Supplementary Material (ESI) for Chemical Communications

Synthesis and Characterization of a Trigonal Bipyramidal Supramolecular Cage Based Upon Rhodium and Platinum Metal Centers

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Supporting Information

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General Considerations

All manipulations dealing with lithium reagents were carried out under an N_2 atmosphere. 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) was synthesized according to literature procedures.[1-3] Dry THF was obtained from a PureSolv™ solvent purification system. Other solvents were used as received. ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR data were recorded on Varian Inova 400 or Unity Inova 750 MHz instruments. The ^{1}H spectra were referenced to the residual proton of the deuterated solvent. The ^{13}C spectra were referenced to the ^{13}C signals of the deuterated solvents. The ^{31}P spectra were referenced to an external standard of 85% H_3PO_4. The ^{195}Pt spectrum was referenced to an external standard of K_2PtCl_4. Mass spectrometry data was collected on a Bruker Daltons (Billerica, MA) Esquire-LC mass spectrometer equipped with ESI. The infrared spectrum was collected as a KBr pellet using a Bomem B-100 Infrared spectrometer.

X-ray Structure Determination Details

Crystals of **2** and **4** were coated in paratone oil and mounted on a CryoLoop™ and placed on the goniometer head under a stream of nitrogen cooled to 100K. The data was collected on a Bruker APEX CCD diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). The unit cell was determined by using reflections from three different orientations. The data was integrated using SAINT.[4] An empirical absorption correction and other corrections were applied to the data using multi-scan SADABS.[4] Structure solution, refinement, and modeling were accomplished by using the Bruker SHELXTL package.[4,5] The structure was determined by full-matrix least-squares refinement of F^2 and the selection of the appropriate atoms from the generated difference map. Hydrogen atom positions were calculated and $U_{iso}(H)$ values were fixed according to a riding model.

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[1] McAuley, A.; Norman, P. R.; Olubuyide, O. *Inorg. Chem.* **1984**, 1938-1943.
[2] Hay, R. W.; Norman, P. R. *J. Chem. Soc., Dalton* **1979** 1441-1445.
[3] Wang, L.; Wang, C.; Bau, R.; Flood, T. C. *Organometallics* **1996**, *15*, 491-498.
[4] Bruker (1997). SMART (Version 5.625), SAINT (Version 6.22) and SHELXTL (Version 6.10)
[5] Sheldrick, G. M. (1997). SHELX-97. University of Göttingen, Germany

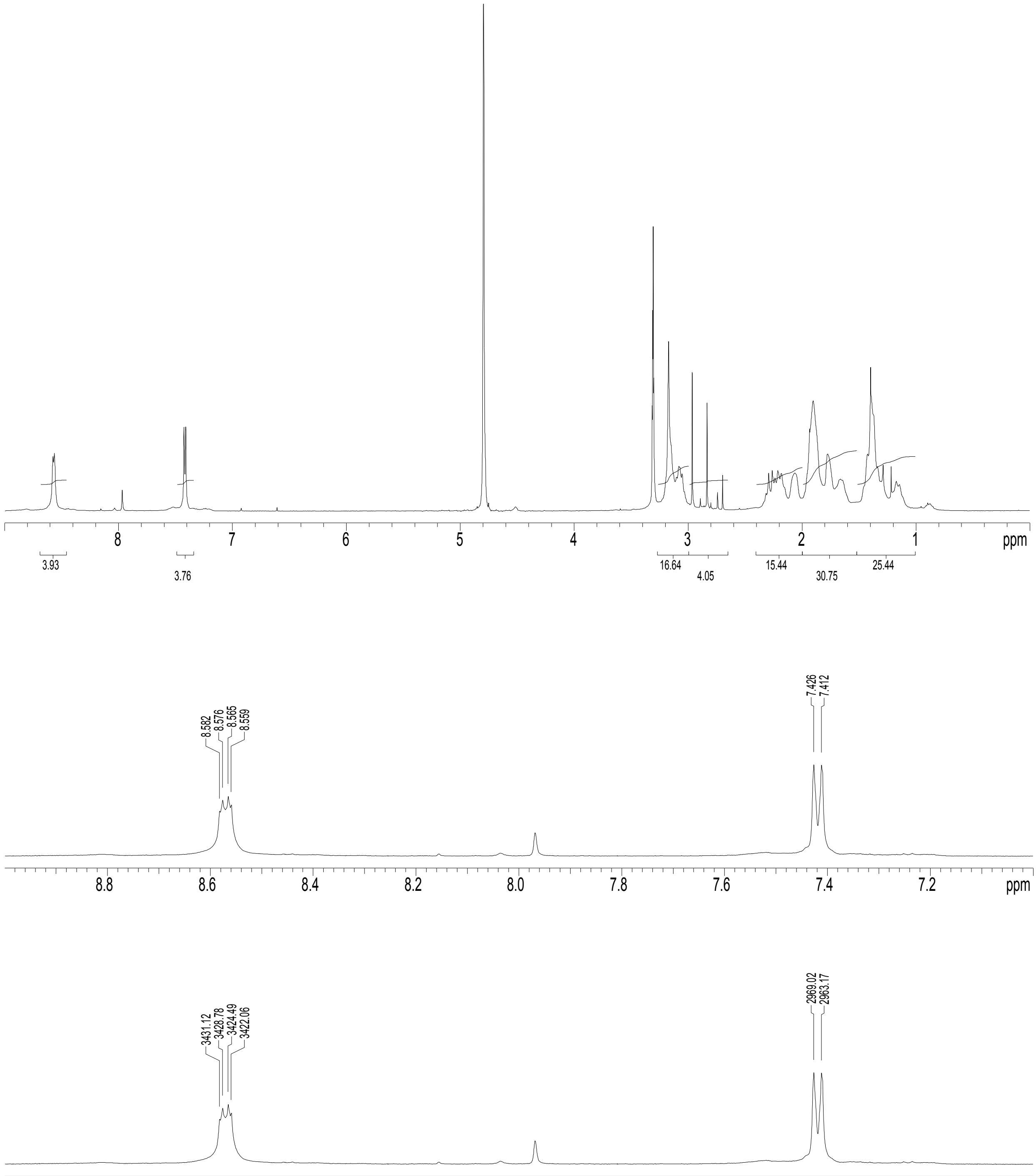
(Me_3tacn)Rh(CCPy)$_3$ (2). (Me_3tacn)$RhCl_3$ (0.761 g, 2.00 mmol) was placed into a Schlenk flask and heated to 50°C in vacuum for one hour. 4-Ethynyl-pyridine (0.722 g, 7.00 mmol) was added to a Schlenk flask and dried under vacuum for one hour at RT. The flask containing the 4-ethynyl-pyridine was filled with ~80 mL of dry THF. The flask containing the alkyne was cooled to -78°C and 4.2 mL of a 1.7 M solution of tert-butyl lithium was added to the flask under nitrogen. The flask containing the (Me_3tacn)$RhCl_3$ was charged with 40 mL of THF and cooled down to -78°C. The flask containing the acetylide was transferred *via* canula to the flask containing the (Me_3tacn)$RhCl_3$. The mixture was kept at -78°C for 4 h and then allowed to warm up to RT. The flask was stirred for 36 h. The volatile components were removed from the mixture by distillation under reduced pressure. The solid was washed with water and quickly filtered to obtain a light brown solid. Yield: 0.65 g, 1.11 mmol, 56%; mp 159-161 °C dec. Crystals suitable for single crystal x-ray diffraction were grown from a concentrated solution of dimethyl sulfoxide. ^{1}H NMR (400 MHz, CD_3OD) δ 3.04-3.15 (m, 6H, N-C*H*H-C*H*H-N), 3.19 (s, 9H, CH_3), 3.26-3.37 (m, 6H, N-CH*H*-CH*H*-N), 7.32 (dd, 6H, $^3J = 4.8$ Hz, $^4J = 1.5$ Hz, m-pyr), 8.32 (dd, 6H, $^3J = 4.8$ Hz, $^4J = 1.5$ Hz, o-pyr); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 52.9 (CH_3), 60.6 (CH_2), 100.2 (d, $^2J_{C\beta\text{-}Rh} = 9.2$ Hz, C_β), 120.2 (d, $^1J_{C\alpha\text{-}Rh} = 48.0$ Hz, C_α), 127.7, 139.5, 149.6 (aromatic); IR (KBr): ν(CC) 2103 (s) cm^{-1}; ES-MS (DMSO) cacld for [M]Na$^+$: *m/z* 603.2, found 603.2; Anal. Calcd for $C_{30}H_{33}N_6Rh$: C, 62.05; H, 5.73; N, 14.48. Found: C, 61.45; H, 5.61; N, 14.10.

(DCPE)Pt(NO_3)$_2$ (3). (DCPE)$PtCl_2$ (1.37 g, 2.0 mmol) was added to 1 L Erlenmeyer flask with a stirbar. CH_2Cl_2 (400 mL) was added to the flask and the solution stirred rapidly. $AgNO_3$ (0.68 g, 4 mmol) was dissolved in water (~5 mL) and added to the flask containing the platinum complex. The complex was stirred for 5 minutes while a white precipitate formed. To this mixture was added 400 mL of acetone. The mixture was allowed to stir for an additional 30 min. The solution was filtered with the aid of Celite® and evaporated under reduced pressure to dryness. The white solid was then taken up in CH_2Cl_2 and allowed to slowly evaporate. The complex was isolated as white crystals. Yield: 1.30 g, 1.87 mmol, 93%; mp 192-194 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.20-1.58 (m, 20H), 1.68-1.96 (m, 20H), 2.02-2.40 (m, 8H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 21.7 ($^1J_{C\text{-}P} = 3.8$ Hz), 22.1 ($^1J_{C\text{-}P} = 3.8$ Hz), 26.2, 27.0, 27.1 ($^1J_{C\text{-}P} = 16.7$ Hz), 27.3, 28.7, 28.7, 29.0, 34.6, 34.9; $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_2Cl_2, ref. 85% H_3PO_4) δ 58.3 ($^1J_{P\text{-}Pt} = 3839$ Hz); ES-MS (CH_2Cl_2) cacld for [M-NO_3]$^+$: *m/z* 679.3, found 679.2; Anal. Calcd for $C_{26}H_{48}N_2P_2PtO_6$: C, 42.09; H, 6.53; N, 3.78. Found: C, 42.10; H, 6.55; N, 3.81.

Trigonal Bipyramidal Cage (4). Compound **2** (0.040 g, 0.069 mmol) was dissolved in 5 mL of CH_2Cl_2. Compound **3** (0.077 g, 0.104 mmol) was dissolved in 5 mL of CH_2Cl_2. The combination of the solutions of **2** and **3** formed a thick orange oil upon mixing. The CH_2Cl_2 was decanted off and the oily liquid was washed with 2X5 mL portions of CH_2Cl_2. The oil was then dissolved in methanol and allowed to slowly crystallize by slow evaporation yielding a yellow crystalline solid. Yield: 0.098 g, 0.029 mmol, 85%. Crystals suitable for single crystal x-ray diffraction were grown from a solution of acetonitrile and toluene. ^{1}H NMR (749.8 MHz, CD_3OD) δ 1.17 (m, 12H), 1.39 (m, 38H), 1.66 (m, 12H), 1.77 (m, 12H), 1.90 (m, 36H), 2.07 (m, 12H), 2.13-2.36 (m, 25H), 3.01-3.25 (m, 39H), 7.42 (d, 12H, $^3J = 5.9$ Hz, m-pyr), 8.60 (dd, 12H, $^3J = 7.0$ Hz, $^3J = 2.4$ Hz, o-pyr); $^{13}C\{^1H\}$ NMR (188.5 MHz, CD_3OD) δ 22.6, 22.8, 26.9, 27.7 ($^1J_{C\text{-}P} = 11.9$ Hz), 27.9 ($^1J_{C\text{-}P} = 12.9$ Hz), 29.6, 30.1, 35.5, 35.6, 53.2, 60.8, 100.8 (d, $^2J_{C\beta\text{-}Rh} = 9.0$

Hz, C_β), 131.0, 131.3 (d, $^1J_{C\alpha\text{-}Rh} = 47.5$ Hz, C_α), 142.7, 150.6; $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_3OD, ref. 85% H_3PO_4) δ 59.0 ($^1J_{P\text{-}Pt} = 3113$ Hz); $^{195}Pt\ \{^1H\}$ NMR (85.549 MHz, CD_3OD, ref. K_2PtCl_4) δ -1674.281 ($^1J_{P\text{-}Pt} = 3134$ Hz); IR (KBr): ν(CC) 2103 (s) cm^{-1}; ES-MS (CD_3OD) cacld for $[M\text{-}6NO_3]^{+6}$, $[M\text{-}5NO_3]^{+5}$, $[M\text{-}4NO_3]^{+4}$, $[M\text{-}3NO_3]^{+3}$, $[M\text{-}2NO_3]^{+2}$,: *m/z* 502.0, 614.8, 784.1, 1066.1, 1630.1, found 502.4, 615.7, 784.6, 1066.2, 1630.5; Anal. Calcd for $C_{138}H_{210}N_{18}Rh_2P_6Pt_3O_{18}$: C, 45.95; H, 6.25; N, 7.45. Found: C, 45.50; H, 6.41; N, 7.09; an unknown amount of solvent occupies the void spaces of the crystalline material used for this analysis.

^{1}H Spectra of **4**



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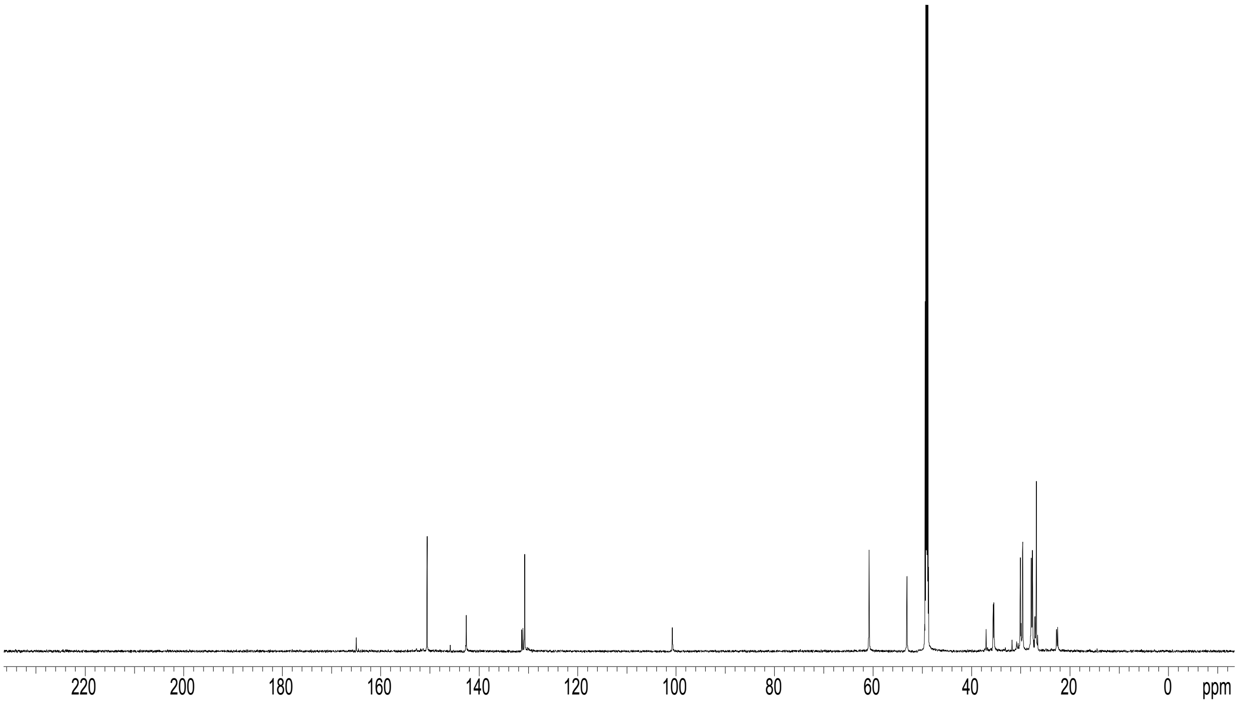

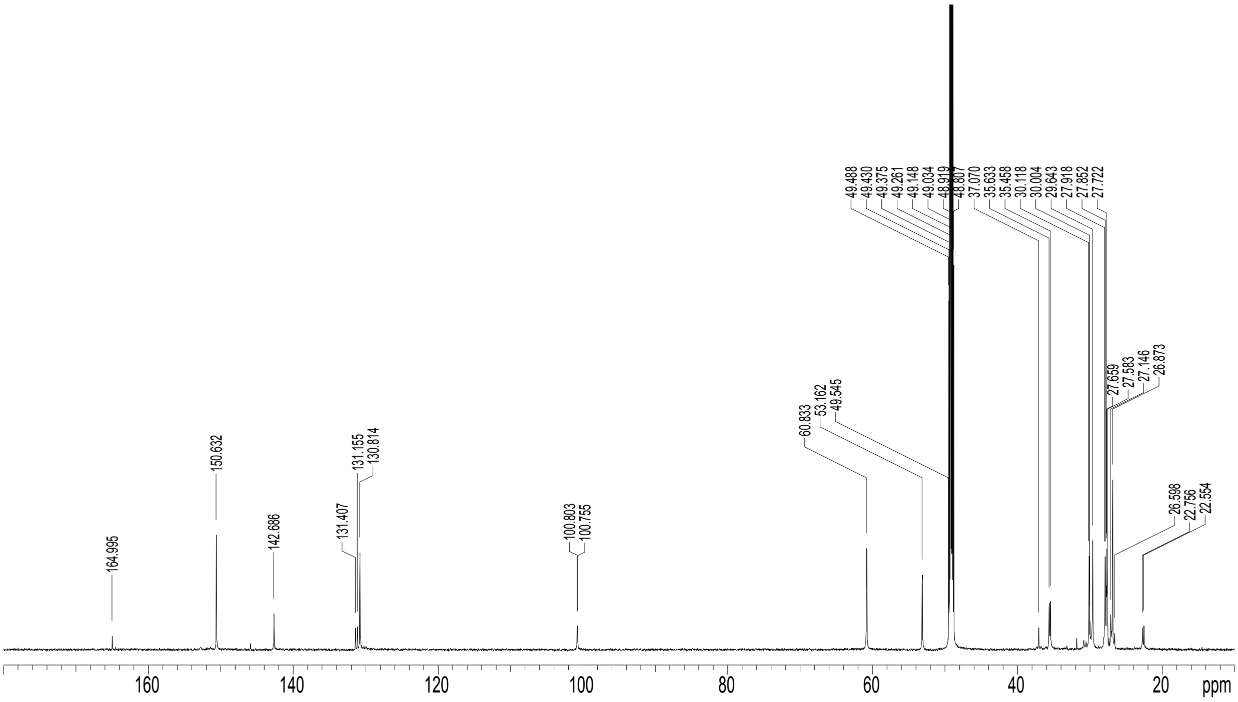

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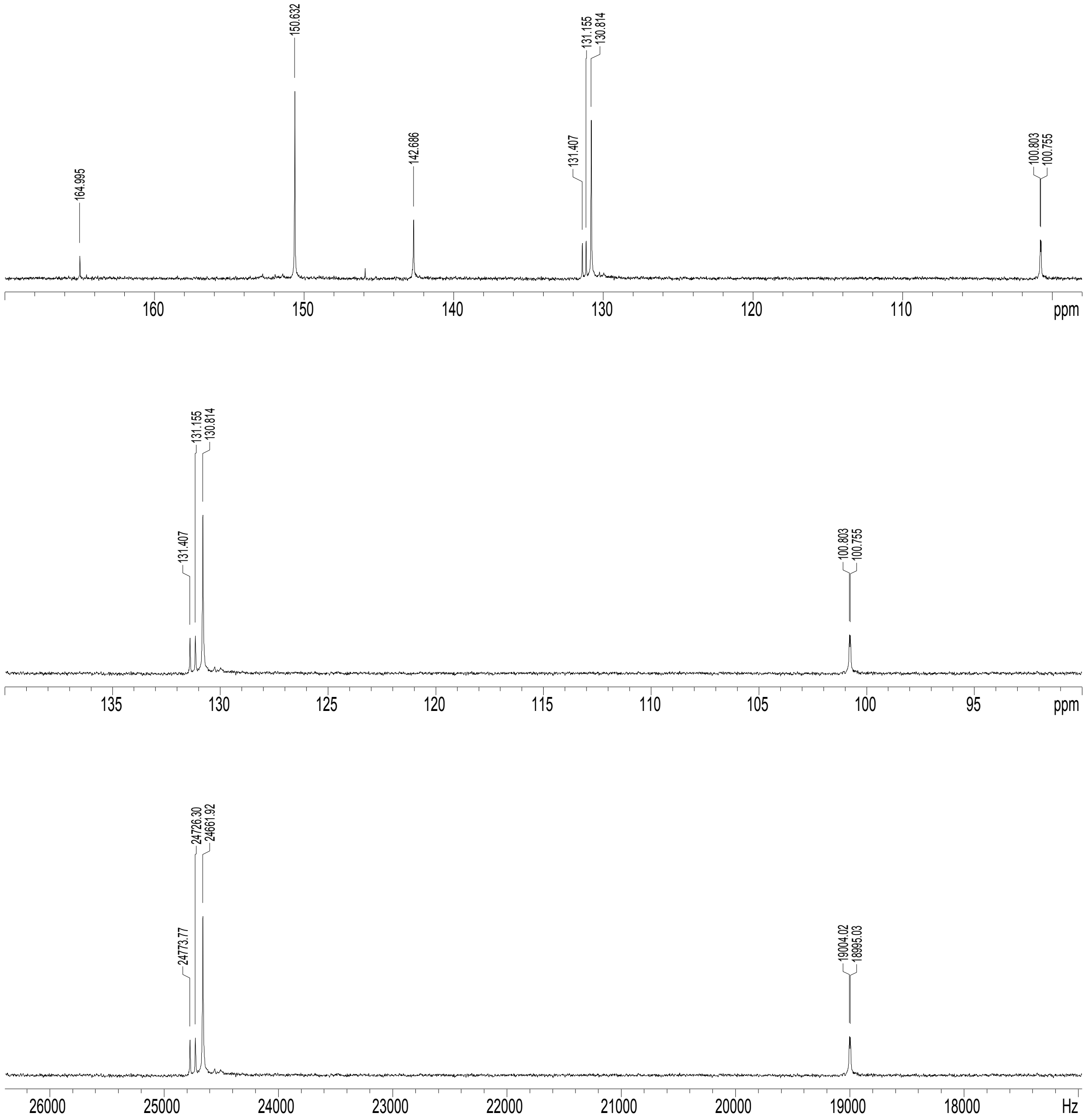
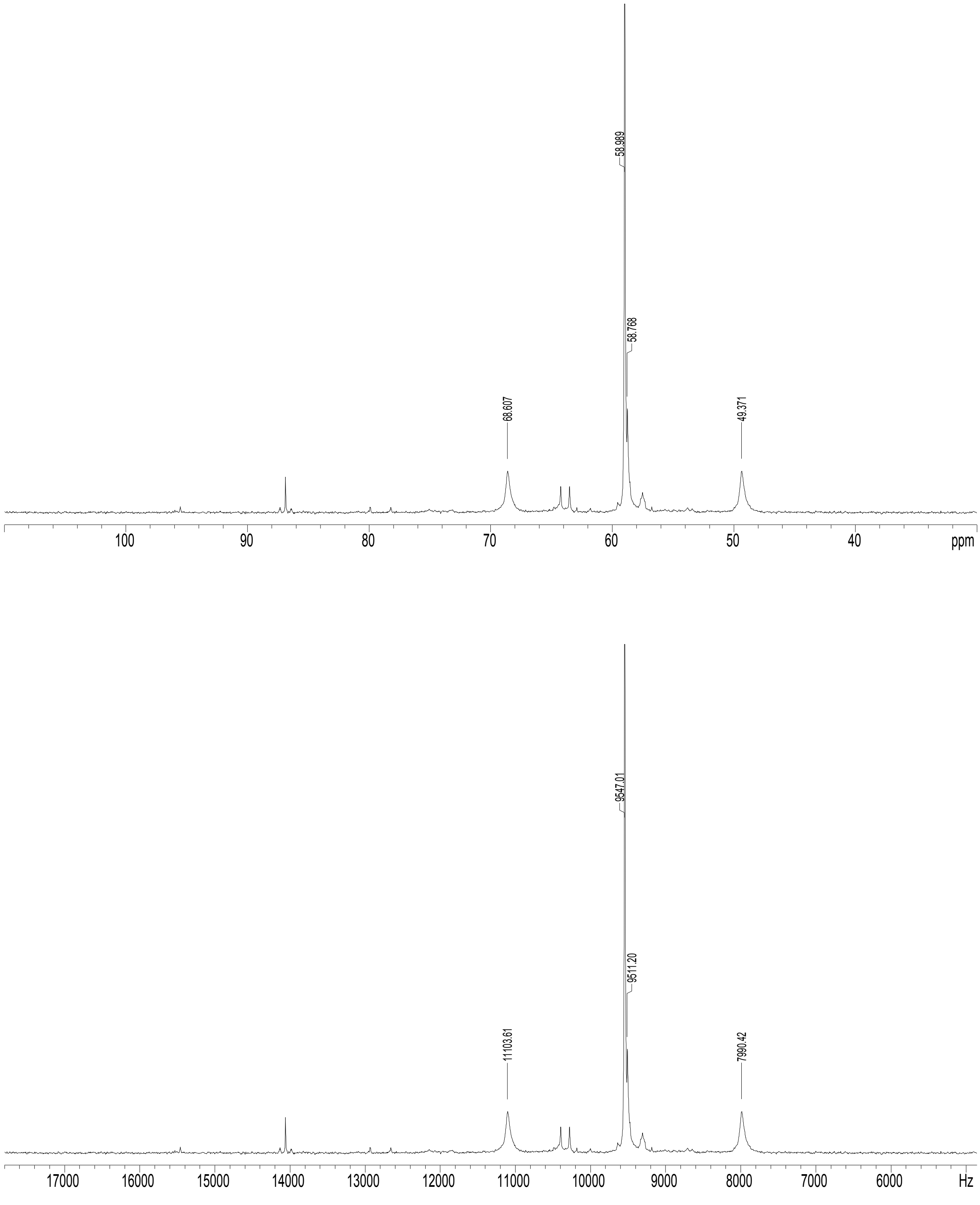
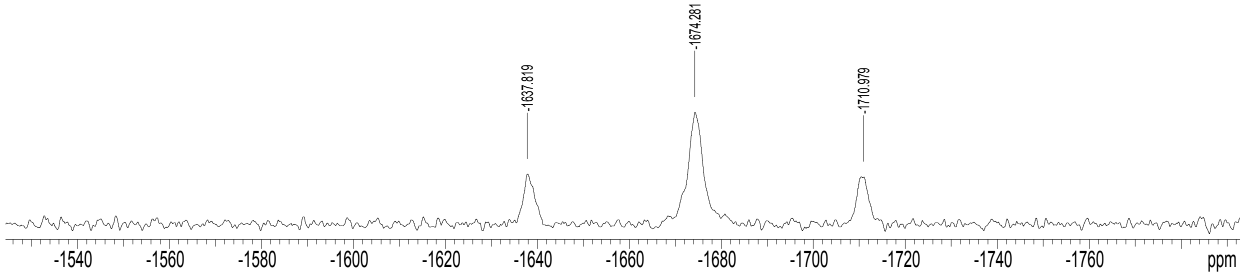
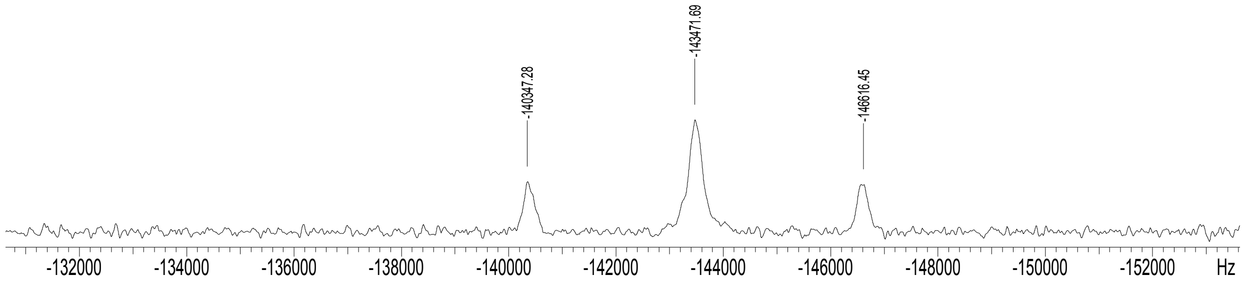


^{31}P Spectra of **4**

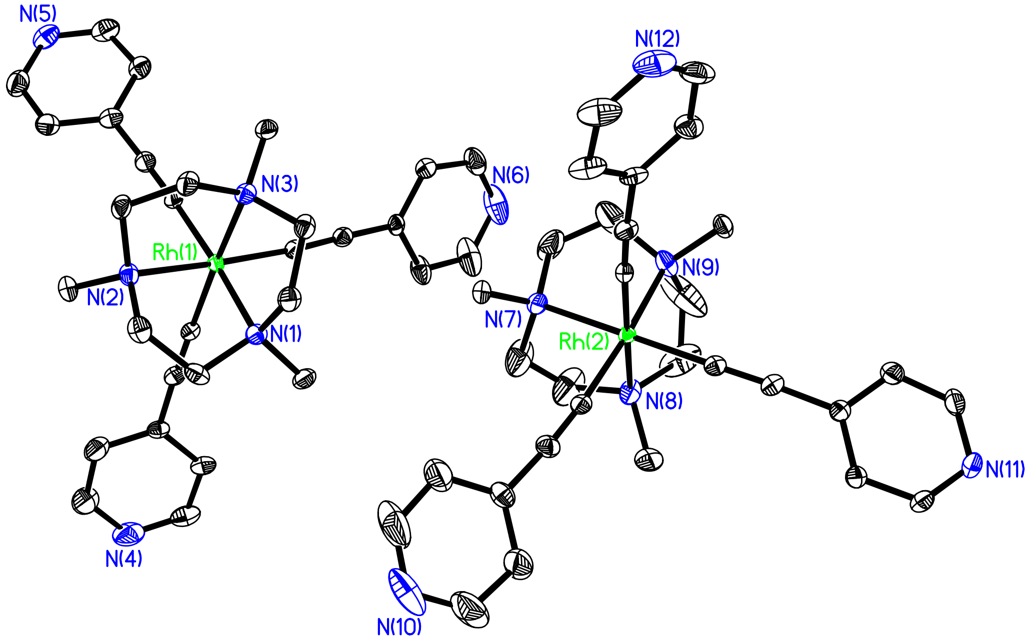


^{195}Pt Spectra of **4**





X-ray Structure of 2
Asymmetric Unit



X-ray Structure of 2
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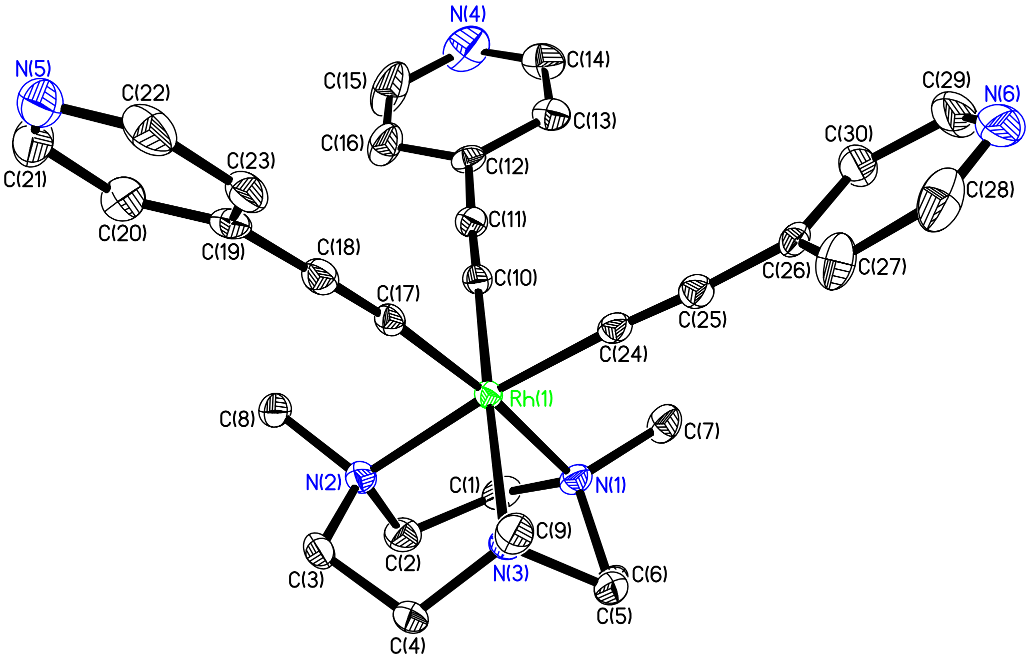

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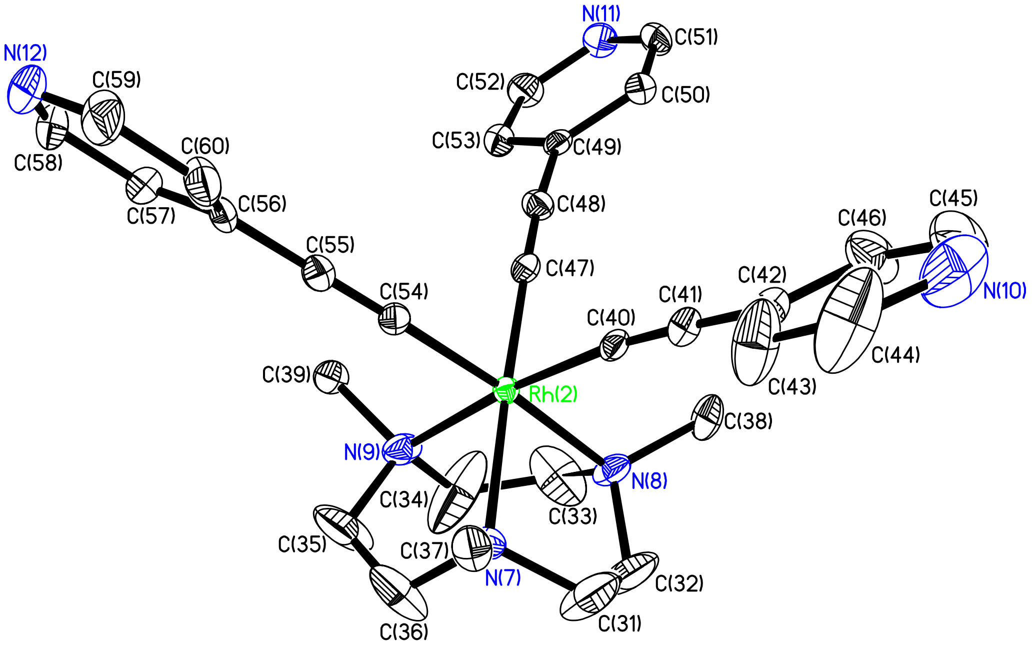
Molecule 2



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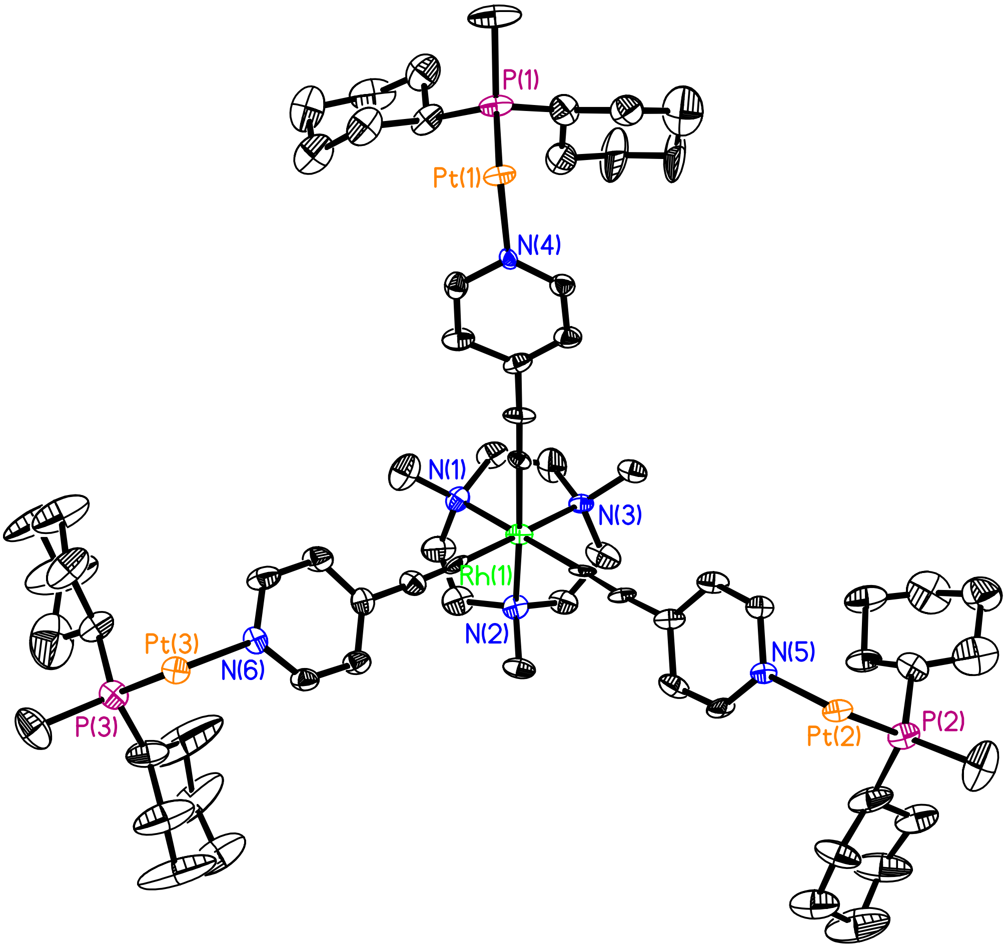

X-ray Structure of 4
Trigonal Bipyramidal Cage