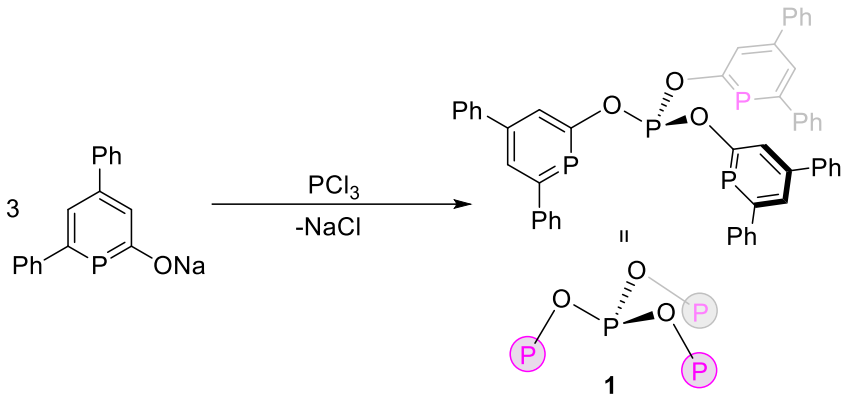
Supporting Information

S1: Synthetic Details

General: All manipulations were performed under an inert atmosphere of dry nitrogen, using standard Schlenk techniques and glovebox. Dry, oxygen-free solvents were employed. Sodium 3,5-diphenyl-phosphinin-2-olate was prepared following literature preocedure,[1] while all other starting materials were purchased from commercial sources. NMR spectra were recorded on Bruker Avance 400 MHz (^{1}H, 400.1 MHz; ^{13}C, 100.5 MHz; ^{31}P, 161.9 MHz) or Bruker Avance 600 MHz spectrometers (^{1}H, 600.2 MHz; ^{13}C, 150.8 MHz; ^{31}P, 242.9 MHz). All spectra were obtained in the solvent indicated at 25 °C except mentioned otherwise. The chemical shifts (δ) were measured according to IUPAC and expressed in ppm relative to $SiMe_4$ (^{1}H, ^{13}C), and 85 % H_3PO_4 (^{31}P). Coupling constants *J* are reported in Hertz [Hz] as absolute values. Single crystal X-ray diffraction data was collected on an Agilent Technologies SuperNova X-RAY diffractometer system equipped with a Cu sealed tube (λ = 1.54178) at 40 kV and 30 mA. Because of high sensitivity of these compounds or the contamination of solvents, the elemental analyses gave unsatisfying results. The high purity of these isolated compounds has been proved mainly by NMR spectra. ESI-MS/APCI-MS spectra were measured on Bruker ESI/APCI-Q-TOF maxis 4G. UV-Vis absorption spectra were

recorded using a Shimadzu UV Vis/NIR UV-3600 spectrophotometer. Solid-state IR spectra were obtained on a Perkin-Elmer Frontier FT-IR spectrometer in the region of 500-4000 cm^{-1} using ATR technique. Melting points (M. P.) were measured on jiahang JH-30 apparatus.

Preparation of 1:



Phosphorus trichloride (92 mg, 0.67 mmol) in Et_2O (1 mL) was added to a stirred solution of sodium 3,5-diphenyl-phosphinin-2-olate (570 mg, 2.0 mmol) in Et_2O (10 mL) at room temperature. After stirring for 0.5 hour, some white precipitates appeared. After filtration, the remaining solid was extracted with dichloromethane to remove the salts. Then, the solvent was removed under reduced pressure, and the remaining residue was washed with hexane and dried *in vacuo* to afford **1** as a pale-yellow powder (373 mg, 0.45 mmol), 68 % yield. M. P. = 164 °C. ^{1}H NMR (CD_2Cl_2, 400.1 MHz): δ = 8.13 (m, 3 H, $C_{ar}H$), 7.96 (m, 3 H, $C_{ar}H$), 7.70 (m, 12 H, $C_{ar}H$), 7.49 (m, 18 H, $C_{ar}H$); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 150.8 MHz): δ = 184.4 (d, $^{1}J_{PC}$ = 46.7 Hz, OCP), 171.6 (d, $^{1}J_{PC}$ = 49.8 Hz, CPC), 145.9 (C_{ar}), 142.9 (d, $^{2}J_{PC}$ = 27.1 Hz, PCC), 141.0 (C_{ar}), 129.7 (C_{ar}), 129.0 (d, *J* = 12.1 Hz, C_{ar}), 128.3 (d, *J* = 15.1 Hz, C_{ar}), 127.8 (C_{ar}), 127.6 (C_{ar}), 125.8 (C_{ar}); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz): δ = 151.8 (d, $^{3}J_{PP}$ = 68.0 Hz), 127.9 (q, $^{3}J_{PP}$ 68.0 Hz). IR (ATR, [cm^{-1}]): 3052, 3023, 1572, 1488, 1372, 1105, 955, 868, 759, 695; UV/Vis (THF, λ (nm) ε ($M^{-1}cm^{-1}$)): 306 (79650); APCI-TOF-MS: calc. for $C_{51}H_{36}O_3P_4^{+}$: 821.16877, ($[M+H]^{+}$), found: 821.16809.

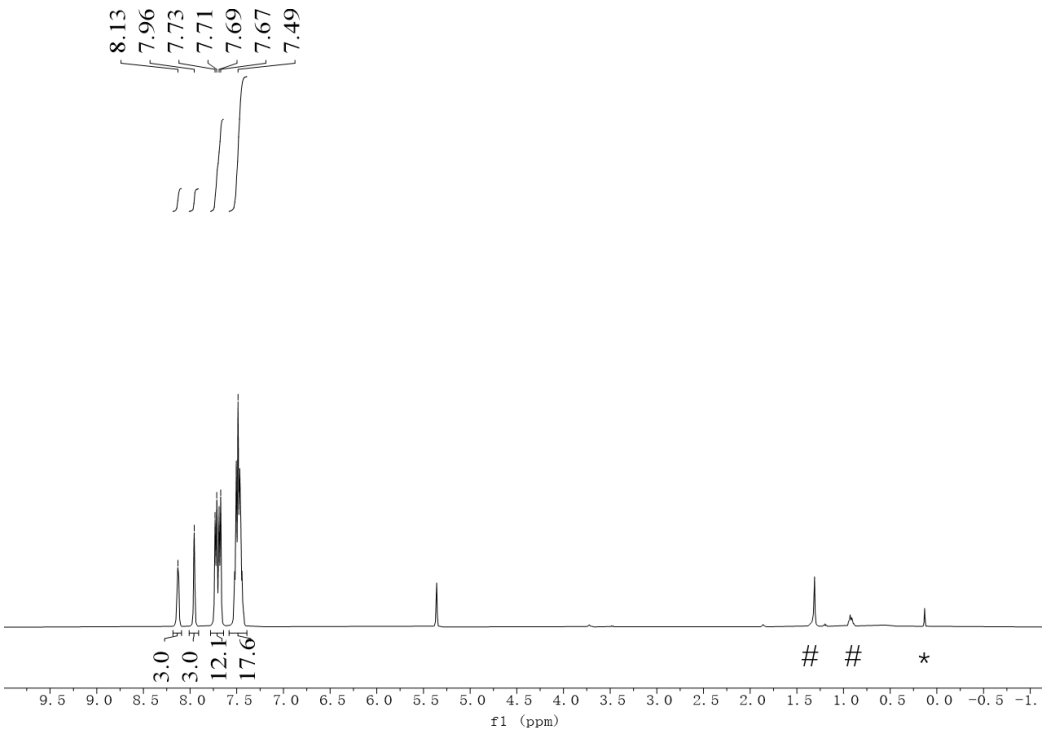


Figure S1. ^{1}H NMR spectrum of **1** in CD_2Cl_2. $^{\#}$Hexane, * Silicone grease.

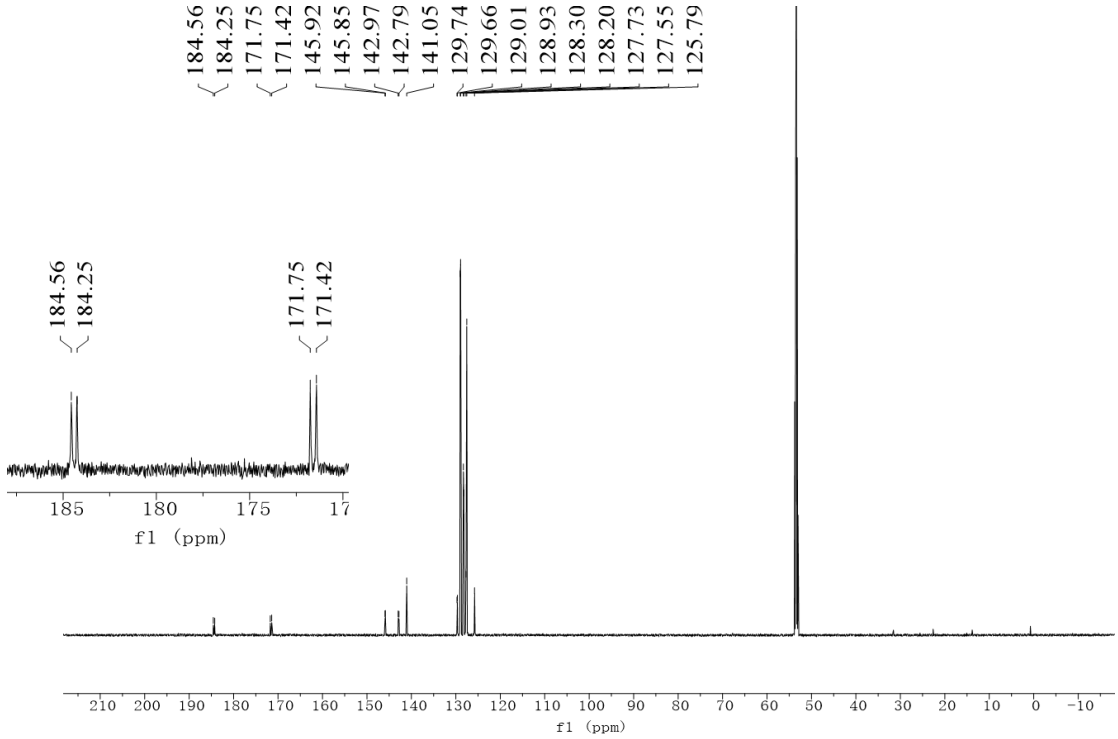


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2.

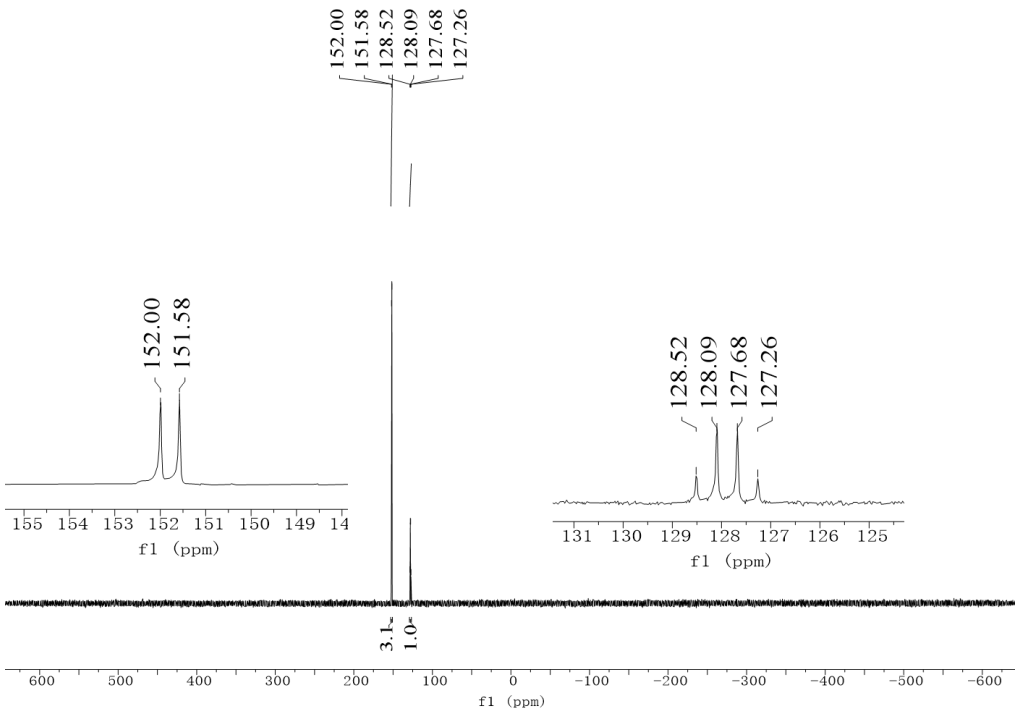


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in CD_2Cl_2.

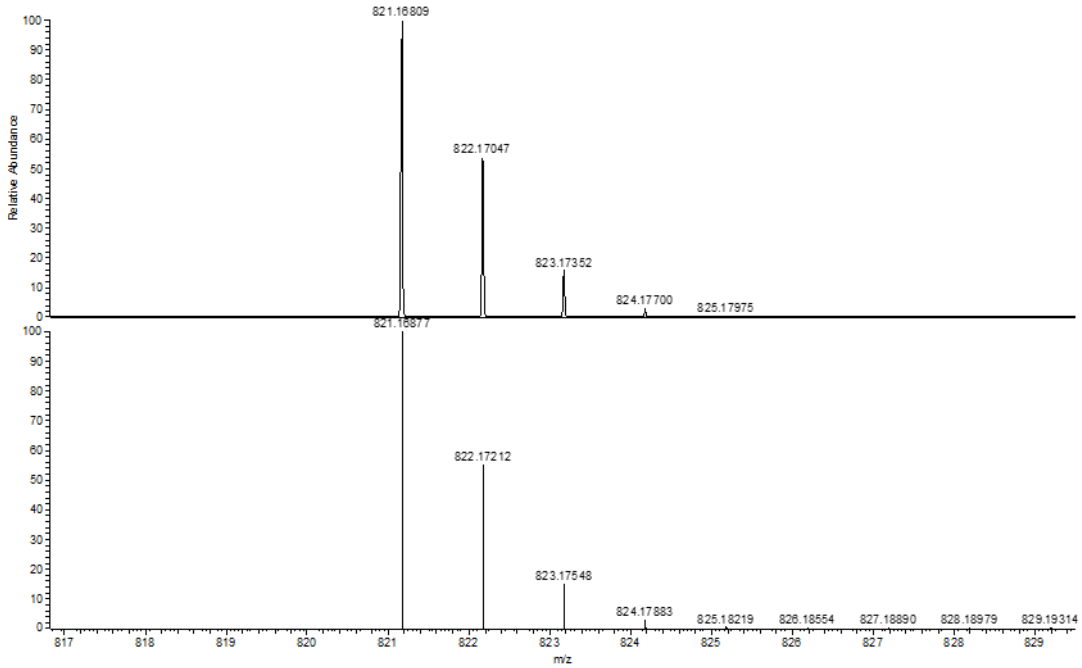


Figure S4. APCI-TOF-MS of **1**.

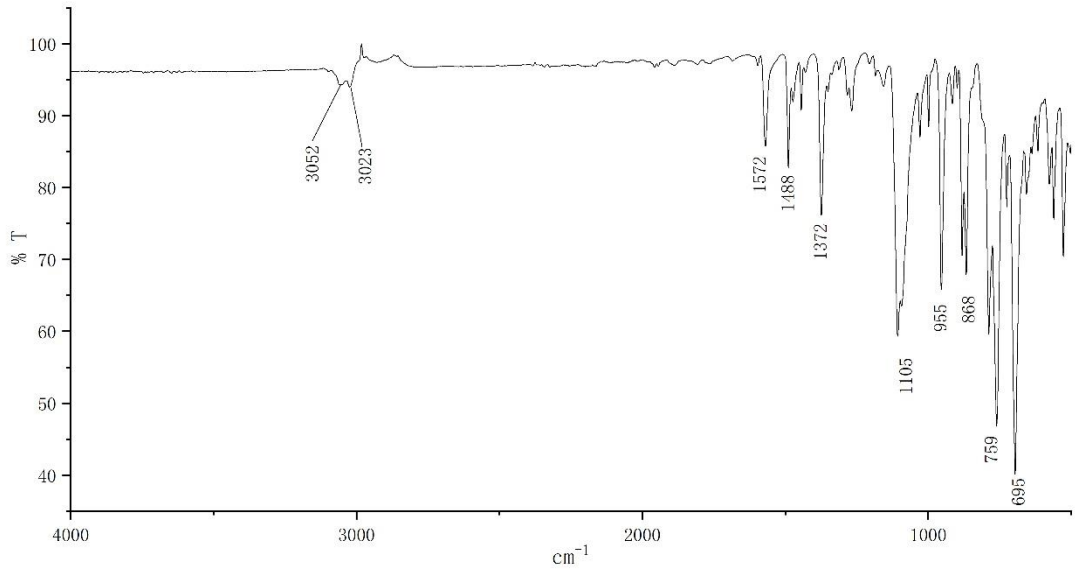
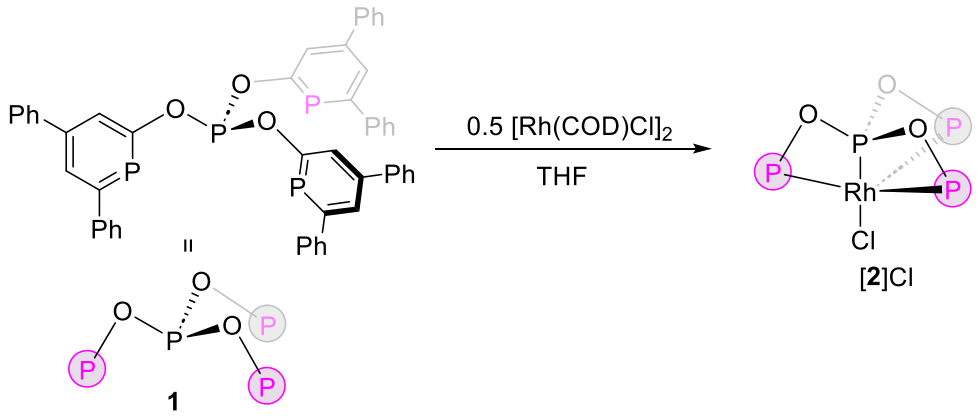


Figure S5. IR spectrum of **1**

Preparation of [2]Cl:



$[Rh(cod)Cl]_2$ (100 mg, 0.22 mmol) in THF (5mL) was added to a stirred solution of **1** (350 mg, 0.43 mmol) in THF (10 mL) at room temperature. After stirring for 2 hours, the solvent was removed under reduced pressure. The remaining solid was washed with hexane and dried *in vacuo* to afford a red powder [**2**]Cl (370 mg, 0.39 mmol), 90.3 % yield. M. P. = 134 °C. ^{1}H NMR (CD_2Cl_2, 400.1 MHz): δ = 8.07 (m, 3 H, $C_{ar}H$), 7.99 (m, 9 H, $C_{ar}H$), 7.65 (m, 6 H, $C_{ar}H$), 7.49 (m, 18 H, $C_{ar}H$); ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2): δ = 173.7 (C_{ar}), 161.5 (t, J = 15.1 Hz, C_{ar}), 141.2 (C_{ar}), 140.8 (C_{ar}), 139.2 (dd, J = 12.1 Hz, J = 5.0 Hz, C_{ar}), 131.4 (dd, J = 11.1 Hz, J = 5.9 Hz, C_{ar}), 129.2 (C_{ar}), 128.9

(C_{ar}), 128.6 (C_{ar}), 128.2 (C_{ar}), 127.3 (C_{ar}), 119.8 (d, J = 20.8 Hz, C_{ar}); $^{31}P\{^{1}H\}$ NMR (161.9 MHz, CD_2Cl_2): 218.8 (dq, $^{1}J_{RhP}$ = 155.4 Hz, $^{2}J_{PP}$ = 25.9 Hz, phosphite), 137.3 (dd, $^{1}J_{RhP}$ = 170.0 Hz, $^{2}J_{PP}$ = 25.9 Hz, phosphinine); IR (ATR, [cm^{-1}]): 3055, 3031, 1493, 1399, 1347, 1134, 1075, 951, 889, 827, 756, 728, 690; UV/Vis (THF, λ (nm) ε ($M^{-1}cm^{-1}$)): 300 (93130), 361 (52280); 409 (79610); 471 (38140); APCI-TOF-MS: calc. for $C_{51}H_{36}O_3P_4Rh^+$: 923.0664 ([M]$^+$), found: 923.0647.

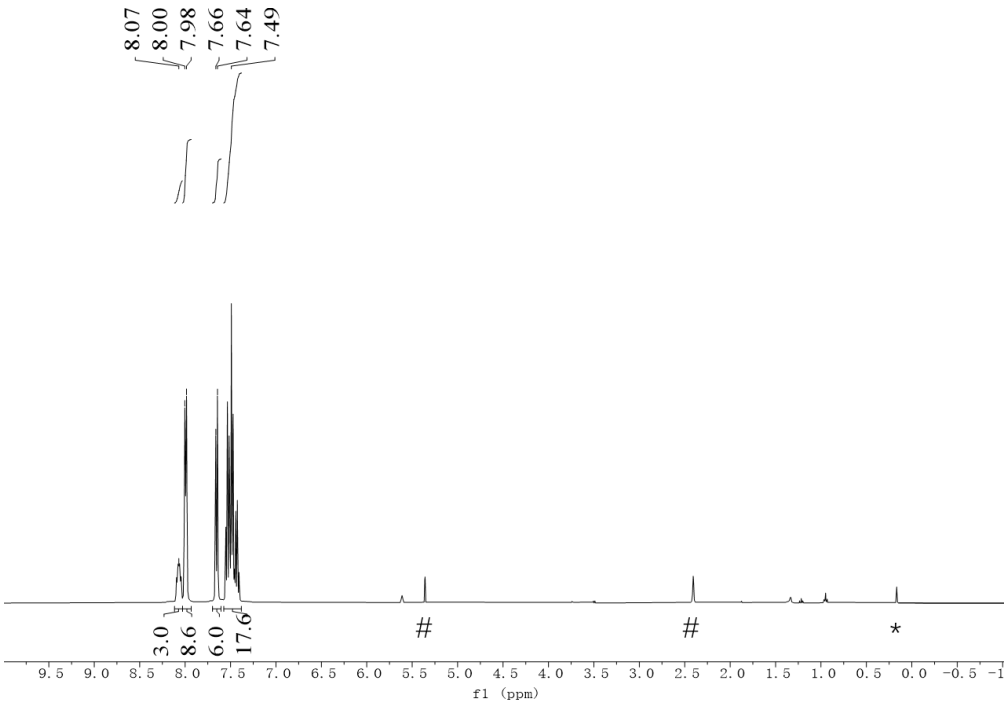


Figure S6. ^{1}H NMR spectrum of [**2**]Cl in CD_2Cl_2. $^{\#}$COD, *Silicon grease.

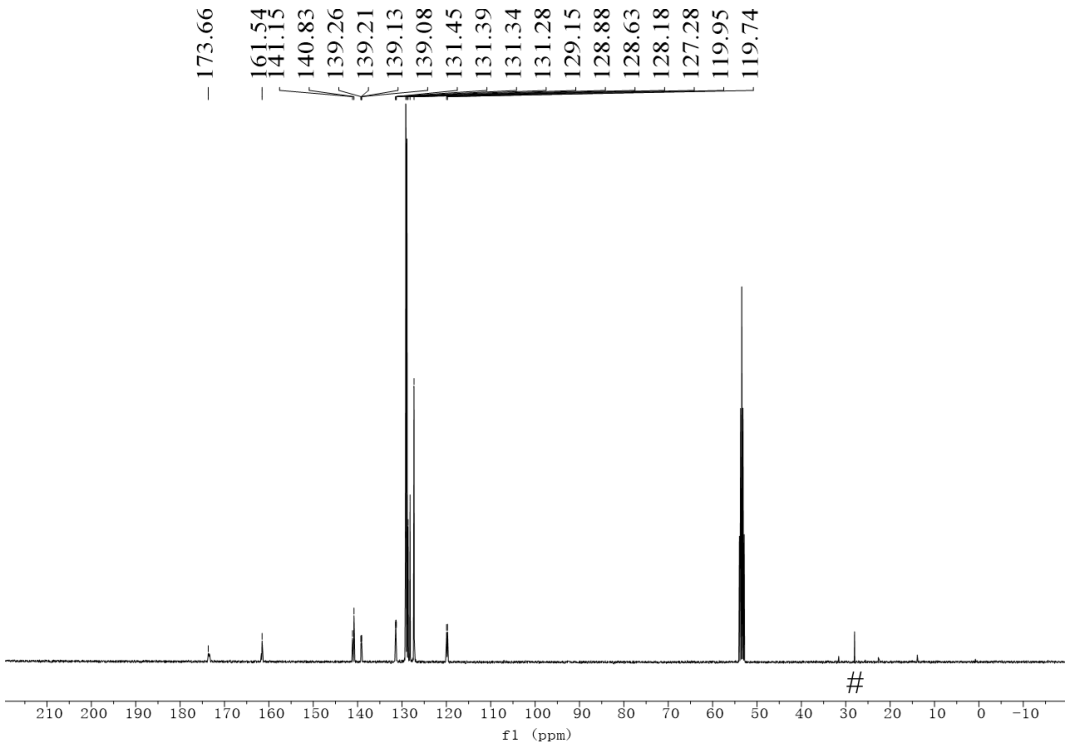


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of [**2**]Cl in CD_2Cl_2. $^{\#}$COD.

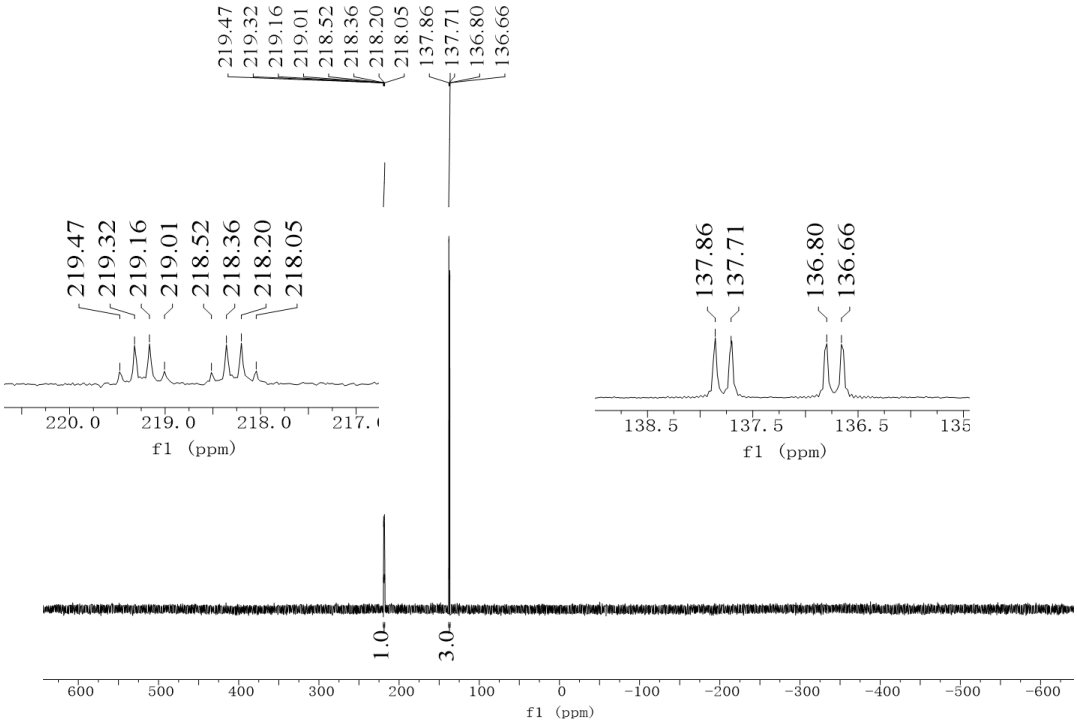


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of [**2**]Cl in CD_2Cl_2.

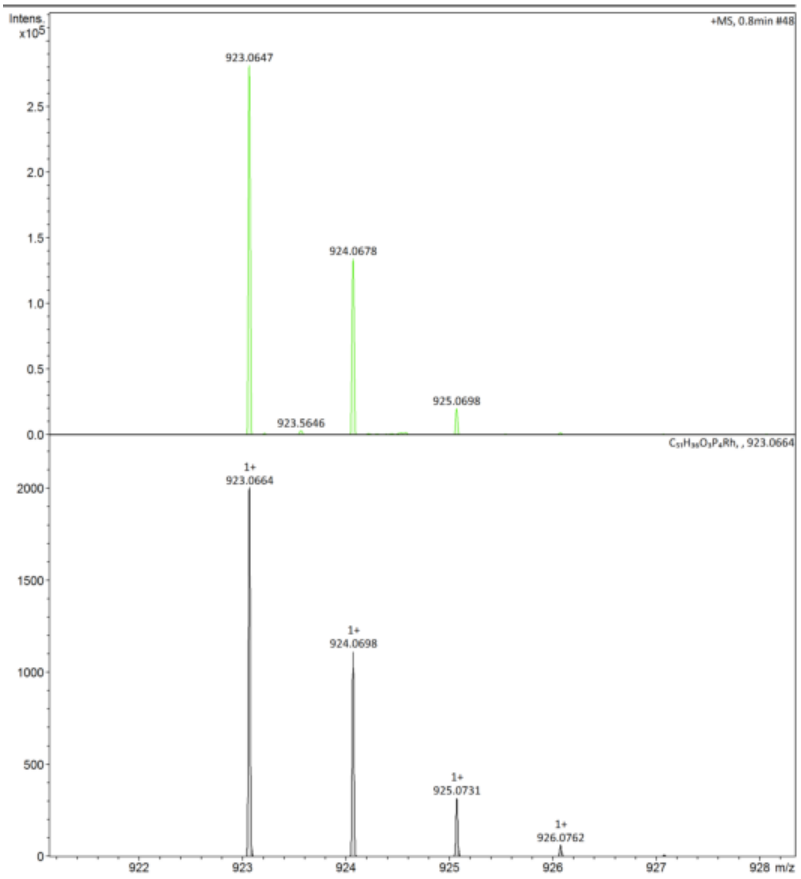


Figure S9. APCI-TOF-MS of [**2**]Cl.

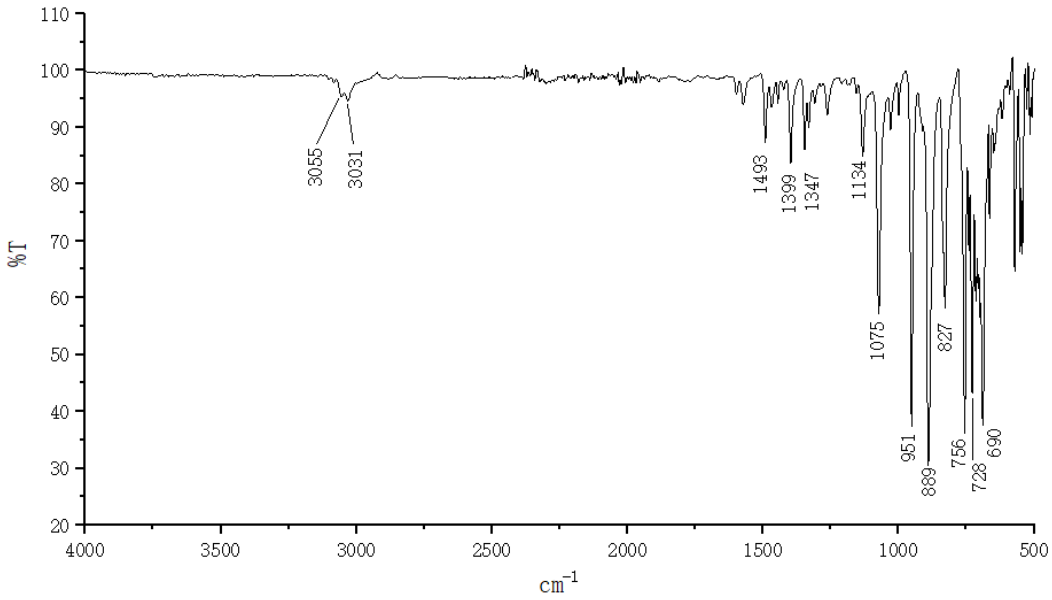
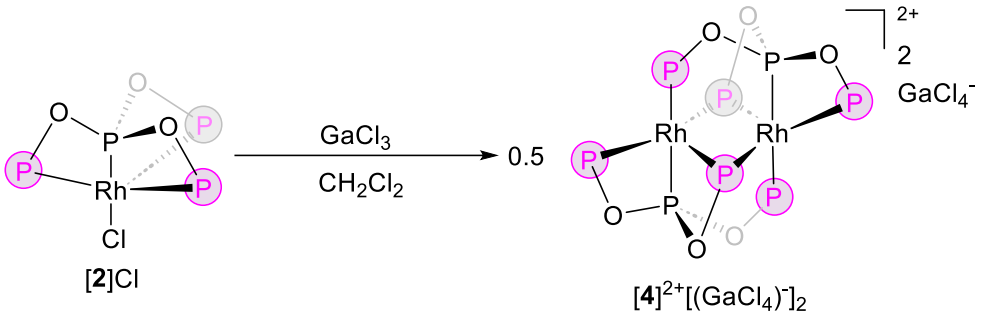


Figure S10. IR spectrum of [**2**]Cl**.**

Preparation of $[4]^{2+}[(GaCl_4)^-]_2$:



$GaCl_3$ (19 mg, 0.11 mmol) in dichloromethane (3 mL) was added to a stirred solution of [**2**]Cl (110 mg, 0.11 mmol) in dichloromethane (10 mL) at room temperature. After stirring for 2 hours, the solvent was removed under reduced pressure. The remaining solid was washed with hexane and dried *in vacuo* to afford $[4]^{2+}[(GaCl_4)^-]_2$ as a green-black powder (110 mg, 0.048 mmol), 87 % yield. M. P. > 250 °C. $^{31}P\{^1H\}$NMR (CD_2Cl_2, 161.9 MHz, 203 K): δ = 170.9 (m, phosphite), 134.9 (m, η_1-P), 98.7 (m, η_1-P), 59.8 (m, μ_2-P); IR (ATR, [cm^{-1}]): 3054, 3027, 2962, 1563, 1099, 958, 889, 760, 694; UV/Vis (THF, λ (nm) ε (M^{-1} cm^{-1})): 347 (114040), 385 (94800); 604 (48540), 666 (33320); APCI-TOF-MS: calc. for $C_{51}H_{36}O_3P_4Rh^+$: 923.0664 ([M]$^+$), found: 923.0623.

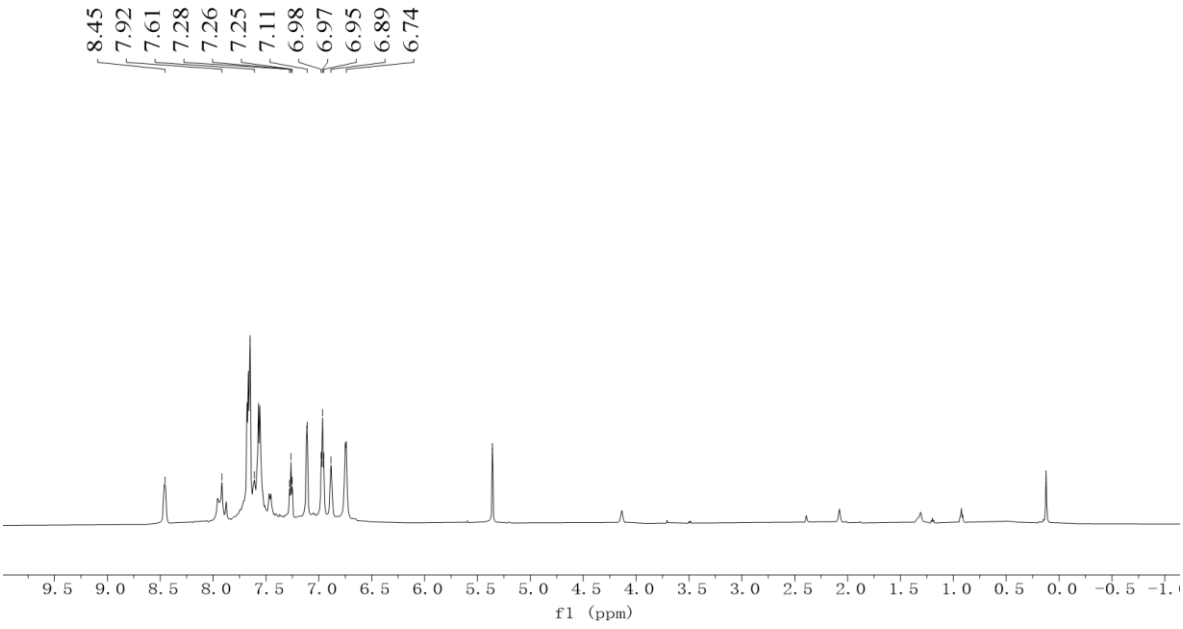


Figure S11. ^{1}H NMR spectrum of $[4]^{2+}[(GaCl_4)^-]_2$ in CD_2Cl_2 at 297K.

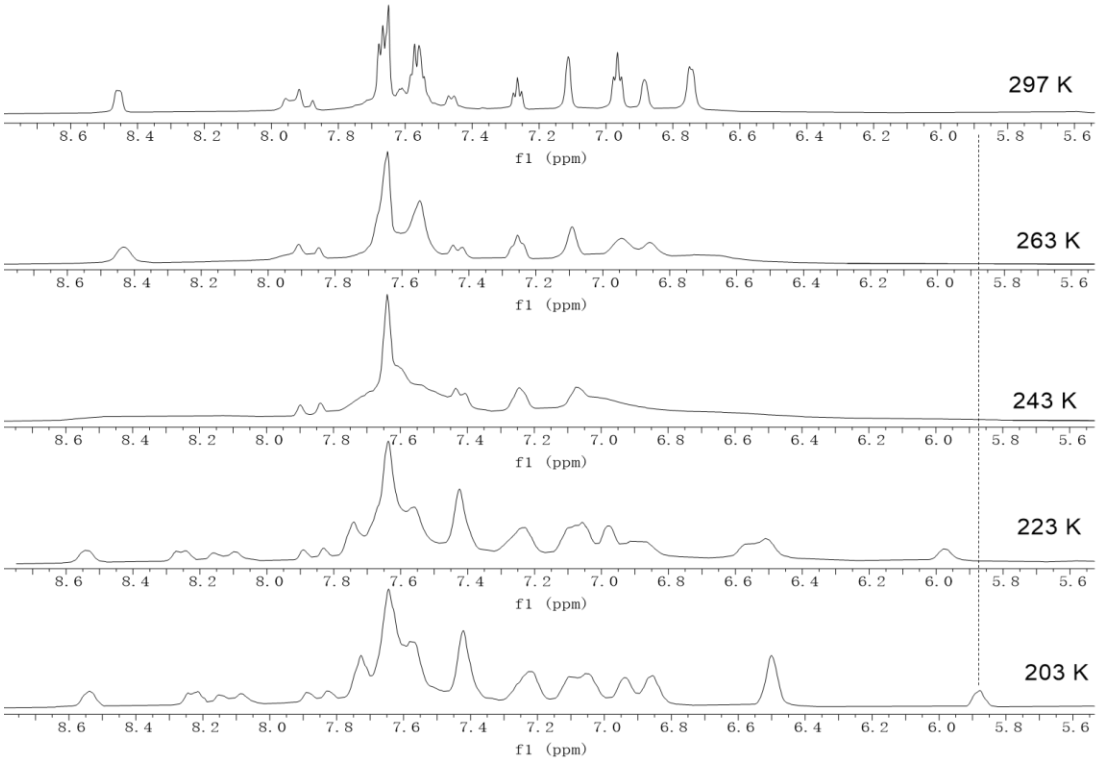


Figure S12. Variable temperature ^{1}H NMR spectrum of $[\mathbf{4}]^{2+}[(GaCl_4)^-]_2$ in CD_2Cl_2. (A new peak at 5.9 ppm appeared gradually upon cooling to 203 K).

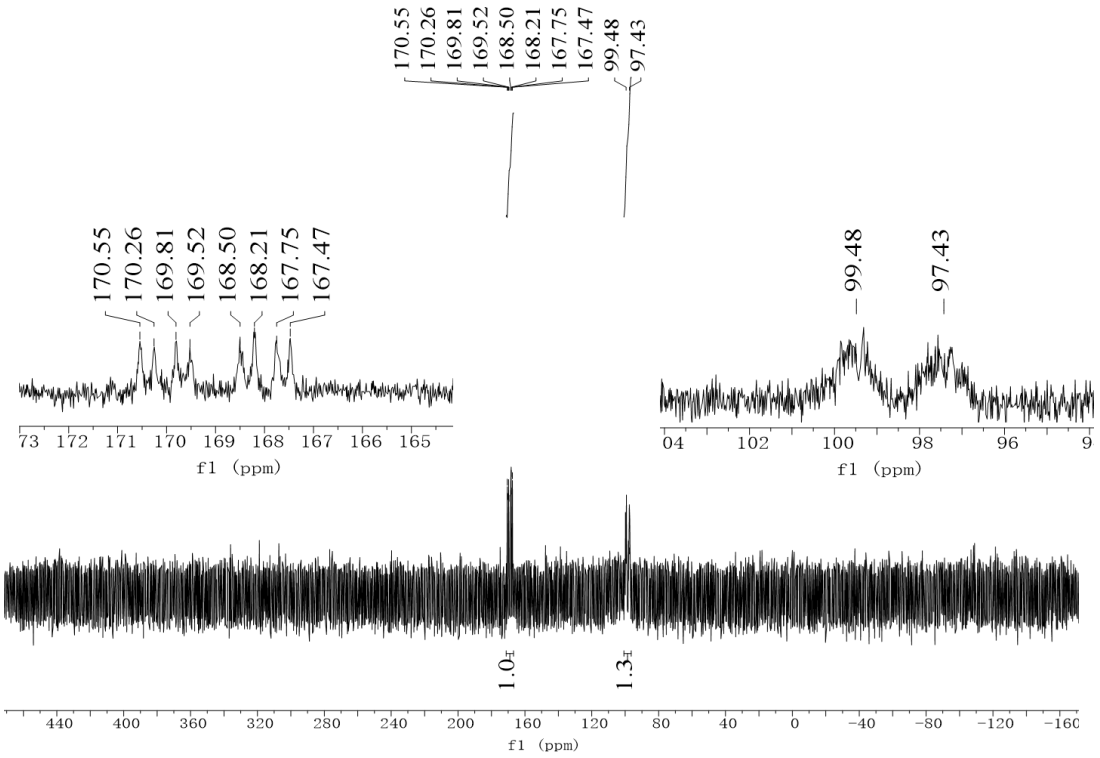


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of $[\mathbf{4}]^{2+}[(GaCl_4)^-]_2$ in CD_2Cl_2 at 297K.

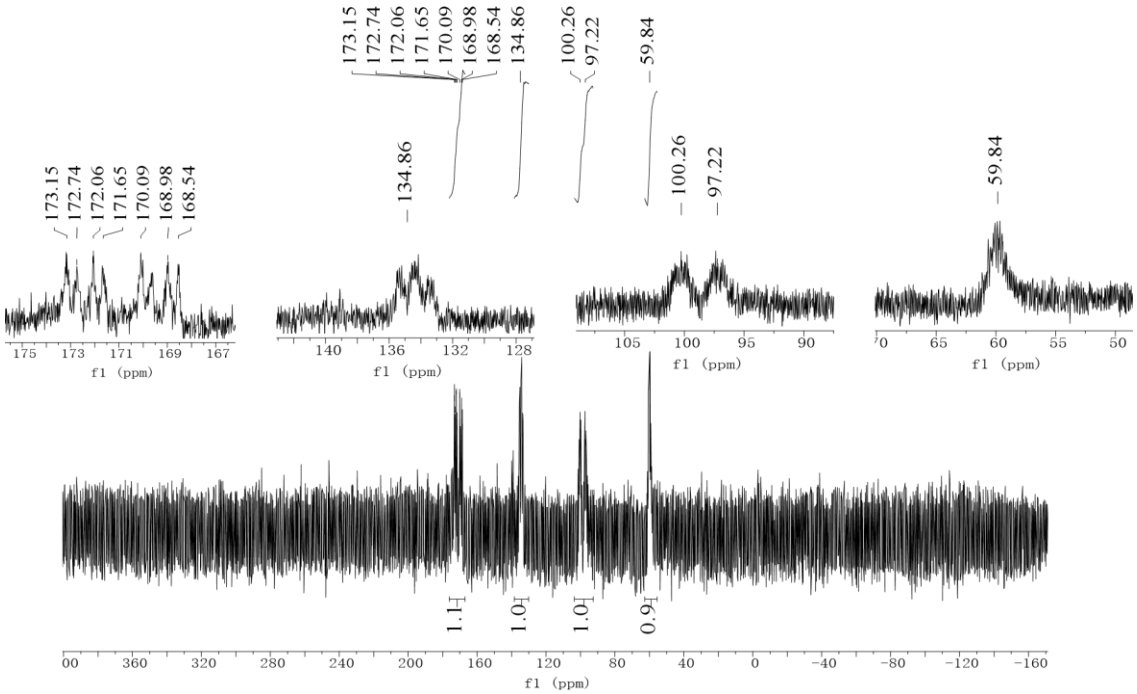


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of $[\mathbf{4}]^{2+}[(GaCl_4)^-]_2$ in CD_2Cl_2 at 203K.

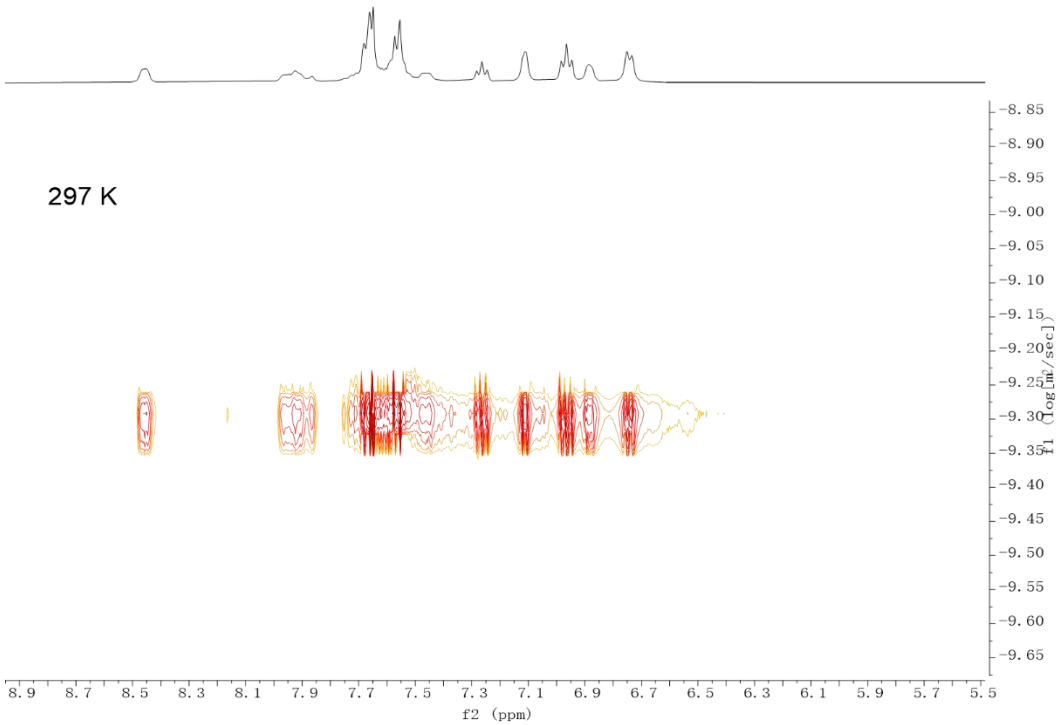


Figure S15. DOSY NMR spectrum of $[\mathbf{4}]^{2+}[(GaCl_4)^-]_2$ in CD_2Cl_2 at 297K.

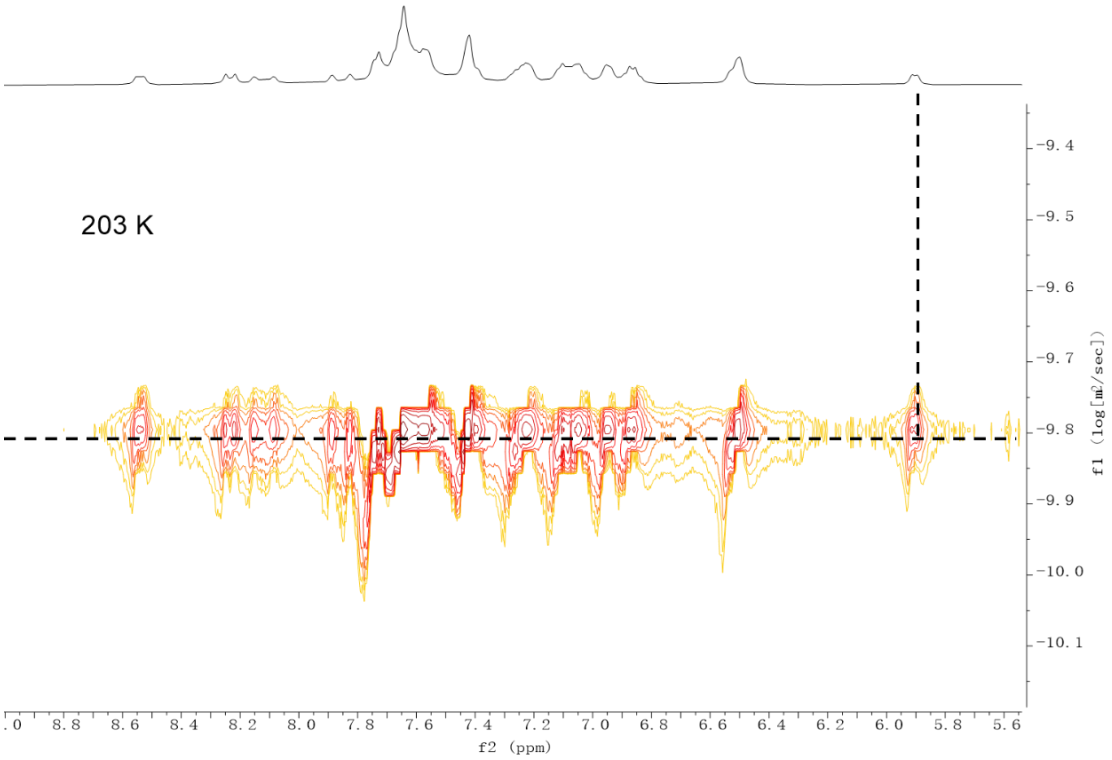


Figure S16. DOSY NMR spectrum of [**4**]$^{2+}$[$(GaCl_4)^-$]$_2$ in CD_2Cl_2 at 203 K (new peak at 5.9 ppm).

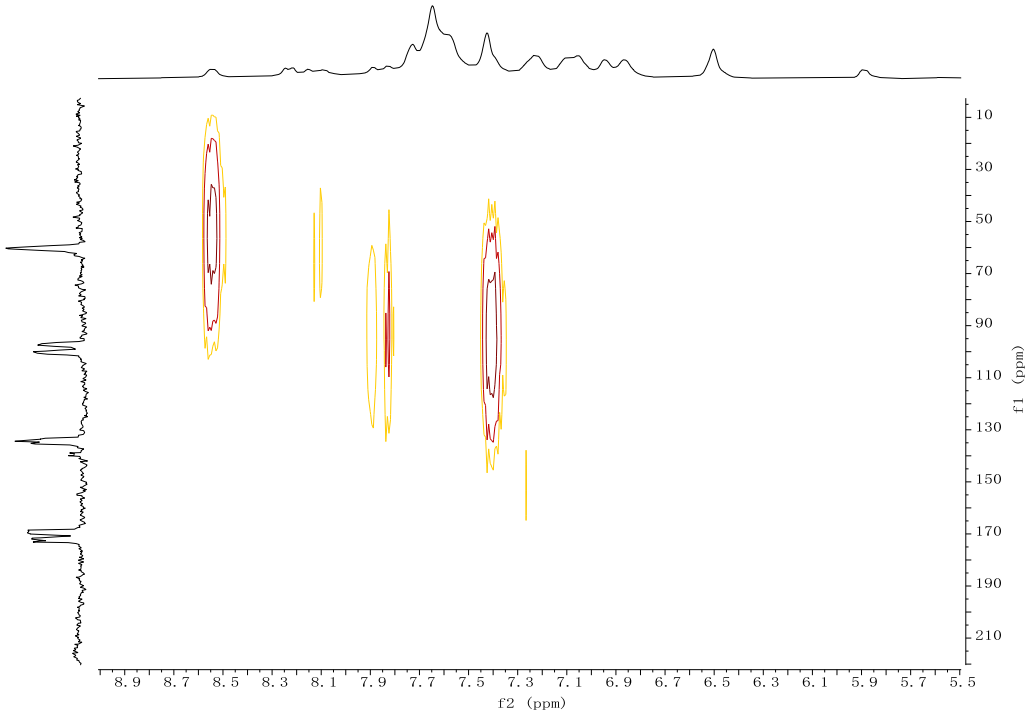


Figure S17. ^1H-^{31}P HMBC NMR spectrum of [**4**]$^{2+}$[$(GaCl_4)^-$]$_2$ in CD_2Cl_2 at 203 K.

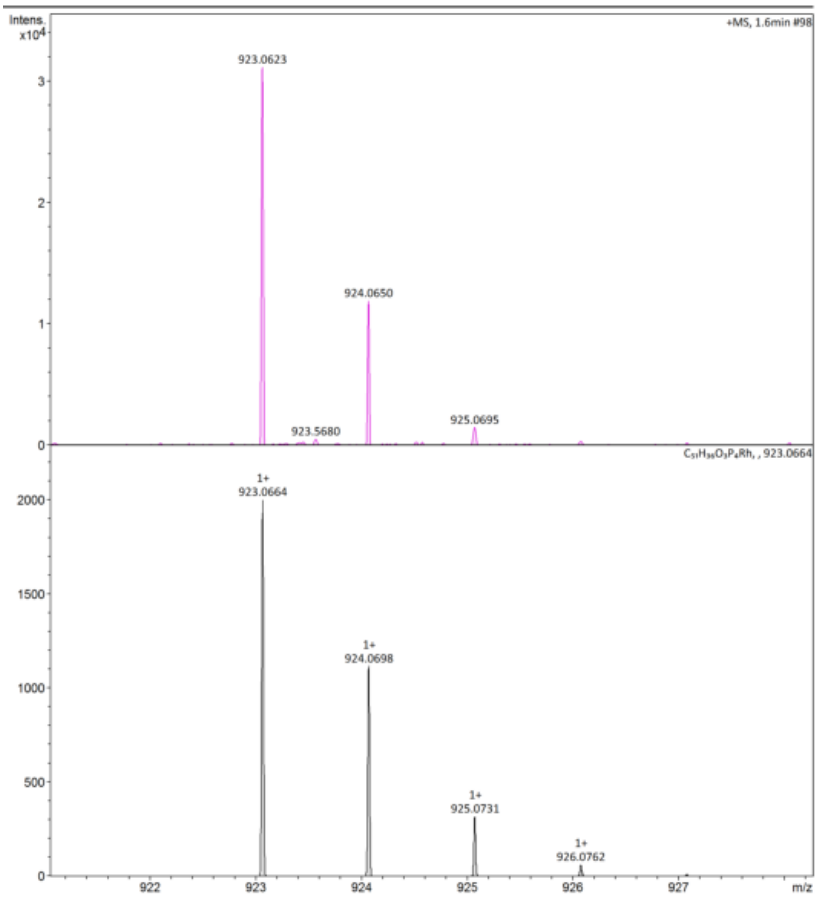


Figure S18. APCI-TOF-MS of $[\mathbf{4}]^{2+}[(GaCl_4)^-]_2$.

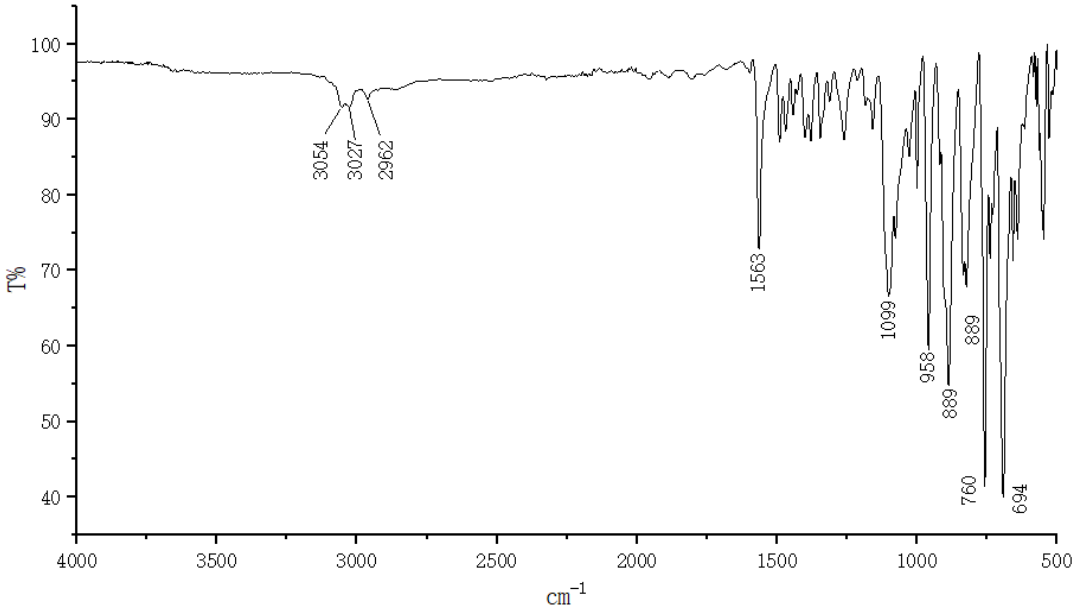
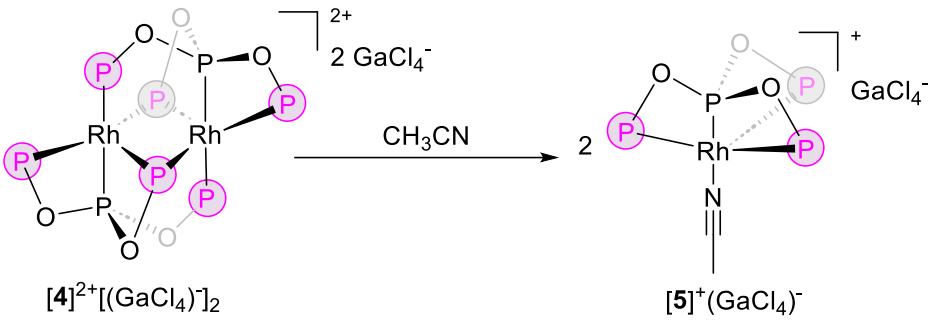


Figure S19. IR spectrum of $[\mathbf{4}]^{2+}[(GaCl_4)^-]_2$.

Preparation of $[5]^{+}(GaCl_4)^{-}$:



Acetonitrile (10 mL) was added to $[\mathbf{4}]^{2+}[(GaCl_4)^{-}]_2$ (220 mg, 0.10 mmol) at room temperature. After stirring for 1 hour, the solvent was removed under reduced pressure, then the remaining solid was washed with hexane and dried *in vacuo* to afford $[\mathbf{5}]^{+}(GaCl_4)^{-}$ as a red powder (181 mg, 0.154 mmol), 77 % yield. M. P. = 174 °C. ^{1}H NMR (CD_2Cl_2, 400.1 MHz): δ = 8.12 (m, 6 H, $C_{ar}H$), 7.7 (m, 12 H, $C_{ar}H$), 7.6 (m, 18 H, $C_{ar}H$), 1.92 (s, 3 H, ACN); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.5 MHz): δ = 172.5 (C_{ar}), 160.6 (t, J = 10.1 Hz, C_{ar}), 143.1 (m, C_{ar}), 140.2 (m, C_{ar}), 139.5 (dd, J = 11.9 Hz, J = 5.1 Hz, C_{ar}), 132.5 (dd, J = 10.6 Hz, J = 5.7 Hz, C_{ar}), 129.4 (m, C_{ar}), 129.3 (m, C_{ar}), 129.1 (m, C_{ar}), 128.8 (m, C_{ar}), 128.5 (dd, J = 7.5 Hz, J = 4.5 Hz, C_{ar}), 127.4 (m, C_{ar}), 120.9 (d, J = 20.1 Hz, C_{ar}), 4.64 (ACN); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz): δ = 212.4 (dq, $^{1}J_{RhP}$ = 155.4 Hz, $^{2}J_{PP}$ = 25.9 Hz, phosphite), 138.5 (dd, $^{1}J_{RhP}$ = 166.8 Hz, $^{2}J_{PP}$ = 25.9 Hz, phosphinine); IR (ATR, [cm^{-1}]): 3054, 3024, 1565, 1493, 1394, 1345, 1260, 1077, 953, 885, 833, 760, 691; UV/Vis (THF, λ (nm) ε ($M^{-1}cm^{-1}$)): 361 (32900), 409 (49800), 467 (25450); ESI-TOF-MS: calc. for $C_{53}H_{39}O_3P_4NRh^{+}$: 964.0930 ($[M]^{+}$), found: 964.0906.

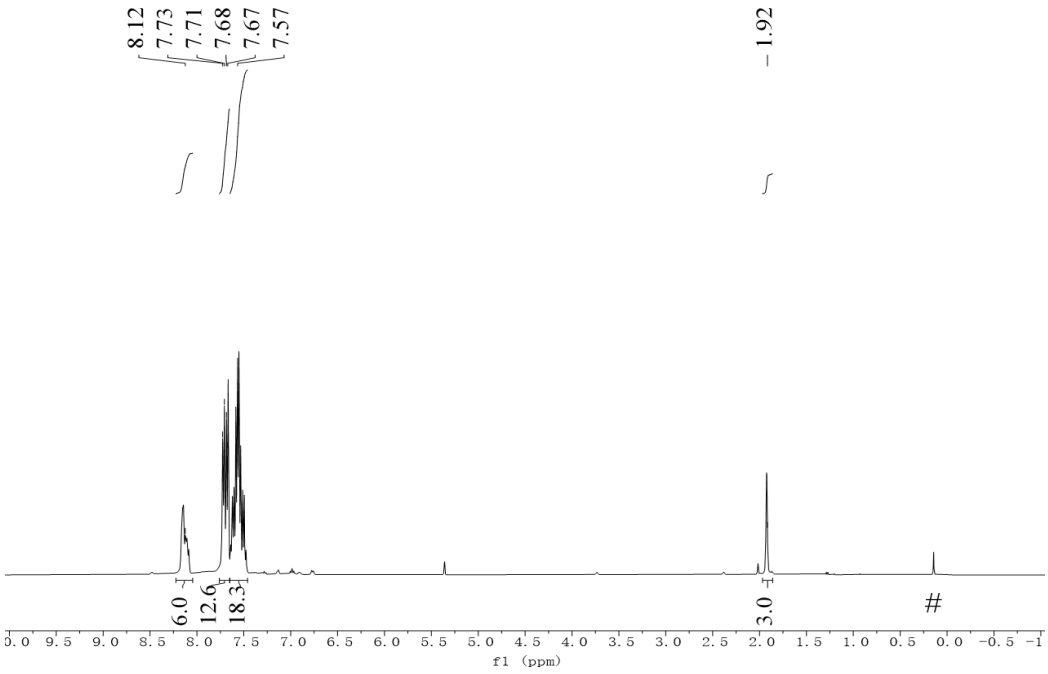


Figure S20. ^{1}H NMR spectrum of $[\mathbf{5}]^{+}(GaCl_4)^{-}$ in CD_2Cl_2. $^{\#}$ silicone grease.

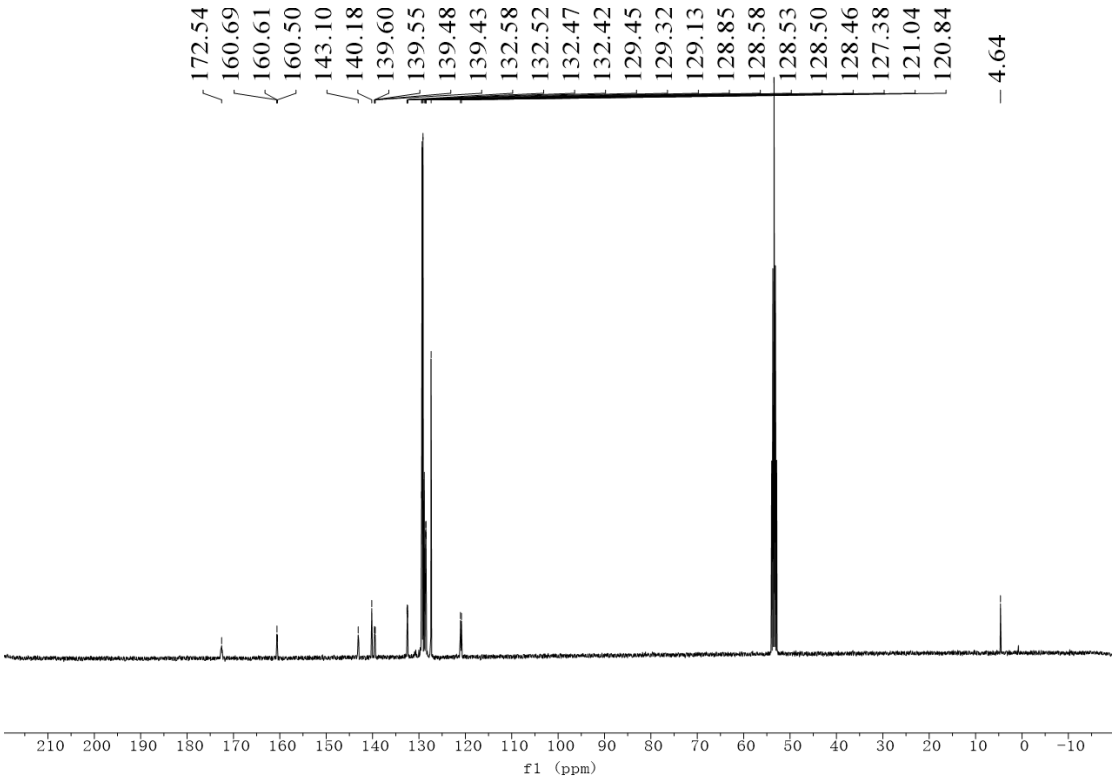


Figure S21. ^{13}C NMR spectrum of $[\mathbf{5}]^{+}(GaCl_4)^{-}$ in CD_2Cl_2.

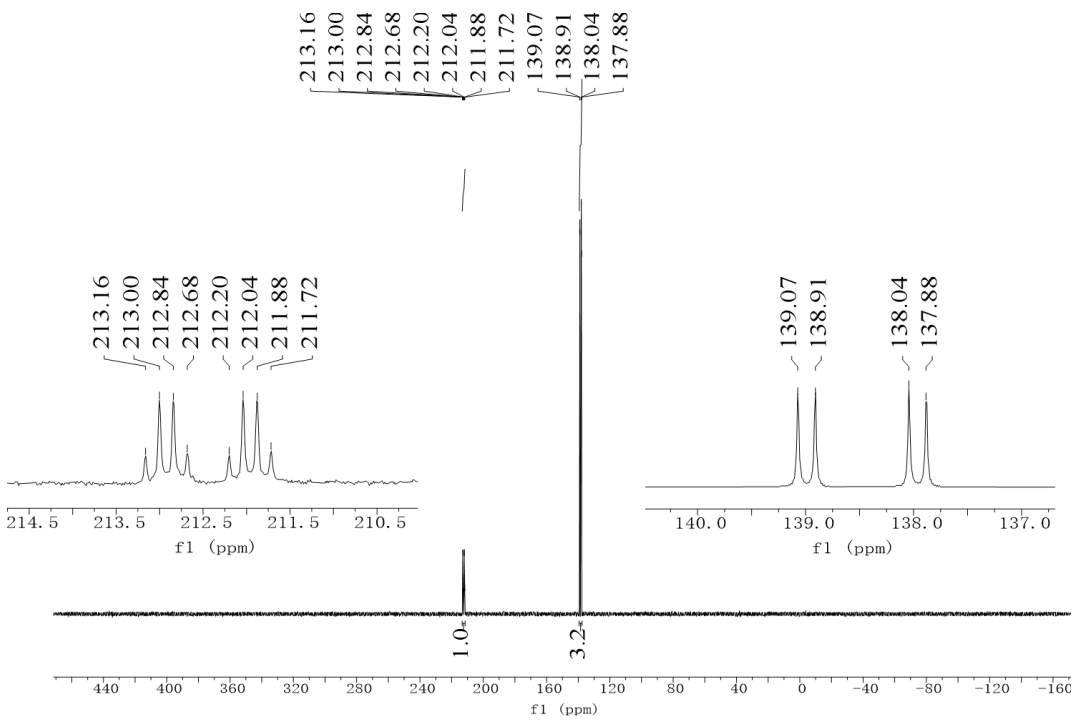


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of $[\mathbf{5}]^{+}(GaCl_4)^{-}$ in CD_2Cl_2.

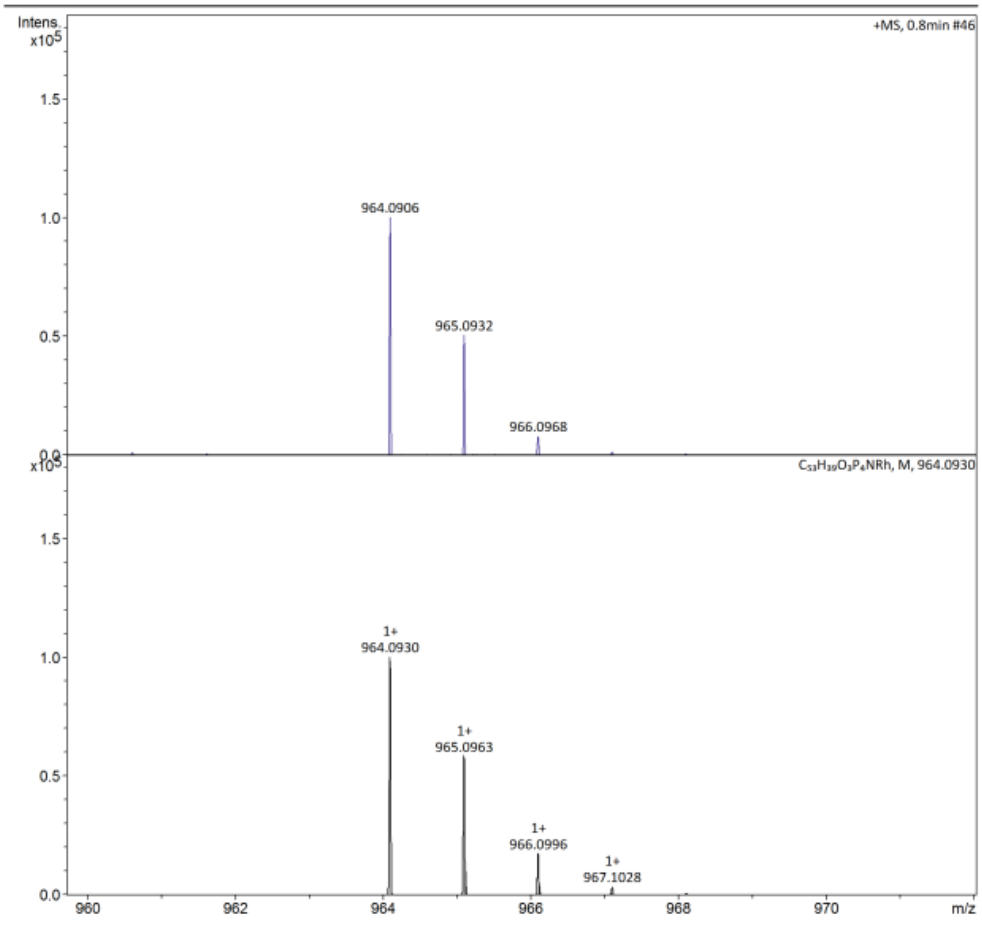


Figure S23. ESI-TOF-MS of $[\mathbf{5}]^{+}(GaCl_4)^{-}$.

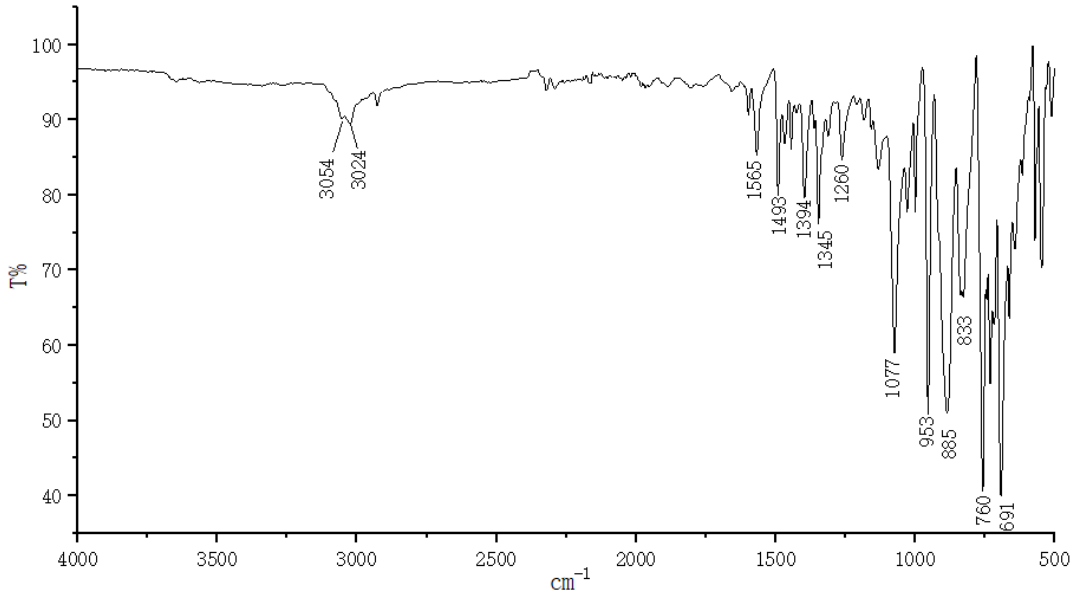
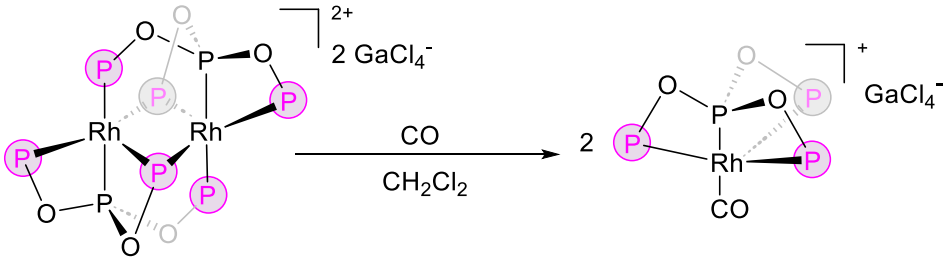


Figure S24. IR spectrum of $[\mathbf{5}]^{+}(GaCl_4)^{-}$.

Preparation of $[\mathbf{6}]^{+}(GaCl_4)^{-}$:



$[\mathbf{4}]^{2+}[(GaCl_4)^{-}]_2$ $[\mathbf{6}]^{+}(GaCl_4)^{-}$

In a Schlenk tube, the solution of $[\mathbf{4}]^{2+}[(GaCl_4)^{-}]_2$ (227 mg, 0.10 mmol) in dichloromethane (5 mL) was first frozen by liquid nitrogen, then the dinitrogen was pumped off under reduced pressure and replaced with CO gas. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the remaining residue was washed with hexane and dried *in vacuo* to afford $[\mathbf{6}]^{+}(GaCl_4)^{-}$ as a red powder (198 mg, 0.17 mmol), 83 % yield. M. P. = 183 °C. ^{1}H NMR (CD_2Cl_2, 400.1 MHz): δ = 8.31 (m, 3 H, $C_{ar}H$), 8.23 (m, 3 H, $C_{ar}H$), 7.62 (m, 30 H, $C_{ar}H$); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.5 MHz): 192.1 (s, CO) 172.9 (m, C_{ar}), 160.8 (m, C_{ar}), 144.5 (m, C_{ar}), 139.7 (m, C_{ar}), 138.4 (dd, J = 11.1 Hz, J = 5.0 Hz, C_{ar}), 133.0 (m, C_{ar}), 129.9 (m, C_{ar}), 129.6 (m, C_{ar}), 129.4 (m, C_{ar}), 129.3 (m, C_{ar}), 128.3 (dd, J = 8.1 Hz, J = 4.6 Hz, C_{ar}), 127.5 (m, C_{ar}), 121.8 (m, C_{ar}); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz) δ = 225.3 (dq, $^{1}J_{RhP}$ = 122.2 Hz, $^{2}J_{PP}$ = 34.0 Hz, phosphite),

139.0 (dd, $^{1}J_{RhP}$ = 161.9 Hz, $^{2}J_{PP}$ = 34.0 Hz, phosphinine); IR (ATR, [cm^{-1}]): 3054, 3024, 2096 (CO), 1563, 1491, 1397, 1346, 1077, 956, 898, 758, 697, 546; UV/Vis (THF, λ (nm) ε ($M^{-1}cm^{-1}$)): 405 (48960); APCI-TOF-MS: calc. for $C_{52}H_{36}O_4P_4Rh^+$: 951.0614 ($[M]^+$), found: 951.0644.

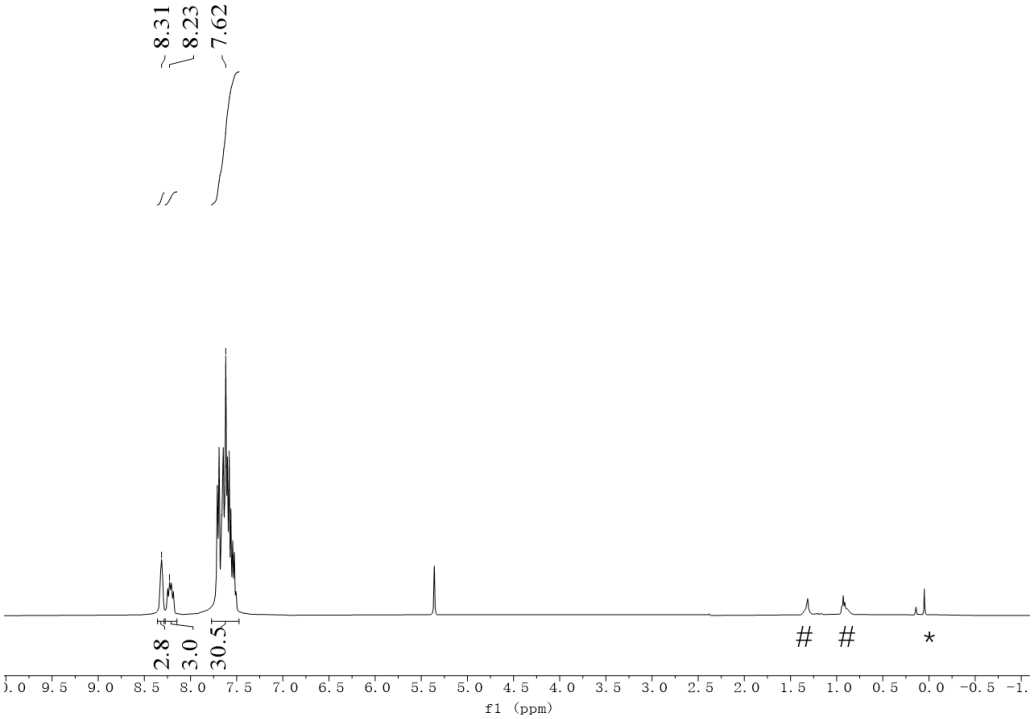


Figure S25. ^{1}H NMR spectrum of $[\mathbf{6}]^+(GaCl_4)^-$ in CD_2Cl_2. $^{\#}$Hexane, *Silicon grease.

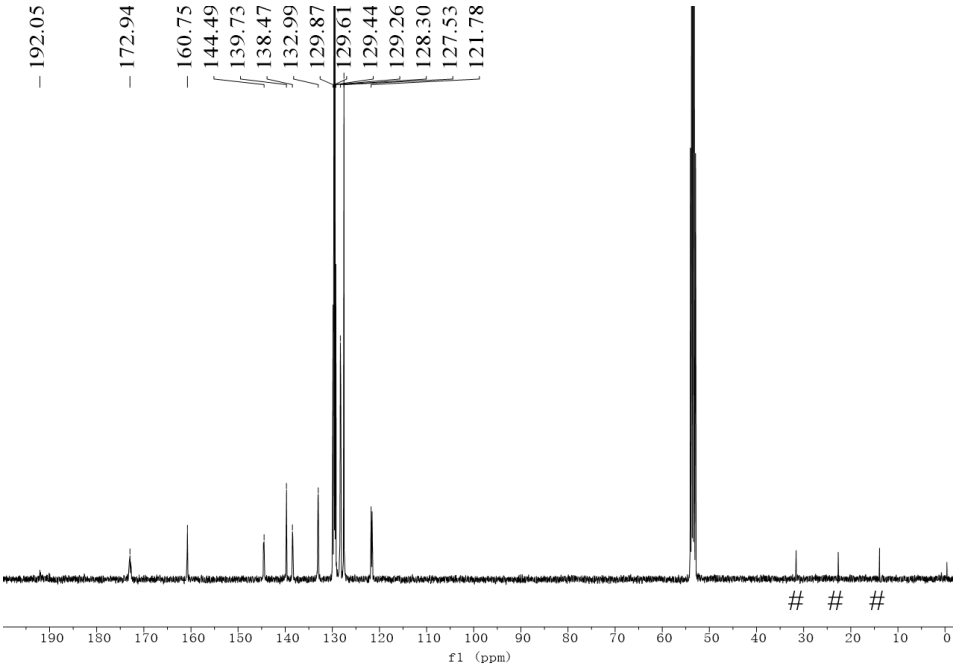


Figure S26. ^{13}C NMR spectrum of $[\mathbf{6}]^+(GaCl_4)^-$ in CD_2Cl_2.$^{\#}$Hexane.

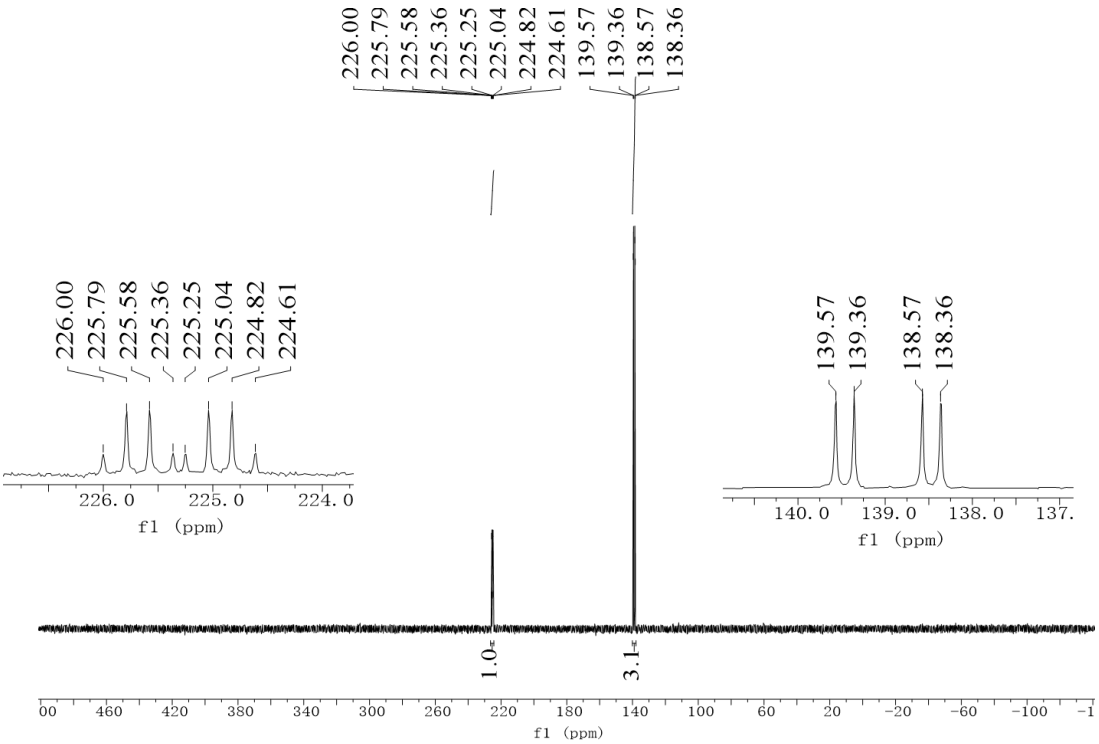


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of $[\mathbf{6}]^{+}(GaCl_4)^{-}$ in CD_2Cl_2.

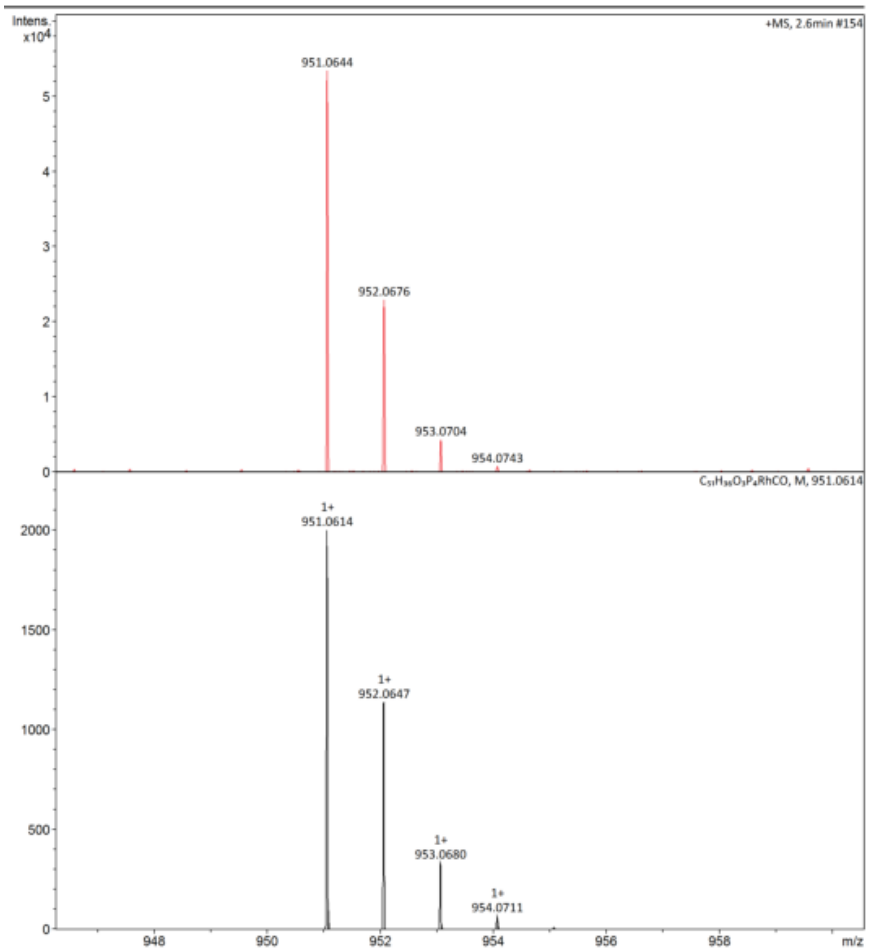


Figure S28. APCI-TOF-MS of $[\mathbf{6}]^{+}(GaCl_4)^{-}$.

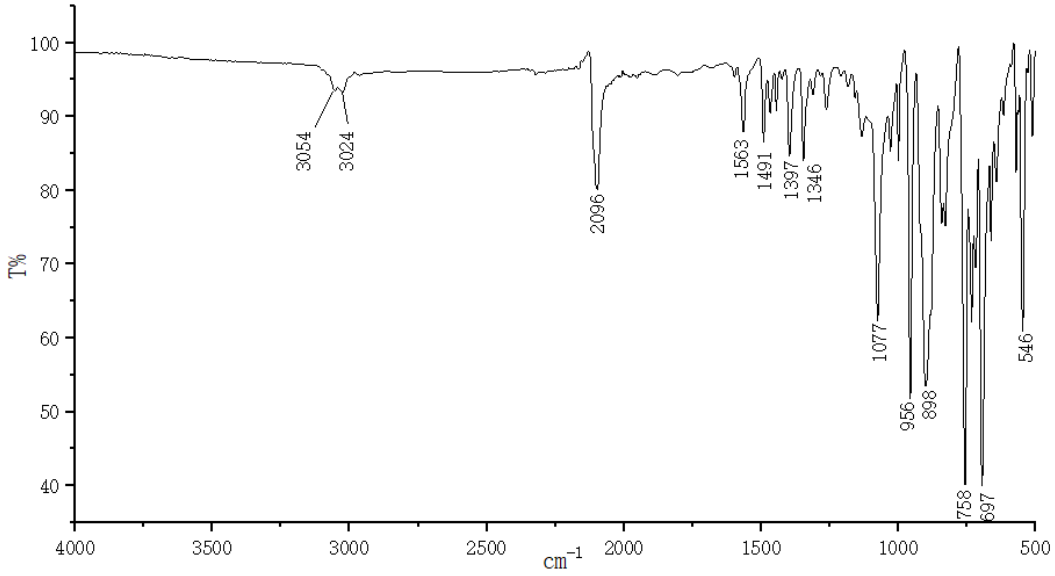
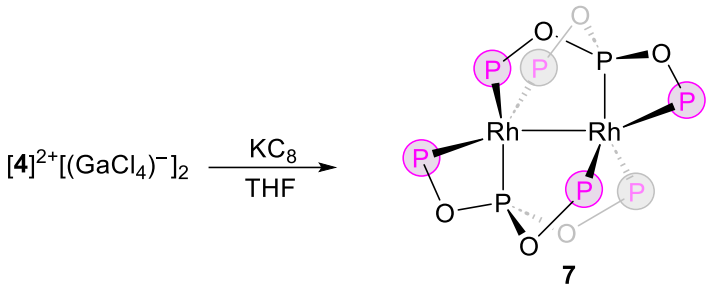


Figure S29. IR spectrum of $[\mathbf{6}]^{+}(GaCl_4)^{-}$.

Preparation of 7:



KC_8 (12 mg, 0.088 mmol) was added to a stirred solution of $[\mathbf{4}]^{2+}[(GaCl_4)^{-}]_2$ (90 mg, 0.039 mmol) in THF (10 mL) at room temperature. After stirring for 2 hours, all the precipitates were filtered off, and the solvent was removed under reduced pressure. The remaining residue was extracted with toluene, washed with hexane and dried *in vacuo* to afford **7** as a red-brown powder (60 mg, 0.032 mmol), 82 % yield. M. P. = 158 °C. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz, 213 K): δ = 224.9 (m, phosphite), δ = 166.2 (m, phosphinine), δ = 160.5 (m, phosphinine); IR (ATR, [cm^{-1}]): 3019, 1599, 1499, 1342, 1264, 1126, 957, 878, 957, 693; UV/Vis (THF, λ (nm) ε (mol^{-1} L cm^{-1})): 397 (81020); ESI-TOF-MS: calc. for $C_{102}H_{72}O_6P_8Rh_2^{+}$: 1846.1334 ($[M]^{+}$), found: 1846.1280.

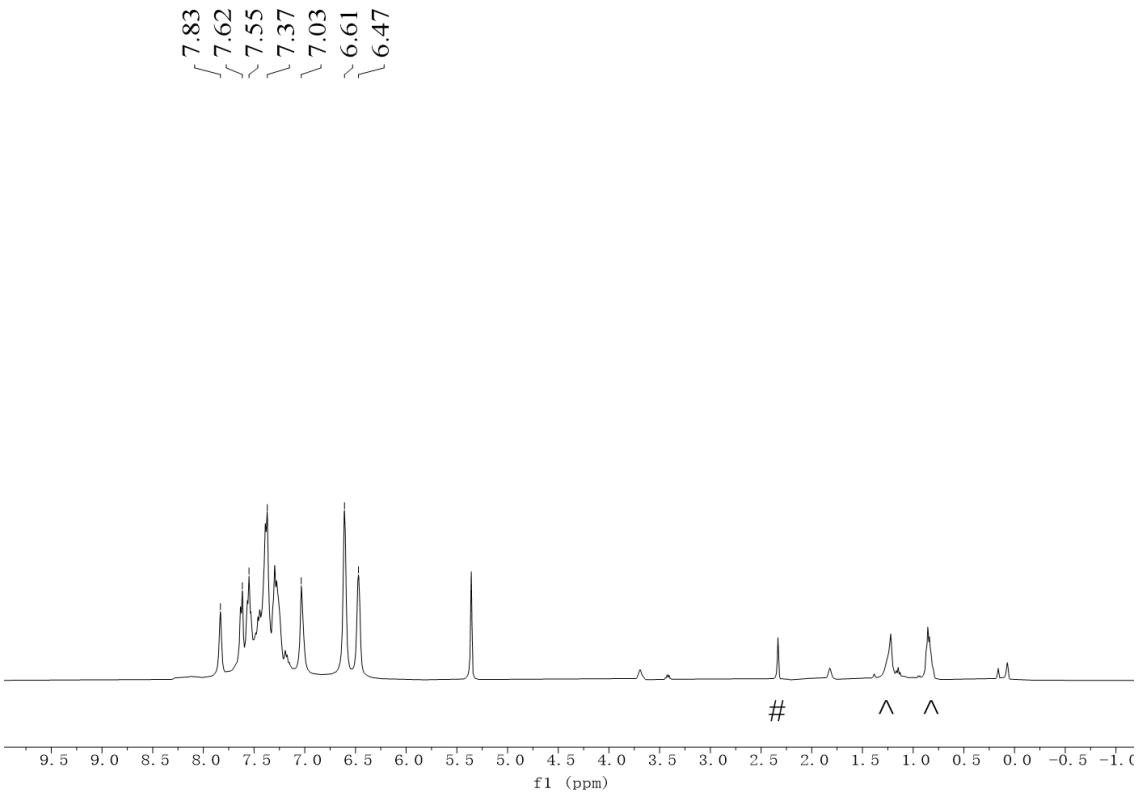


Figure S30. ^{1}H NMR spectrum of **7** in CD_2Cl_2 at 213 K. ^Hexane. #Toluene.

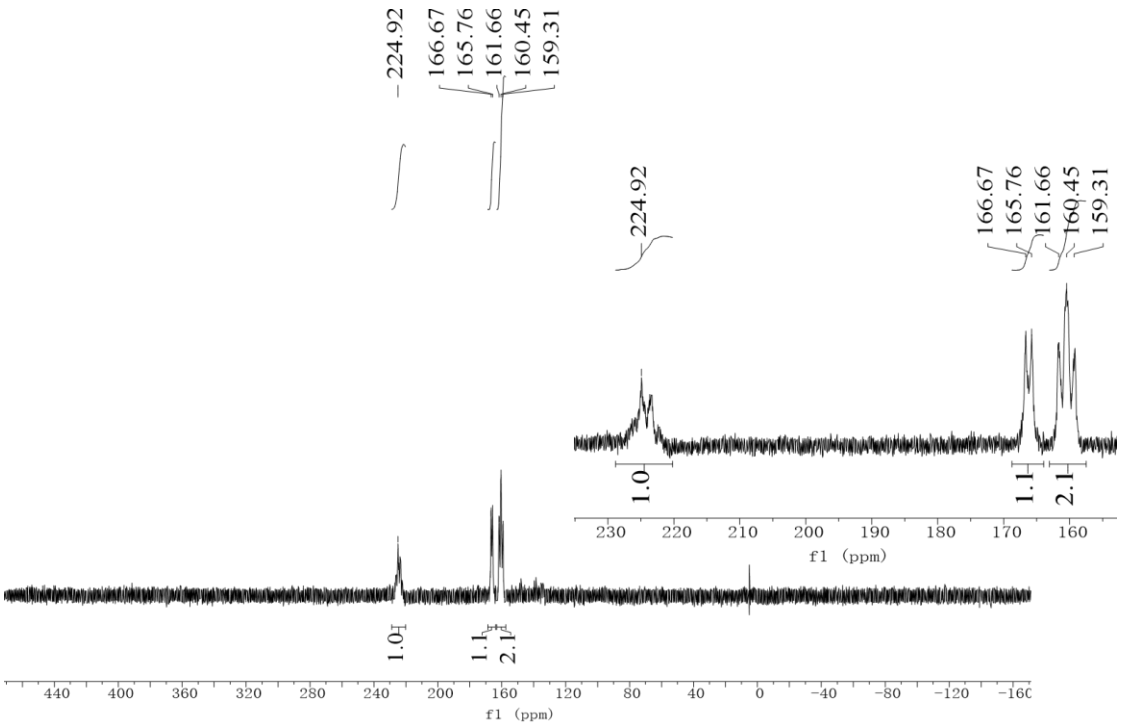


Figure S31. ^{31}P{^{1}H} NMR spectrum of **7** in CD_2Cl_2 at 213 K.

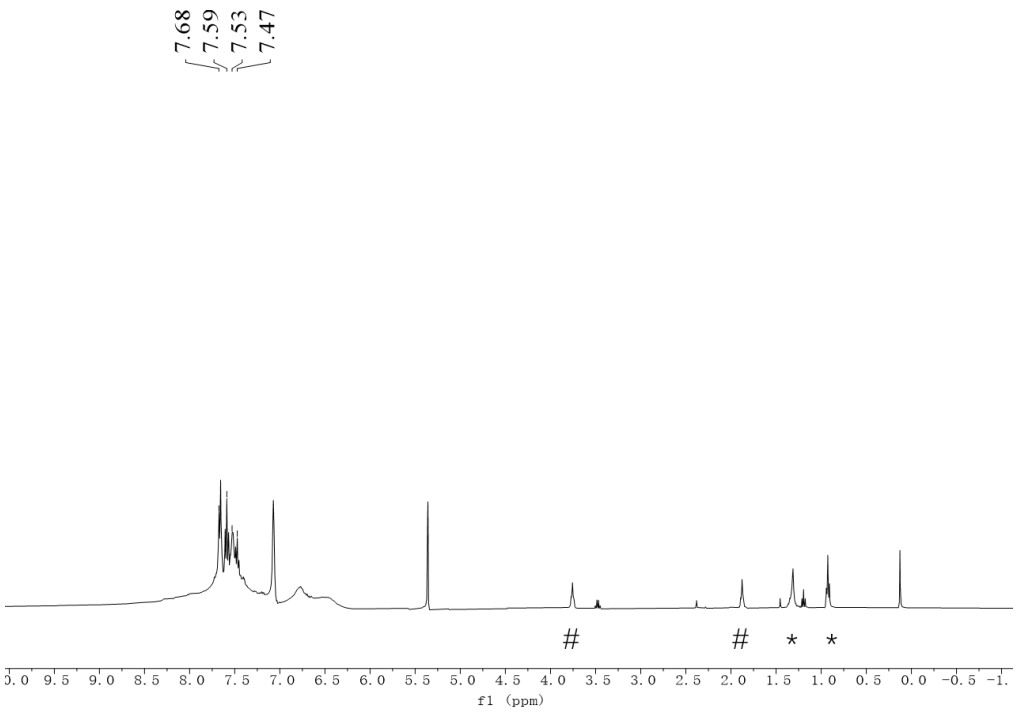


Figure S32. ^{1}H NMR spectrum of **7** in CD_2Cl_2 at 297 K. $^{\#}$THF. *Hexane.

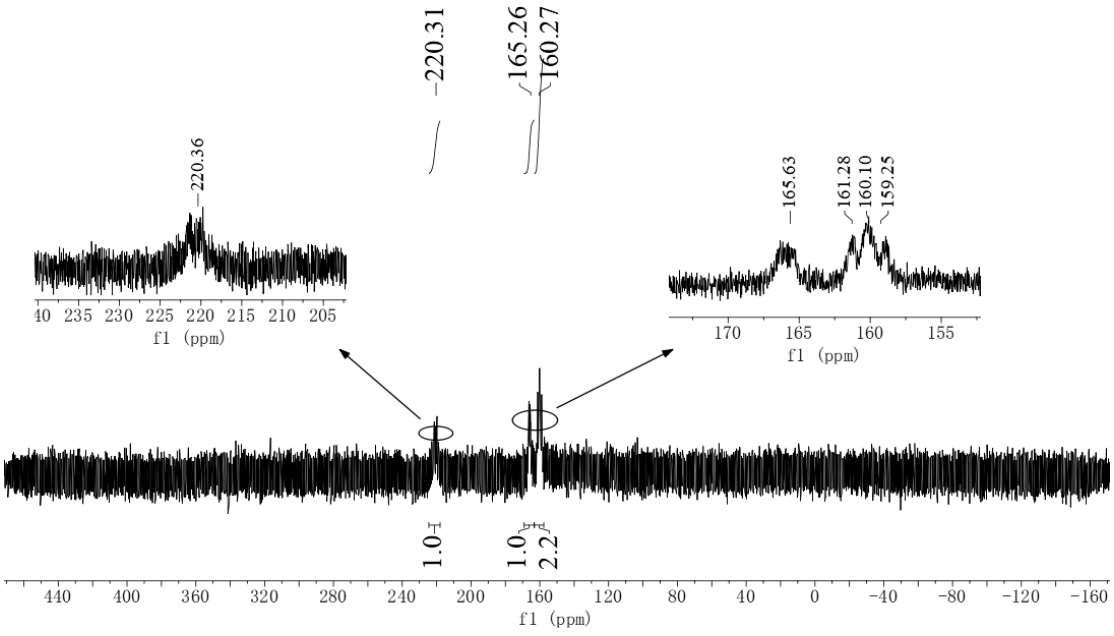


Figure S33. ^{31}P{^{1}H} NMR spectrum of **7** in CD_2Cl_2 at 297 K.

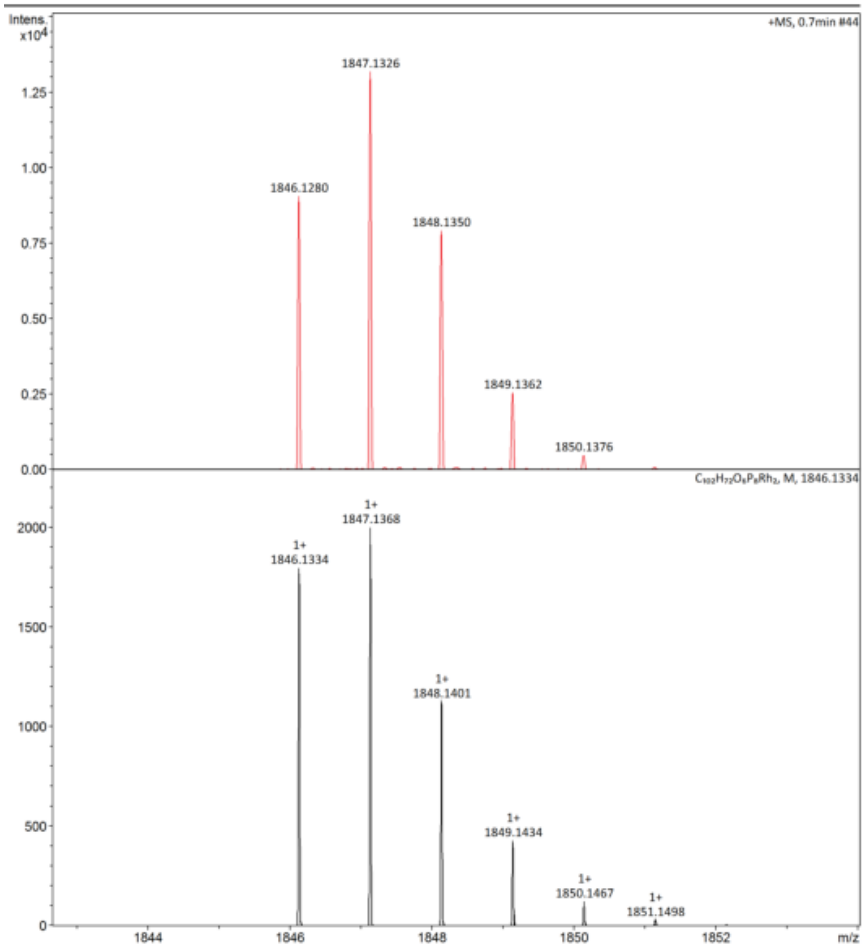


Figure S34. ESI-TOF-MS of **7**.

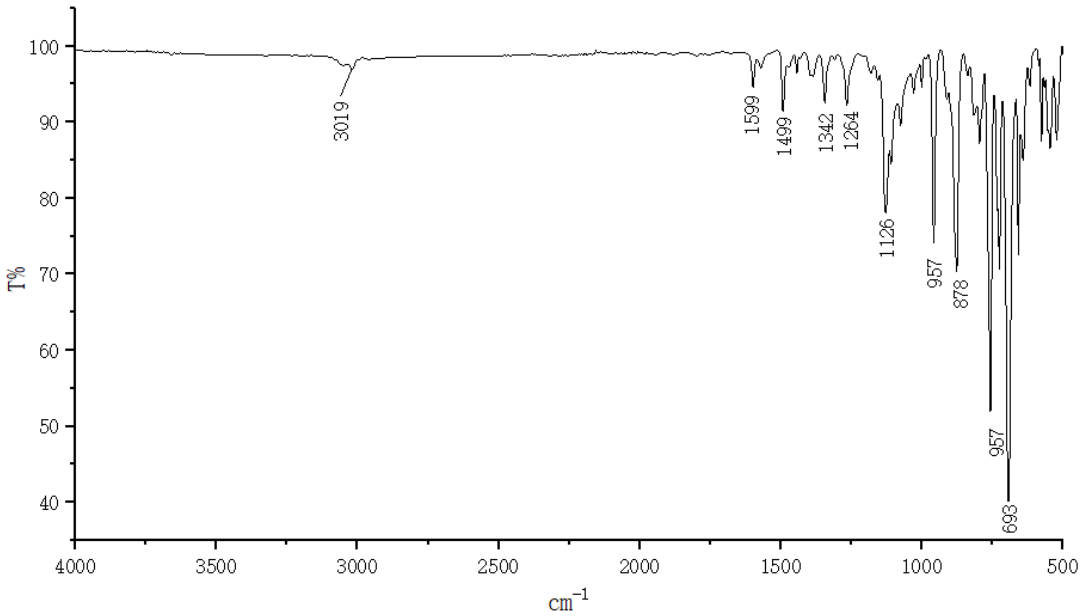
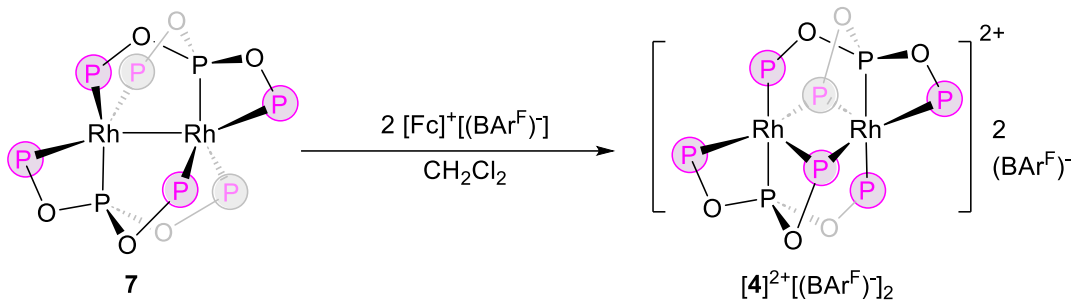


Figure S35. IR spectrum of **7**.

Preparation of $[\mathbf{4}]^{2+}[(BAr^F)^-]_2$:



$[Fc]^+[BAr^F]^-$(90 mg, 0.086 mmol) in dichloromethane (3 mL) was added to a stirred solution of **7** (80 mg, 0.043 mmol) in dichloromethane (10 mL) at room temperature. After stirring for 2 hours, the solvent was removed under reduced pressure. The remaining solid was successively washed with toluene and hexane, then dried *in vacuo* to afford $[\mathbf{4}]^{2+}[(BAr^F)^-]_2$ as a green-black powder (126 mg, 0.035 mmol), 82 % yield. M. P. > 250 °C. $^{31}P\{^1H\}$NMR (CD_2Cl_2, 161.9 MHz): δ = 169.2 (m, phosphite), 97.8 (m, η_1-P); IR (ATR, [cm^{-1}]): 3066, 1567, 1354, 1275, 1110, 960, 882, 837, 770, 709, 695, 682; UV/Vis (THF, λ (nm) ε (mol^{-1} L cm^{-1})): 345 (84120), 483 (27020), 607 (51790), 662 (38640); APCI-TOF-MS: calc. for $C_{51}H_{36}O_3P_4Rh^+$: 923.0664 ($[M]^+$), found: 923.0629.

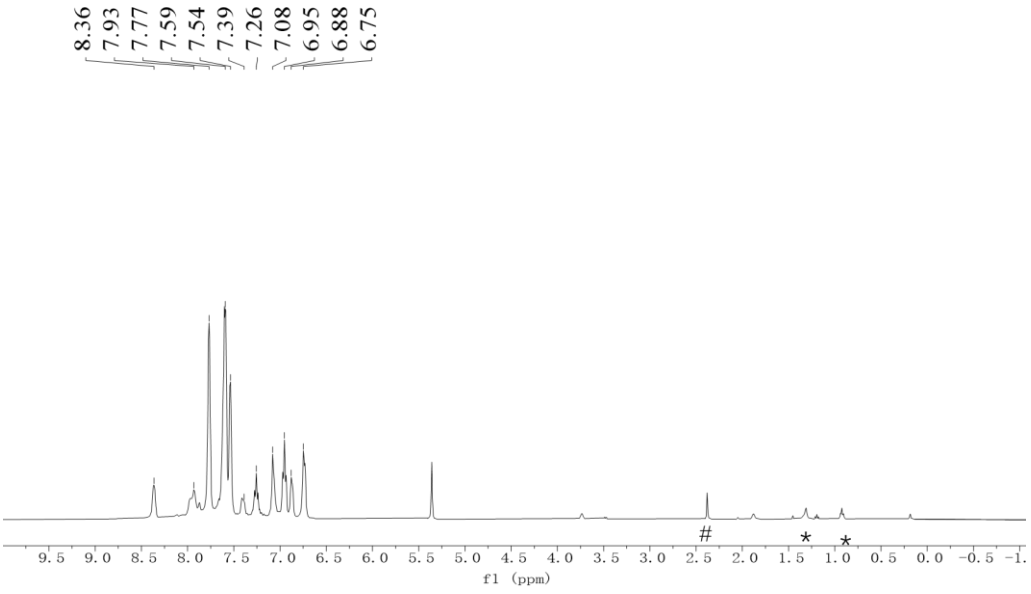


Figure S36. ^1H NMR spectrum of $[\mathbf{4}]^{2+}[(BAr^F)^-]_2$ in CD_2Cl_2 at 297 K #Toluene,*Hexane.

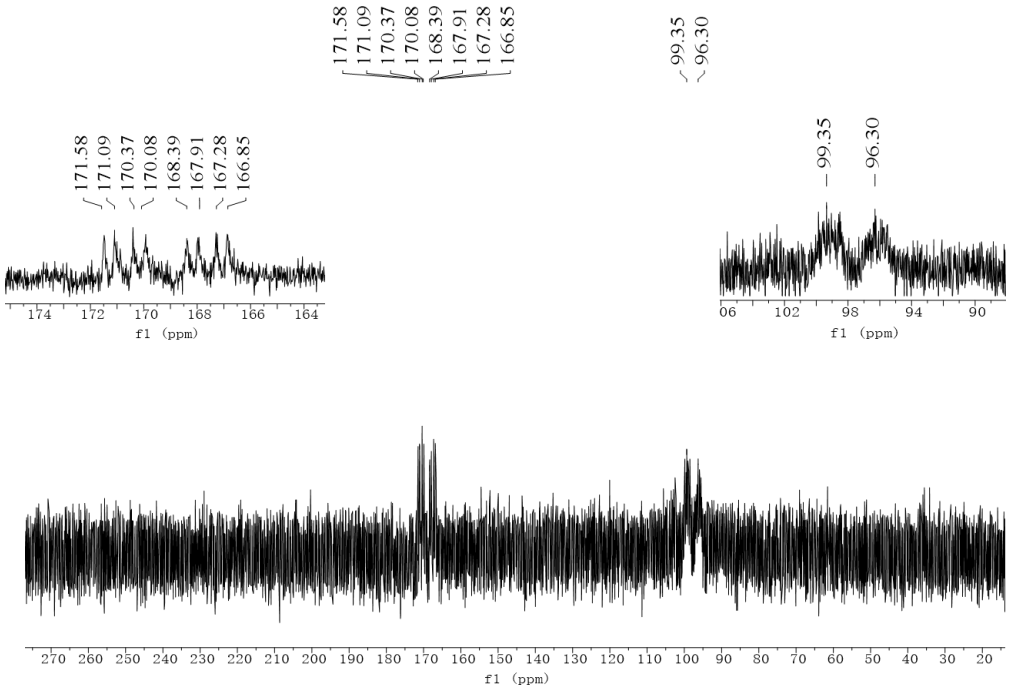


Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum of $[\mathbf{4}]^{2+}[(BAr^{F})^{-}]_2$ in CD_2Cl_2 at 297 K.

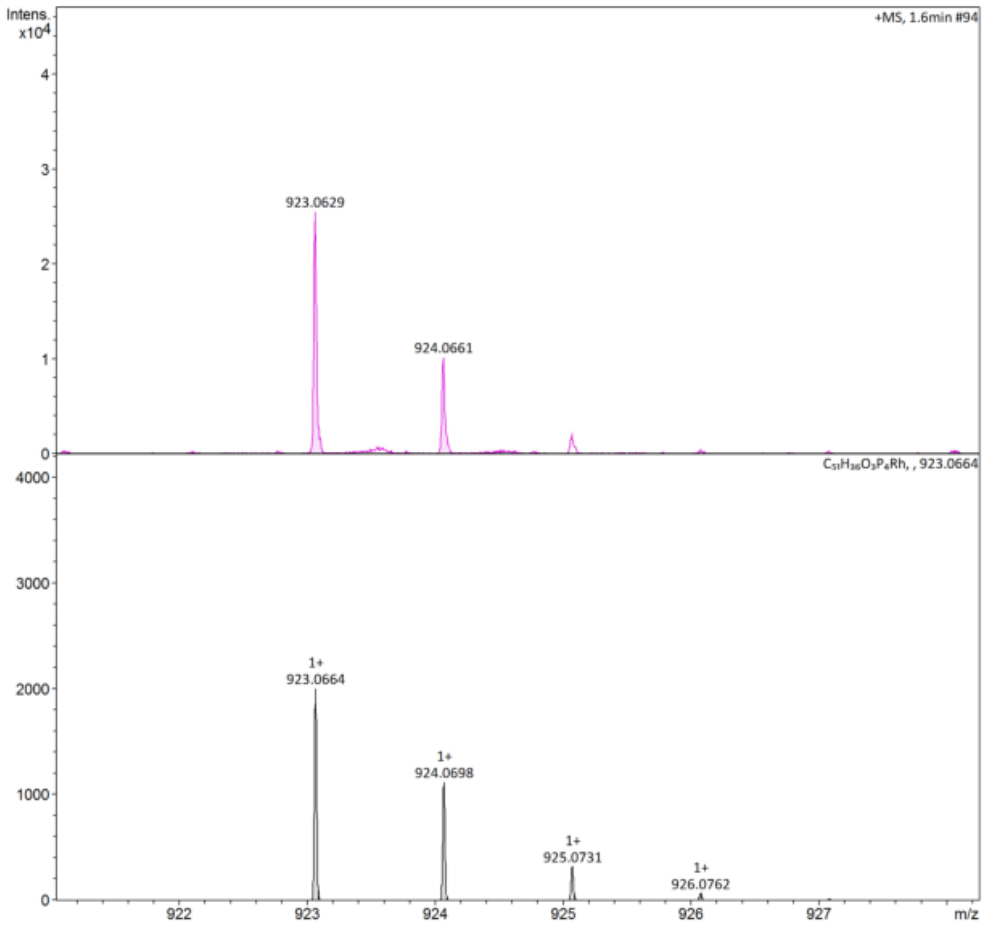


Figure S38. APCI-TOF-MS of $[\mathbf{4}]^{2+}[(BAr^{F})^{-}]_2$.

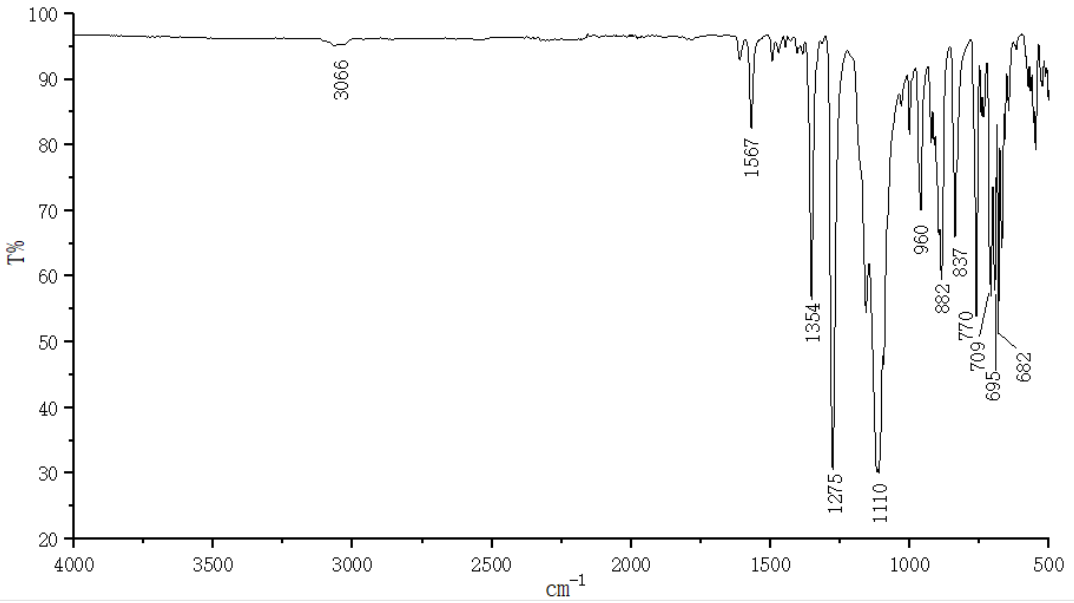


Figure S39. IR spectrum of $[\mathbf{4}]^{2+}[(BAr^F)^-]_2$.

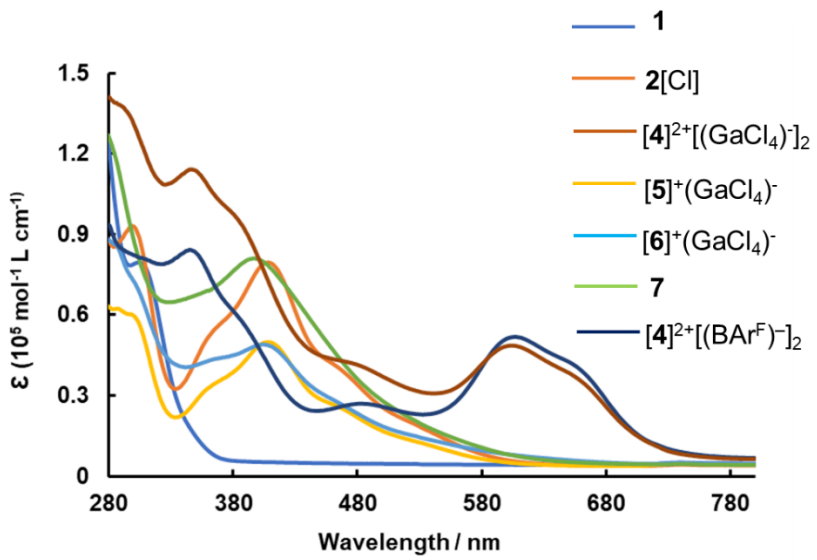


Figure S40. UV/Vis absorption spectra for 10^{-5} M THF solution, while complex $[\mathbf{4}^{2+}][(GaCl_4)^-]_2$ and $[\mathbf{4}^{2+}][(BAr^F)^-]_2$ in dichloromethane.

S2: X-Ray Diffraction Studies

These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, or by emailing data_request@ccdc.cam.ac.uk. The CCDC reference numbers for this paper are CCDC 2302402-2302405.

Table S1. Crystal data and structure refinement

Compounds	**[2]Cl**	**$[6]^{+}[BAr^{F}]^{-}$**
Empirical formula	$C_{102}H_{73}Cl_2O_6P_8Rh_2$	$C_{84}H_{48}BF_{24}O_4P_4Rh$
Formula weight	1919.08	1814.82
Temperature/K	150.00(10)	150.00(10)
Crystal system	tetragonal	triclinic
Space group	$P4_1$	P-1
a/Å	19.27277(12)	12.6282(8)
b/Å	19.27277(12)	15.4080(9)
c/Å	49.9982(6)	21.6077(12)
α/°	90	77.086(5)
β/°	90	73.804(5)
γ/°	90	84.818(5)
Volume/$Å^3$	18571.3(3)	3933.6(4)
Z	8	2
$\rho_{calc}g/cm^3$	1.373	1.532
μ/mm^{-1}	5.133	0.407
F(000)	7816.0	1820.0
Crystal size/mm^3	0.16 × 0.14 × 0.12	0.5 × 0.5 × 0.4
Radiation	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.914 to 148.82	5.428 to 60.314
Index ranges	-19 ≤ h ≤ 24, -19 ≤ k ≤ 23, -62 ≤ l ≤ 61	-17 ≤ h ≤ 15, -21 ≤ k ≤ 20, -29 ≤ l ≤ 30
Reflections collected	193095	59159
Independent reflections	37011 [R_{int} = 0.0663, R_{sigma} = 0.0501]	19422 [R_{int} = 0.0567, R_{sigma} = 0.0619]
Data/restraints/parameters	37011/5474/1991	19422/24/1090
Goodness-of-fit on F^2	1.122	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0812, wR_2 = 0.2162	R_1 = 0.0456, wR_2 = 0.1057
Final R indexes [all data]	R_1 = 0.1049, wR_2 = 0.2287	R_1 = 0.0699, wR_2 = 0.1180
Largest diff. peak/hole / e $Å^{-3}$	1.83/-1.45	0.99/-0.71
Flack parameter	0.501(17)	

to be continued.

Compounds	**$[4]^{2+}[(GaCl_4)^{-}]_2$**	**7**
Empirical formula	$C_{104}H_{76}Cl_{12}Ga_2O_6P_8Rh_2$	$C_{126}H_{120}O_{12}P_8Rh_2$
Formula weight	2440.06	2279.79
Temperature/K	150.00(10)	149.99(10)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
a/Å	15.28780(10)	15.87110(10)
b/Å	16.0822(2)	33.0914(3)

c/Å	22.0950(2)	21.7367(2)
α/°	98.6030(10)	90
β/°	106.9000(10)	109.9920(10)
γ/°	92.9220(10)	90
Volume/Å^3	5113.54(9)	10728.12(17)
Z	2	4
ρ_{calc}g/cm^3	1.585	1.412
μ/mm^{-1}	7.671	4.127
F(000)	2448.0	4728.0
Crystal size/mm^3	0.17 × 0.16 × 0.14	0.12 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.586 to 132.02	5.084 to 148.296
Index ranges	-11 ≤ h ≤ 18, -18 ≤ k ≤ 19, -26 ≤ l ≤ 26	-19 ≤ h ≤ 19, -27 ≤ k ≤ 40, -27 ≤ l ≤ 25
Reflections collected	59935	66736
Independent reflections	17731 [R_{int} = 0.0263, R_{sigma} = 0.0265]	21196 [R_{int} = 0.0425, R_{sigma} = 0.0440]
Data/restraints/parameters	17731/128/1210	21196/116/1360
Goodness-of-fit on F^2	1.037	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1170	R_1 = 0.0632, wR_2 = 0.1610
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.1184	R_1 = 0.0743, wR_2 = 0.1674
Largest diff. peak/hole / e Å^{-3}	2.94/-1.59	2.25/-1.62

S3: DFT calculations

All calculations were carried out using the Gaussian 16 quantum mechanical package.[2] Geometry optimizations were carried out using density functional theory (DFT) at the B3LYP-D3(BJ)/def2-SVP level of theory. At each of the optimized structures, vibrational analysis was performed to ensure that the geometry corresponds to an energy minimum. NBO calculations at the B3LYP-D3(BJ)/def2-SVP level of theory were carried out using NBO 7.0 program.[3]

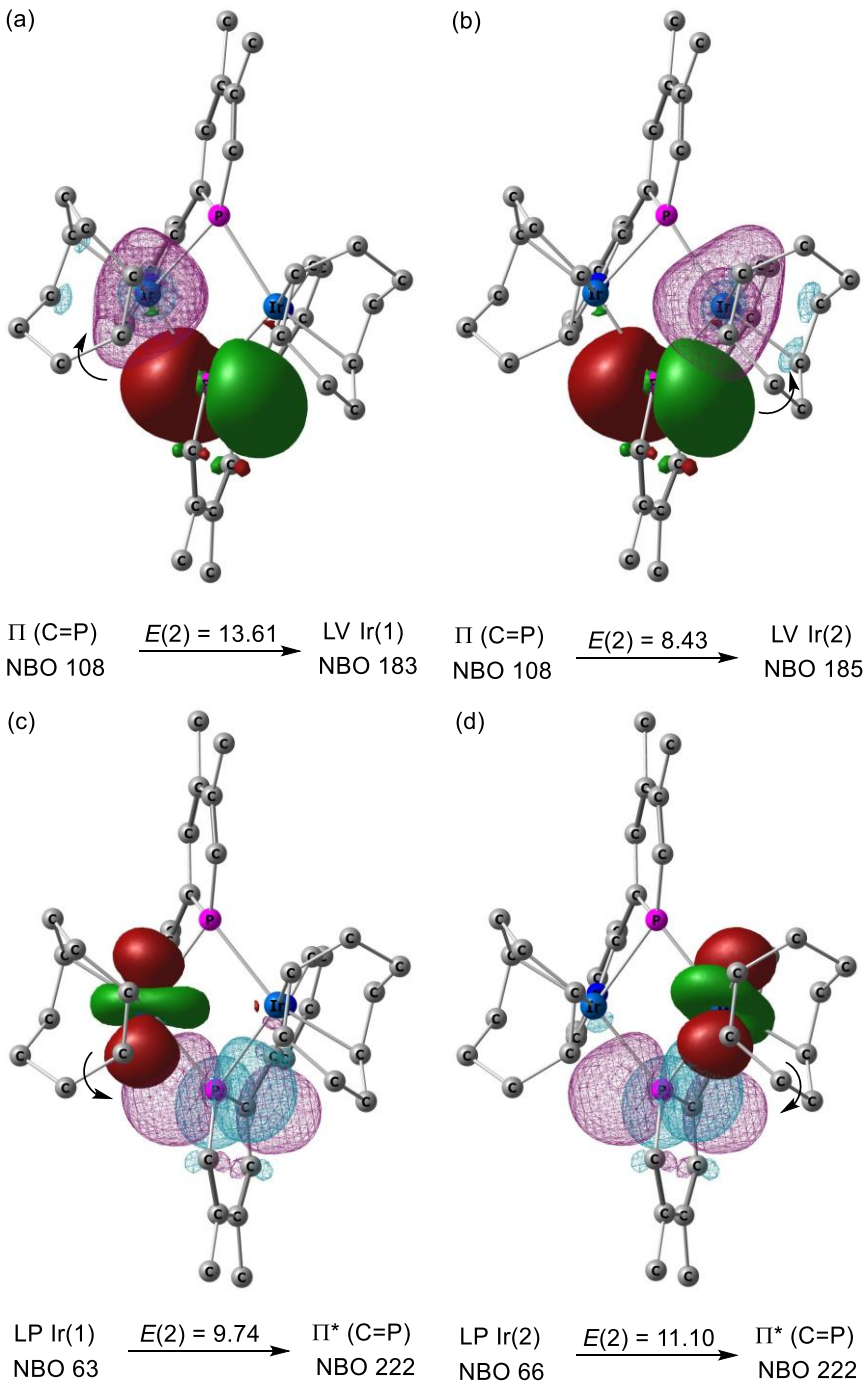


Figure S41. Second order perturbation analysis of **A** (isovalue = 0.05).

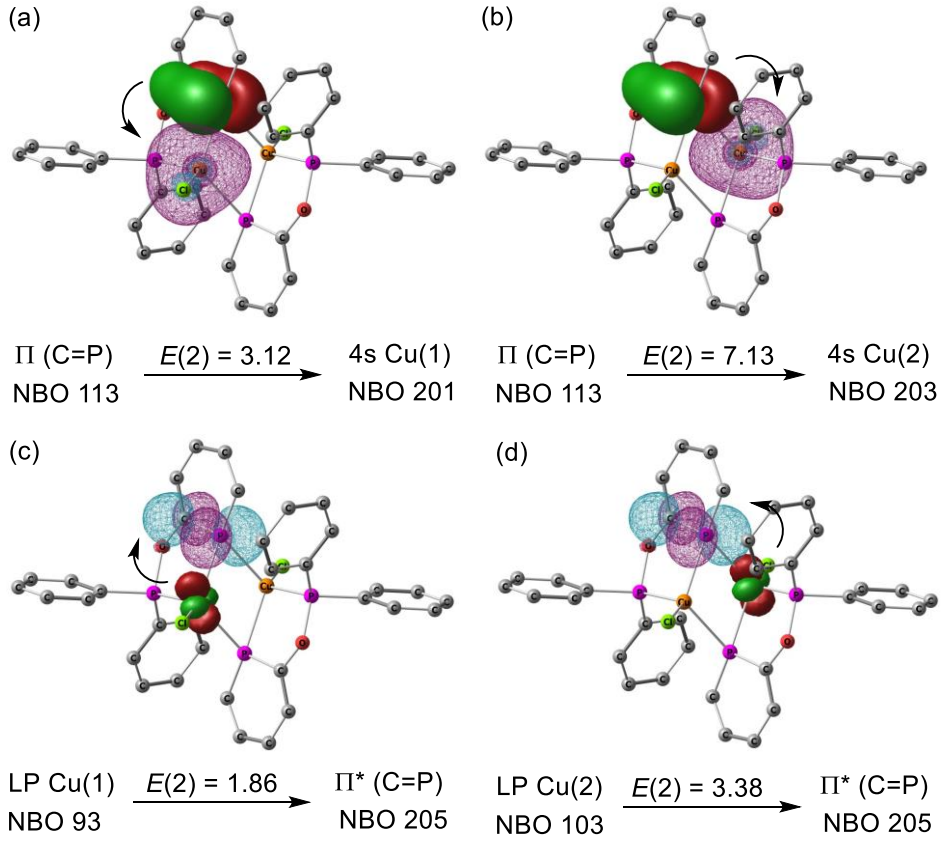


Figure S42. Second order perturbation analysis of **B** (isovalue = 0.05).

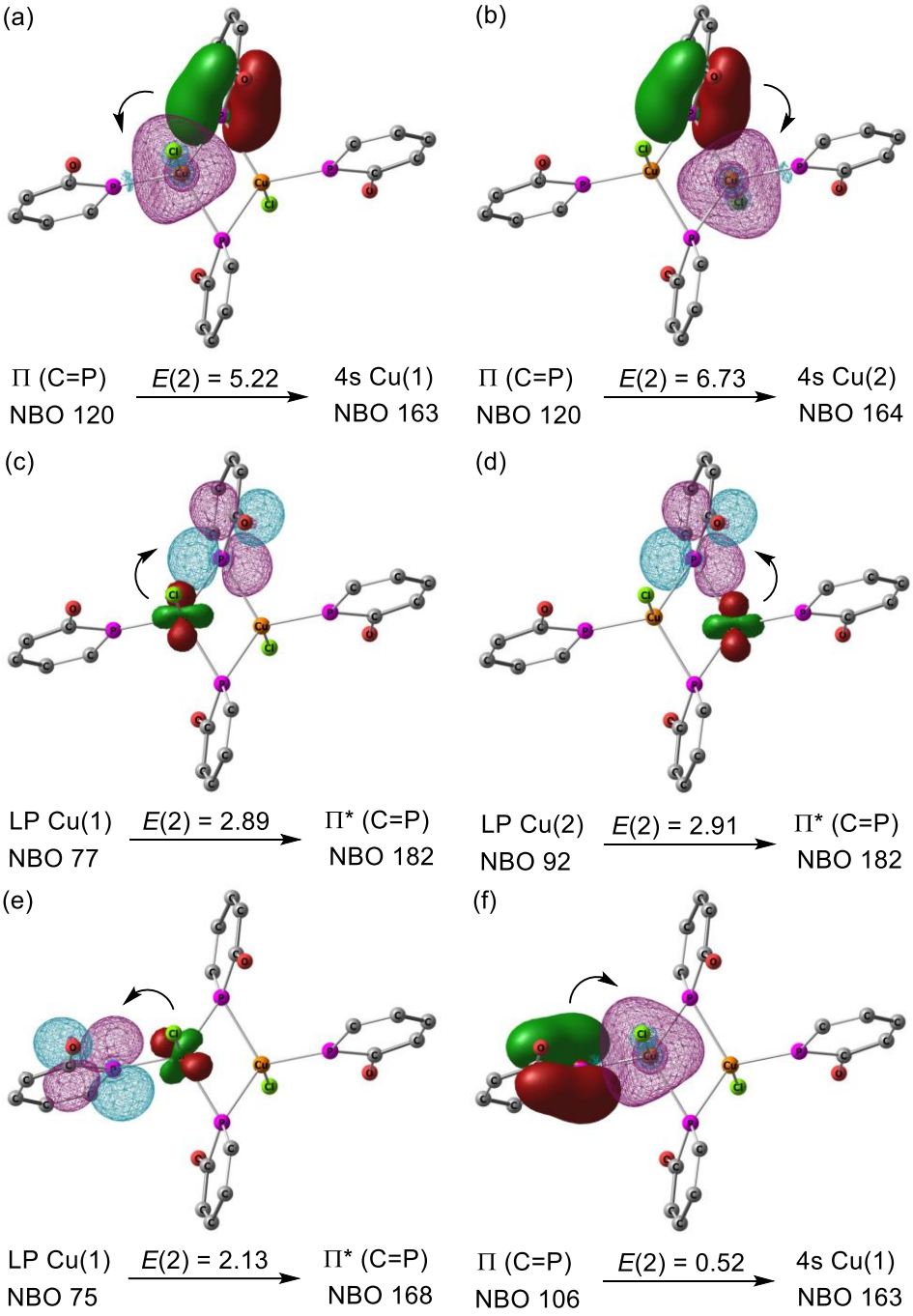


Figure S43. Second order perturbation analysis of **C** (isovalue = 0.05).

Cartesian Coordinates:

^{H}[**4**]$^{2+}$

Rh	-0.25168300	-0.84476200	1.1096020
P	0.54878200	0.75211400	2.4774280
P	1.69499900	2.42141700	-0.1679860
P	0.09372700	-2.11004700	2.9673010
P	-1.67736800	0.99669800	0.4490090
O	2.02138300	1.43020100	2.3538920
O	0.66709200	0.26686400	4.0349530
O	-0.38582500	2.10167100	2.5256300
C	0.13185400	-3.70091100	3.6135100
C	0.83871400	-1.56679400	5.5708870
H	1.11772800	-0.84661200	6.3442730
C	3.37672800	3.28654900	1.8399060
H	3.74125700	3.17763300	2.8650250

C	-2.53106300	3.06201500	2.0928120
H	-2.34606100	3.73688600	2.9326600
C	0.56470900	-1.08977000	4.2999780
C	-3.74714300	3.13361200	1.3959000
C	0.44810700	-3.93375700	4.9562560
H	0.44321900	-4.97130300	5.3011050
C	0.77399400	-2.93479700	5.8796310
C	2.52480700	3.72008900	-0.9377420
C	3.90261900	4.28788000	1.0197280
C	2.39299000	2.39209900	1.4276560
C	-1.54973800	2.14032700	1.7719290
C	-4.09441400	2.28037100	0.3391770
H	-5.07718500	2.40969000	-0.1225060
C	3.49517100	4.49179500	-0.3039510
H	3.96792900	5.29406700	-0.8765940
C	-3.27040900	1.27502900	-0.1624610
Rh	0.25168300	0.84476200	-1.1096020
P	-0.54878200	-0.75211400	-2.4774280
P	-1.69499900	-2.42141700	0.1679860
P	-0.09372700	2.11004700	-2.9673010
P	1.67736800	-0.99669800	-0.4490090
O	-2.02138300	-1.43020100	-2.3538920
O	-0.66709200	-0.26686400	-4.0349530
O	0.38582500	-2.10167100	-2.5256300
C	-0.13185400	3.70091100	-3.6135100
C	-0.83871400	1.56679400	-5.5708870
H	-1.11772800	0.84661200	-6.3442730
C	-3.37672800	-3.28654900	-1.8399060
H	-3.74125700	-3.17763300	-2.8650250
C	2.53106300	-3.06201500	-2.0928120
H	2.34606100	-3.73688600	-2.9326600
C	-0.56470900	1.08977000	-4.2999780
C	3.74714300	-3.13361200	-1.3959000
C	-0.44810700	3.93375700	-4.9562560
H	-0.44321900	4.97130300	-5.3011050
C	-0.77399400	2.93479700	-5.8796310
C	-2.52480700	-3.72008900	0.9377420
C	-3.90261900	-4.28788000	-1.0197280
C	-2.39299000	-2.39209900	-1.4276560
C	1.54973800	-2.14032700	-1.7719290
C	4.09441400	-2.28037100	-0.3391770
H	5.07718500	-2.40969000	0.1225060
C	-3.49517100	-4.49179500	0.3039510
H	-3.96792900	-5.29406700	0.8765940
C	3.27040900	-1.27502900	0.1624610
H	-0.09716300	-4.54043800	2.9530190
H	1.00240400	-3.23480700	6.9042110
H	-2.27459900	-3.91930600	1.9820980
H	-4.67155200	-4.94101400	-1.4369970
H	-3.60725600	0.65143900	-0.9944390
H	-4.47065300	3.88797900	1.7110720
H	0.09716300	4.54043800	-2.9530190
H	-1.00240400	3.23480700	-6.9042110
H	2.27459900	3.91930600	-1.9820980
H	4.67155200	4.94101400	1.4369970
H	3.60725600	-0.65143900	0.9944390
H	4.47065300	-3.88797900	-1.7110720

[H]7

Rh	1.28126515	-0.24001417	0.6025554
Rh	-1.28129457	-0.23999015	-0.6025217
P	-1.93748931	0.51627862	1.3563164
P	1.93761148	0.51538699	-1.3565606
P	1.00975183	1.80482566	1.7255213
P	-3.45715914	-0.75102057	-0.8211084
P	-1.00938187	1.80449481	-1.7261797
P	-0.25919111	-1.87624817	-1.8208302
P	0.25872226	-1.87577496	1.8211551
P	3.45705199	-0.75130400	0.8213949
O	-3.61928072	0.61569481	1.4636183
O	-1.68465431	-0.30618631	2.7920540
O	3.61942354	0.61440417	-1.4639213
O	1.69219684	2.03579308	-1.9340998
O	-1.69178076	2.03679220	1.9334044
O	1.68461613	-0.30741703	-2.7920883
C	-0.58803326	4.10140409	1.7789758
H	-1.59157434	4.53155717	1.8331579
C	6.05676774	-1.39514330	1.4413274
H	6.77466637	-1.87377462	2.1141577
C	-6.05696422	-1.39486388	-1.4406489
H	-6.77494143	-1.87371580	-2.1132382
C	-0.49828921	2.71328398	1.8059905
C	0.49888158	2.71259231	-1.8066994
C	0.17693996	-4.32275296	-3.0226043
H	-0.11628262	-5.36773361	-3.1633366
C	1.76817867	-2.53645641	-3.5996780
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C	-0.51594859	-1.78451055	-2.61371634
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P	0.02901575	2.02104769	1.95623832

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Cl	3.10326332	1.06949869	-0.43700768

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H	8.725215	3.612210	9.823266
P	5.810462	6.834864	12.320386

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