SUPPORTING INFORMATION

$[Rh_2(MEPY)_4]$ and $[BiRh(MEPY)_4]$: Convenient Syntheses and Computational Analysis of Strikingly Dissimilar Siblings

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Supporting Crystallographic Information

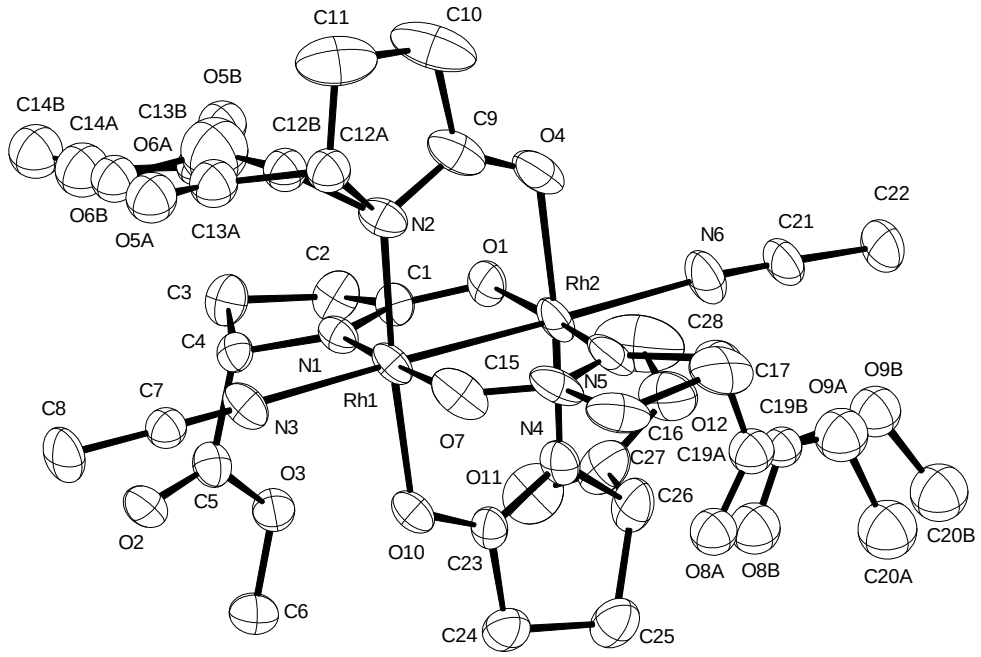


Figure S1. Structure of [RhRh(5*S*-MEPY)$_4$]·2MeCN (**1b**) in the solid state. H atoms have been removed for clarity.

X-Ray Crystal Structure Analysis of Complex 1b. $C_{28}H_{38}N_6O_{12}Rh_2$, M_r = 856.46 g · mol^{-1}, red prism, crystal size 0.131 x 0.073 x 0.072 mm^3, orthorhombic, space group $P2_12_12_1$ [19], a = 10.0391(16) Å, b = 18.827(3) Å, c = 19.385(3) Å, V = 3663.8(10) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.553 g · cm^3, λ = 0.71073 Å Å, μ(*Mo*-K_α) = 0.964 mm^{-1}, Gaussian absorption correction (T_{min} = 0.91, T_{max} = 0.95), Bruker-AXS Kappa Mach3 APEX-II-diffractometer with Iμs X-ray source , 2.299 < θ < 33.405°, 115805 measured reflections, 14225 independent reflections, 9394 reflections with $I > 2\sigma(I)$, R_{int} = 0.2101, 432 parameters, absolute structure parameter = −0.01(3), S = 0.950, residual electron density 1.3 (0.89 Å from Rh2) / −1.8 (0.85 Å from Rh1) e · Å^{-3}.

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.056 [$I > 2\sigma(I)$], wR_2 = 0.133. **CCDC-2068752**.

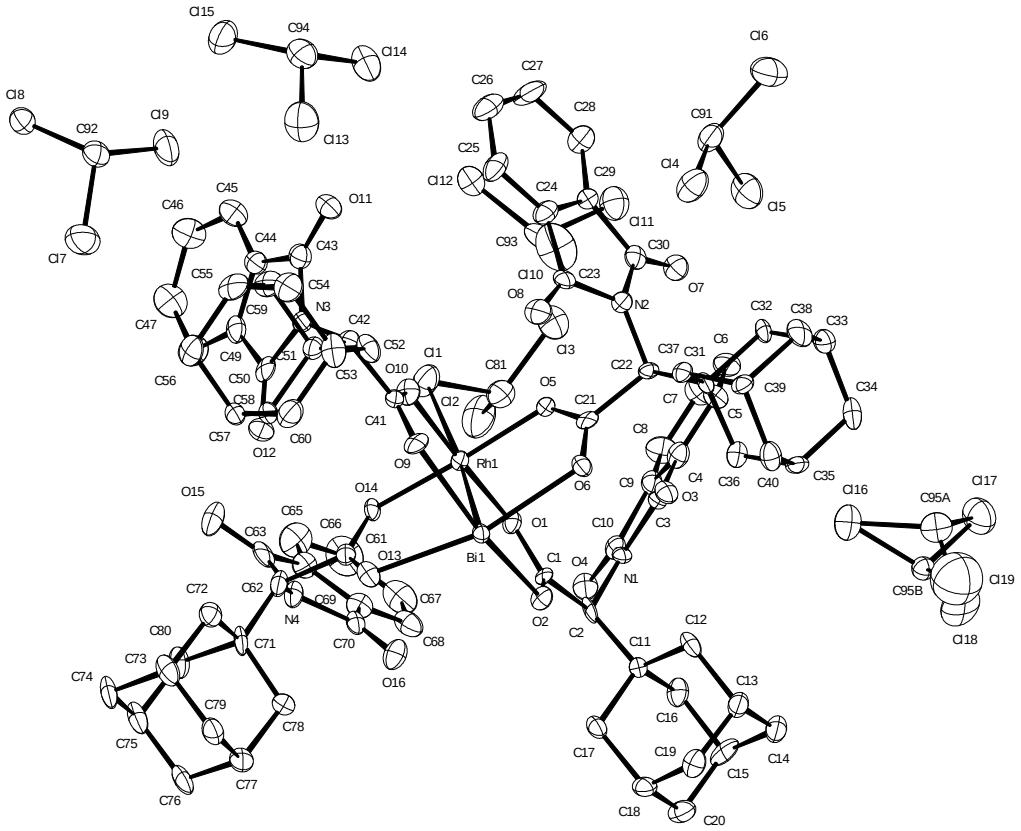


Figure S2. Structure of [BiRh(*S*-PTAD)$_4$] (**10a**) in the solid state. H atoms have been removed for clarity.

X-Ray Crystal Structure Analysis of Complex 10a. $C_{86}H_{86}BiCl_{18}N_4O_{16}Rh$, M_r = 2381.57 g · mol^{-1}, yellow prism, crystal size 0.12 x 0.06 x 0.04 mm^3, monoclinic, space group $P2_1$ [4], a = 14.8828(10) Å, b = 15.4447(18) Å, c = 20.427(3) Å, β = 91.462(6)°, V = 4693.9(9) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.685 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 2.626 mm^{-1}, Gaussian absorption correction (T_{min} = 0.62, T_{max} = 0.79), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode, 2.738 < θ < 28.281°, 53501 measured reflections, 22830 independent reflections, 18274 reflections with $I > 2\sigma(I)$, R_{int} = 0.0579, 1143 parameters, absolute structure parameter = −0.015(3), S = 1.054, residual electron density 1.6 (0.93 Å from Bi1) / −1.1 (0.94 Å from Bi1) e · Å^{-3}.

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.051 [$I > 2\sigma(I)$], wR_2 = 0.103. **CCDC-2068750**.

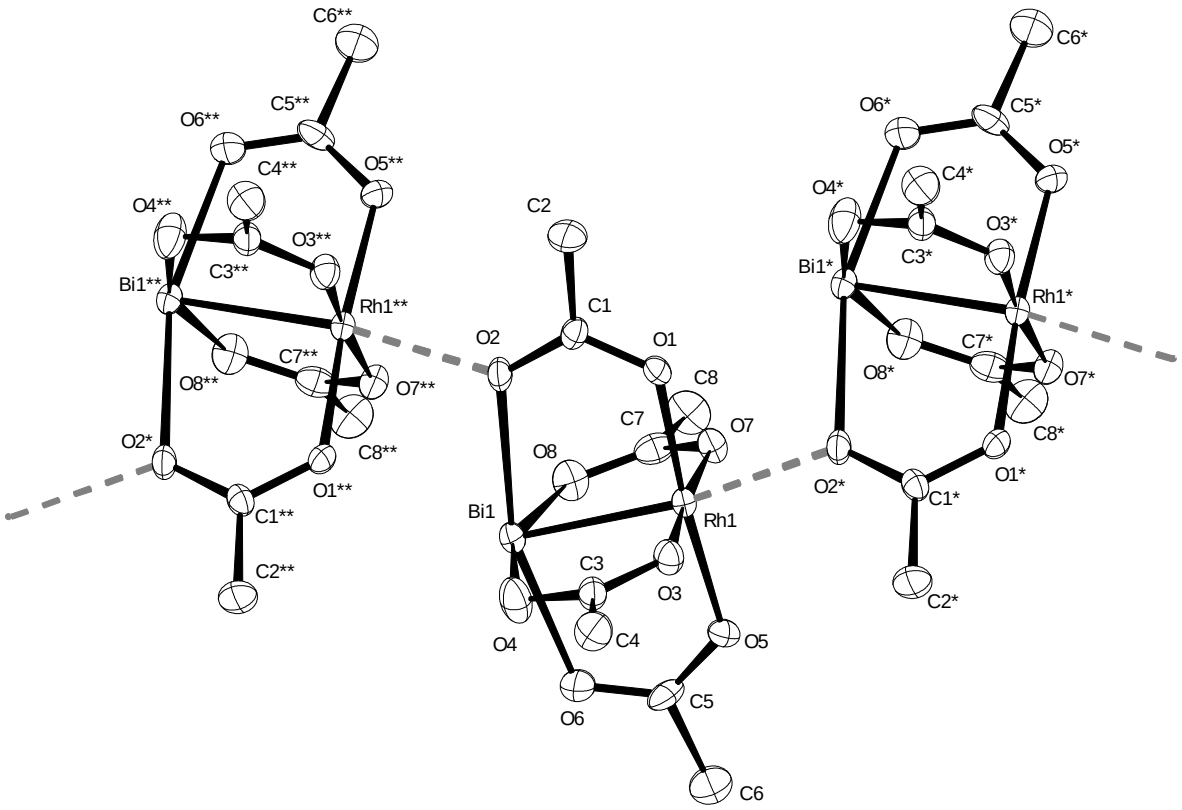


Figure S3. Structure of [BiRh(OAc)$_4$] (**12**) in the solid state. H atoms have been removed for clarity.

X-ray Crystal Structure Analysis of Complex 12. $C_8H_{12}BiO_8Rh$, M_r = 548.07 g · mol^{-1}, yellow needle, crystal size 0.06 x 0.02 x 0.02 mm^3, monoclinic, space group *Cc* [9], a = 12.2910(4) Å, b = 11.4179(4) Å, c = 9.4318(7) Å, β = 92.033(5)°, V = 1322.80(12) Å^3, T = 100(2) K, Z = 4, D_{calc} = 2.752 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 14.560 mm^{-1}, Gaussian absorption correction (T_{min} = 0.47, T_{max} = 0.73), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode, 3.217 < θ < 36.058°, 15443 measured reflections, 5361 independent reflections, 4156 reflections with $I > 2\sigma(I)$, R_{int} = 0.0538, 167 parameters, absolute structure parameter = −0.033(5), S = 1.028, residual electron density 1.4 (0.44 Å from Bi1) / −1.8 (0.73 Å from Bi1) e · Å^{-3}.

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.037 [$I > 2\sigma(I)$], wR_2 = 0.075. **CCDC-2068749**.

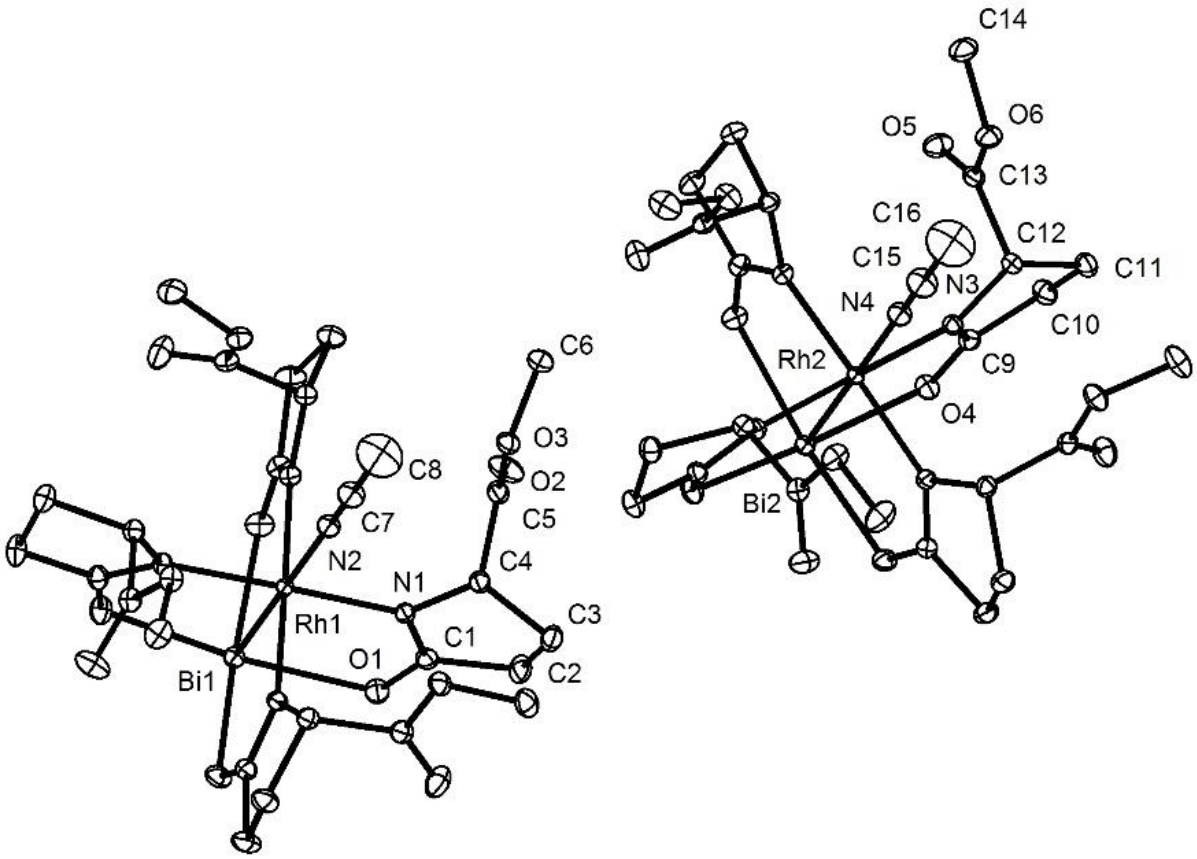


Figure S4. Structure of [BiRh(5*S*-MEPY)$_4$]·NCMe (**13**) in the solid state. H atoms have been removed for clarity.

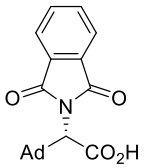
X-Ray Crystal Structure Analysis of Complex 13. $C_{26}H_{35}BiN_5O_{12}$, M_r = 921.48 g · mol^{-1}, yellow prism, crystal size 0.161 x 0.122 x 0.114 mm^3, tetragonal, space group *P4* [75], *a* = 11.3085(5) Å, *b* = 11.3085(5) Å, *c* = 12.0596(5) Å, *V* = 1542.21(15) Å^3, *T* = 100(2) K, *Z* = 2, D_{calc} = 1.984 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 6.303 mm^{-1}, Gaussian absorption correction (T_{min} = 0.57, T_{max} = 0.66), Bruker-AXS Kappa Mach3 APEX-II-diffractometer with Iμs X-ray source, 1.689 < θ < 41.810°, 133624 measured reflections, 10534 independent reflections, 9897 reflections with $I > 2\sigma(I)$, R_{int} = 0.0219, 213 parameters, absolute structure parameter = −0.0202(8), *S* = 1.070, residual electron density 0.9 (0.50 Å from N2) / −1.0 (0.05 Å from Bi1) e · Å^{-3}.

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.013 [$I > 2\sigma(I)$], wR_2 = 0.032. **CCDC- 2068751**.

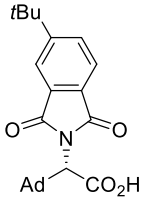
Additional Experimental Data

Chiral Ligands

(*S*-PTAD−H). A mixture of (1*S*)-(adamantan-1-yl)(carboxy)methanaminium chloride (491 mg, 2.0 mmol),[1] phthalic anhydride (296 mg, 2.0 mmol) and Et_3N (306 µL, 2.2 mmol) in toluene (15 mL) was stirred at 125°C for 2 h using a Dean-Stark apparatus to collect the released water. The reaction was quenched with aqueous HCl (1 M, 15 mL) and the resulting solution was extracted with EtOAc (2×30 mL). The combined organic layers were washed with brine (2×20 mL), dried over Na_2SO_4 and concentrated in vacuo. The white residue was purified by flash chromatography using CH_2Cl_2/MeOH (96:4) as eluent to obtain the desired product as a white solid (380 mg, 70%). The recorded data matched with those reported in the literature.[2]



(*S*-^{tert}PTAD−H). A mixture of (1*S*)-(-adamantan-1-yl)(carboxy)methanaminium chloride (722 mg, 2.938 mmol),[1] 5-(*tert*-butyl)isobenzofuran-1,3-dione (660 mg, 3.232 mmol) and Et_3N (491 µL, 3.528 mmol) in toluene (35 mL) was stirred at 125°C for 4 h, using a Dean-Stark apparatus to collect the water. The reaction was quenched with aqueous HCl (1 M, 15 mL) and the resulting solution was extracted with EtOAc (2×30 mL). The combined organic layers were washed with brine (2×20 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography using CH_2Cl_2/MeOH (97:3) as eluent to obtain the desired product as a white solid (1.12 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.76 (q, *J* = 7.9 Hz, 2H), 4.57 (s, 1H), 1.98 (d, *J* = 13.6 Hz, 6H), 1.74 (d, *J* = 11.5 Hz, 3H), 1.64 (s, 6H), 1.37 ppm (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): *δ* = 173.4, 168.8, 168.4, 159.1, 131.9, 131.4, 129.0, 123.6, 121.0, 60.9, 39.5, 37.8, 36.7, 35.9, 31.3, 28.6 ppm; IR (ATR): $\tilde{\nu}$ = 1775, 1711, 1619, 1430, 1366, 1349, 1180, 1092, 755, 693, 654, 566 cm^{-1}; HRMS (ESI$^-$) for $C_{24}H_{28}NO_4$ [*M*−H]$^-$: calcd: 394.20238, found: 394.20242.



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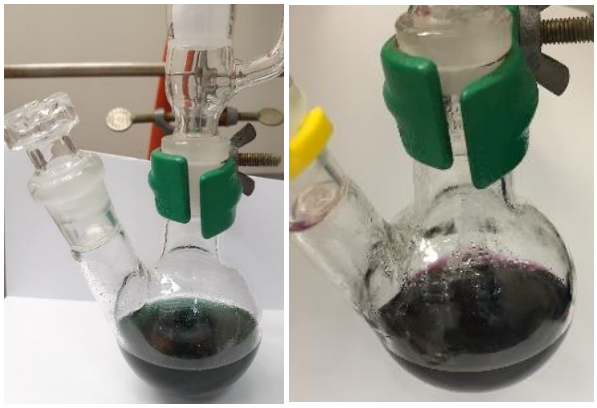
Illustrated Procedure for the Preparation and Isolation of [Rh_2(5*S*-MEPY)$_4$]·2 MeCN (1b).

A two-necked 50 mL, round bottom flask equipped with a magnetic stir bar, an inert gas adapter on the side neck, and a Soxhlet apparatus topped by a reflux condenser, which also carries an inert gas adapter, was evacuated, flame-dried, and allowed to cool to ambient temperature before it was refilled with argon. A thimble containing a layer of dry sand and a layer of dry K_2CO_3 (4.4 g) was introduced into the Soxhlet apparatus[3] under Ar before the gas adapter on the side neck was replaced by a glass stopper.



The flask was charged with chlorobenzene (22.5 mL), which had been degassed prior to use by passing a stream of Ar through it for 20 min. Next, commercial [$Rh_2(OAc)_4$] (300.0 mg, 679 µmol) was added, followed by methyl 2-pyrrolidone-5*S*-carboxylate (**7**, 5*S*-MEPY-H, 651.0 mg, 4.7 mmol). The flask was immersed into a pre-heated oil bath (145°C) and the mixture stirred at this temperature for 13 h, causing a color change from green to dark red.[4]

[3] Alternatively, a frit with a bridging side arm as shown on the photograph can be used instead of a Soxhlet extractor and a thimble

[4] Reaction time and temperature are important parameters to avoid accumulation of isomeric [Rh_2(5*S*-MEPY)$_4$] complexes and complexes resulting from incomplete substitution oft he acetate ligands by MEPY, which result in

The mixture was allowed to reach ambient temperature and the solvent was evaporated in high vacuum (10^{-3} mbar) to give a deep blue/violet solid material. An aliquot of this compound was purified by sublimation (130°C, 10^{-3} mbar) to give $[Rh_2(5S\text{-MEPY})_4]\cdot 2(S\text{-MEPY-H})_2$ (**1c**). The crude blue compound was dissolved in MeCN (20 mL) under air to give a dark red solution.

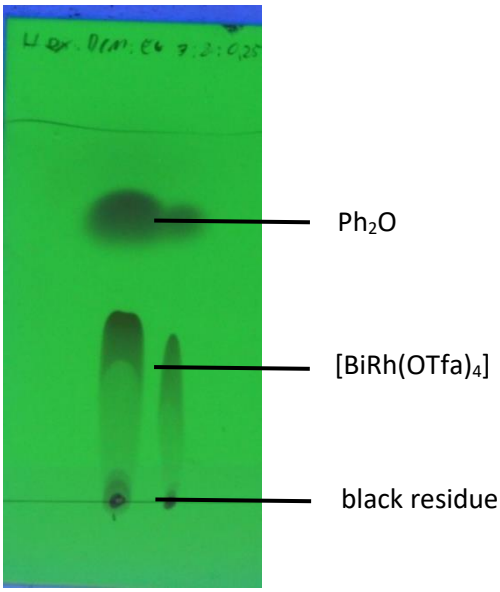
Silica gel (8 g) was added with stirring, resulting in decolorization of the solution. The now dark red solid material was filtered off and carefully rinsed with MeCN (3 x 50 mL); the combined MeCN filtrates were discarded. The still red silica was then washed with MeOH (3 x 50 mL) until it was colorless, and the combined blue MeOH filtrates were evaporated on a rotary evaporator to leave a violet solid material. This purification step was repeated three times.

lower yields of product and/or may compromise the performance of the catalyst, see: C. J. Welch, Q. Tu, T. Wang, C. Raab, P. Wang, X. Jia, X. Bu, D. Bykowski, B. Hohenstaufen, M. P. Doyle, *Adv. Synth. Catal*. **2006**, *348*, 821-825.

A flame-dried Schlenk flask containing a magnetic stir bar was charged with this solid material. The compound was then heated in vacuum (10^{-3} mbar) for 14 h to 100°C with gentle stirring until the solid had taken a turquoise color.

The flask was refilled with Ar and allowed to cool to ambient temperature before dry MeCN (1 mL) was introduced. After stirring for 5 min, the remaining solvent was evaporated and the product dried in vacuum to furnish the title complex as a red/violet solid material (473 mg, 81%). $[\alpha]_D^{20}$ = −335.7 (0.014 g/100 mL, $CHCl_3$); δ = 4.32 – 4.27 (m, 2H), 3.95 (d, J = 8.7 Hz, 2H), 3.71 (s, 6H), 3.68 (s, 6H), 2.63 – 2.59 (m, 4H), 2.31 – 2.21 (m, 10H), 2.20 – 211 (m, 4H), 1.97 – 1.82 ppm (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 188.6, 188.3, 175.5, 175.2, 115.4, 66.8, 66.7, 52.1, 51.9, 31.8, 31.6, 26.1, 25.4, 3.07 ppm; IR (film) $\tilde{\nu}$ = 2950, 1729, 1608, 1428, 1279, 1193, 1168, 1117, 1043, 987, 686, 595 cm^{-1}; HRMS (ESI^+): m/z calcd. for $C_{28}H_{38}N_6O_{12}Rh_2$ [M+Na−(2×MeCN)]$^+$: 797.00190; found: 797.00231.

[BiRh(OTfa)$_4$] (9). [Rh$_2$(OTfa)$_4$]·2MeCN (**8**) (534 mg, 0.722 mmol) was heated to 80°C under high vacuum (10^{-3} mbar) for 1 h to remove the axially bound ligands; during this time, the color of the sample changed from purple to green. Next, Bi(OTfa)$_3$ (415 mg, 0.757 mmol),[5] freshly ground Bi metal (817 mg, 3.91 mmol), toluene (40 mL), Ph$_2$O (1.1 mL, 6.93 mmol) and trifluoroacetic acid (200 µL, 2.61 mmol) were added. The mixture was stirred at 115°C bath temperature for 16 h and the reaction progress was monitored by ^{19}F NMR analysis. The remaining Bi metal was allowed to settle and the supernatant was removed via cannula. The yellow filtrate was concentrated in vacuo. Most of the remaining Ph$_2$O was sublimed onto a cold (−30°C) sublimation finger at 50°C under high vacuum (10^{-3} mbar). The residue was purified by flash chromatography (toluene/MeCN, gradient 100:0 ⟶ 90:10); some black residue sticks on top of the column, whereas a broad yellow-brown band containing the product was collected (see the adjacent photographs). Evaporation of the product-containing fraction afforded the title complex as a yellow powder (855 mg, 82%). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): δ −74.2 ppm.



TLC plate of the crude reaction mixture showing the distinct separation of [BiRh(OTfa)$_4$] from side products (eluent: hexanes/CH_2Cl_2/EtOAc, 7:2:0.25)

The yellow band of [BiRh(OTfa)$_4$] is eluted with toluene/MeCN (gradient 100:0 ⟶ 90:10), whereas the black impurities stick on top of the column.

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Computational Details

All calculations presented in this publication were carried out with the ORCA 4.2 program package.[1,2] All geometries were optimized at DFT level using the BP86[3] functional and the ZORA-def2-TZVP basis set.[4] The D3 version of Grimme's dispersion correction including Becke–Johnson damping (D3(BJ))[5,6] was applied together with the scalar relativistic zeroth-order regular approximation (ZORA Hamiltonian).[7,8] The resolution-of-identity (RI) approximation was utilized with the corresponding SARC/J auxiliary basis set[9,10] to speed up the calculation of the two-electron integrals.[11–13] The calculations include the implicit solvent effects by employing the conductor–like polarizable continuum model (CPCM)[14–17] using the Van-der-Waals Gaussian surface type for CH_2Cl_2 solvent. In all cases, a fine integration grid (grid7, nofinalgrid) was used as well as very tight SCF convergence criteria. Stationary points were characterized by the numeric calculation of the Hessian. This level of theory is noted as BP86-D3(BJ)-CPCM/ZORA-def2-TZVP. The molecular orbitals were visualized by Avogadro, using an isosurface value of 0.08.

References

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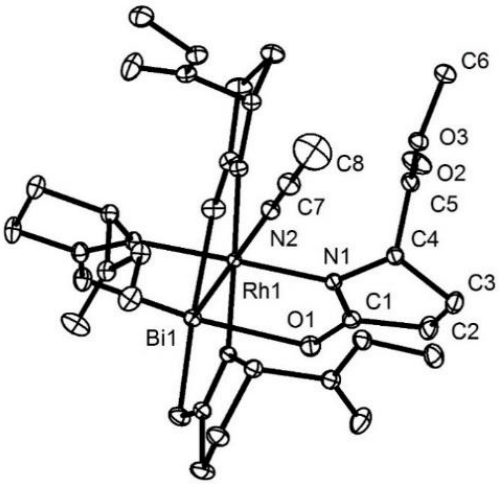
Geometric Structures

[BiRh(5*S*-MEPY)$_4$]·MeCN

X-Ray Structure



DFT-optimized structure

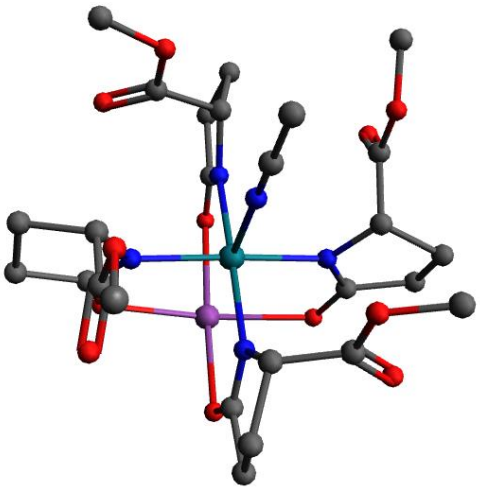


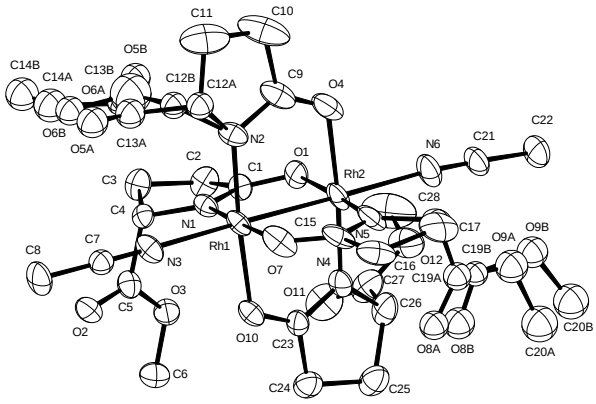
Figure S5. Structure of [BiRh(5*S*-MEPY)$_4$]·MeCN in the solid state (left); DFT-optimized structure (right).

Table S1. Selected Bond Lengths [Å] of [BiRh(5*S*-MEPY)$_4$]·MeCN; the crystallographic data refer to the two independent molecules in the unit cell

	X-Ray	**DFT**
Bi–Rh	2.573(2) / 2.577(2)	2.61
Bi–O (average)	2.37	2.40 – 2.41
Rh–N (average)	2.06	2.07
Rh–$NCCH_3$	2.231(3) / 2.240(3)	2.18

[RhRh(5*S*-MEPY)$_4$]·2MeCN

X-Ray Structure



DFT optimized structure

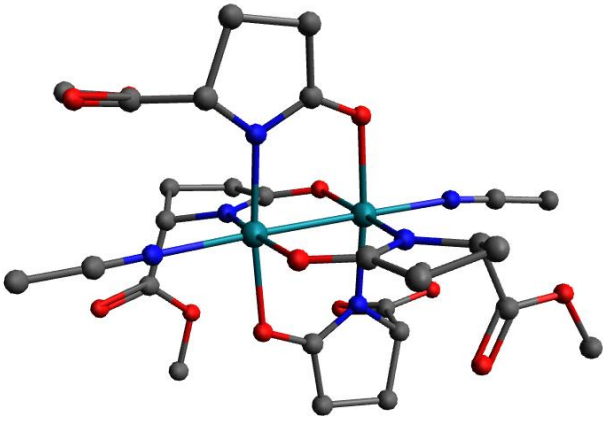


Figure S6. Structure of [RhRh(5*S*-MEPY)$_4$]·2MeCN in the solid state (left); DFT-optimized structure (right).

Table S2. Selected Bond Lengths [Å] of [RhRh(5*S*-MEPY)$_4$]·2MeCN

	X-Ray	**DFT**
Rh−Rh	2.455(1)	2.50
Rh−O (average)	2.08	2.11
Rh−N	2.01	2.02 – 2.04
Rh−NCMe	2.211(6) / 2.229(6)	2.15 / 2.14

[BiRh(5*S*-MEPY)$_4$] and [RhRh(5*S*-MEPY)$_4$] (without axial ligands each)

[BiRh(5*S*-MEPY)$_4$] **[RhRh(5*S*-MEPY)$_4$]**

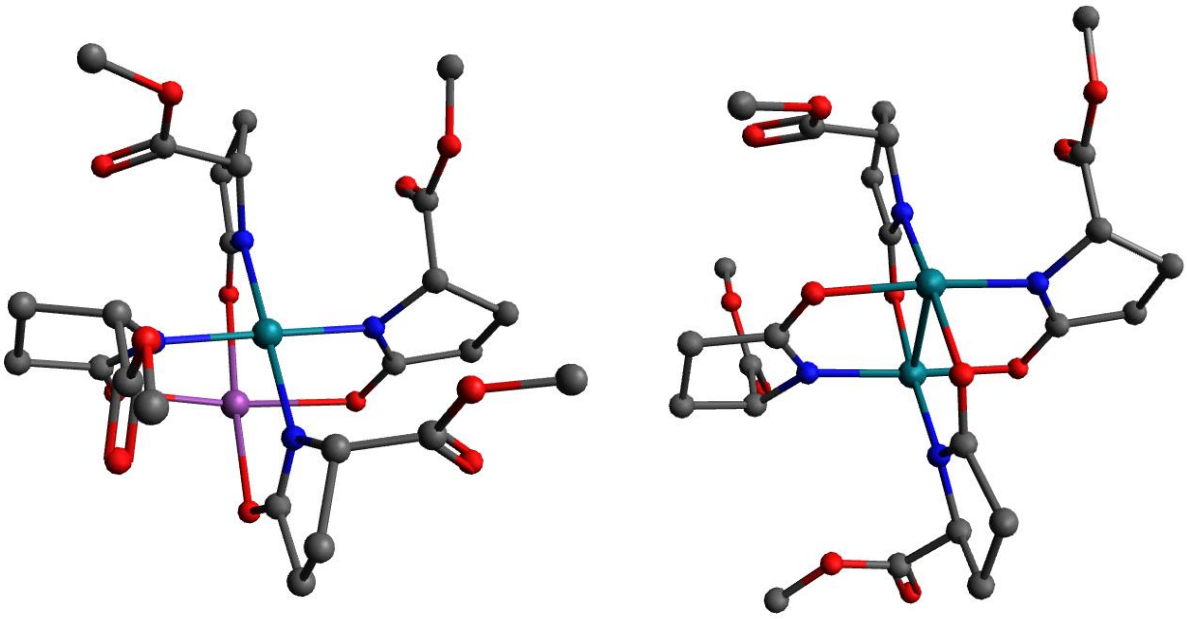


Figure S7. Structures of [BiRh(5*S*-MEPY)$_4$] (left) and [RhRh(5*S*-MEPY)$_4$] (right) as optimized by DFT.

Table S3. Selected Bond Lengths [Å] of [BiRh(5*S*-MEPY)$_4$] and [RhRh(5*S*-MEPY)$_4$] as optimized by DFT

	[BiRh(5*S*-MEPY)$_4$]	**[RhRh(5*S*-MEPY)$_4$]**
M−Rh	2.59	2.44
M−O	2.40	2.10
Rh−N	2.05	2.01 – 2.02

Electronic Structures

Table S4. Energies of molecular orbitals (eV) without axial ligands.

MO	[RhRh(5*S*-MEPY)$_4$]	[BiRh(5*S*-MEPY)$_4$]
LUMO+5	−1.40 eV	−1.11 eV
LUMO+4	−1.41 eV	−1.30 eV
LUMO+3	−1.48 eV	−1.44 eV
LUMO+2	−1.48 eV	−1.46 eV
LUMO+1	−1.81 eV	−1.46 eV
LUMO	−3.71 eV	−2.55 eV
	Δ 0.50 eV	Δ 2.10 eV
HOMO	−4.21 eV	−4.65 eV
HOMO−1	−4.86 eV	−5.70 eV
HOMO−2	−4.90 eV	−5.70 eV
HOMO−3	−5.44 eV	−5.73 eV
HOMO−4	−5.75 eV	−6.07 eV
HOMO−5	−6.03 eV	−6.10 eV
HOMO−6	−6.24 eV	−6.10 eV

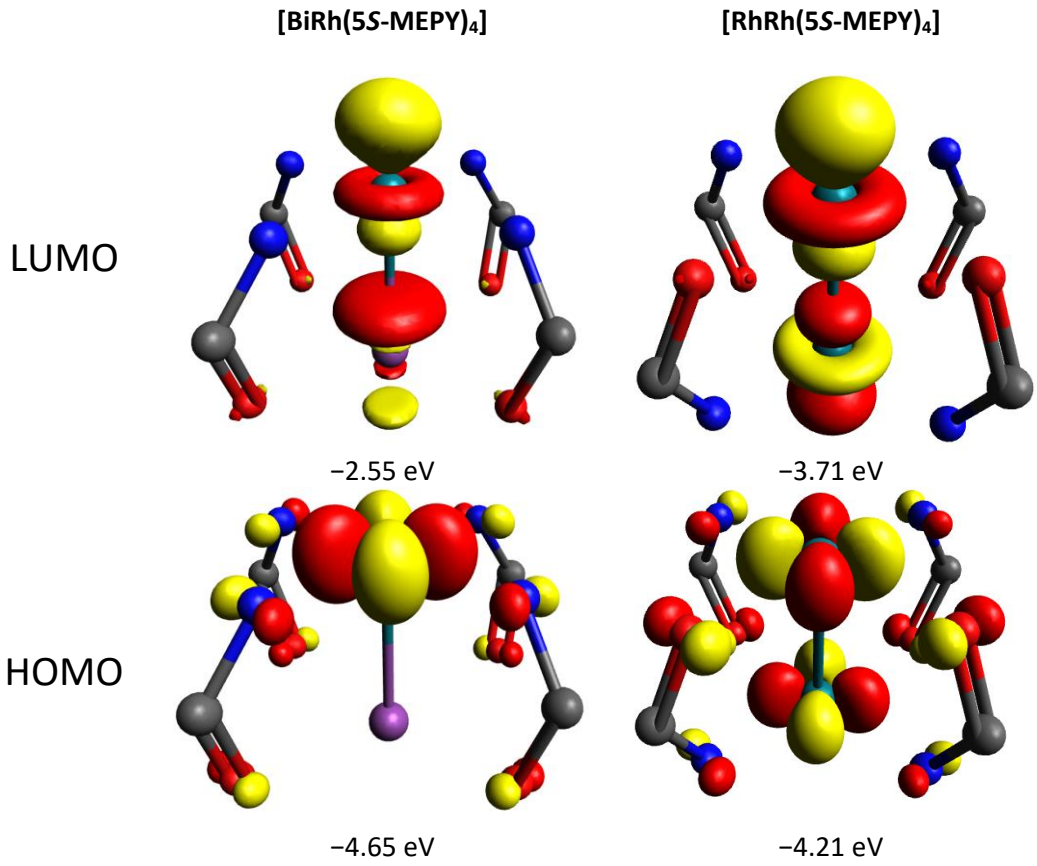


Figure S8. Molecular Orbitals Scheme: HOMO and LUMO.

Molecular Orbital Energy Diagrams

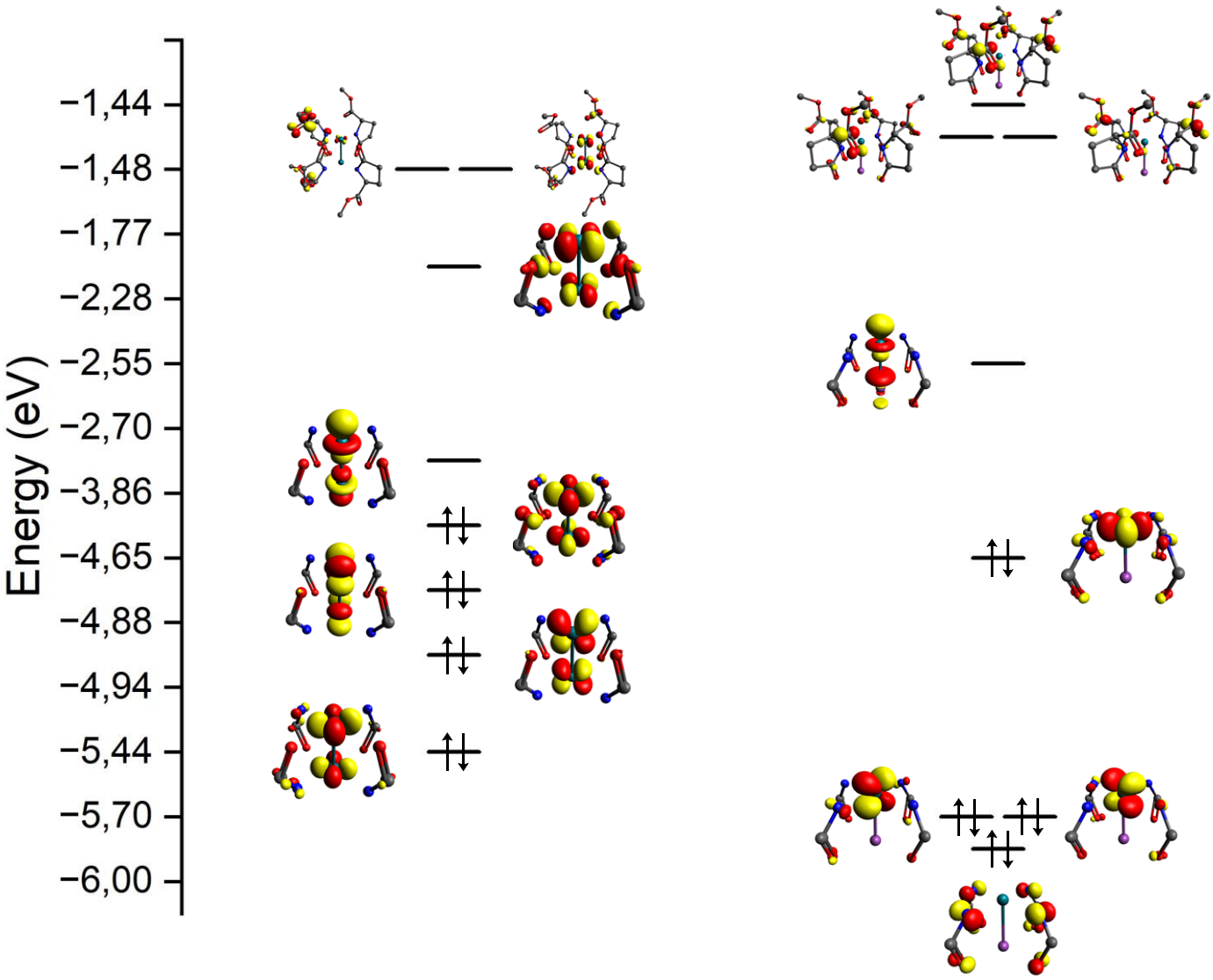
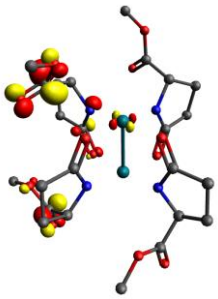
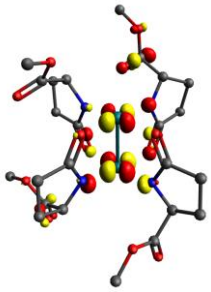


Figure S1. Molecular Orbital Scheme for [RhRh(5*S*-MEPY))$_4$] (left) and [BiRh(5*S*-MEPY)$_4$] (right). The structures are truncated for sake of clarity.

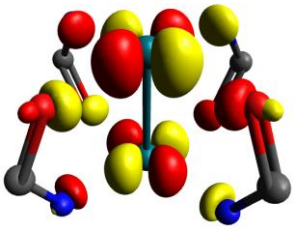
Molecular Orbital Scheme of [RhRh(5*S*-MEPY)$_4$]



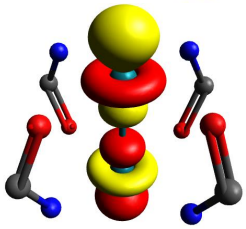
−1.48 eV
LUMO+2, LUMO+3

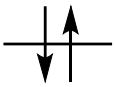


−1.81 eV
LUMO+1

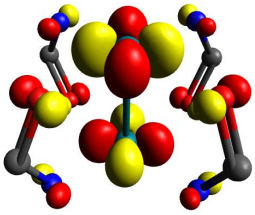


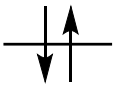
−3.71 eV
LUMO



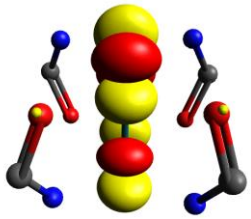


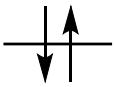
−4.21 eV
HOMO



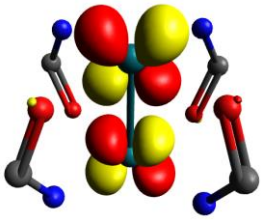


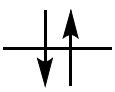
−4.86 eV
HOMO−1



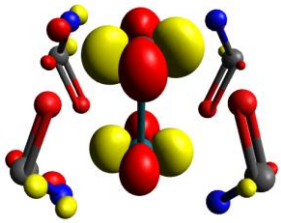


−4.90 eV
HOMO−2

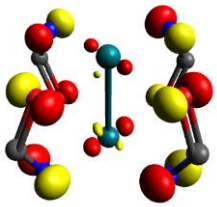


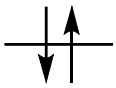


−5.44 eV
HOMO−3

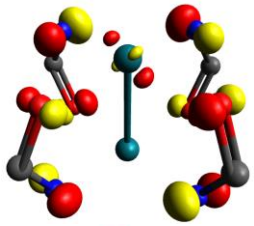


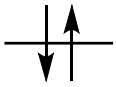
−5.75 eV
HOMO−4



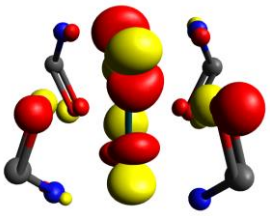


−6.03 eV
HOMO−5

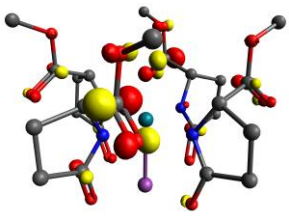


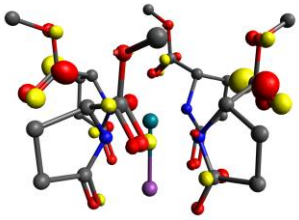


−6.24 eV
HOMO−6

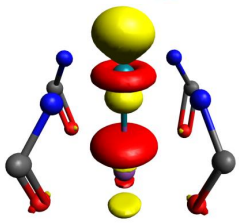


Molecular Orbital Scheme of [BiRh(5*S*-MEPY)$_4$]

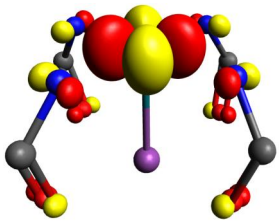




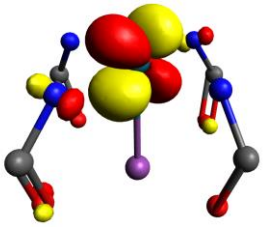
−1.46 eV
LUMO+1, LUMO+2

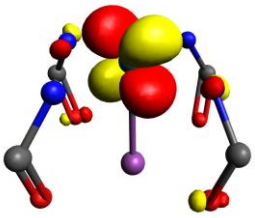


−2.55 eV
LUMO

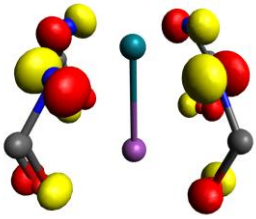


−4.65 eV
HOMO

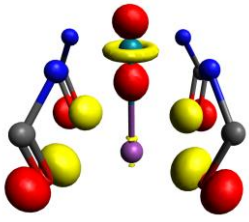




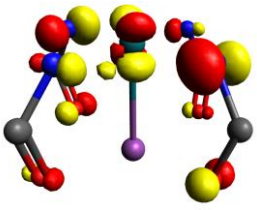
−5.70 eV
HOMO−1, HOMO−2

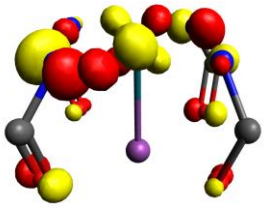


−5.73 eV
HOMO−3



−6.07 eV
HOMO−4



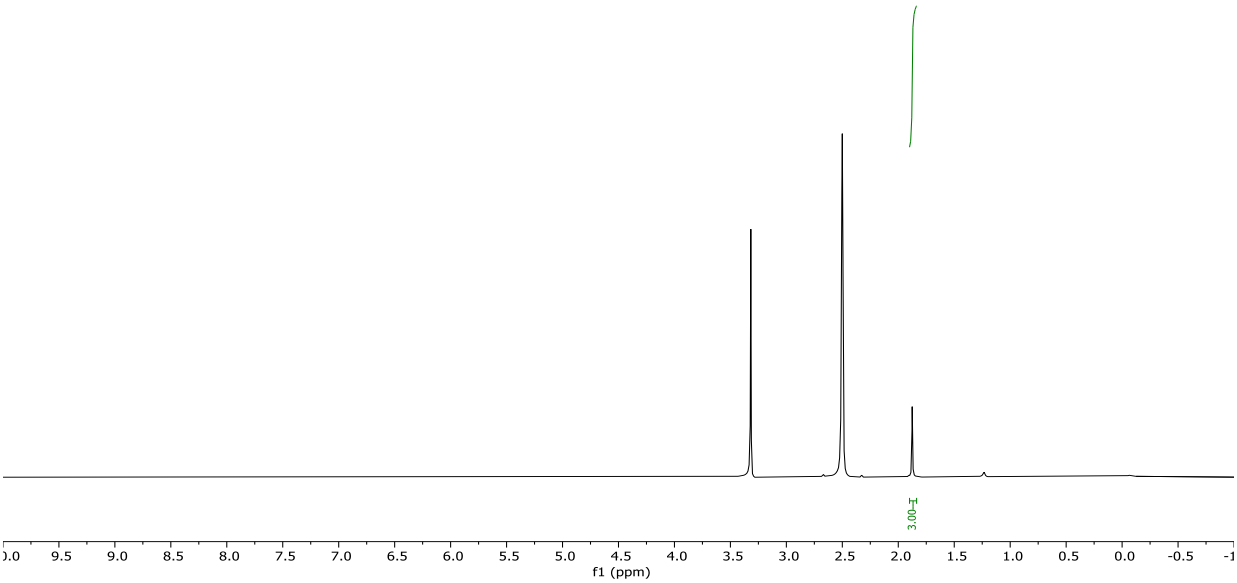


−6.10 eV
HOMO−5, HOMO−6

Spectra

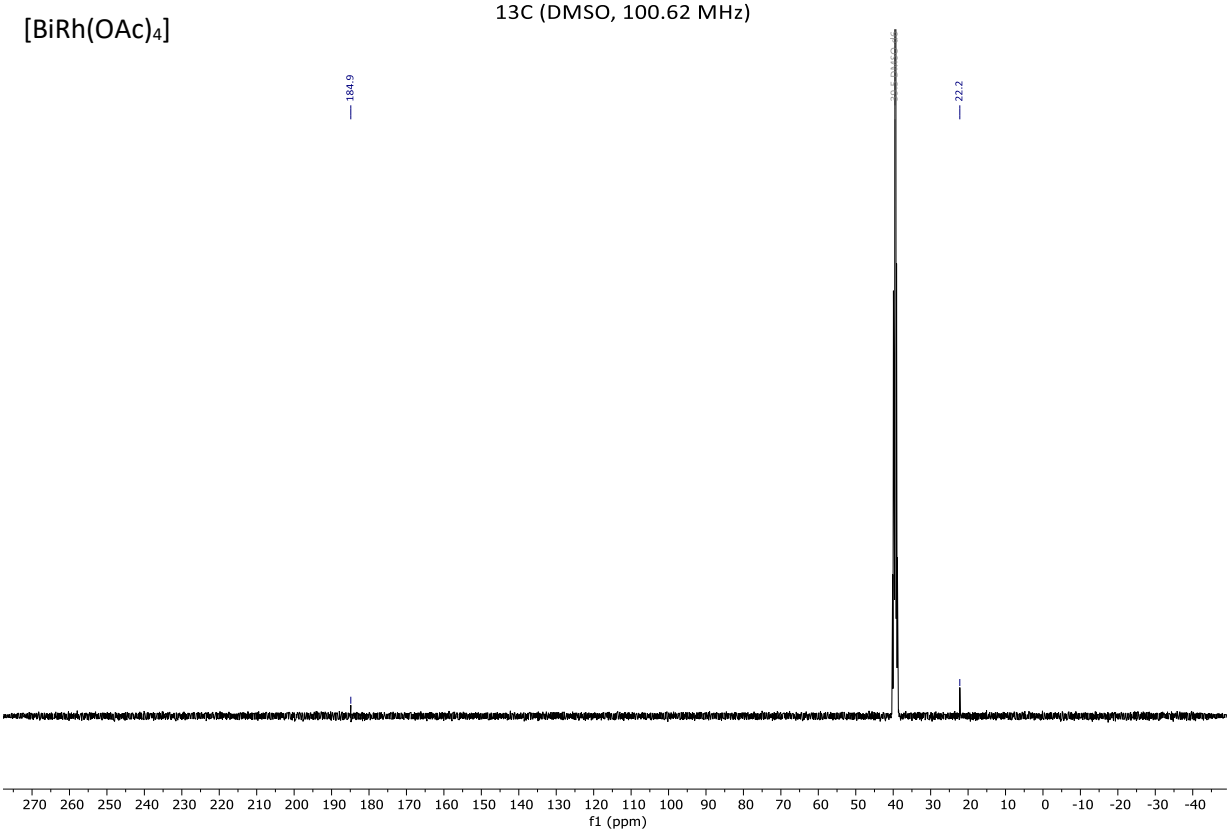
[BiRh(OAc)$_4$]

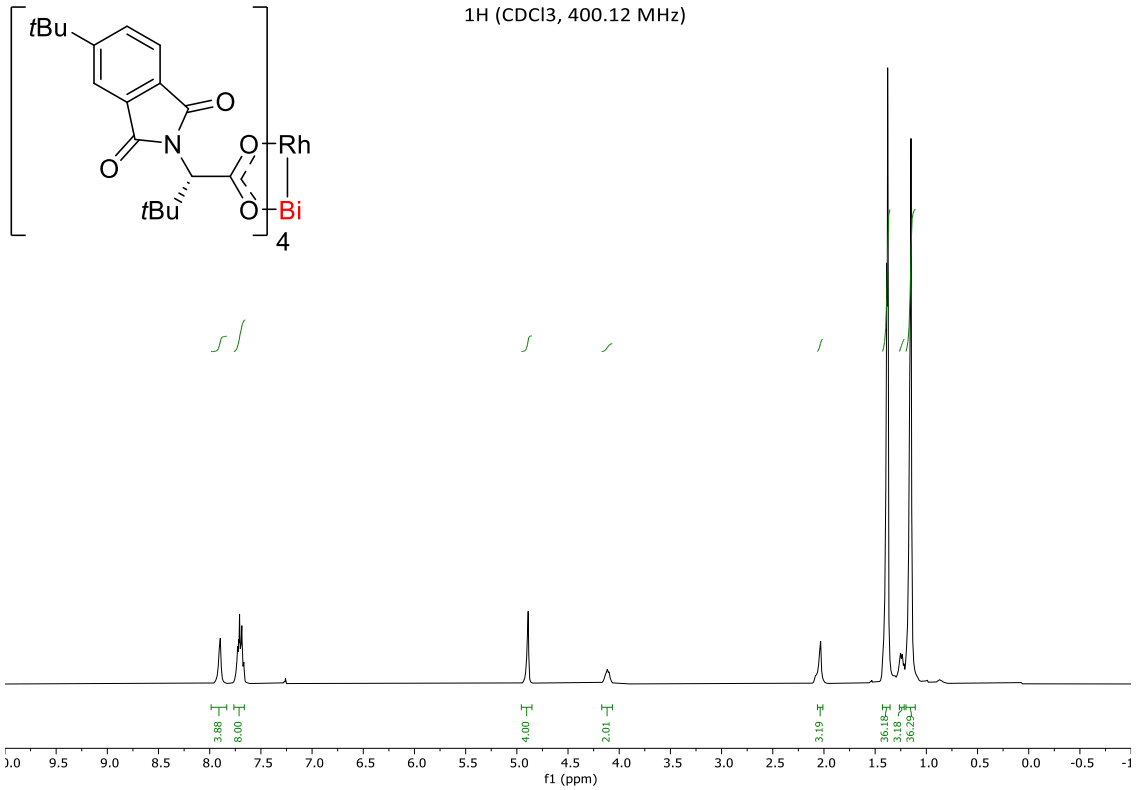
1H (DMSO, 400.12 MHz)

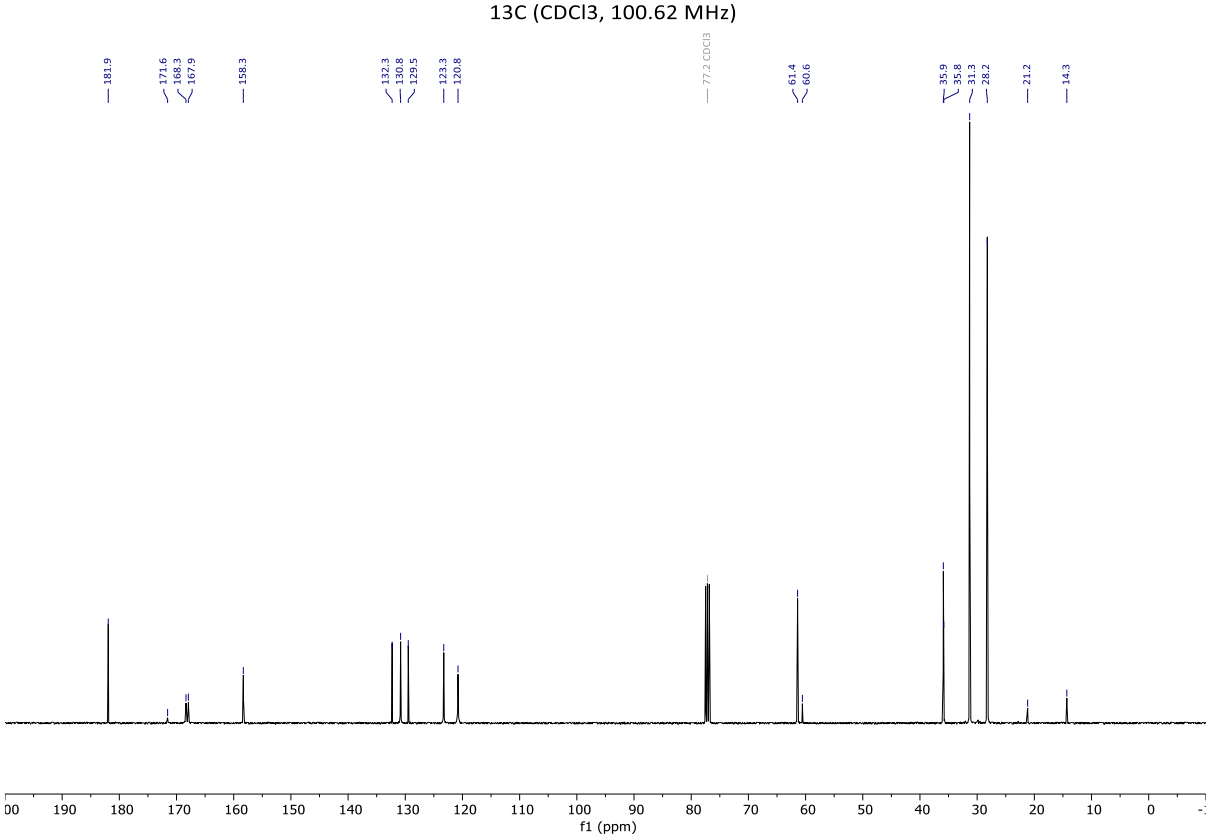


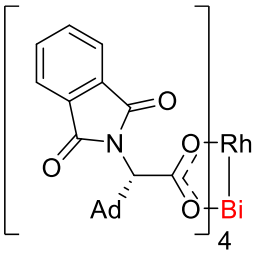
[BiRh(OAc)$_4$]

13C (DMSO, 100.62 MHz)

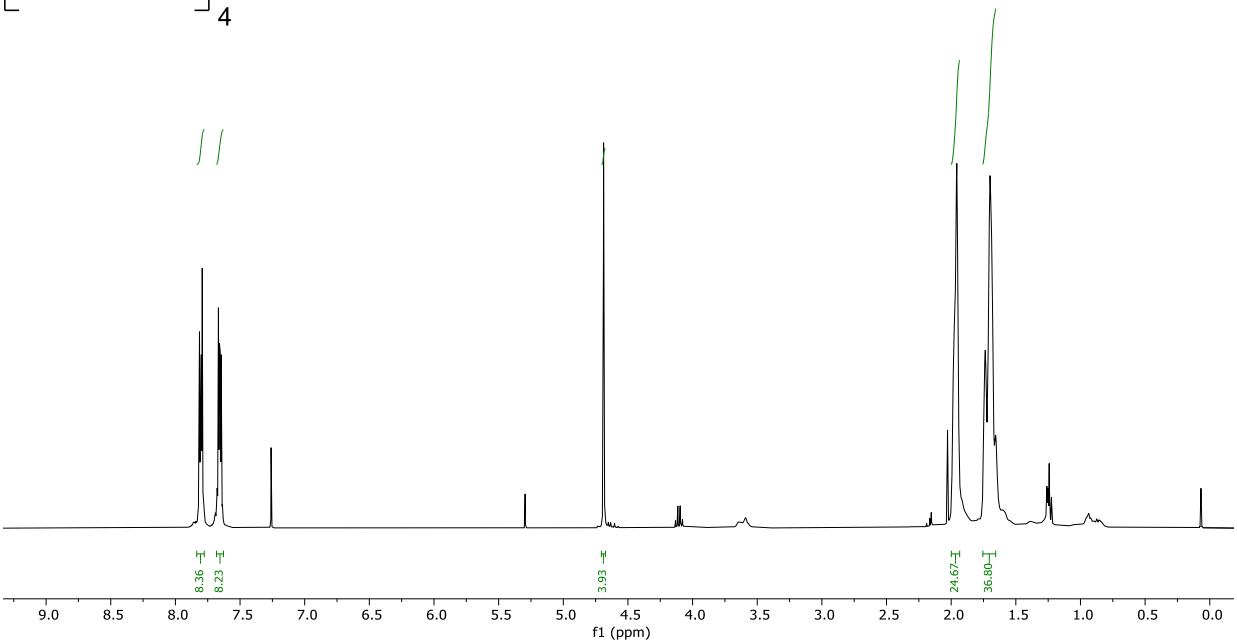



tBu
O
N
O
O
Rh
tBu
O
Bi
4
1H (CDCl3, 400.12 MHz)
3.88
8.00
4.00
2.01
3.19
36.18
3.18
36.29
f1 (ppm)

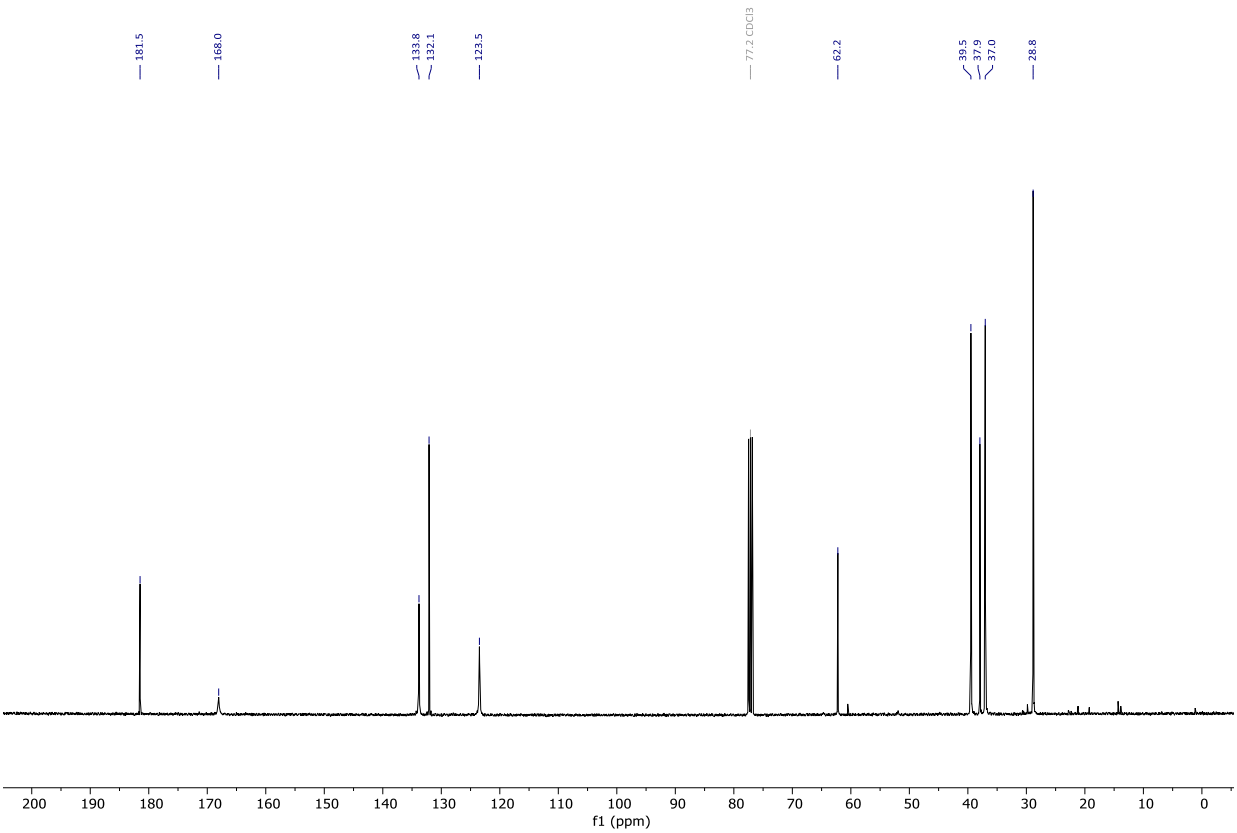

13C (CDCl3, 100.62 MHz)
181.9
171.6
168.3
167.9
158.3
132.3
130.8
129.5
123.3
120.8
77.2 CDCl3
61.4
60.6
35.9
35.8
31.3
28.2
21.2
14.3
f1 (ppm)

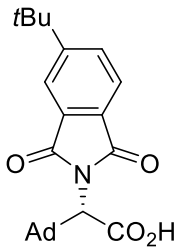


1H (CDCl3, 400.12 MHz)



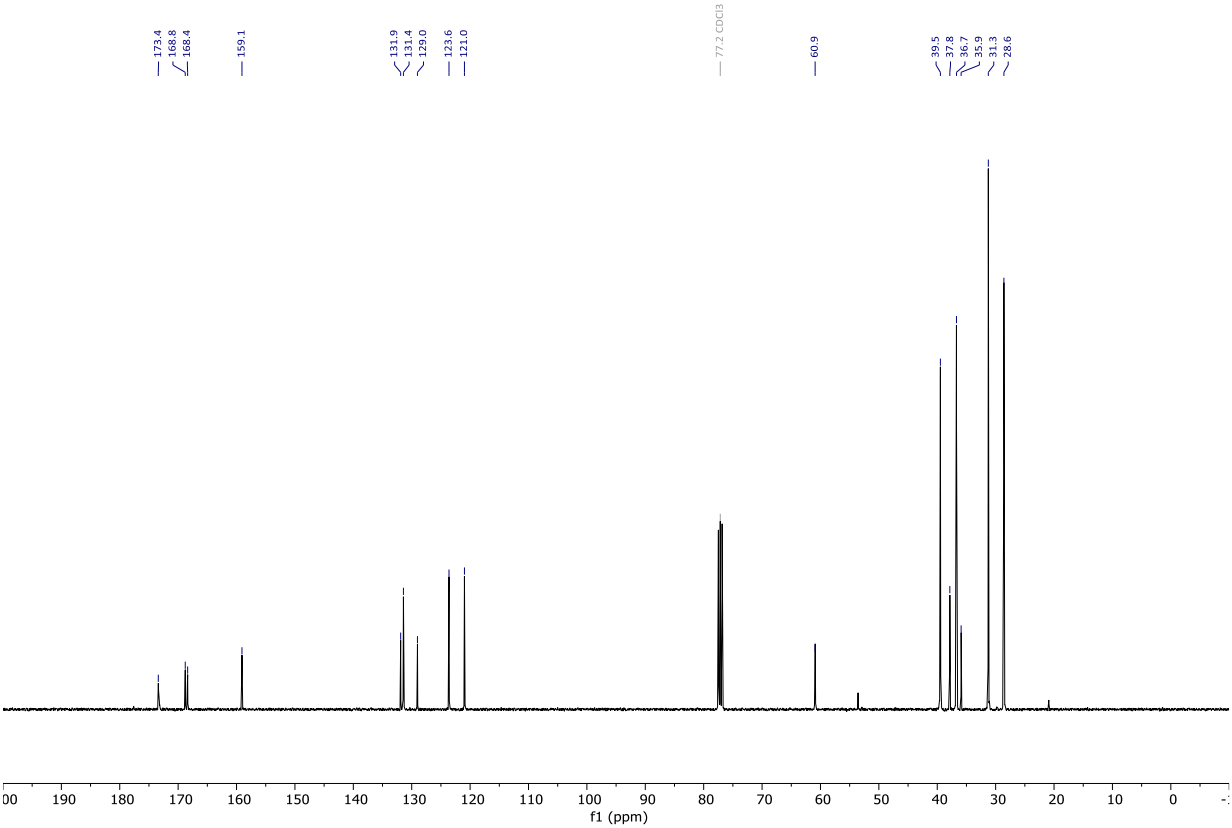
13C (CDCl3, 100.62 MHz)

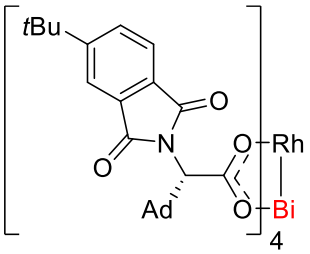




1H (CDCl3, 400.12 MHz)

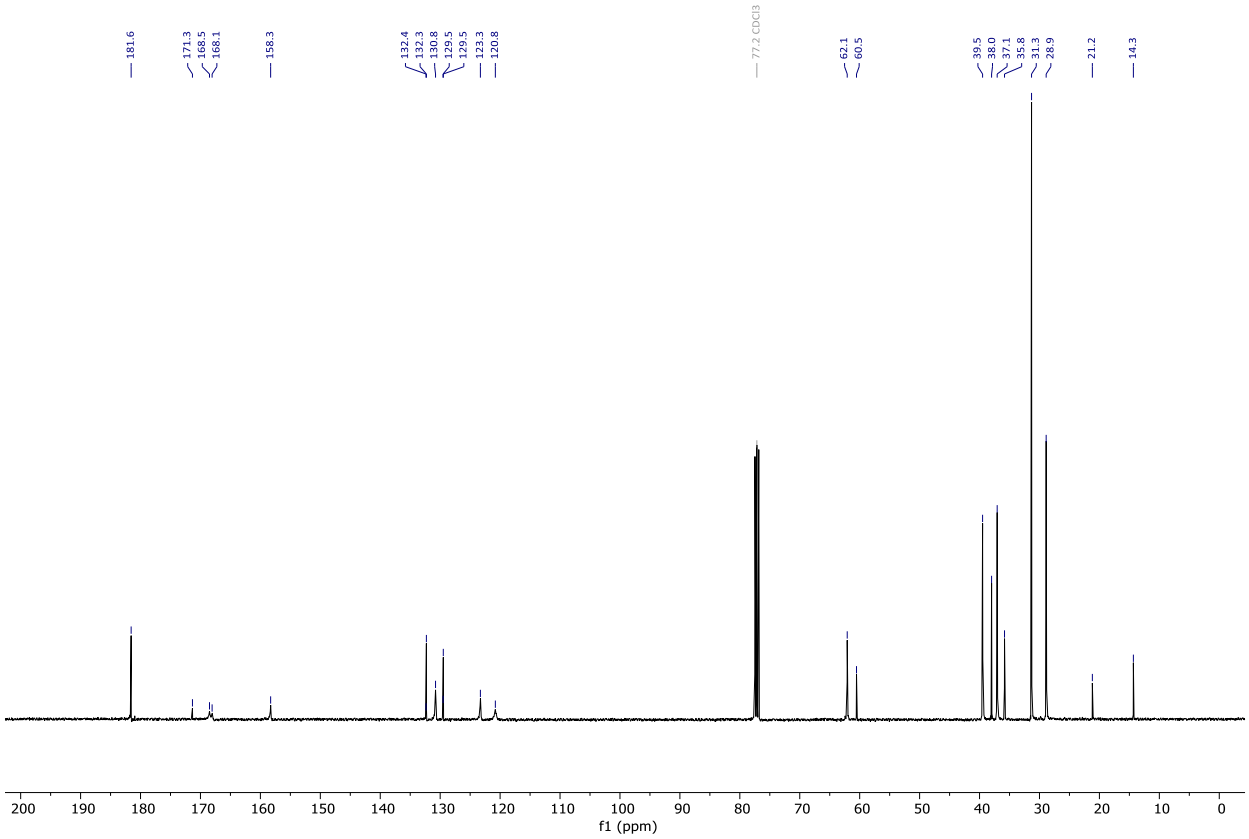
13C (CDCl3, 100.62 MHz)



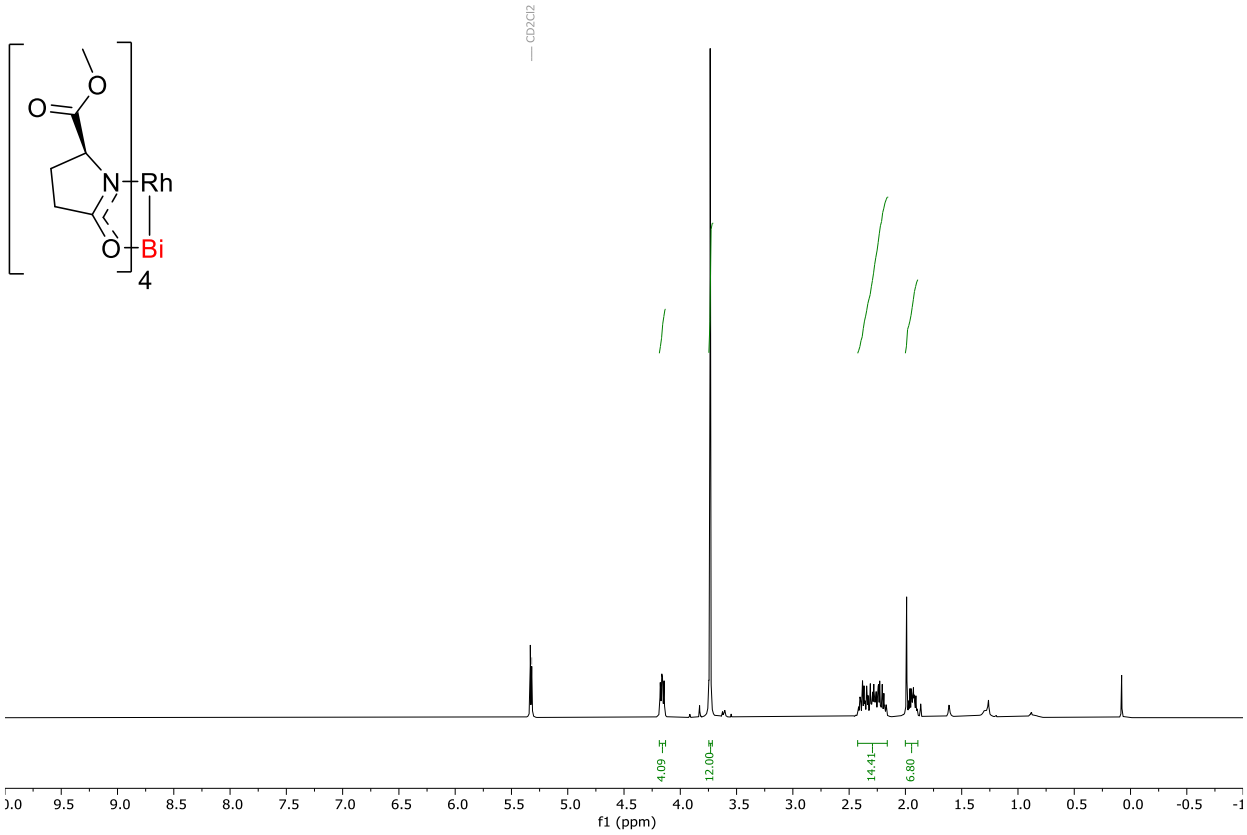


1H (CDCl3, 400.12 MHz)

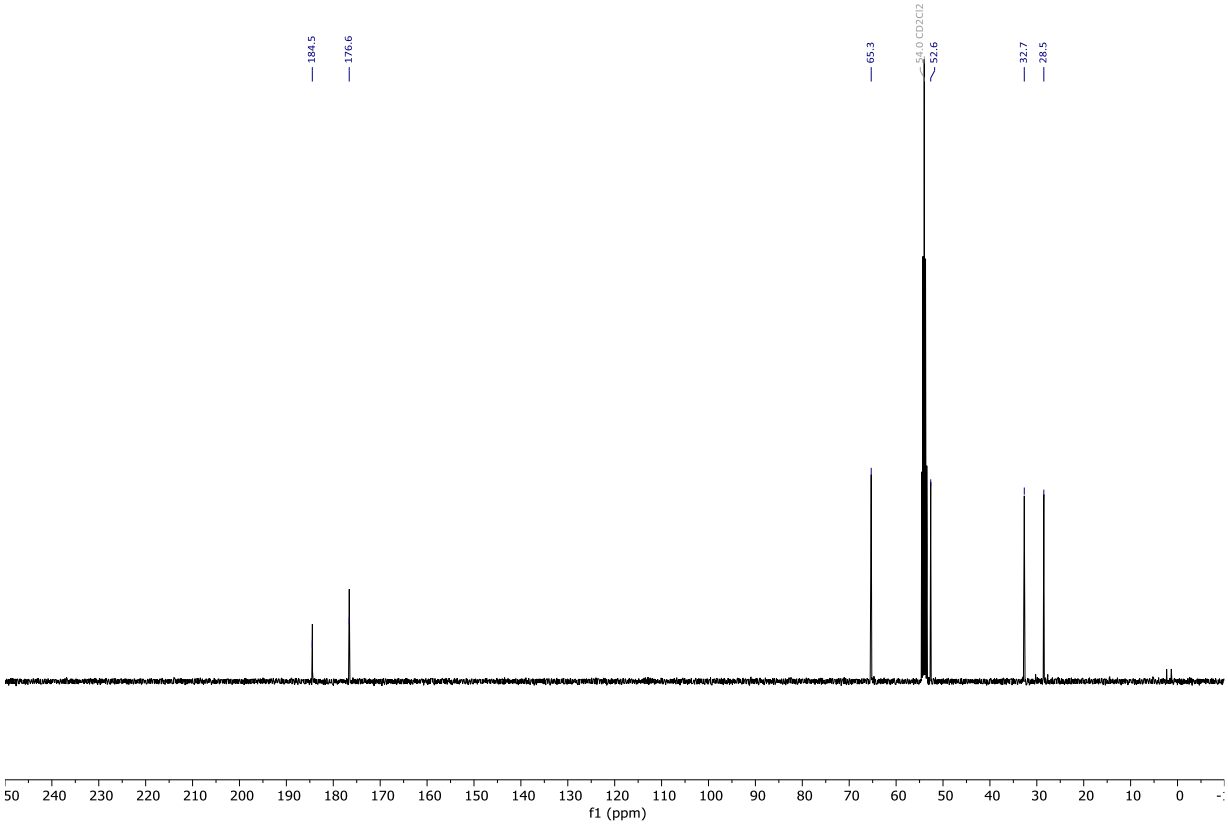
13C (CDCl3, 100.62 MHz)

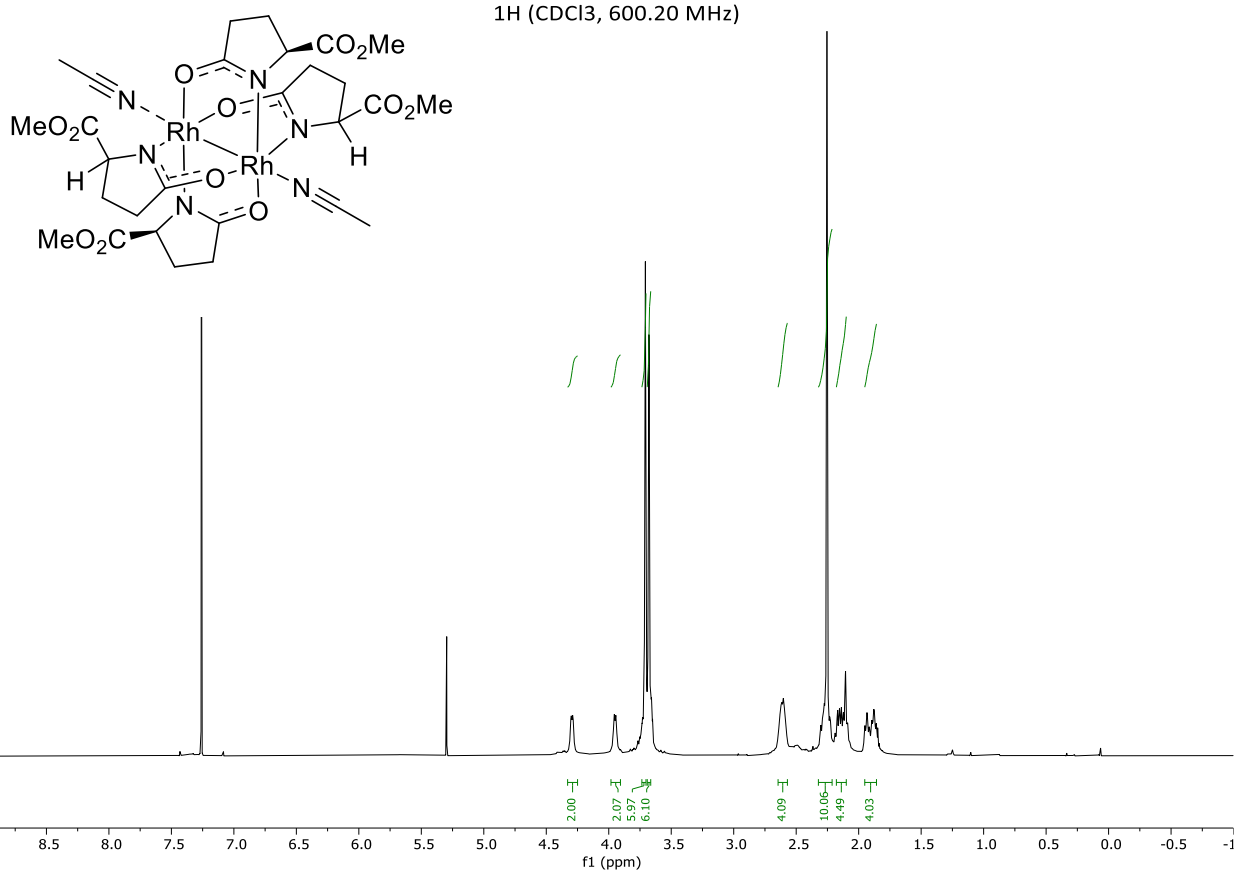


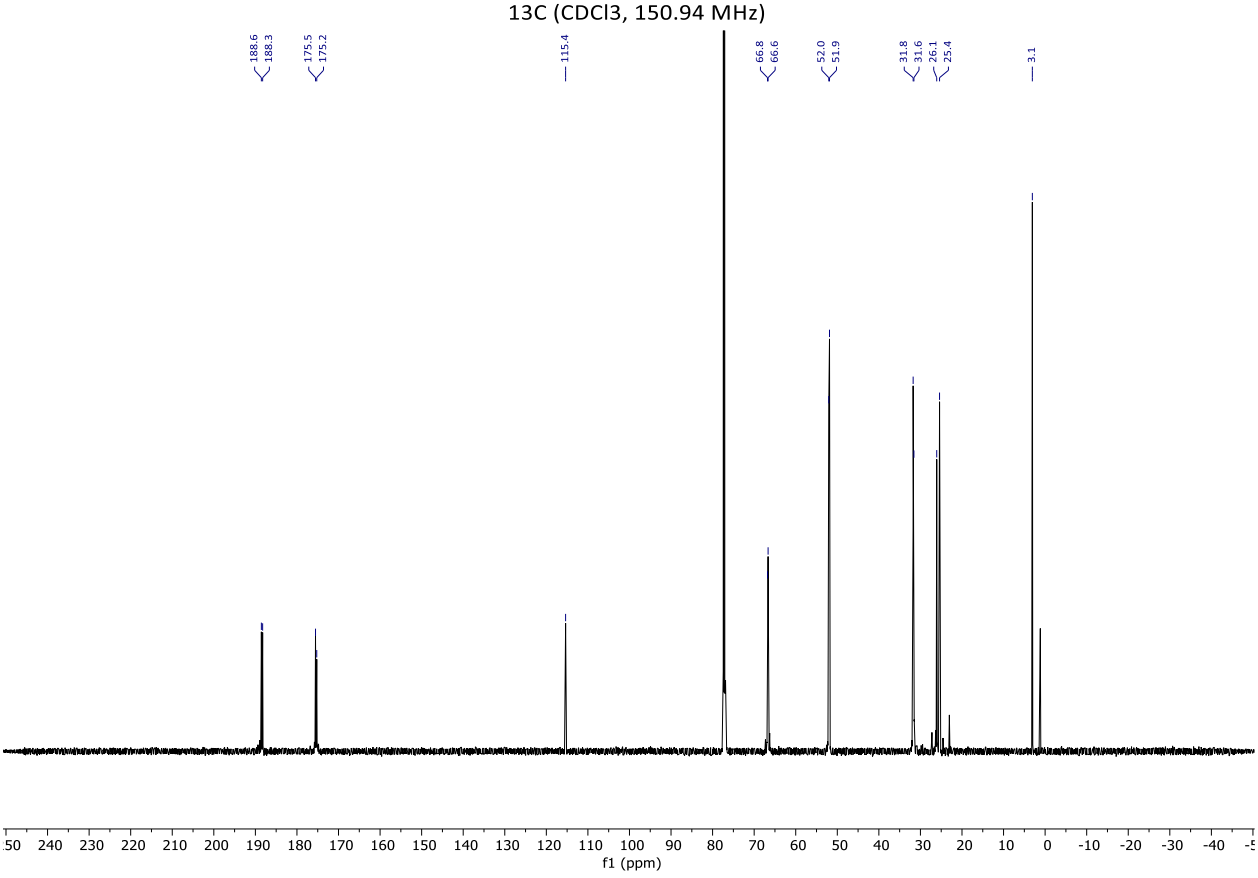
1H (CD2Cl2, 400.12 MHz)

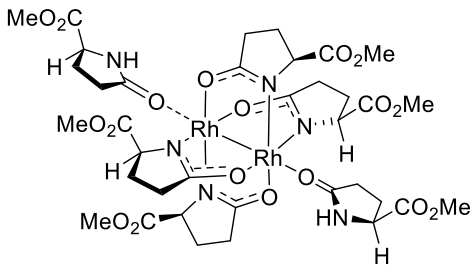


13C (CD2Cl2, 100.62 MHz)

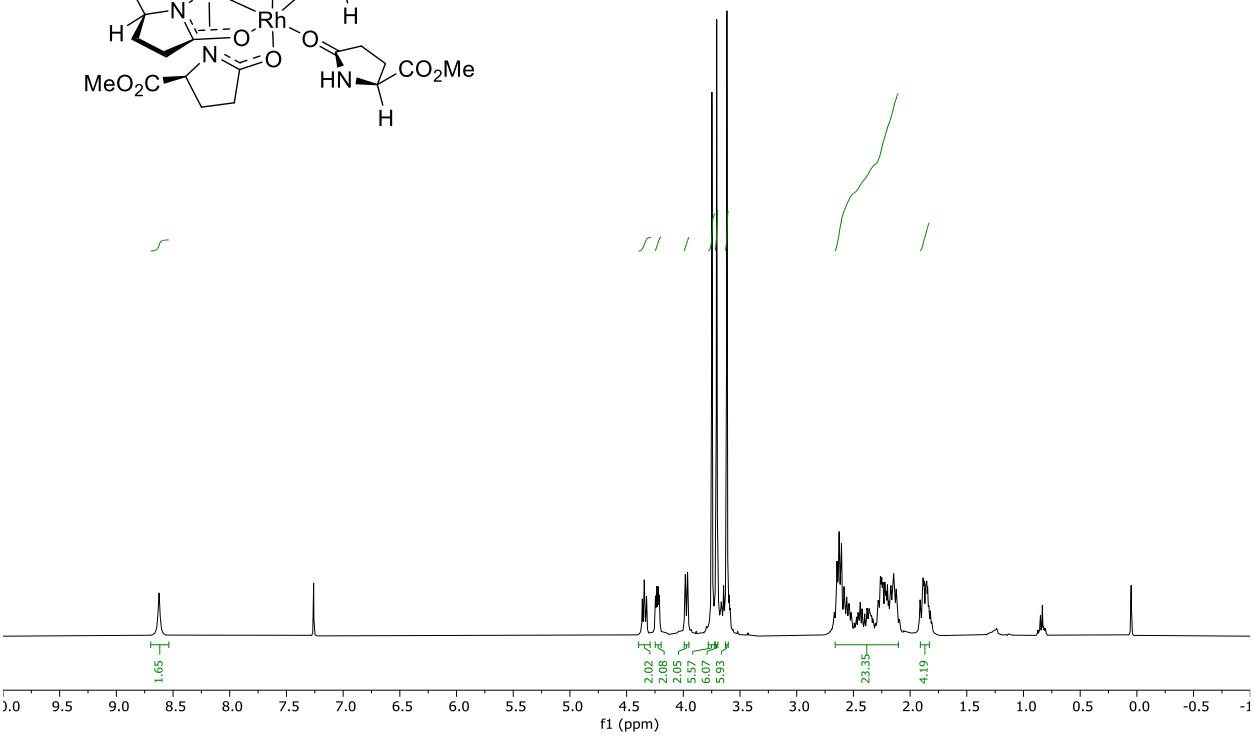



1H (CDCl3, 600.20 MHz)
CO2Me
MeO2C
Rh
Rh
H
2.00
2.07
5.97
6.10
4.09
10.06
4.49
4.03
f1 (ppm)

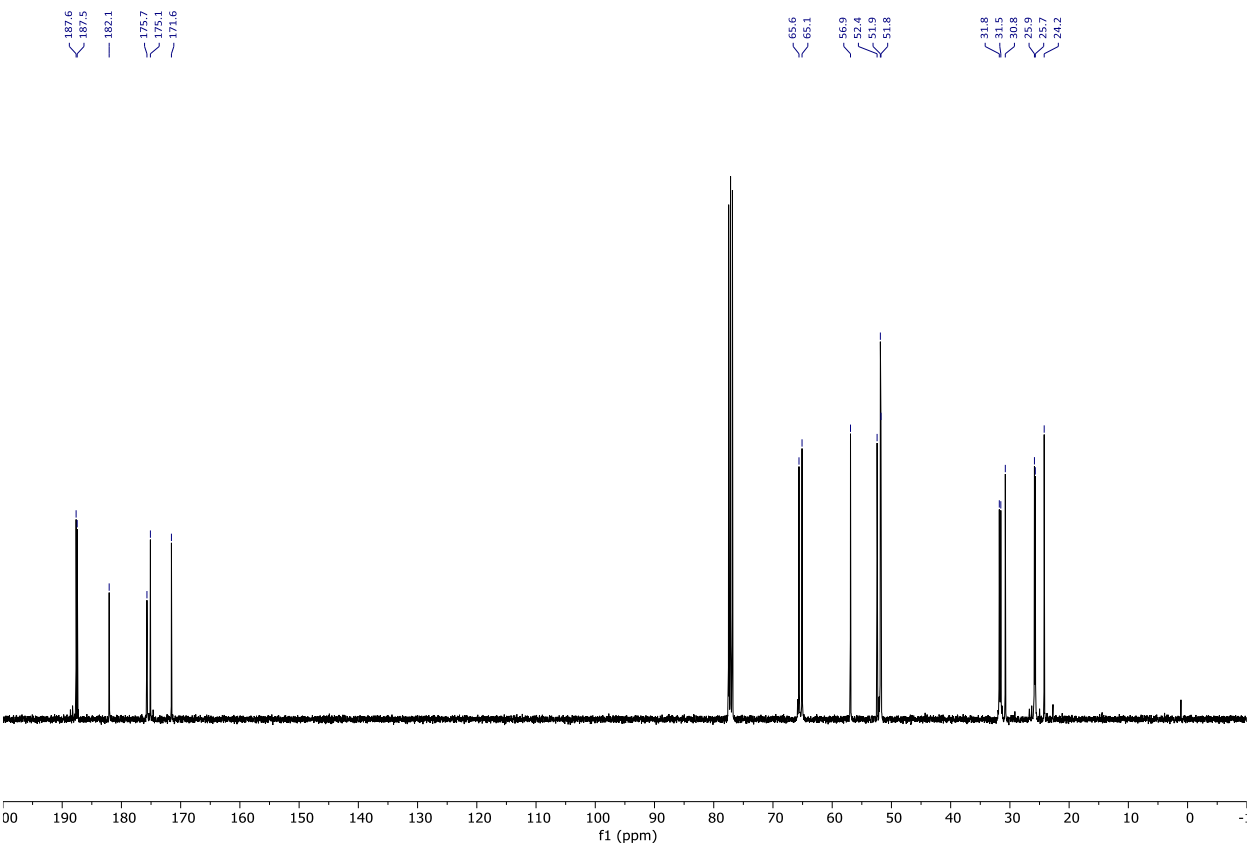

13C (CDCl3, 150.94 MHz)
188.6
188.3
175.5
175.2
115.4
66.8
66.6
52.0
51.9
31.8
31.6
26.1
25.4
3.1
f1 (ppm)

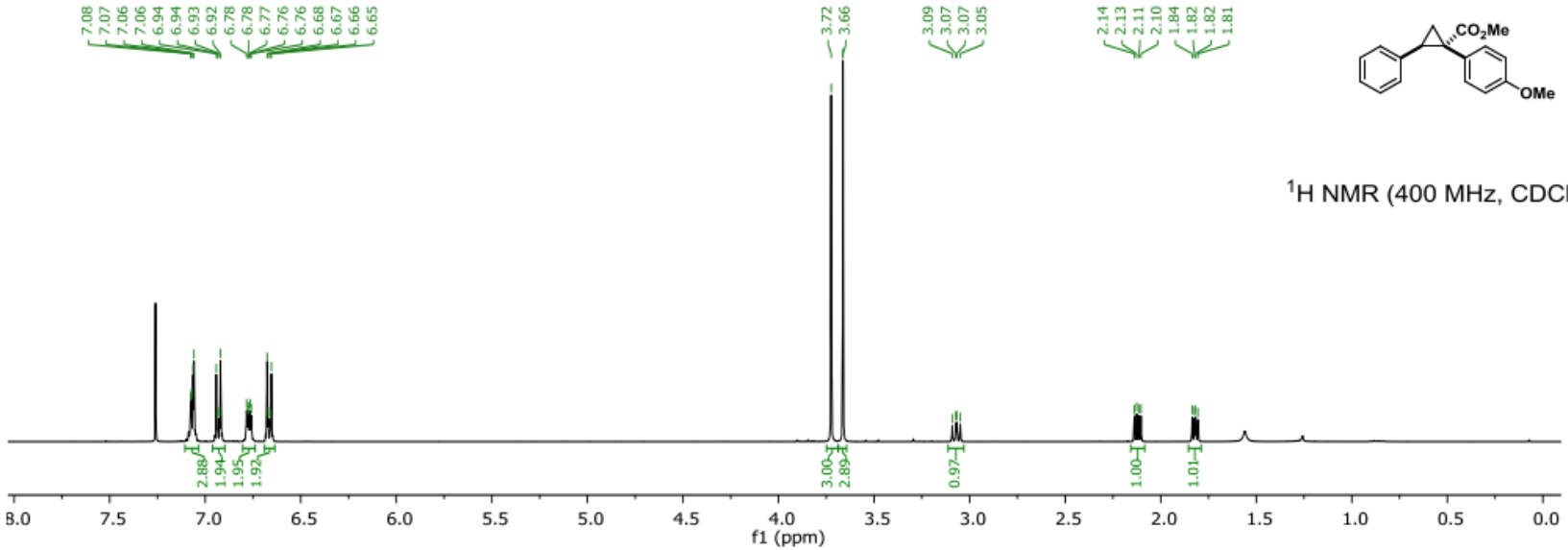


1H (CDCl3, 400.12 MHz)

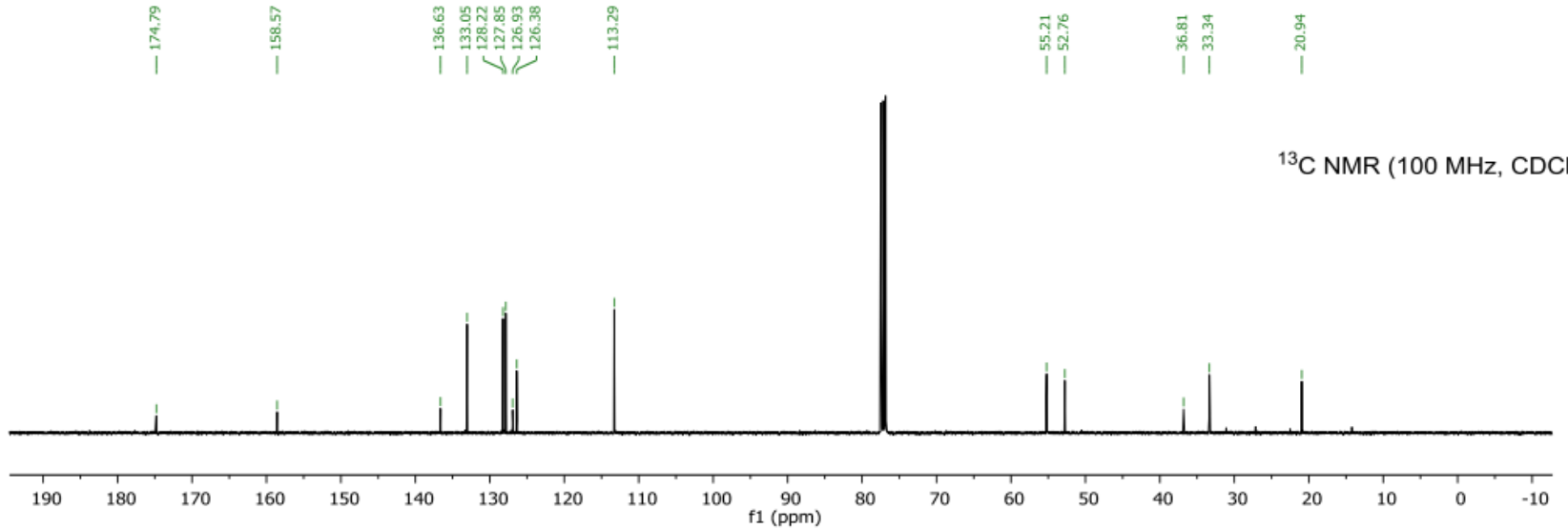


13C (CDCl3, 100.62 MHz)





^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

Cartesian Coordinates and Electronic Energies

Cartesian coordinates (in Å) and electronic energies (in a.u.). Calculations reported at BP86-D3(BJ)-CPCM/ZORA-def2-TZVP level.

Cartesian Coordinates of [RhRh(MEPY)$_4$·2MeCN			
86	E = −12000.058831422017		
Rh	3.75859638	9.72477119	12.2378933
Rh	6.12772809	9.37083194	12.953055
O	6.58966986	8.61152475	11.0443895
O	1.36281544	7.17006434	9.65384348
O	3.31067738	6.20380347	10.2936691
O	6.60349303	11.3045646	12.2644988
O	1.43550422	12.9118032	10.0377323
O	3.12903177	11.7168313	9.12097382
O	3.32981781	10.6061455	14.1088115
O	7.89177273	8.88221856	16.9526465
O	3.2483289	7.85670908	13.0655578
O	6.5656021	5.37279918	11.8698987
O	8.42458496	5.7507306	13.1135114
N	4.34359957	8.82718833	10.5217211
N	4.39050349	11.554513	11.6113671
N	1.7186047	9.96743741	11.6288818
N	5.48974713	7.54677402	13.5507685
N	5.53468071	10.2089017	14.6969345
N	8.15823874	9.04409452	13.5731799
C	5.58803843	8.46067208	10.2627647
C	5.71956091	7.80355529	8.90444706
H	5.88790145	6.72544981	9.04733664
H	6.57933829	8.20630265	8.35314238
C	4.3664584	8.1102337	8.24619046
H	4.43969146	9.0097975	7.62106847
H	3.98471868	7.29213268	7.62309334
C	3.43476494	8.42887801	9.45086975
H	2.73454622	9.23949233	9.22755398
C	2.57206142	7.2256195	9.8204597
C	2.57850565	5.0027675	10.634236
H	2.04412986	4.61949184	9.75562995
H	1.86365103	5.21425211	11.4393479
H	3.33608993	4.28806023	10.9683544
C	0.63034194	10.0188183	11.2255799
C	-0.707957	10.098757	10.6836222
H	-0.8356257	11.061564	10.1688003
H	-1.4517772	10.0186831	11.4882283
H	-0.8638129	9.28125349	9.96617283
C	5.61534426	12.0013988	11.8464312
C	5.73916331	13.4952155	11.6342269
C	4.41103751	13.8710579	10.9679256
C	3.48399481	12.6549211	11.2890772
C	2.553145	12.4230232	10.1132064
C	2.32396304	11.5565023	7.9263986
C	4.30909663	10.6491913	14.9311177
C	4.16780962	11.2294385	16.3242329
H	3.58988696	10.5290044	16.9463119
H	3.62359599	12.1825662	16.3012149
C	5.62652695	11.364666	16.7856869
C	6.39465608	10.3715083	15.8632994
C	6.60107799	9.03909404	16.5781375
C	8.18544675	7.66909194	17.6912759
H	7.57654989	7.6209575	18.6025793
C	9.20438958	8.74168703	13.9780123
C	10.4862676	8.32693902	14.5053633
H	11.2860974	8.55046101	13.7862125
H	10.467906	7.24485342	14.6964398
H	10.6914087	8.85468274	15.4469879
C	4.22579284	7.16053231	13.5091393
C	4.03532018	5.76435146	14.0657186
H	3.80272355	5.0735799	13.2429592
H	3.19337498	5.73853349	14.7702465
C	5.39339211	5.46870602	14.7196962
H	5.71925632	4.42824077	14.5992219
H	5.36477636	5.70311869	15.7909144
C	6.35733253	6.47791729	14.036072
C	7.09517422	5.81904954	12.8732884
C	9.21647245	5.12365061	12.0729645
H	9.11622574	5.68577266	11.1361332
H	8.89103085	4.08710596	11.9189669
H	10.2482796	5.1559436	12.4348408
O	5.72096369	8.23390236	16.8294923
H	4.5427692	13.9576632	9.88109014
H	6.62324759	13.7442396	11.0328087
H	5.86459841	13.9695728	12.620625
H	3.9789988	14.8078606	11.3364936
H	5.77177804	11.1477546	17.8511685
H	6.00102052	12.3774341	16.5886043
H	7.37574481	10.7615383	15.5668147

H	7.98371625	6.79018303	17.0657059
H	9.24942125	7.72999596	17.9374379
H	7.09939565	6.87436461	14.7374405
H	2.83411863	12.8677532	12.1525657
H	1.40333987	11.0073236	8.16149947
H	2.94692658	10.984404	7.23285952
H	2.07132203	12.53693	7.50386156

Cartesian Coordinates of [RhRh(MEPY)$_4$]

74 E = −11734.155165757438

Rh	3.82766857	9.70837392	12.2797167
Rh	6.12320156	9.29069341	12.9976987
O	6.59257097	8.46956735	11.1374902
O	1.30295244	7.28708365	10.0118913
O	3.2226967	6.11883181	10.3206645
O	6.71354992	11.1635346	12.2870833
O	1.49691694	12.6224761	10.1485751
O	3.27597501	11.7020383	9.08421199
O	3.38744583	10.6430076	14.0952187
O	7.75334928	8.60667319	16.9607887
O	3.21977692	7.88623618	13.1026278
O	6.57008806	5.13730263	11.9929796
O	8.28000674	6.4115022	12.7760209
N	4.36417246	8.75886101	10.5877623
N	4.51851259	11.4879046	11.6167241
N	5.44152858	7.50908479	13.6215324
N	5.56406131	10.164369	14.7251081
C	5.59235222	8.33248396	10.3453905
C	5.70090974	7.6305704	9.01122026
H	5.83930798	6.5535946	9.18874346
H	6.57041133	7.99163881	8.44675884
C	4.35398806	7.95552218	8.34518226
H	4.45450968	8.82298983	7.68037636
H	3.94264577	7.12269532	7.76289672
C	3.4341298	8.35722604	9.53250878
H	2.76817732	9.18921516	9.27864371
C	2.52120829	7.21929208	9.98696787
C	2.43360133	4.97179408	10.7229366
H	1.79356403	4.64526229	9.89337169
H	1.81260354	5.22678593	11.5904504
H	3.16130801	4.19629023	10.9786057
C	5.7618475	11.8916572	11.8293763
C	5.94523319	13.3636531	11.5389716
C	4.62759301	13.7568354	10.8567767
C	3.64988843	12.6095124	11.2571528
C	2.67467645	12.3032552	10.130751
C	2.43465233	11.4845351	7.92207011
C	4.35389271	10.6553724	14.9391086
C	4.21780031	11.2494933	16.3237993
H	3.58628966	10.5883925	16.936029
H	3.73222164	12.2331115	16.2830293
C	5.67323279	11.301803	16.8154947
C	6.40265828	10.2594773	15.9163309
C	6.47977735	8.90844895	16.6265928
C	7.92780572	7.37866659	17.716789
H	7.36870722	7.43399232	18.6590697
C	4.17073256	7.14877741	13.5501249
C	3.94544501	5.74505373	14.0624791
H	3.66394853	5.09583547	13.2222584
H	3.12097045	5.725448	14.7874971
C	5.30920444	5.36943218	14.66726
H	5.60842917	4.33926579	14.4432395
H	5.29716528	5.50109702	15.7560085
C	6.29356303	6.39818988	14.0652271
C	7.04037213	5.8843111	12.8348539
C	9.02592127	6.12300964	11.5648149
H	8.49876746	6.55178695	10.7039944
H	9.1398961	5.03942649	11.4379239
H	9.99901225	6.60281343	11.7031623
O	5.51944247	8.20768021	16.8952399
H	4.75260893	13.7679093	9.76663386
H	6.83474887	13.5424987	10.9211153
H	6.09586178	13.8850605	12.4975213
H	4.24278049	14.7327888	11.1721254
H	5.78205195	11.0806943	17.8840403
H	6.11076503	12.289339	16.6215942
H	7.4185373	10.5799988	15.6520164
H	7.57823179	6.52048107	17.1292174
H	9.00254304	7.30574174	17.9051907
H	7.03079745	6.75613434	14.7953818
H	3.06929535	10.9613068	7.20119423
H	2.09854986	12.4473958	7.51729847
H	1.5638672	10.8732703	8.19002057
H	3.03318325	12.8928956	12.1246071

Cartesian Coordinates of [BiRh(MEPY)$_4$]·MeCN			
80	E = −29420.354933194278		
C	4.40802365	3.125648	7.52233652
C	3.78115225	1.78240242	7.84373905
C	3.57614176	1.84981217	9.36084691
H	3.74441477	0.89423919	9.87276425
H	2.56513987	2.20133831	9.59866917
C	4.58212084	2.95042216	9.80473341
H	4.17945887	3.56450673	10.6165459
C	5.86374623	2.29190979	10.2996272
C	7.07526848	1.66207069	12.2431515
H	6.94391488	1.76712264	13.3238759
H	8.01360351	2.13135425	11.9219148
H	7.07178705	0.6049413	11.9501108
C	5.64819509	5.66188627	12.0153927
C	5.64353119	5.66835741	13.4588903
Bi	5.64657765	5.65597785	6.06260177
N	4.81418582	3.76140061	8.61071919
N	5.65087122	5.65748507	10.8561372
O	4.51147085	3.5510745	6.32027075
O	6.68291293	1.72761896	9.59556325
O	5.94431807	2.35104259	11.6502309
Rh	5.65120333	5.65609762	8.67517964
C	6.88685948	8.18831476	7.51821115
C	7.5114142	9.53326874	7.83751545
H	6.81044873	10.3285823	7.54117906
H	8.43736016	9.6751003	7.26529572
C	7.72755483	9.46266877	9.35281105
H	7.56505382	10.4170123	9.86885522
H	8.74002934	9.10886058	9.58110869
C	6.72463738	8.36142432	9.80155954
H	7.13120627	7.74735376	10.6115214
C	5.44468616	9.01856399	10.3029951
C	4.24398474	9.64854286	12.2532318
H	4.37889055	9.5392383	13.3330847
H	3.30434107	9.18112367	11.9330429
H	4.24718546	10.7068286	11.9642827
N	6.48757995	7.55077652	8.60822887
O	6.77786372	7.76357282	6.31641266
O	4.62121228	9.5821068	9.60334673
O	5.37256718	8.961169	11.6541141
C	8.18141704	4.4167567	7.51771004
C	9.525927	3.79126844	7.83706748
H	10.3217266	4.49033362	7.53756335
H	9.6658109	2.86344542	7.26740359
C	9.45719657	3.57971968	9.35306947
H	10.4124714	3.74247149	9.86731176
H	9.10227408	2.56845505	9.58488576
C	8.35784514	4.58530141	9.80034137
H	7.74464611	4.18206673	10.6125943
C	9.0177488	5.86578945	10.2966773
C	9.65723332	7.06867055	12.2427488
H	9.55503655	6.93363165	13.3233005
H	9.18928225	8.00924047	11.9261761
H	10.7135391	7.06382394	11.9467344
N	7.5455972	4.81943305	8.60748764
O	7.7552852	4.5226783	6.31613805
O	9.58039412	6.68679605	9.59343884
O	8.96392469	5.94138301	11.6478597
C	3.11883347	6.89594784	7.52264256
C	1.77446337	7.52055985	7.8443672
H	0.97855563	6.82109329	7.54602062
H	1.63311043	8.44839265	7.27511144
C	1.84565009	7.73184629	9.36039031
H	0.89134297	7.56831552	9.87615999
H	2.20028186	8.74328822	9.5920735
C	2.94630139	6.72676958	9.80552826
H	3.56078731	7.13066365	10.6164505
C	2.28884151	5.44556091	10.3032794
C	1.66099448	4.23813352	12.2500212
H	1.77044318	4.36968056	13.3302741
H	2.12916757	3.29985767	11.9268771
H	0.60266473	4.24137148	11.9612621
N	3.75641842	6.49292565	8.61118768
O	3.54345451	6.79088539	6.32047263
O	1.72430622	4.62455081	9.60160835
O	2.3473786	5.36905206	11.654193
H	4.4764165	0.98474346	7.54041545
H	2.85049327	1.6455246	7.2779476
H	6.50114588	6.2461533	13.8294926
H	5.71204551	4.63762943	13.8328366
H	4.71331334	6.1248723	13.8236614

Cartesian Coordinates of [BiRh(MEPY)$_4$]			
74	E = −29287.406796620849		
C	4.35603858	3.17007722	7.565822
C	3.72295255	1.83399198	7.8944181
C	3.59926301	1.87704763	9.42301026
H	3.78359893	0.91073538	9.90810002
H	2.60489297	2.23256871	9.71550008
C	4.64503532	2.95836885	9.8347714
H	4.29579005	3.56842316	10.6783718
C	5.93575432	2.26025489	10.2496158
C	7.18017902	1.49865019	12.1262329
H	7.0672937	1.53935709	13.2133489
H	8.12858607	1.95745882	11.8211252
H	7.13631372	0.46326827	11.7667115
Bi	5.64962368	5.65784998	6.07680603
N	4.82477248	3.77895745	8.64063075
O	4.41582804	3.62486578	6.36791764
O	6.71269577	1.70953803	9.48962335
O	6.06327034	2.26021619	11.5963591
Rh	5.65267103	5.6566138	8.66239122
C	6.94243783	8.14642634	7.5643023
C	7.57018073	9.48518271	7.89339048
H	6.89959506	10.2872441	7.54895702
H	8.52830198	9.60389796	7.3710936
C	7.70607151	9.43455142	9.4205809
H	7.53138715	10.3987205	9.91341024
H	8.70115663	9.07139216	9.70153104
C	6.66037205	8.35452109	9.83426249
H	7.00983781	7.74444402	10.6777441
C	5.37034612	9.05333708	10.2504626
C	4.1293252	9.81658859	12.1286631
H	4.2444719	9.7775029	13.2156053
H	3.18090516	9.35612508	11.8261028
H	4.17112027	10.8515708	11.7677277
N	6.47951573	7.53422859	8.63990372
O	6.88027309	7.69301965	6.3660807
O	4.59064238	9.60123673	9.49129719
O	5.2460686	9.05572438	11.5975397
C	8.14006147	4.364107	7.56222211
C	9.4786185	3.73525552	7.89012089
H	10.2809638	4.40413611	7.54304158
H	9.59516463	2.77600663	7.36940537
C	9.43050259	3.6022804	9.41765056
H	10.3958184	3.77644187	9.90842336
H	9.06625302	2.60834238	9.7012995
C	8.35282594	4.65042712	9.83115684
H	7.74403265	4.30386142	10.6767319
C	9.05448404	5.94030281	10.2430049
C	9.82462434	7.18350423	12.1170039
H	9.78909724	7.0697873	13.2042201
H	9.36385158	8.13188308	11.8147854
H	10.8583616	7.14045322	11.7526686
N	7.53029305	4.82960922	8.63812791
O	7.68452484	4.42430957	6.36470666
O	9.60077183	6.71827473	9.48090728
O	9.06109757	6.0666987	11.5898846
C	3.16329436	6.94997878	7.56769858
C	1.82496123	7.57788164	7.89827901
H	1.02246595	6.90882115	7.55185367
H	1.70700416	8.53752809	7.37862957
C	1.87541458	7.70938756	9.42586208
H	0.91092889	7.53450176	9.91800693
H	2.23980513	8.7031824	9.70979686
C	2.95406309	6.66102966	9.83659275
H	3.563926	7.00686165	10.6817338
C	2.25306224	5.37062631	10.2479016
C	1.48143364	4.12792683	12.1215801
H	1.51520431	4.24235374	13.2087822
H	1.94348841	3.17973372	11.8206847
H	0.44820806	4.16983999	11.755663
N	3.77485208	6.48353958	8.64214996
O	3.61704798	6.89101776	6.36944459
O	1.70794917	4.59207688	9.48560307
O	2.24486961	5.24495167	11.5948896
H	4.38378653	1.02838616	7.53976263
H	2.75949871	1.72554583	7.37957262