

Supporting Information for

Oxygenation of a Ruthenium Complex Bearing A PBP-Pincer Ligand Induced a Formation of Boronato Ligand with A Weak Ru–O Bond

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Experimental Section

General

The ^1H , $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on 600, 500 or 400 MHz spectrometers with residual protiated solvent for ^1H , deuterated solvent for $^{13}\text{C}\{^1\text{H}\}$, an external $\text{BF}_3\cdot\text{OEt}_2$ for $^{11}\text{B}\{^1\text{H}\}$, and an external 85% H_3PO_4 for $^{31}\text{P}\{^1\text{H}\}$ used as reference. Elemental analyses were performed by A Rabbit Science Co., Ltd. (<http://www.rabbit-sc.jp/>) using yanaco CHN corder MT-5. X-ray crystallographic analyses were recorded on a Rigaku VariMax Saturn CCD diffractometer. IR spectrum was measured on a Shimadzu IRAffinity and is uncorrected. Melting point was measured on a MPA100 Optimelt Automated Melting Point System and is uncorrected. Toluene (dehydrated, Kanto Chemical Co., Inc.) was purified by passing through a solvent purification system (Grass Contour). Benzene- d_6 (Kanto Chemical Co., Inc.) was dried by distillation over sodium-benzophenone followed by vacuum transfer. All other solvents (Kanto Chemical Co., Inc.) and *N*-methylnmorpholine *N*-oxide (Wako Pure Chemical Industries, Ltd.) were used as received. Hydroborane ligand precursor **1**^[1] and $\text{Ru}(\text{CO})_3(\text{cod})$ ^[2] were synthesized by a literature procedures.

Synthesis of [PBP]Ru(H)(CO)₂ (**2**)

A mixture of **1** (314 mg, 0.719 mmol) and Ru(CO)₃(cod) (264 mg, 0.900 mmol) in toluene (12.0 mL), prepared in a glovebox, was stirred at 100 °C for 5 h on the outside of glovebox. The resulting suspension was filtered and the filtrate was evaporated under reduced pressure. The crude product was adsorbed on silica gel and it was charged on the top of a silica gel column to be purified. Eluting with a solvent mixture (hexane : Et₂O = 8 : 1) gave a colorless solid of **2** (153 mg, 0.309 mmol, 42 %). ¹H NMR (C₆D₆, 500 MHz) δ -9.31 (t, ²J_{PH} = 23 Hz, 1H), 1.09 (vt, ³J_{PH} = 8 Hz, 18H), 1.24 (vt, ³J_{PH} = 8 Hz, 18H), 3.58 (d of vt, *J* = 12, 3 Hz, 2H), 3.71 (d, *J* = 12 Hz, 2H), 6.91 (dd, *J* = 6, 3 Hz, 2H), 7.11 (dd, *J* = 6, 3 Hz, 2H); ³¹P NMR (C₆D₆, 202 MHz) δ 122.2 (s); ¹¹B NMR (C₆D₆, 160 MHz) δ 53.1 (brs); ¹³C NMR (C₆D₆, 126 MHz) δ 29.7 (vt, ²J_{PC} = 3 Hz, CH₃), 30.0 (vt, ²J_{PC} = 3 Hz, CH₃), 36.1 (vt, ¹J_{PC} = 9 Hz, 4°), 36.6 (vt, ¹J_{PC} = 5 Hz, 4°), 43.6 (vt, ¹J_{PC} = 17 Hz, CH₂), 108.5 (CH), 118.2 (CH), 140.4 (vt, ³J_{PC} = 6 Hz, 4°), 205.4 (br m, CO), 207.4 (br m, CO); mp: 150-240 °C (dec.); IR (KBr) 1994, 1967, 1894 cm⁻¹; Anal. calcd. For C₂₆H₄₅BN₂O₂P₂Ru: C, 52.76; H, 7.67; N, 4.74. Found: C, 52.50; H, 7.76; N, 4.82.

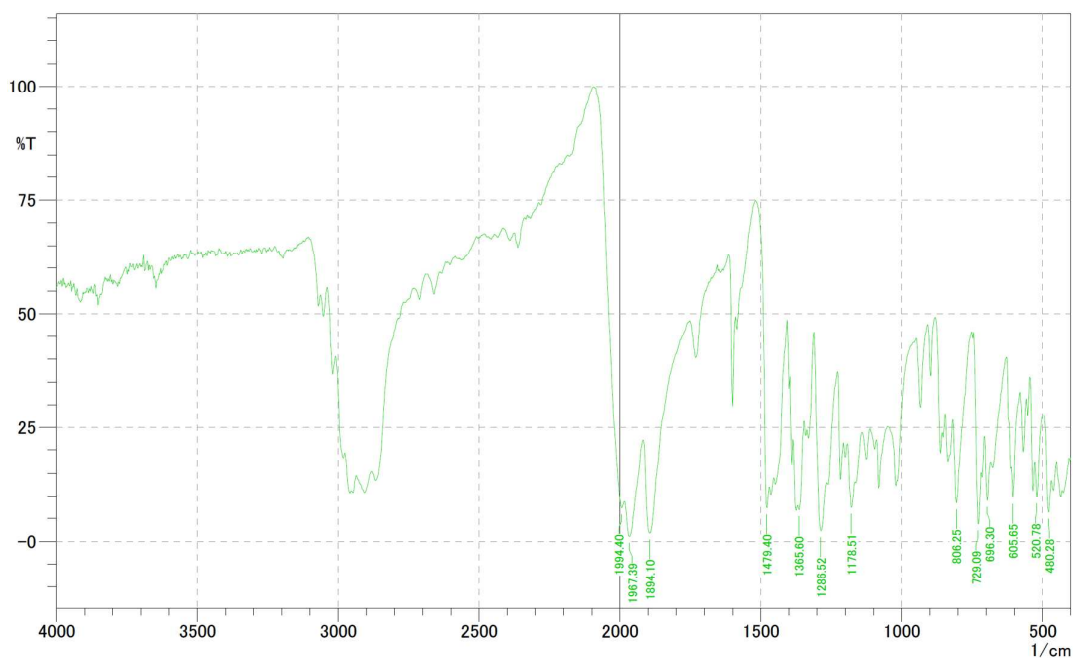


Figure S1. Infrared spectrum of **2** (KBr)

Oxidation of **2** to form **4**

In a glovebox, a solution of **2** (130.0 mg, 0.219 mmol) in CH₂Cl₂ (2.0 mL) was added to a solution of *N*-methylmorpholine *N*-oxide (50.9 mg, 0.435 mmol) in CH₂Cl₂ (2.0 mL), and then the resulting solution was stirred at room temperature for 20 min. The resulting suspension was filtered and the filtrate was evaporated under reduced pressure. Recrystallization of the crude product from toluene at -35 °C in a refrigerator of glovebox gave colorless crystals of **4** (63.4 mg, 0.109 mmol, 50%). ¹H NMR (C₆D₆, 500 MHz) δ -6.08 (t, ²J_{PH} = 12 Hz, 1H), 1.05 (vt, ³J_{PH} = 6 Hz, 18H), 1.35 (vt, ³J_{PH} = 6 Hz, 18H), 3.73 (vt, *J* = 3 Hz, 1H), 3.76 (vt, *J* = 3 Hz, 1H), 4.12 (vt, *J* = 3 Hz, 1H), 4.14 (vt, *J* = 3 Hz, 1H), 6.88 (dd, *J* = 6, 3 Hz, 2H), 7.10 (dd, *J* = 6, 3 Hz, 2H); ³¹P NMR (C₆D₆, 202 MHz) δ 115.9 (s); ¹¹B NMR (C₆D₆, 160 MHz) δ 22.7 (brs); ¹³C NMR (C₆D₆, 126 MHz) δ 30.0 (vt, ²J_{PC} = 3 Hz, CH₃), 31.1 (vt, ²J_{PC} = 3 Hz, CH₃), 35.4 (vt, ¹J_{PC} = 6 Hz, 4°), 37.1 (vt, ¹J_{PC} = 3 Hz, 4°), 43.2 (vt, ¹J_{PC} = 9 Hz, CH₂), 109.0 (CH), 118.3 (CH), 141.2 (br), 202.1 (br, CO), 203.6 (br, CO); mp: 120-200 °C (dec.); IR (KBr) 2029, 1956, 1915, and 1467 cm⁻¹; Anal. calcd. For C₂₆H₄₅BN₂O₃P₂Ru: C, 51.41; H, 7.47; N, 4.61. Found: C, 51.37; H, 7.21; N, 4.67.

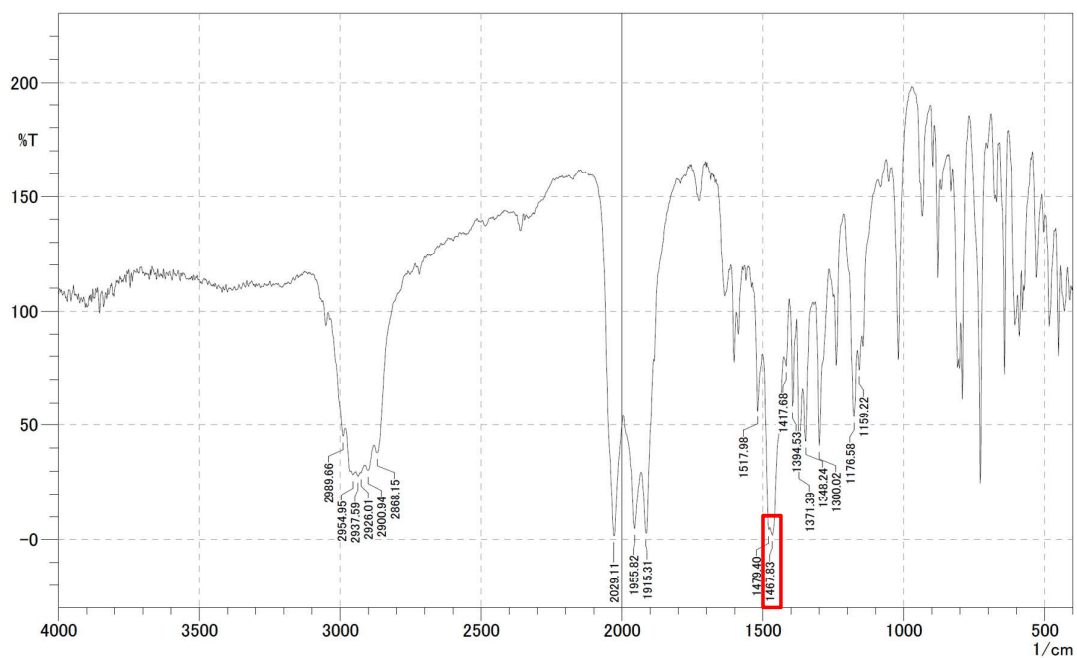


Figure S2. Infrared spectrum of **4** (KBr)

Details for X-ray crystallography

Details of the crystal data and a summary of the intensity data collection parameters for **2** and **4** are listed in Table S1. A suitable crystal was mounted with a mineral oil to the glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71070$ Å). All the following procedure for analysis, Yadokari-XG 2009^[3] was used as a graphical interface. The structure was solved by direct methods with (SIR-97)^[4] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).^[5] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms except hydride ligand were placed using AFIX instructions. Hydride ligand H1 was located on a residue of the Fourier map and was refined isotropically. The resulting CIF files and its checkCIF file is also attached as supporting information.

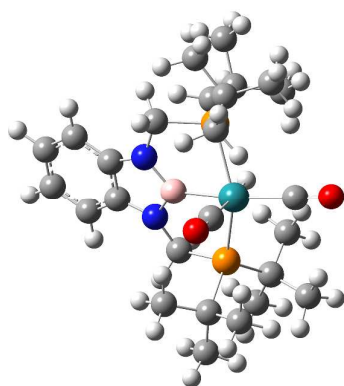
Table S1. Crystallographic data and structure refinement details for **2**·CHCl₃ and **4**

	2 ·CHCl ₃	4
CCDC deposit #	956437	956438
formula	C ₂₇ H ₄₆ BCl ₃ N ₂ O ₂ P ₂ Ru	C ₂₆ H ₄₅ BN ₂ O ₃ P ₂ Ru
fw	710.83	607.46
T (K)	193(2)	113(2)
cryst syst	<i>Monoclinic</i>	<i>Orthorhombic</i>
space group	<i>P2₁/n</i>	<i>Pbca</i>
<i>a</i> , (Å)	19.308(6)	11.472(4)
<i>b</i> , (Å)	8.596(3)	37.285(14)
<i>c</i> , (Å)	21.611(7)	13.446(5)
α , (°)	90	90
β , (°)	109.343(5)	90
γ , (°)	90	90
<i>V</i> , (Å ³)	3384.3(19)	5752(4)
<i>Z</i>	4	8
D _{calc.} (g/cm ³)	1.395	1.403
μ (mm ⁻¹)	0.821	0.686
F(000)	1472	2544
cryst size (mm)	0.20×0.15×0.10	0.60×0.20×0.05
2 θ range, (°)	1.73-25.00	2.18-25.00
reflns collected	22350	29952
indep reflns/ <i>R</i> _{int}	5939/0.0718	5028/0.0835
params	439	376
GOF on F^2	1.174	1.177
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.0753, 0.1385	0.0587, 0.0883
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0904, 0.1465	0.0797, 0.0957

Computational Details.

All optimizations (B3LYP, LANL2DZ for Rh and cc-pVDZ for others) were performed by Gaussian 09 (rev. C.01)^[6] running on a Fujitsu PRIMERGY RX 300 S7 system at Research Center for Computational Science in National Institutes of Natural Sciences. The crystal structures of **2** and **4** were used for the initial structure for optimization and all the optimized structures were confirmed to have no imaginary frequency (scaled with a factor of 0.970). Wiberg Bond Indices were estimated by using NBO 3.1 program (E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.).

Optimized structure of **2**

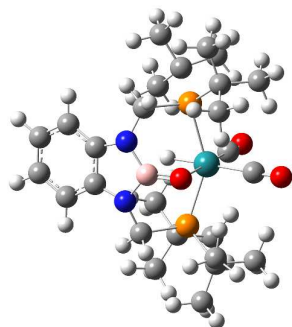


Cartesian coordinate for **2**

Ru	0.0422100	-1.0144270	-0.1847840
C	0.0667220	-2.9262140	0.3482500
O	0.0724500	-4.0191720	0.7235200
C	0.0762840	-1.2164610	-2.1225520
O	0.1004650	-1.2857960	-3.2786670
P	2.3641040	-0.3307550	0.1588300
P	-2.3358820	-0.4666370	0.0058100
B	-0.0306350	1.0797580	-0.3105640
N	1.0317750	2.0050360	-0.0110980
C	0.5215550	3.3071240	-0.0146350
C	-0.8654700	3.2390310	-0.3587900
N	-1.1980700	1.8936950	-0.5414370
C	3.5417940	-0.4055250	-1.3883140
C	3.2937990	-1.0055140	1.7265910
C	-3.6765430	-1.4628850	-0.9855830
C	-2.9346620	-0.2277170	1.8444660
C	2.2863280	-1.0700490	2.8925200
H	1.8345700	-0.0904450	3.1120060
H	1.4697140	-1.7745870	2.6938180
H	2.8227430	-1.4017600	3.7986340
C	4.4690860	-0.1156650	2.1860370
H	5.2731710	-0.0338790	1.4463380
H	4.1432460	0.9005580	2.4547830
H	4.9082560	-0.5597980	3.0963390
C	3.8042920	-2.4324280	1.4534260
H	3.0087030	-3.0879640	1.0683460
H	4.6425600	-2.4488130	0.7423470
H	4.1685000	-2.8729530	2.3975760
C	5.0034290	-0.0149970	-1.1031540
H	5.5266750	-0.7543830	-0.4810160

H	5.5462200	0.0399290	-2.0628880
H	5.0939310	0.9727250	-0.6255280
C	3.5140120	-1.8271220	-1.9839770
H	3.9477210	-2.5739800	-1.3043800
H	2.4965150	-2.1516440	-2.2369760
H	4.1107500	-1.8392830	-2.9126270
C	2.9889350	0.5881440	-2.4334820
H	3.0923880	1.6344710	-2.1101250
H	3.5692230	0.4736320	-3.3651790
H	1.9349350	0.4111550	-2.6762520
C	-3.0618630	-1.8160430	-2.3531300
H	-2.7270290	-0.9293580	-2.9124070
H	-2.2076070	-2.4969080	-2.2481980
H	-3.8272800	-2.3227270	-2.9659820
C	-4.9749700	-0.6705170	-1.2444970
H	-5.5067240	-0.3898250	-0.3281470
H	-4.7925040	0.2430770	-1.8305190
H	-5.6590210	-1.3003120	-1.8399640
C	-3.9977360	-2.7816770	-0.2584630
H	-3.0830300	-3.3392530	-0.0037810
H	-4.5782430	-2.6290480	0.6625370
H	-4.6024840	-3.4225790	-0.9233320
C	-2.5866070	-1.4875100	2.6601150
H	-3.1134750	-2.3836830	2.3041570
H	-1.5073390	-1.6889950	2.6339560
H	-2.8805410	-1.3258760	3.7118790
C	-4.4415770	0.0613820	1.9732560
H	-5.0657080	-0.7941890	1.6821520
H	-4.6680680	0.2822570	3.0305630
H	-4.7557160	0.9395270	1.3880590
C	-2.1761690	0.9694200	2.4558990
H	-1.0880020	0.8340110	2.4048300
H	-2.4314980	1.9251980	1.9749700
H	-2.4603800	1.0506760	3.5193090
C	-2.5012940	1.2945880	-0.7067980
H	-3.2862980	1.8591550	-0.1767420
H	-2.8005610	1.2272040	-1.7676680
C	2.2919180	1.5422600	0.5157370
H	3.1593840	2.0560870	0.0682870
H	2.3489620	1.6930340	1.6084300
H	0.0262750	-0.6164830	1.4079060
C	-1.6286600	4.4009740	-0.4523710
H	-2.6850050	4.3563260	-0.7265070
C	-1.0076900	5.6339960	-0.1886450
H	-1.5939680	6.5529680	-0.2570520
C	0.3457150	5.6996790	0.1562470
H	0.8064510	6.6691140	0.3581680
C	1.1261390	4.5342700	0.2472710
H	2.1823460	4.5898860	0.5199590

Optimized structure of 4



Cartesian coordinate for 4

Ru	0.0001250	-0.9728540	0.1744650
H	0.0000890	0.5908700	0.6367280
O	0.0001120	-0.3579760	-1.9224870
B	-0.0000180	0.9567870	-1.7183640
N	1.1680700	1.8081430	-1.4812040
N	-1.1682980	1.8078940	-1.4813400
P	2.3886460	-0.3202460	-0.0281570
P	-2.3886110	-0.3204960	-0.0282140
C	0.0000300	-1.4767280	1.9737290
O	0.0000220	-1.7926180	3.0900470
C	0.0002160	-2.8618970	-0.4509310
O	0.0002570	-3.9635520	-0.7841790
C	0.7144570	3.0432050	-1.0060040
C	1.4166360	4.1749320	-0.5954140
H	2.5090570	4.1911850	-0.6078930
C	0.6975360	5.3043920	-0.1655800
H	1.2418370	6.1922220	0.1636580
C	-0.6986820	5.3042440	-0.1656640
H	-1.2432100	6.1919590	0.1635090
C	-1.4174910	4.1746320	-0.5955840
H	-2.5099150	4.1906550	-0.6081920
C	-0.7150220	3.0430570	-1.0060890
C	2.4512500	1.2282770	-1.1963020
H	3.1201600	1.9689940	-0.7412560
H	2.9365660	0.8757740	-2.1169630
C	3.5058580	-1.5955120	-0.9711530
C	3.5133870	-2.9375050	-0.2142180
H	4.0581690	-3.6846520	-0.8169470
H	2.5003070	-3.3245940	-0.0447300
H	4.0191530	-2.8691840	0.7583200
C	4.9621400	-1.1377230	-1.1806390
H	5.5498750	-1.1717350	-0.2523670

H	5.0369620	-0.1246910	-1.6054870
H	5.4487450	-1.8253440	-1.8944630
C	2.8593960	-1.8123220	-2.3593300
H	3.0586800	-0.9722930	-3.0416470
H	1.7695320	-1.9301940	-2.3120870
H	3.3027200	-2.7143160	-2.8149450
C	3.2559020	0.3177360	1.5907380
C	3.5427400	-0.8529030	2.5506820
H	4.3888590	-1.4687200	2.2125410
H	2.6710360	-1.5071950	2.6922070
H	3.8138140	-0.4459730	3.5403650
C	4.5729700	1.0819530	1.3419990
H	4.9757800	1.4030920	2.3181460
H	4.4288650	1.9961240	0.7476030
H	5.3446600	0.4728170	0.8565540
C	2.2741110	1.2933790	2.2726620
H	1.3693990	0.7869460	2.6299410
H	1.9598960	2.1130440	1.6085580
H	2.7777300	1.7446440	3.1452090
C	-2.4513950	1.2277070	-1.1967310
H	-2.9362140	0.8748010	-2.1174940
H	-3.1207550	1.9682980	-0.7421370
C	-3.2557890	0.3176700	1.5906310
C	-3.5429600	-0.8529530	2.5504970
H	-2.6714370	-1.5074880	2.6920340
H	-4.3892290	-1.4685170	2.2122810
H	-3.8139690	-0.4460220	3.5401950
C	-2.2739220	1.2931280	2.2727020
H	-2.7776600	1.7445640	3.1450930
H	-1.9593540	2.1126550	1.6086140
H	-1.3694110	0.7865200	2.6302460
C	-4.5726770	1.0821680	1.3417710
H	-5.3442060	0.4734230	0.8555820
H	-4.4281580	1.9966980	0.7480220
H	-4.9758980	1.4027570	2.3179270
C	-3.5057080	-1.5960960	-0.9708830
C	-4.9621140	-1.1386300	-1.1801990
H	-5.4487440	-1.8265520	-1.8937180
H	-5.0372040	-0.1257420	-1.6053390
H	-5.5496460	-1.1724620	-0.2517890
C	-3.5128440	-2.9380360	-0.2138640
H	-4.0183540	-2.8697690	0.7588000
H	-2.4996540	-3.3249480	-0.0446430
H	-4.0576590	-3.6852780	-0.8164440
C	-2.8593350	-1.8128750	-2.3591250
H	-3.3021040	-2.7152830	-2.8144540
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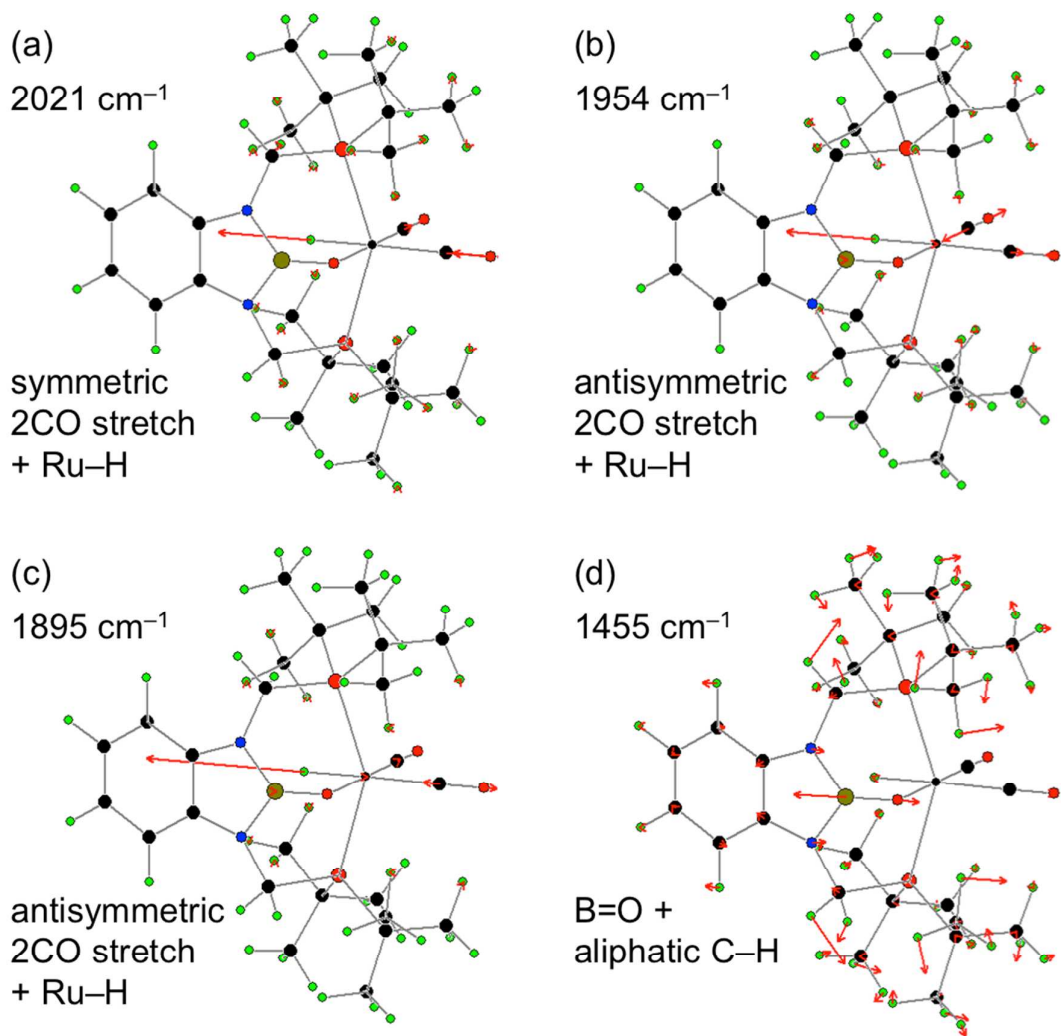


Figure S1. DFT-calculated vibrational mode of **4** and their assignment

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