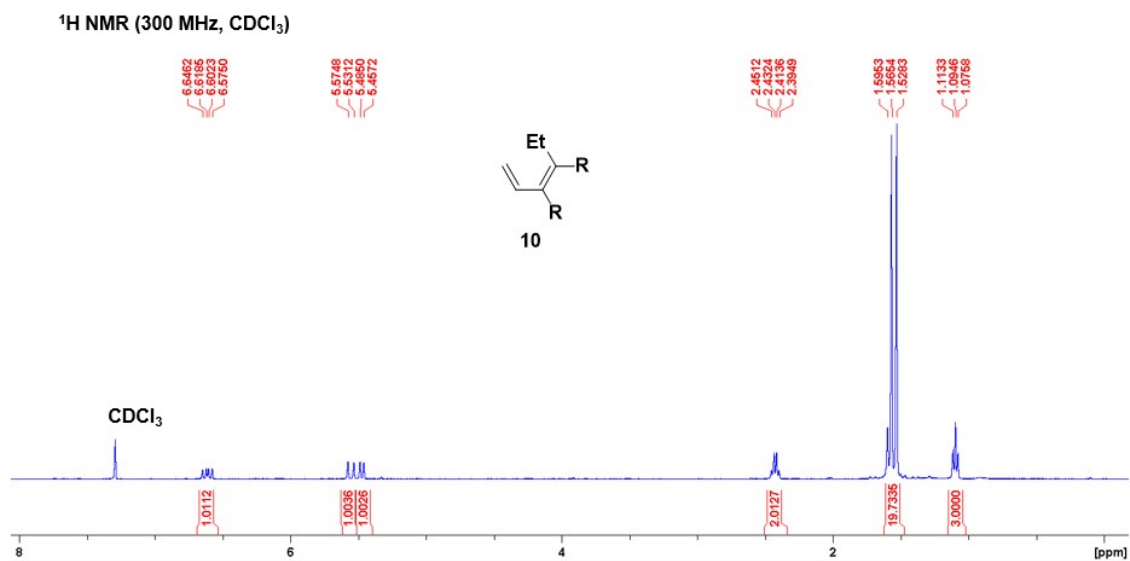


Figure S21. ¹H NMR spectrum of compound **10** (R = CO₂^tBu).

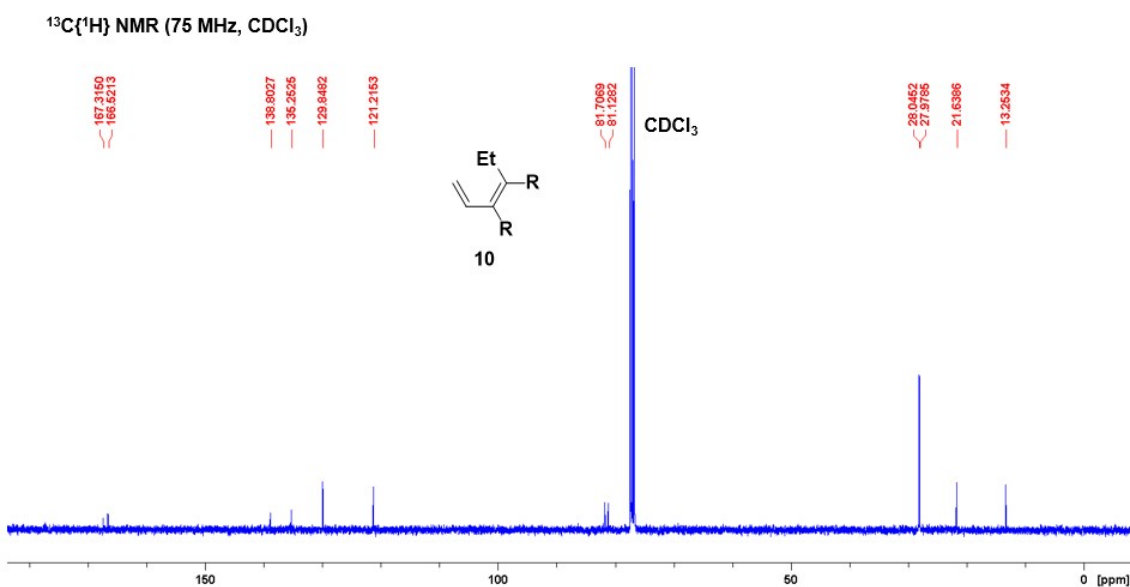


Figure S22. ¹³C{¹H} NMR spectrum of compound **10** (R = CO₂^tBu).

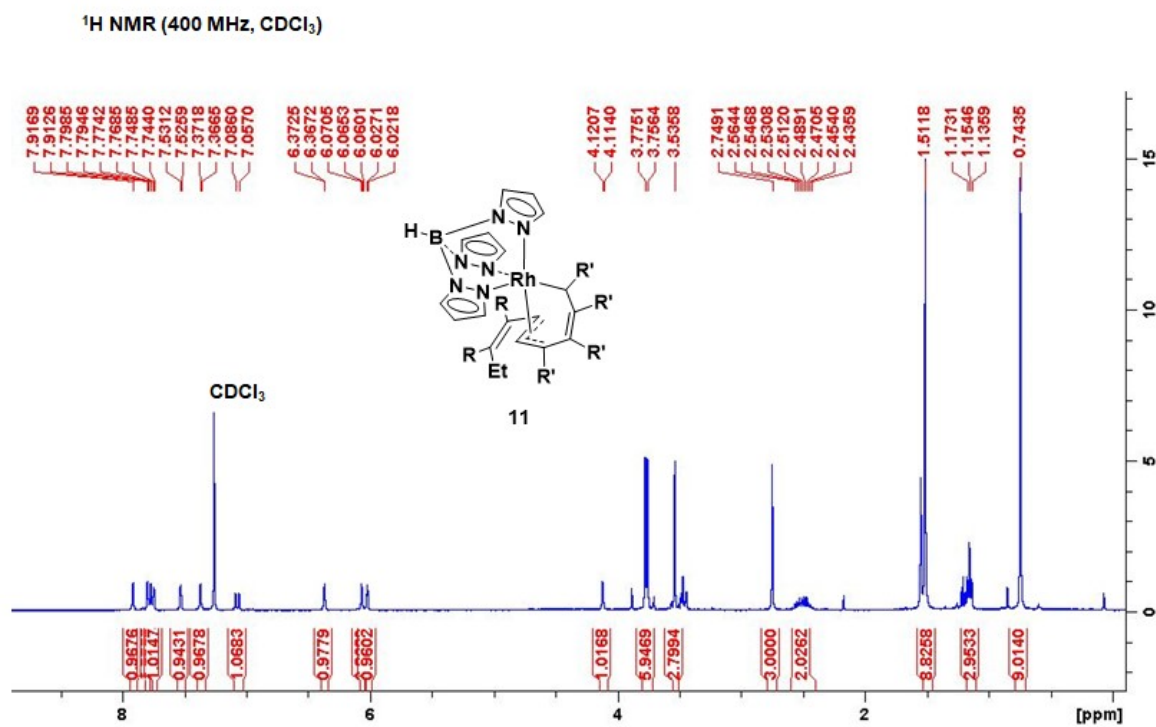


Figure S23. ¹H NMR spectrum of compound **11** (R = CO₂^tBu, R' = CO₂Me).

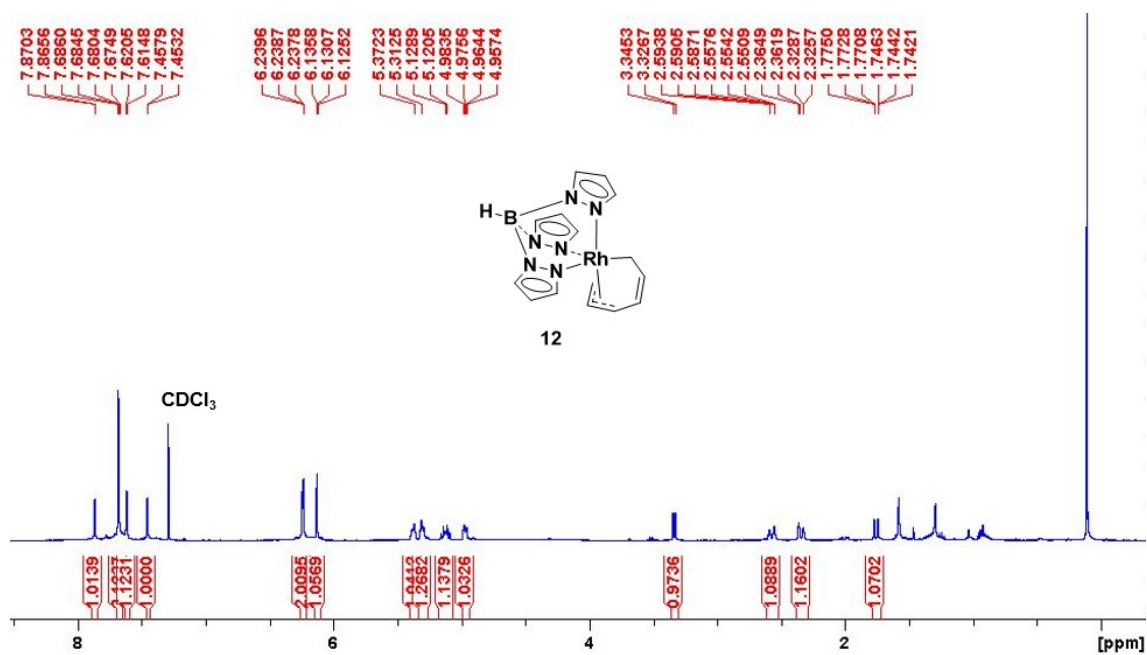


Figure S24. ¹H NMR spectrum of compound **12**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3)

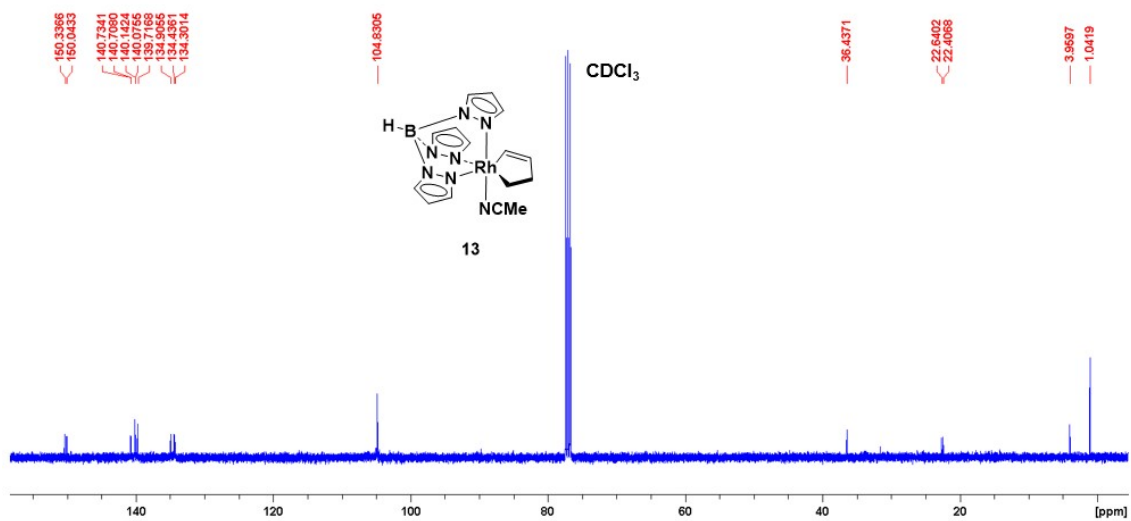


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 13.

^1H NMR (400 MHz, CDCl_3)

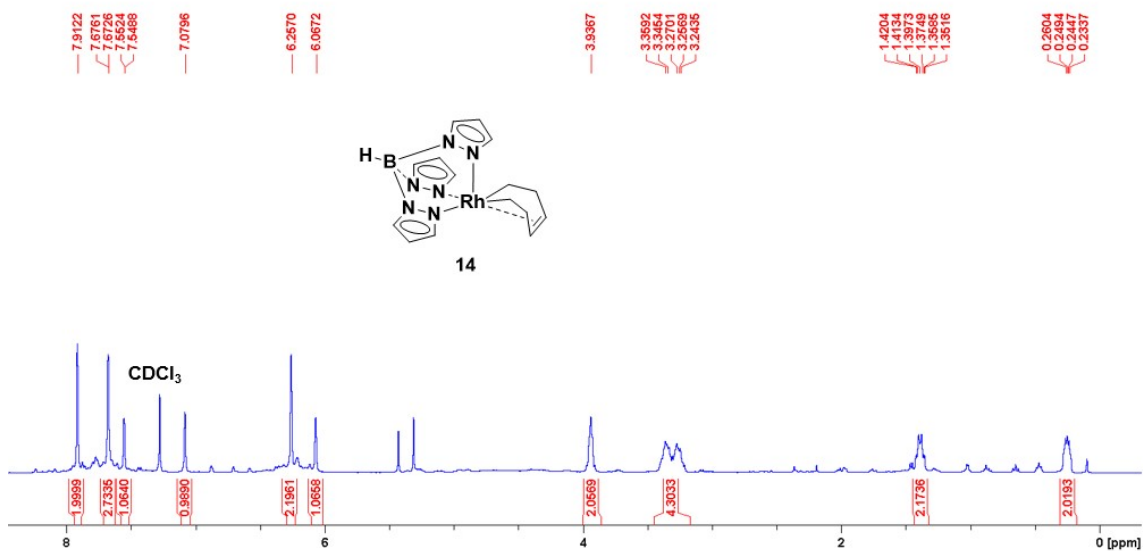


Figure S28. ^1H NMR spectrum of compound 14.

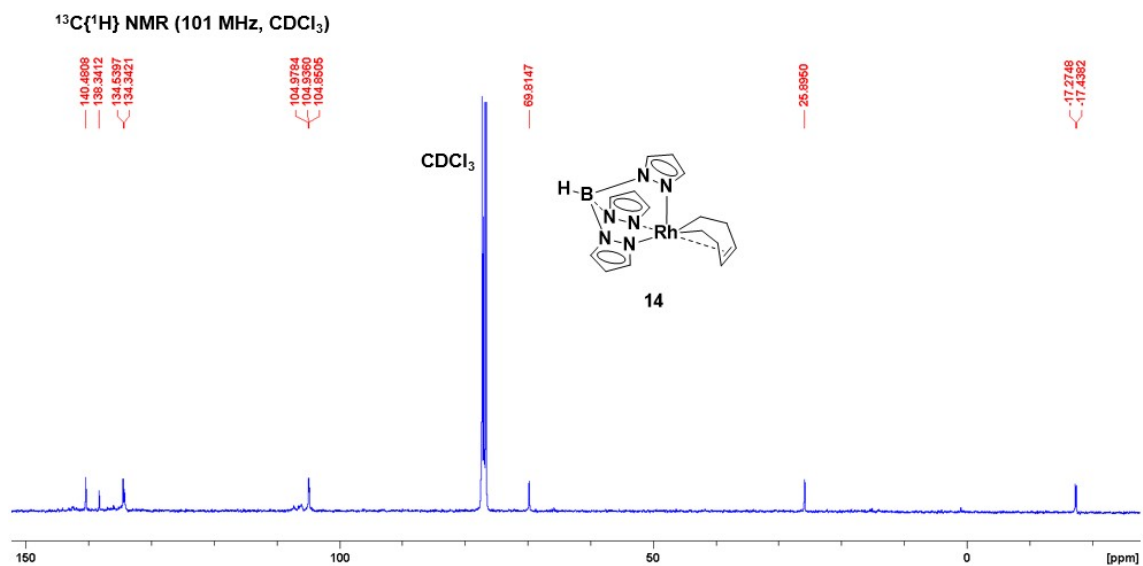


Figure S29. ¹³C{¹H} NMR spectrum of compound 14.

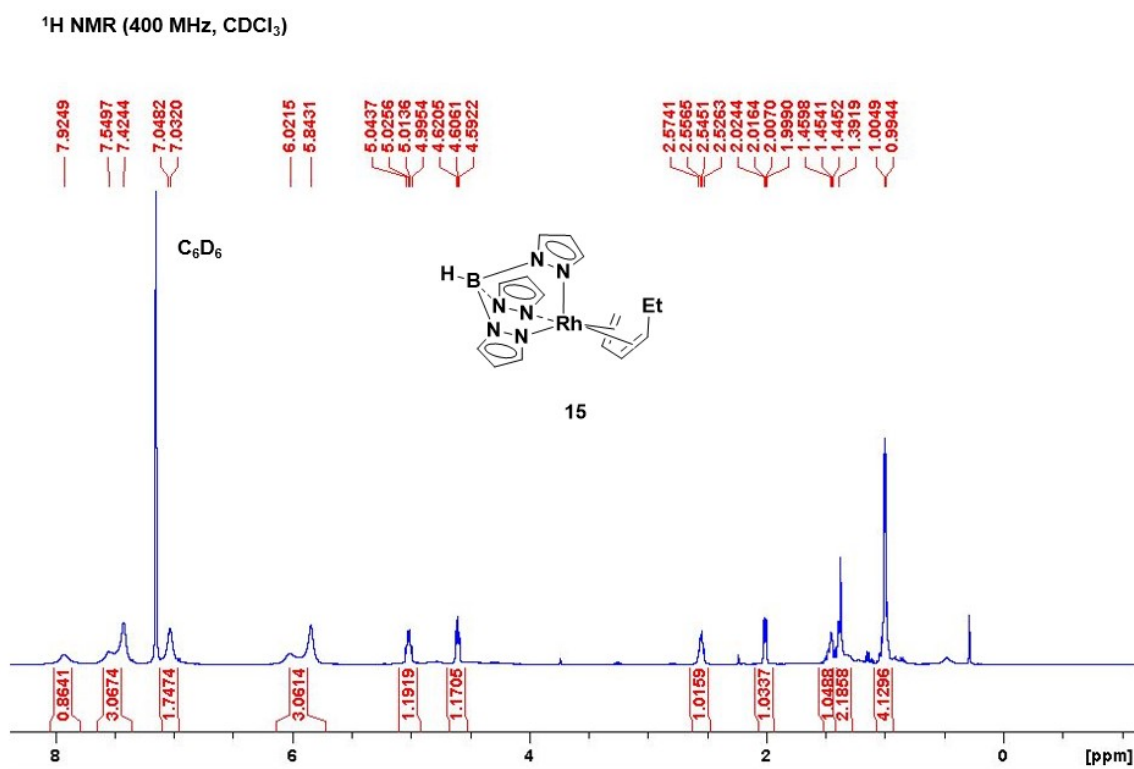


Figure S30. ¹H NMR spectrum of compound 15.

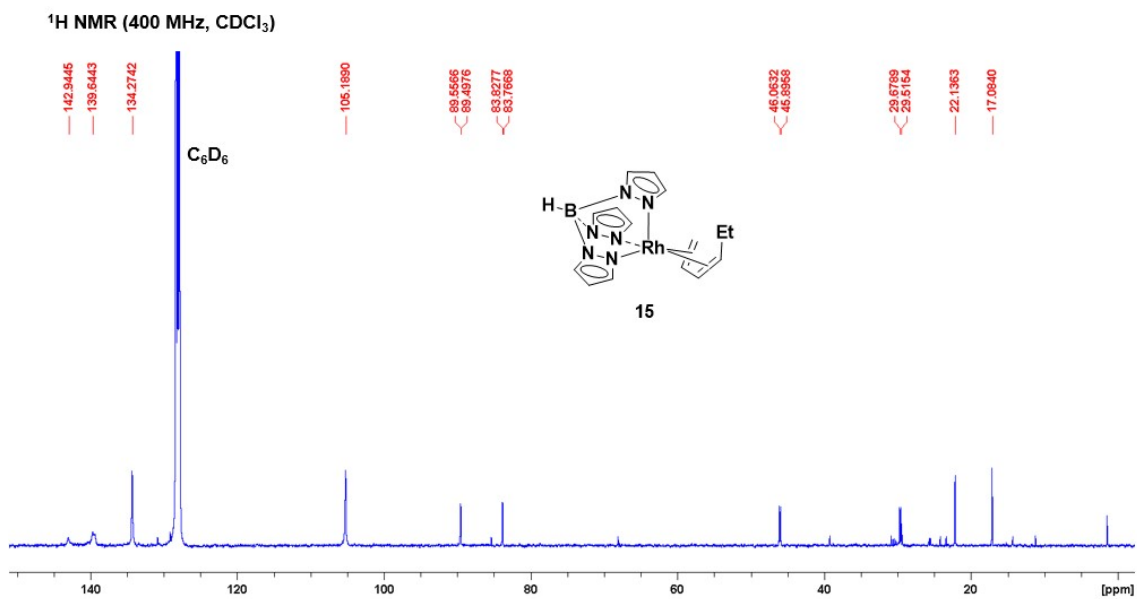


Figure S31. ¹³C{¹H} NMR spectrum of compound **15**.

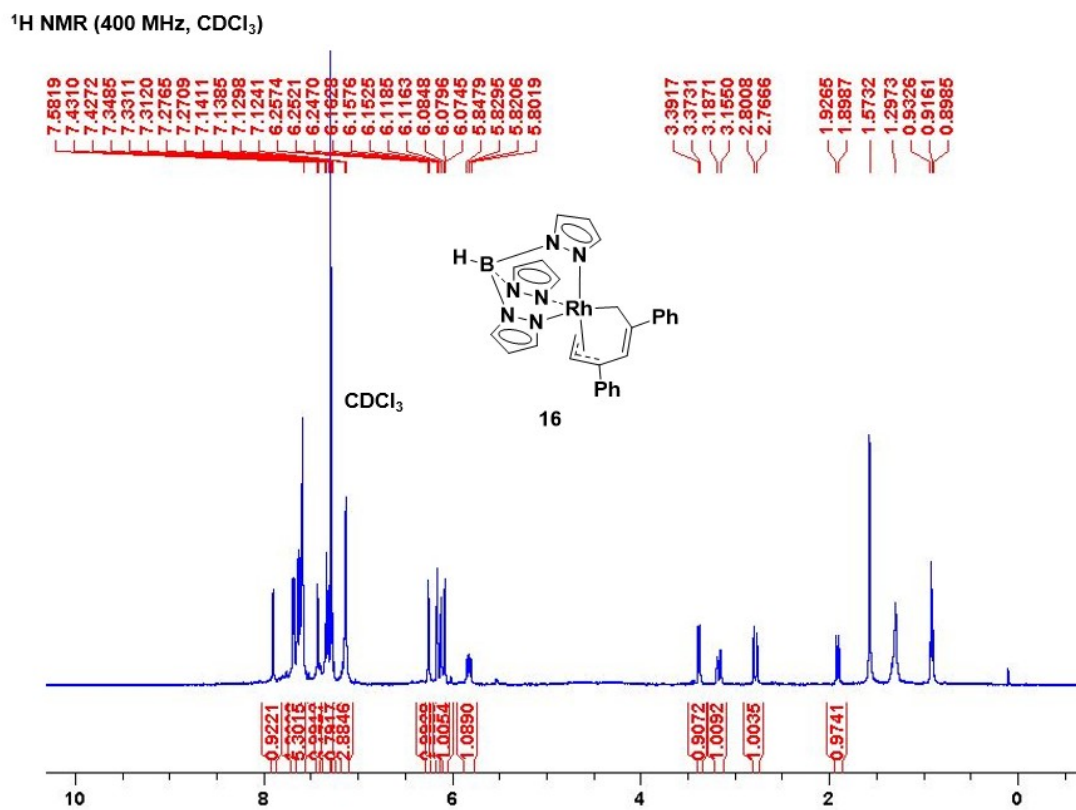


Figure S32. ¹H NMR spectrum of compound **16**.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)

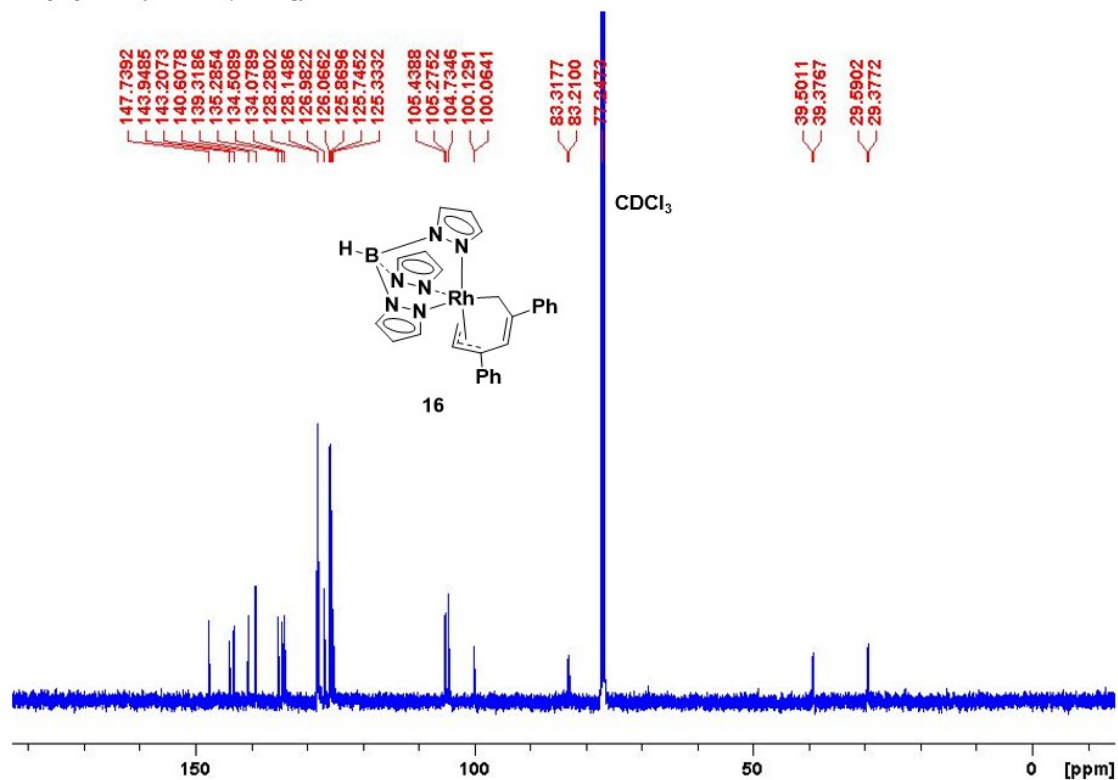


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 16.

^1H NMR (400 MHz, CDCl_3)

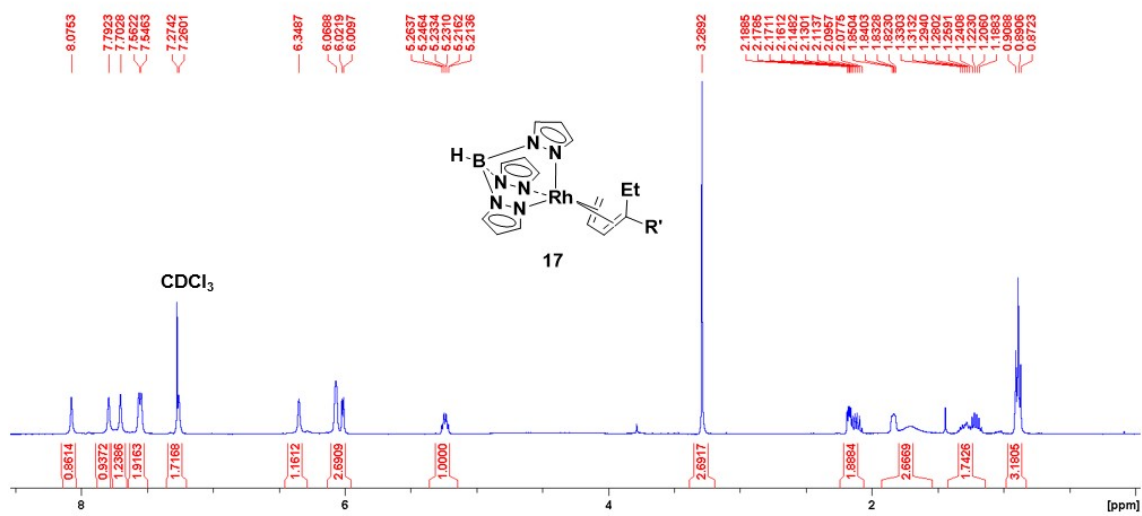


Figure S34. ^1H NMR spectrum of compound 17 ($\text{R}' = \text{CO}_2\text{Me}$).

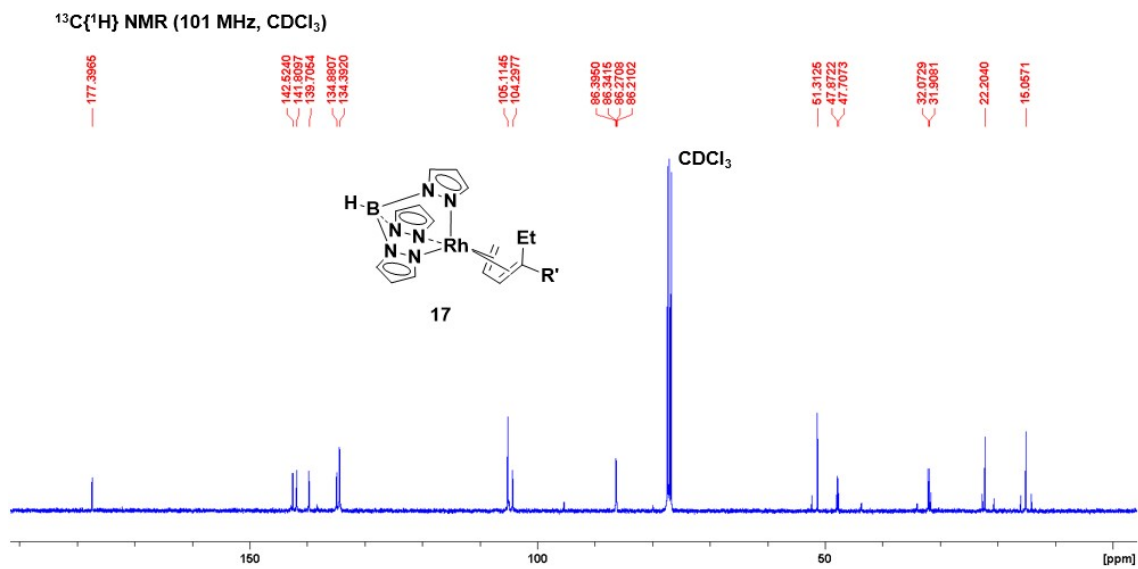


Figure S35. ¹³C{¹H} NMR spectrum of compound **17** (R' = CO₂Me).

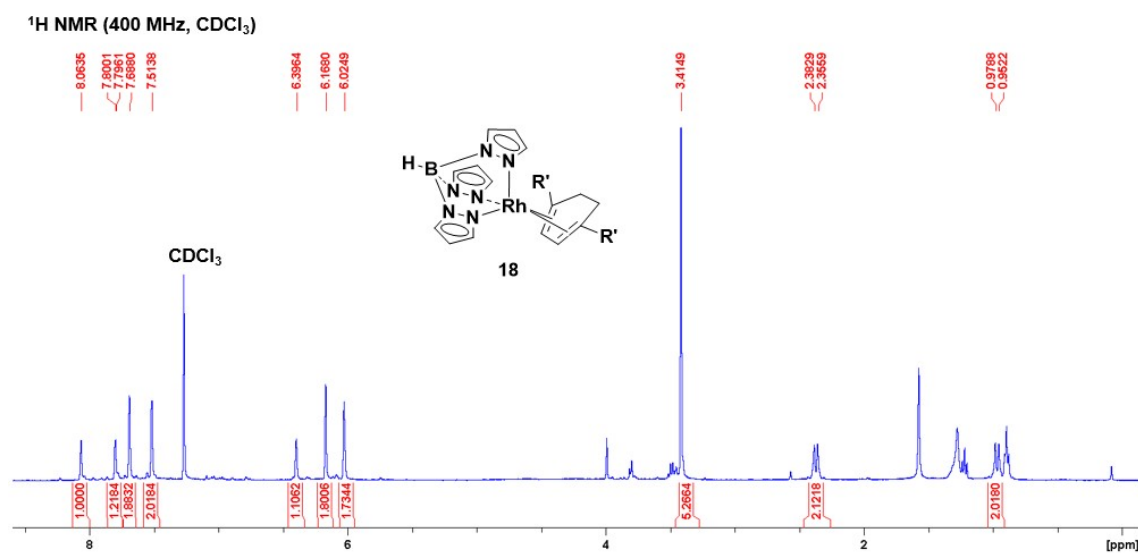


Figure S36. ¹H NMR spectrum of compound **18** (R' = CO₂Me).

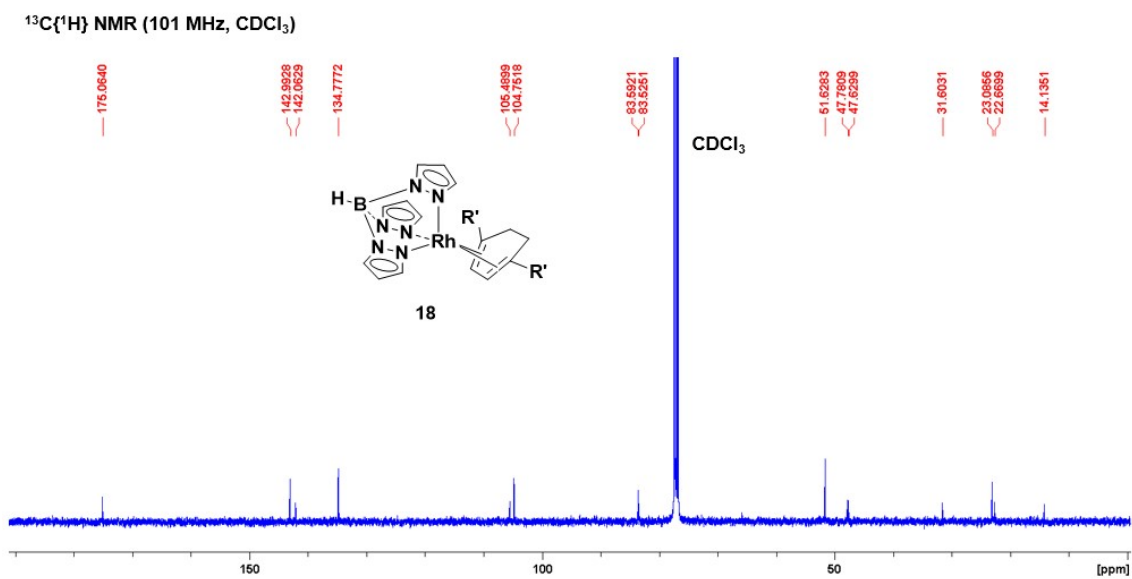


Figure S37. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **18** ($\text{R}' = \text{CO}_2\text{Me}$).

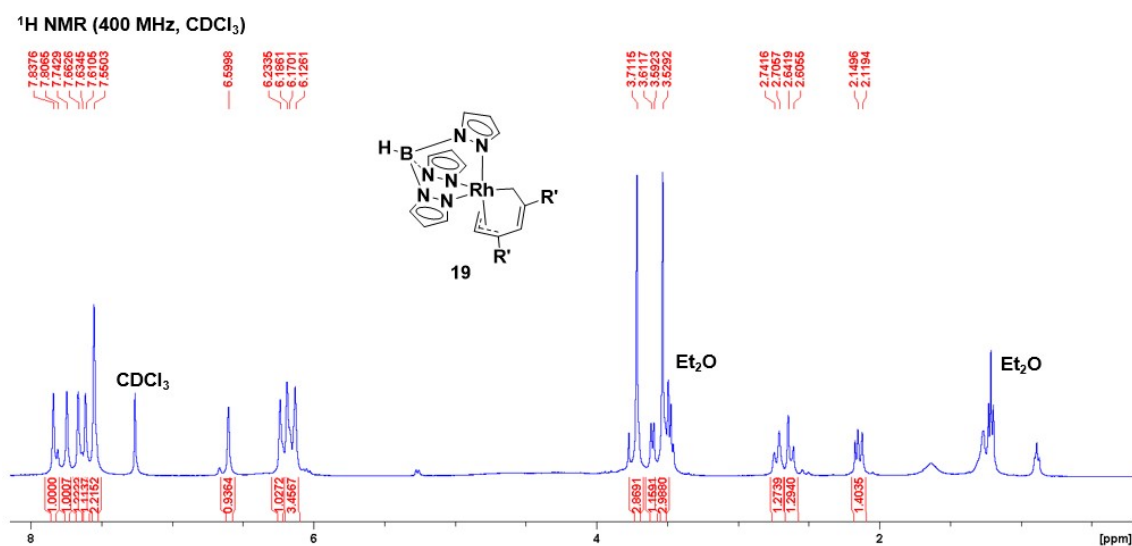


Figure S38. ^1H NMR spectrum of compound **19** ($\text{R}' = \text{CO}_2\text{Me}$).

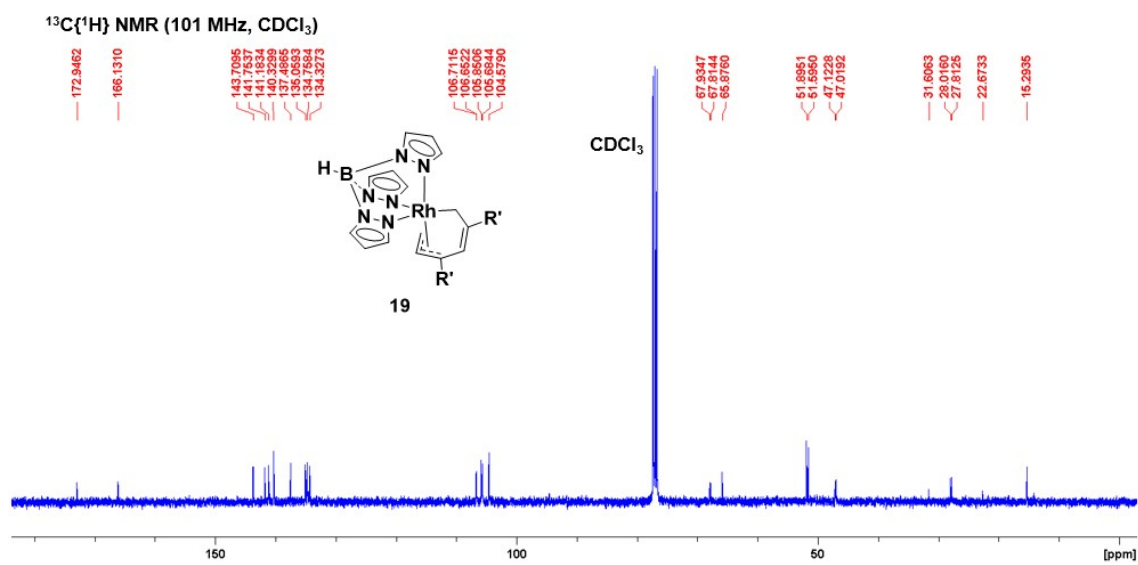


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **19** ($\text{R}' = \text{CO}_2\text{Me}$).