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A Diamino-substituted Carbodiphosphorane as Strong C-Donor and Weak N-Donor: Isolation of Monomeric Trigonal-Planar L·$ZnCl_2$

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1. Experimental Details

1.1 General

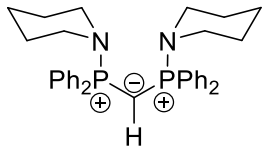
Chemicals. All experiments (if not stated otherwise) were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Argon (99.999%) was a product of *Air Liquide*. Involved solvents were dried using an MBraun SPS 800 (THF, toluene, Et_2O, acetonitrile, *n*-pentane, *n*-hexane) or dried in accordance with standard procedures and stored under an argon atmosphere over molecular sieves. Commercial substrates were used as received unless otherwise stated. $GaCl_3$, $InCl_3$ and $ZnCl_2$ were purchased from Sigma-Aldrich. Compound **3** was prepared according to the literature synthesis by LeFloch.[1]

NMR spectroscopy. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Avance-400 or Avance-250 spectrometers at 25 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (J) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT, APT, HSQC and HMBC experiments.

Elemental analyses were performed on an Elementar vario MICRO cube elemental analyzer.

IR-Spectra were recorded on a Thermo Nicolet iS5 FT-IR in transmission mode with a Specac "Omni-cell" with KBr plates and a 0.1 mm spacer or with a ATR module at 22 °C.

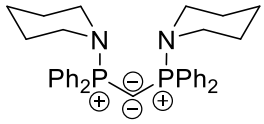
1.2. Preparation of Ylide **1-HBr**



To an oven-dried 50 mL Schlenck-tube, 1.34 g (1.91 mmol, 1 eq.) of compound **3** and 25 mL DCM was added resulting in a yellowish suspension. In another Schlenck-tube, 0.38 mL (3.79 mmol, 2 eq.) of piperidine and 1.93 mL (5.69 mmol, 3 eq.) trihexylamine was combined in 10 mL DCM. The mixture of piperidine and trihexylamine was added to the suspension of compound **3** via dropping funnel over a period of 10 min. This reaction mixture was stirred for 2 hours. After the solvent was removed under reduced pressure the sticky oil was dissolved in 10 ml THF. After 15 mL of pentane was added, a yellow precipitate was observed, which was filtered off. The residual solid was washed ten times with small portions (3 mL) of hot THF (60 °C). After drying under reduced pressure 642 mg (54%) of compound **1-HBr** was obtained as a pale yellow solid.

^{1}H NMR (400 MHz, DCM-d_2) δ 7.73 – 7.55 (t, 4H, $CH_{PPh,para}$), 7.51–7.33 (m, 16H $CH_{,PPh,ortho/meta}$), 3.10–2.84 (m, 8H, $N(CH_2CH_2)_2CH_2$), 2.07 (t, J = 6.4 Hz, 1H, P*CH*P), 1.66–1.51 (m, 8H, $N(CH_2CH_2)_2CH_2$), 1.50-1.36 (m, 4H, $N(CH_2CH_2)_2CH_2$) ppm.**^{31}P {^{1}H} NMR** (162 MHz, DCM-d_2) δ= 39.7 (s) ppm.**^{13}C {^{1}H} NMR** (101 MHz, DCM-d_2) δ 133.4 (s, PPh_{para}), 132.4 (dd, $^3J_{CP}$ =5.1 Hz, $^5J_{CP}$=1.4 Hz, PPh_{meta}), 129.7 (dd, $^2J_{CP}$ = 6.4 Hz, $^4J_{CP}$ = 1.2 Hz, PPh_{ortho}), 126.82(dd, $^1J_{CP}$=117 Hz, $^3J_{CP}$=4.3 Hz, PPh_{ipso}), 46.8 (s, $N(CH_2CH_2)_2CH_2$)) 26.3 (s, $N(CH_2CH_2)_2CH_2$)), 24.6 (s, ($N(CH_2CH_2)_2CH_2$)), 7.27 (t, $^1J_{CP}$ = 143.3 Hz P-*C*-P). **CHNS** for $C_{35}H_{41}N_2P_2Br$: Calc.: C, 66.56; H, 6.54; N, 4.44. Measured: C, 66.22; H, 6.55; N, 4.46.

1.3. Preparation of bisylide **1**



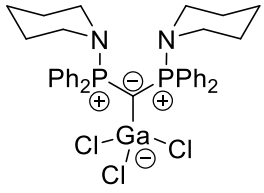
300 mg (0.48 mmol, 1 eq.) of compound **1-HBr.** was dissolved in 10 ml dry THF. The colorless solution was cooled to 0 °C and 96 mg (0.48 mmol, 1 eq.) potassium hexamethyldisilazide in 7 mL dry THF was slowly added. The solution was stirred for 2 hours at 0 °C and concentrated at reduced pressure. The green solid was washed three times with 5 mL of pentane and dried in vacuum giving rise to compound **1** a yellow solid (246 mg, 0.45 mmol, 94%). Single crystals of compound **1** were obtained by slow diffusion of *n*-pentane into a saturated solution of compound **1** in diethyl ether.

^{1}H NMR (400 MHz, THF-d_8) δ 7.9–7.78 (m, 8H, $CH_{PPh,para/ortho}$), 7.29–7.16 (m, 12H $CH_{,PPh,ortho/meta}$), 2.87–2.66 (br, s, 8H, N(CH_2CH$_2$)$_2$CH$_2$), 1.55–1.35 (br, s, 12H, N(CH$_2$$CH_2$)$_2$$CH_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, THF-d_8) δ 138.3 (dd, $^{1}J_{CP}$ = 57.9 Hz, $^{3}J_{CP}$ = 1.1 Hz, PPh$_{ipso}$) 132.9 (dd, $^{3}J_{CP}$ = 5.1 Hz, $^{5}J_{CP}$=1.1 Hz, PPh$_{meta}$), 129.8 (s, PPh$_{para}$), , 128.2 (dd, $^{2}J_{CP}$ = 6.0 Hz, $^{4}J_{CP}$ = 1.3 Hz, PPh$_{ortho}$), 46.8 (s, N(CH_2CH$_2$)$_2$CH$_2$)) 27.5 (s, N(CH$_2$$CH_2$)$_2CH_2$)), 26.3 (s, (N(CH$_2CH_2$)$_2$$CH_2$)), 15.6 (t, $^{1}J_{CP}$= 172.6 Hz, P-C-P) ppm. **^{31}P{^{1}H} NMR** (162 MHz, THF-d_8) δ= 12.5 (s) ppm. **CHNS** for $C_{35}H_{40}N_2P_2$: Calcd.: C: 76.34, H: 7.32, N: 5.09, P: 11.25. Measured: C, 76.04; H, 6.94; N, 4.89.

Table S1. Comparison of the TEP-values of carbenes, phosphines and CDPs.[2]

Compound	TEP [cm^{-1}]
PPh$_3$	2067.5
PEt$_3$	2062.7
PPr$_3$	2061.6
SIPr	2051.5
IPr	2050.5
CDP **A**	2032.0
[C$_3$H$_6$(Ph$_2$P)$_2$C]	2031.9
1	**2031.8**

1.4 Preparation of **1-GaCl$_3$**



A J-Young-NMR tube was filled with 30 mg (0.05 mmol, 1 eq.) of compound **1** and 9.6 mg (0.05 mmol, 1 eq.) of $GaCl_3$. To this mixture, THF was added and the reaction mixture was shaken for one hour. After that, a white precipitate was obtained. The supernatant THF was removed by pipette and the residual was washed three times with small amounts of pentane. The colorless solid was dried in vacuum to yield 24 mg (0.033 mmol, 66%). Single crystals of compound **1-GaCl$_3$** were grown by slow diffusion of pentane into a saturated solution of compound **1-GaCl$_3$** in THF.

^{1}H NMR (400 MHz, DCM-d_2) δ 7.64–7.52 (m, 8H, $CH_{PPh,meta}$), 7.52–7.42 (m, 4H $CH_{,PPh,para}$), 7.41-7.3 (m, 8H, $CH_{PPh,para}$), 3.20–2.99 (br,s, 8H, N(CH_2CH_2)$_2$$CH_2$), 2.07 (t, J = 6.4 Hz, 1H, P*CH*P), 1.64–1.51 (br, s, 4H, N(CH_2CH_2)$_2$$CH_2$), 1.50-1.33 (m, 8H, N($CH_2CH_2$)$_2$$CH_2$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, DCM-d_2) δ 133.9 (dd, $^{3}J_{CP}$ = 4.7 Hz, $^{5}J_{CP}$ = 1.2 Hz, PPh_{meta}), 132.2 (s, PPh_{para}), 130.5 (dd, $^{1}J_{CP}$ = 108.8 Hz, $^{3}J_{CP}$ = 3.7 Hz, PPh_{ipso}), 128.8 (dd, $^{2}J_{CP}$ = 6.6 Hz, $^{4}J_{CP}$ = 1.1 Hz, PPh_{ortho}), 48.7 (s, N(CH_2CH_2)$_2$$CH_2$)) 26.5 (s, N($CH_2CH_2$)$_2$$CH_2$)), 24.9 (s, (N($CH_2CH_2$)$_2$$CH_2$)), 12.6 (t, $^{1}J_{CP}$ =91.8 Hz P-*C*-P) ppm. **^{31}P{^{1}H} NMR** (162 MHz, DCM-d_2) δ = 44.3 (s) ppm.

1.5 Preparation of further metal complexes with **1**

1-Rh. For the syntheses of the metal complexes, **1** was dissolved in THF and stoichiometric amounts of the respective metal chlorides ($Rh(CO)_2$(acac) for **1-Rh**) were added. Immediately after the metal salt was added, the color of the reaction mixture changed from yellow to colorless. After one hour a colorless precipitate was formed which was separated from the solution and washed three times with small amounts of pentane (3 ml). In each of these reactions the formation of the ylide [**1-H**]Cl was observed in the ^{31}P{^{1}H}NMR spectrum which could not be separated from the metal complex (see figures S10-18.).

Further metal halides/precursors:

The preparation of further metal complexes of **1** was performed analogous to **1-Rh**. The process of the reaction was always followed by ^{31}P NMR spectroscopy and isolation was attempted as soon as full conversion or no further changes were observed. Longer reaction times always resulted in reformation of **1-H**, which was found to be impossible to completely remove from the metal complexes.

1-InCl$_3$: ^{1}H NMR (400 MHz, DCM-d_2) δ 7.60-7.32 (br, m, 20H, CH_{PPh}), 2.95-2.85 (br, s, 8H, N(CH_2CH_2)$_2$$CH_2$), 1.96 (t, 0.25H, PC*H*P), 1.45-1.18 (br, m, 12H, N(CH_2CH_2)$_2$CH_2). ^{31}P{^{1}H} NMR (162 MHz, DCM-d_2) δ= 42.5 (s) ppm.

1-GeCl$_2$: ^{1}H NMR (400 MHz, DCM-d_2) δ 7.56-7.2 (br, m, 30H, CH_{PPh}), 3.15-2.97 (br, s, 8H, N(CH_2CH_2)$_2$$CH_2$), 2.9-2.81 (br, s, 6H, N(CH_2CH_2)$_2$$CH_2$, and protonated-species), 1.95 (t, 1H PC*H*P), 1.47-1.18 (br, m, N(CH_2CH_2)$_2$CH_2, and protonated species). ^{31}P{^{1}H} NMR (162 MHz, DCM-d_2) δ= 41.2 ppm.

1-ZnCl$_2$: ^{1}H NMR (400 MHz, DCM-d_2) δ 7.55-7.2 (m, 20H, CH_{PPh}), 3.05-2.92 (br, s, 8H, N(CH_2CH_2)$_2$$CH_2$), 1.43 (br, s, 12H, N($CH_2CH_2$)$_2CH_2$). ^{31}P{^{1}H} NMR (162 MHz, DCM-d_2) δ = 38.9 (s) ppm.

1-Rh(acac)CO$_2$: ^{31}P{^{1}H} NMR (162 MHz, DCM-d_2) δ = 32.9 (d, $^{2}J_{PRh}$ = 6.6 Hz) ppm.

1-CeCl$_3$: No conversion

1-$NdCl_3$: $^{31}P\{^1H\}$ NMR (162 MHz, DCM-d_2) δ = 40.7 (s) ppm.

1-YCl_3: $^{31}P\{^1H\}$ NMR (162 MHz, DCM-d_2) δ = 40.2 (s) ppm.

1-$ZrCl_4$: Only protonation observed.

1-$MoCl_5$: Only protonation observed

2. NMR Spectroscopy

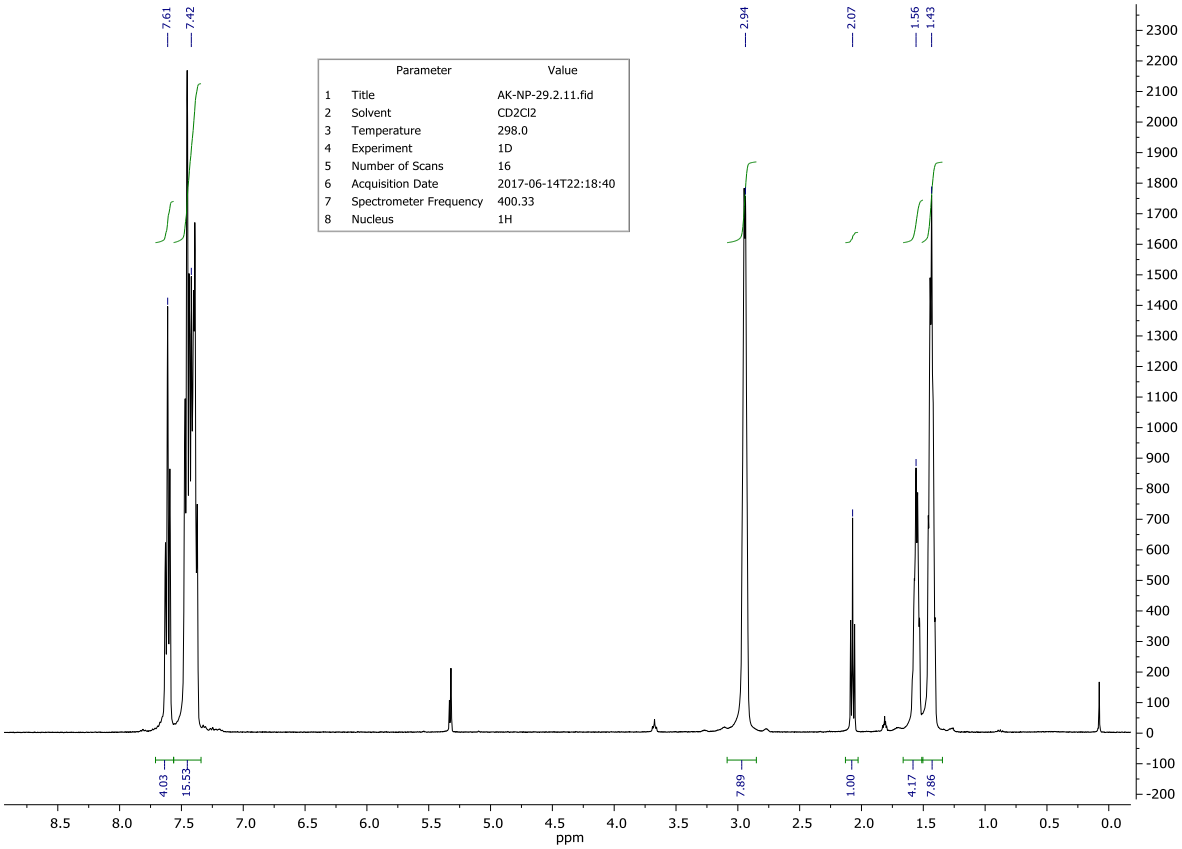


Figure S1. ^{1}H NMR spectrum of compound **1-HBr.**

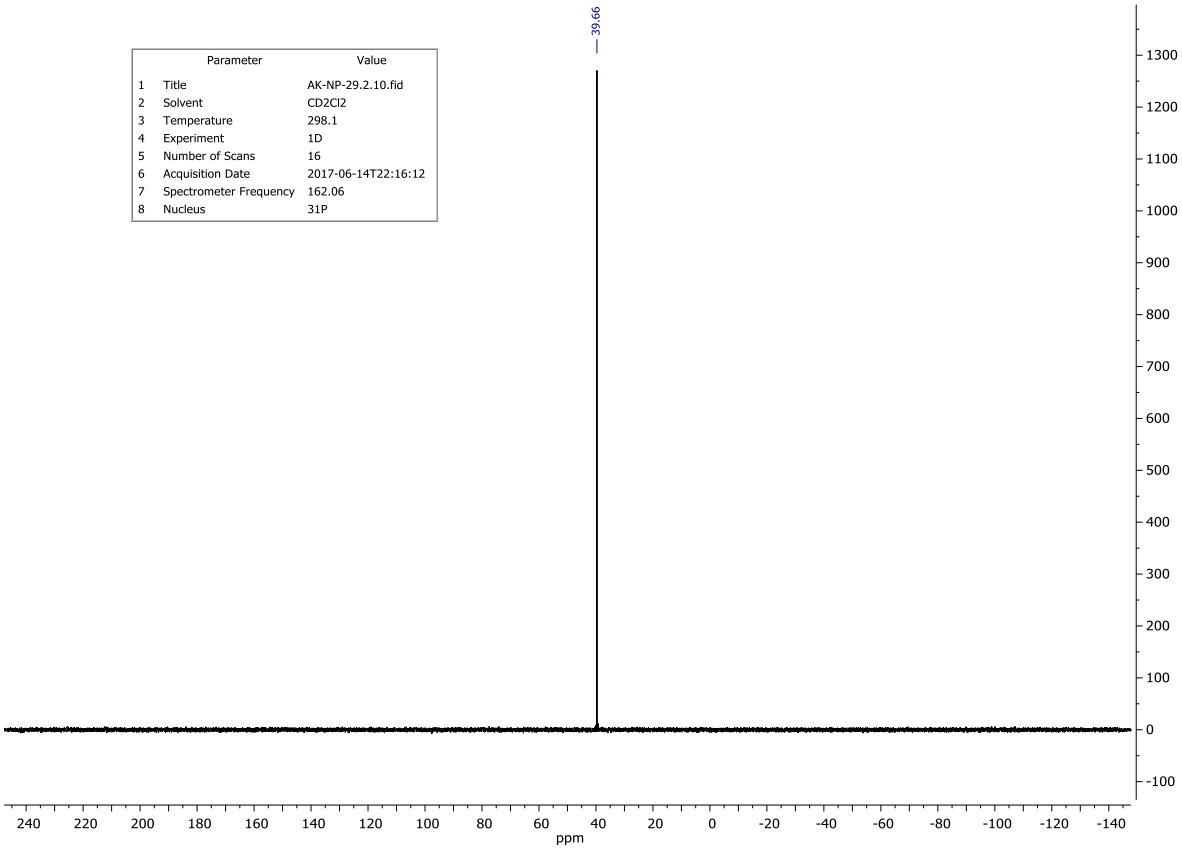


Figure S2. ^{31}P{^{1}H} NMR spectrum of compound **1-HBr.**

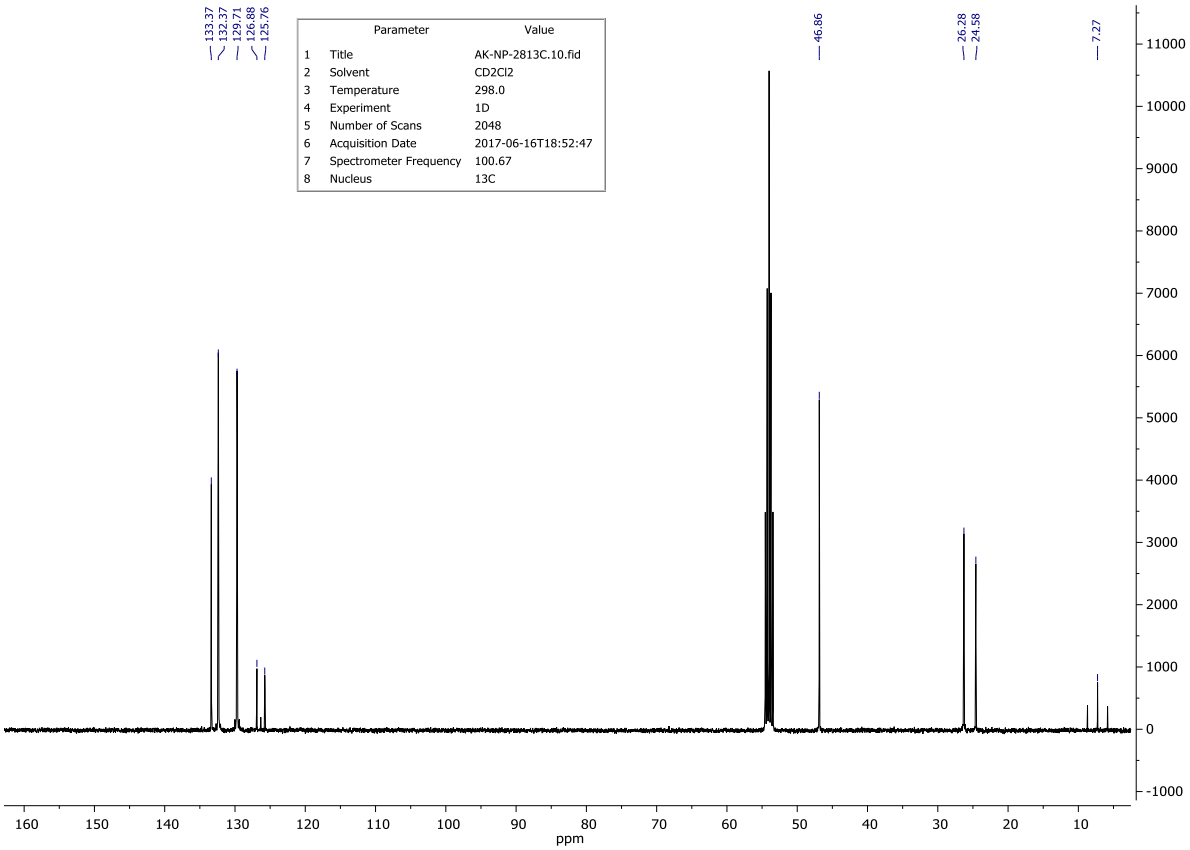


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1-HBr.**

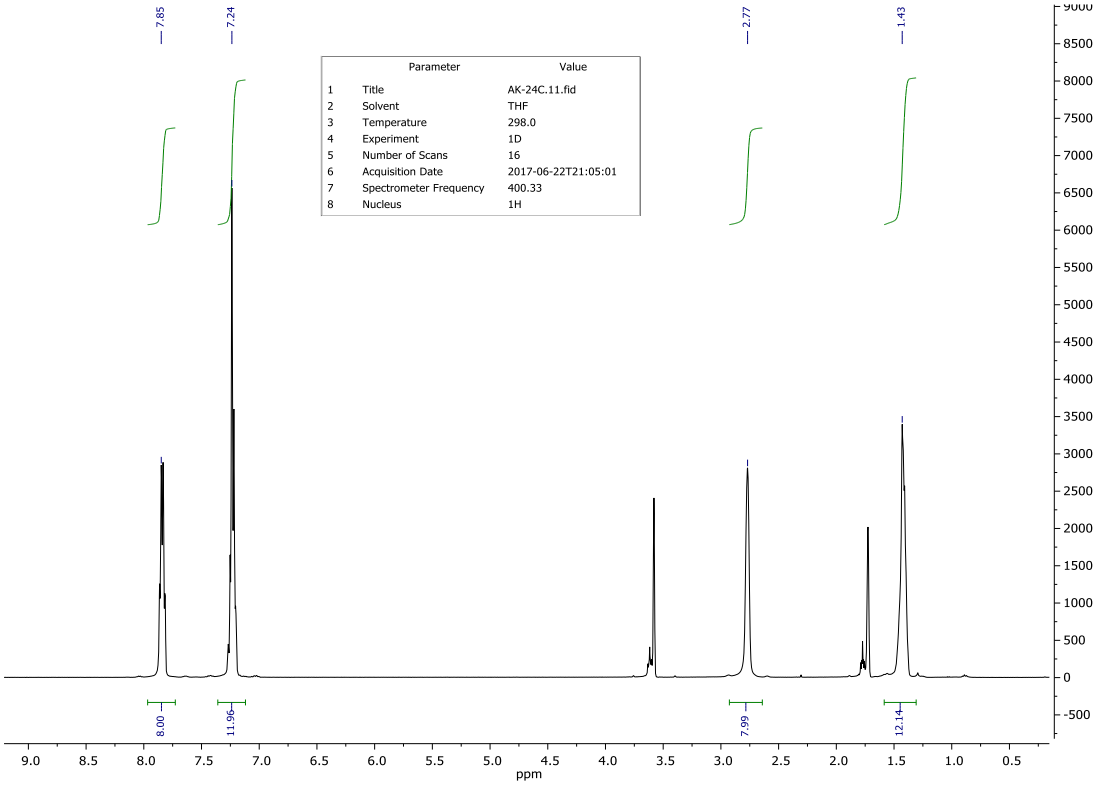


Figure S4. ^{1}H NMR spectrum of compound **1**.

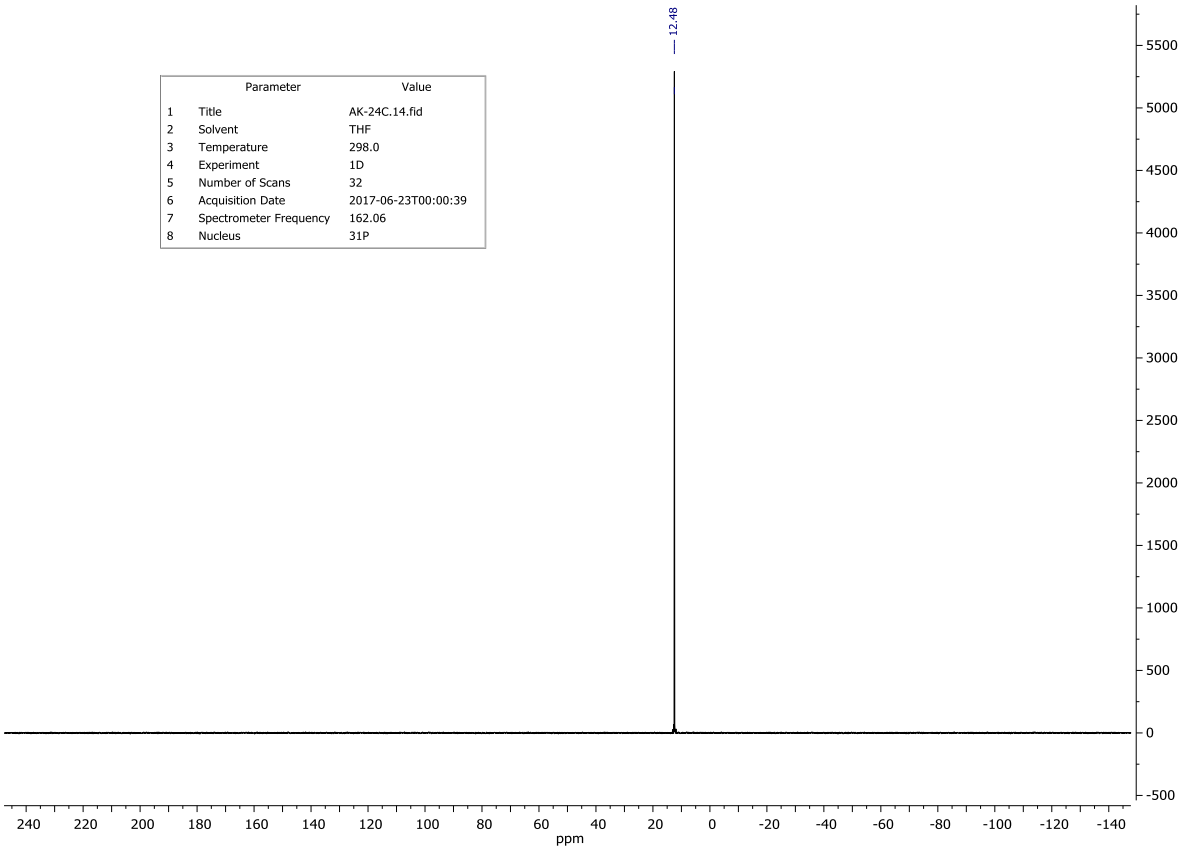


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of compound **1**.

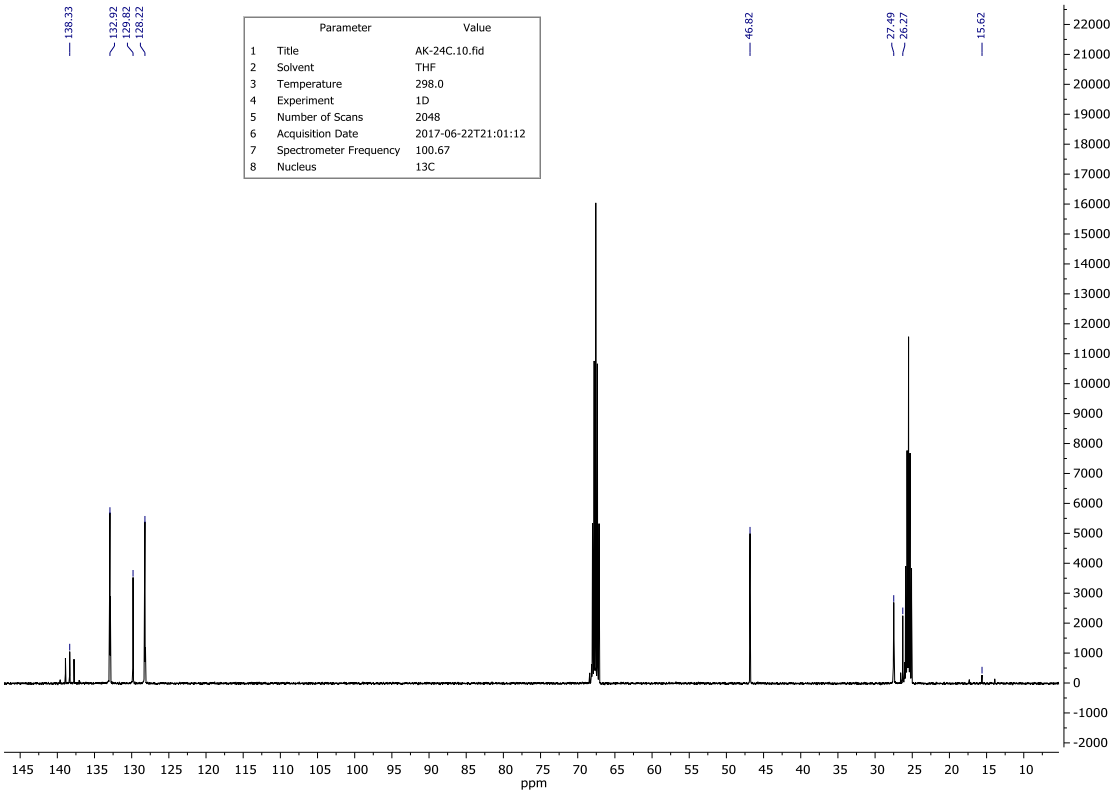


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1**.

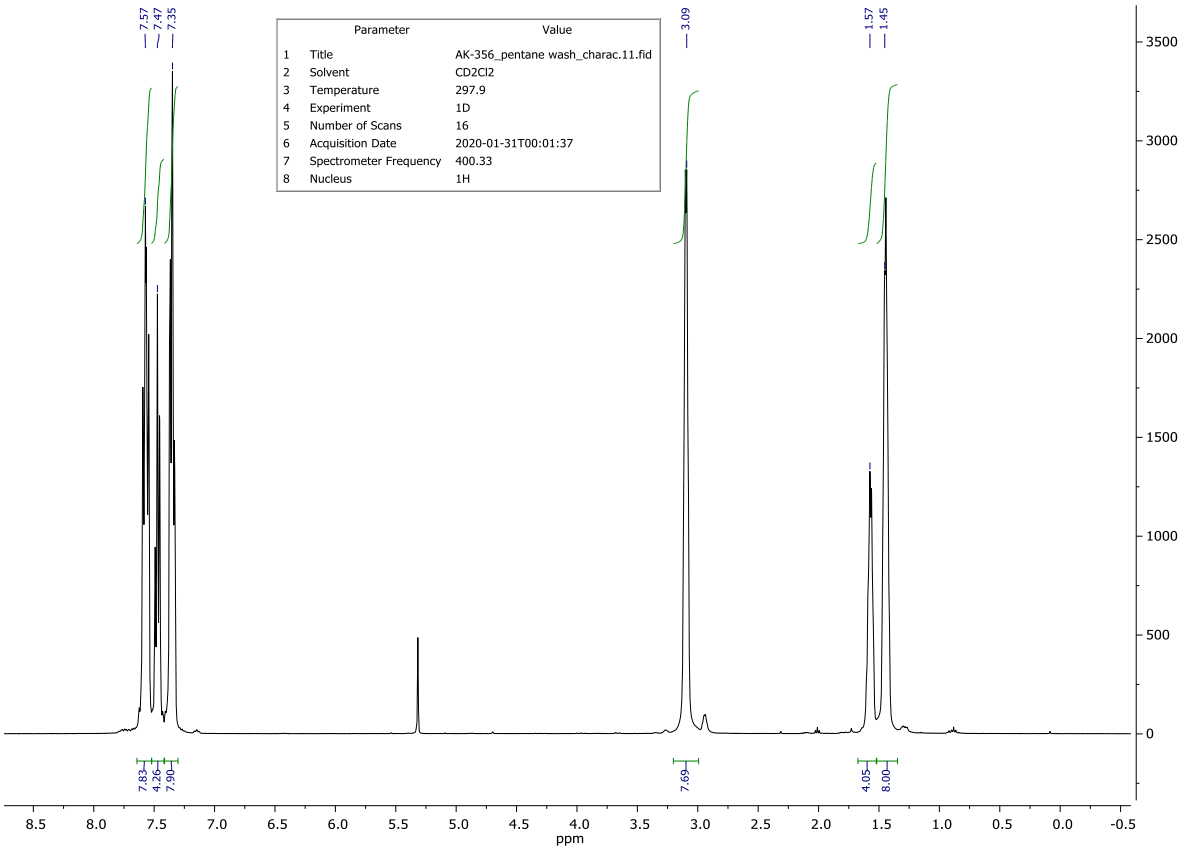


Figure S7. ^{1}H NMR spectrum of compound **1-GaCl$_3$**.

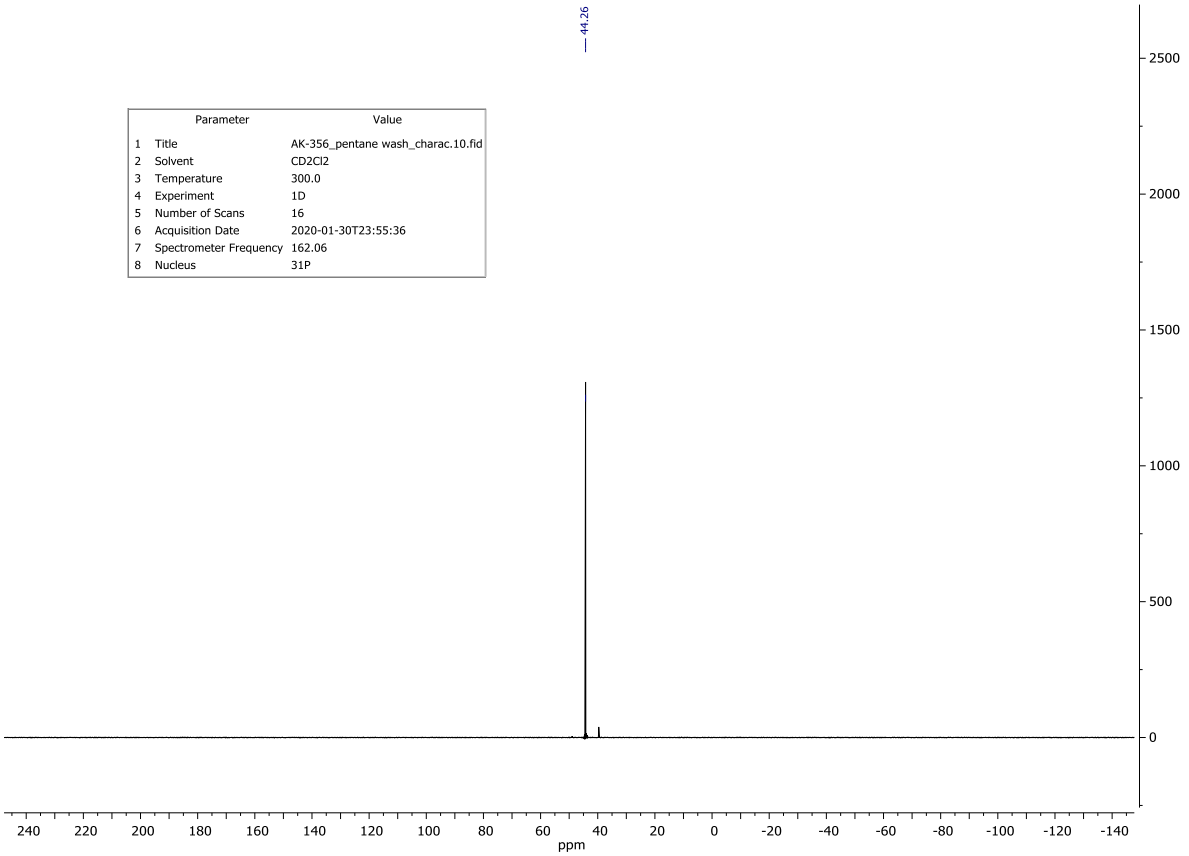


Figure S8. ^{31}P{^{1}H} NMR spectrum of compound **1-GaCl$_3$**.

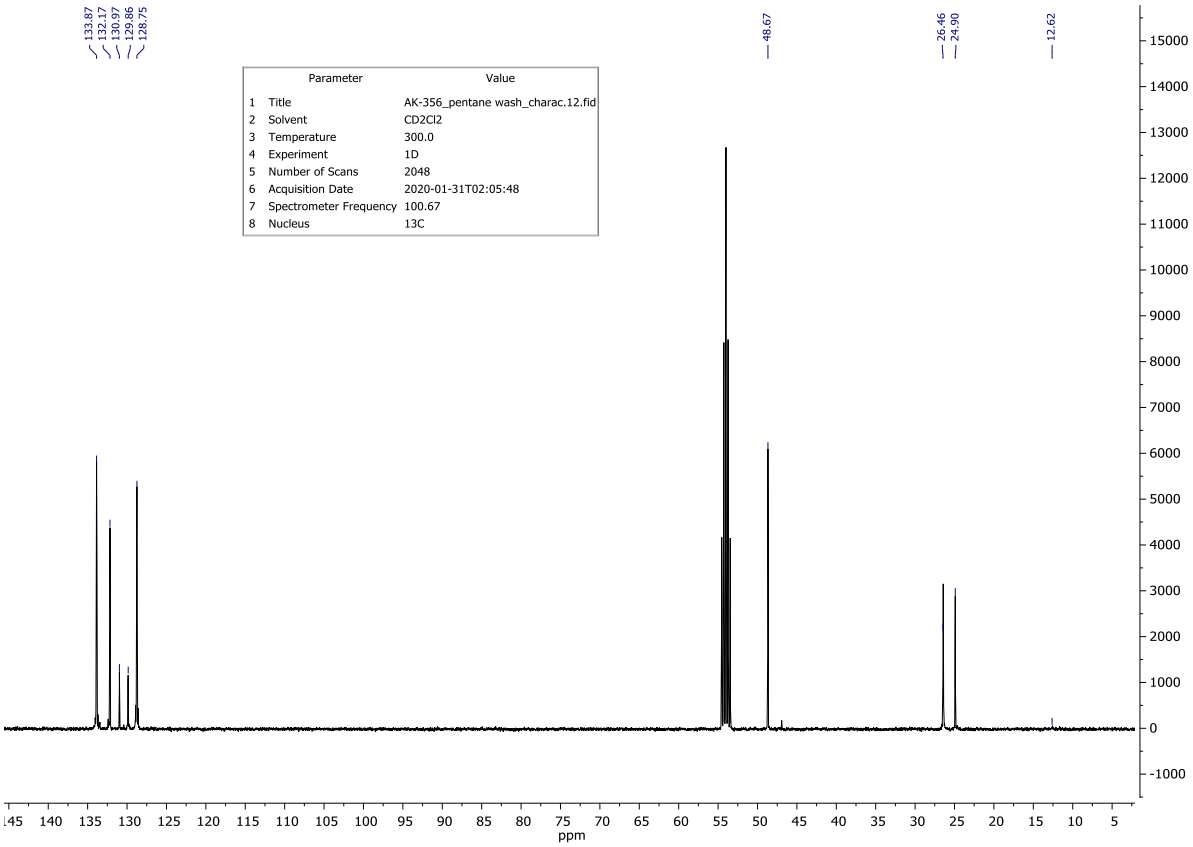


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1-GaCl$_3$**.

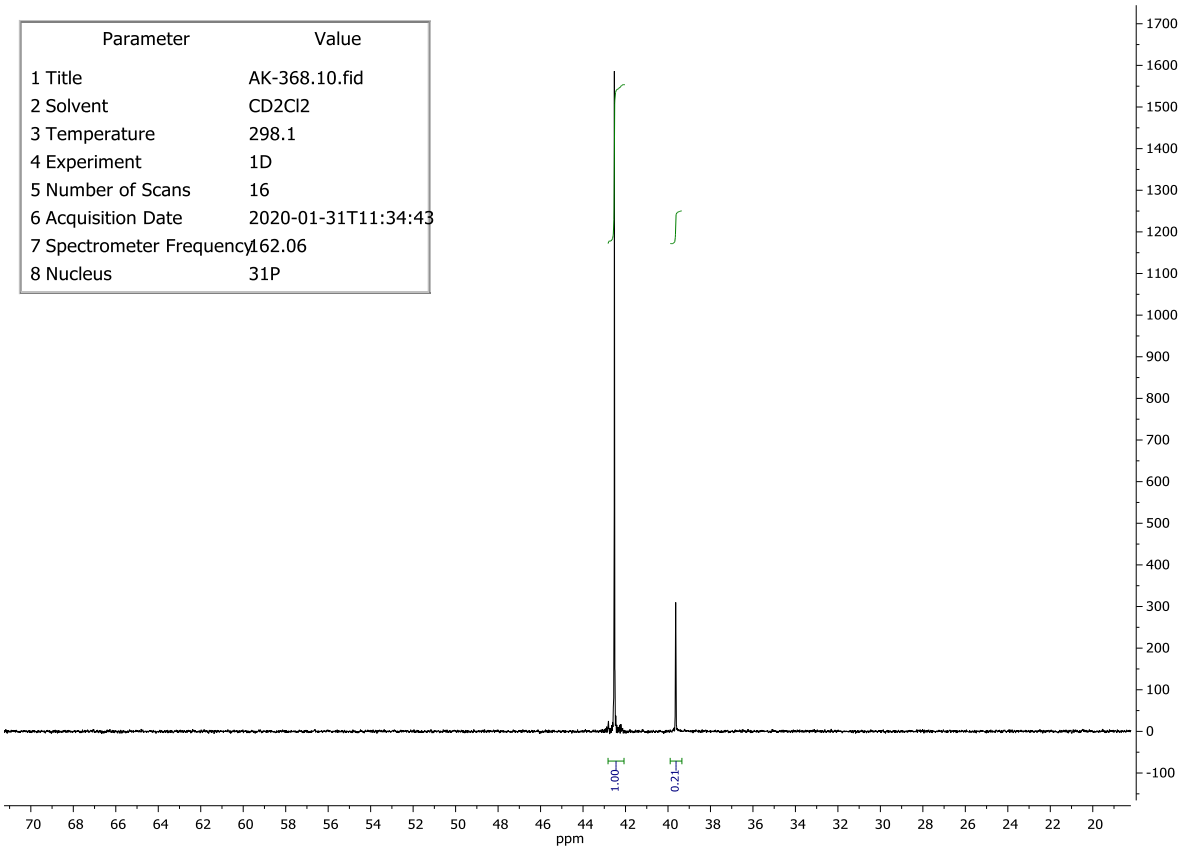


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of compound **1** with $InCl_3$; the signal at 39.7 ppm corresponds to **1-H**.

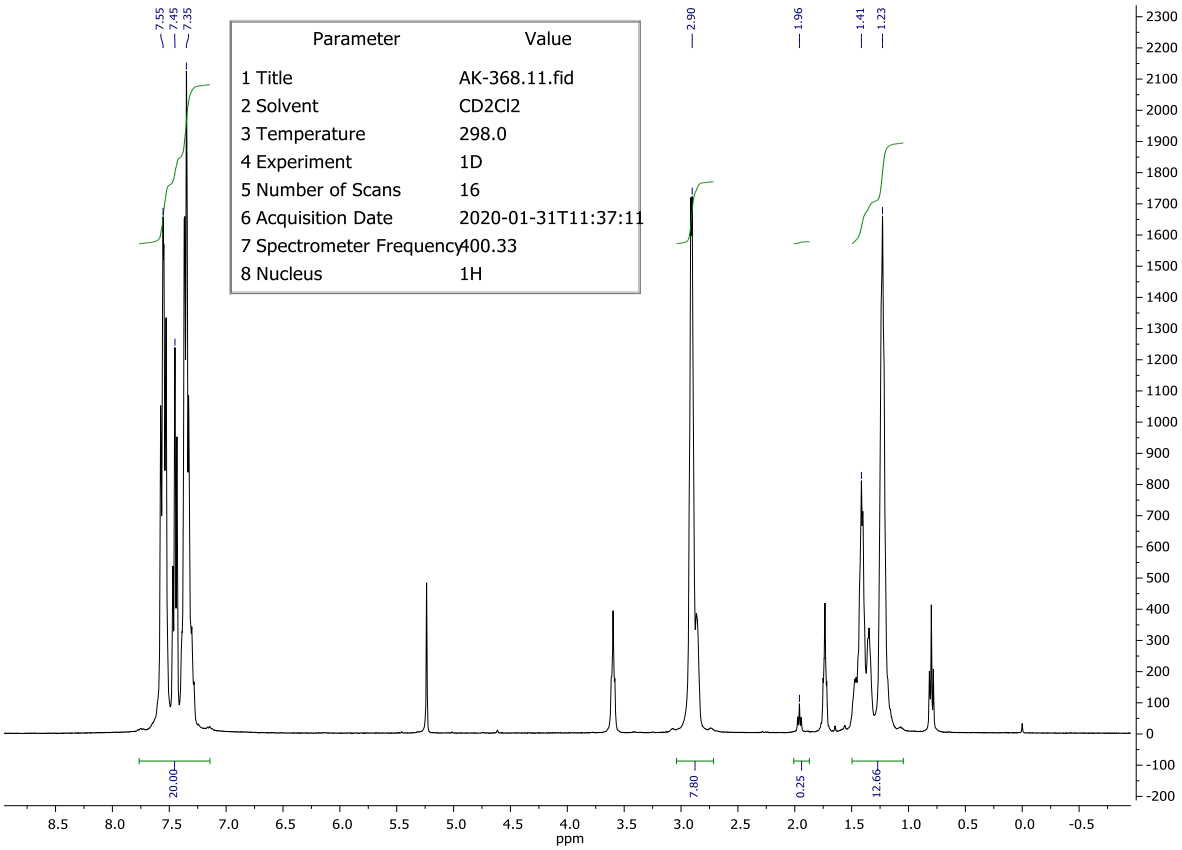


Figure S11. ^{1}H NMR spectrum of the reaction of compound **1** with $InCl_3$.

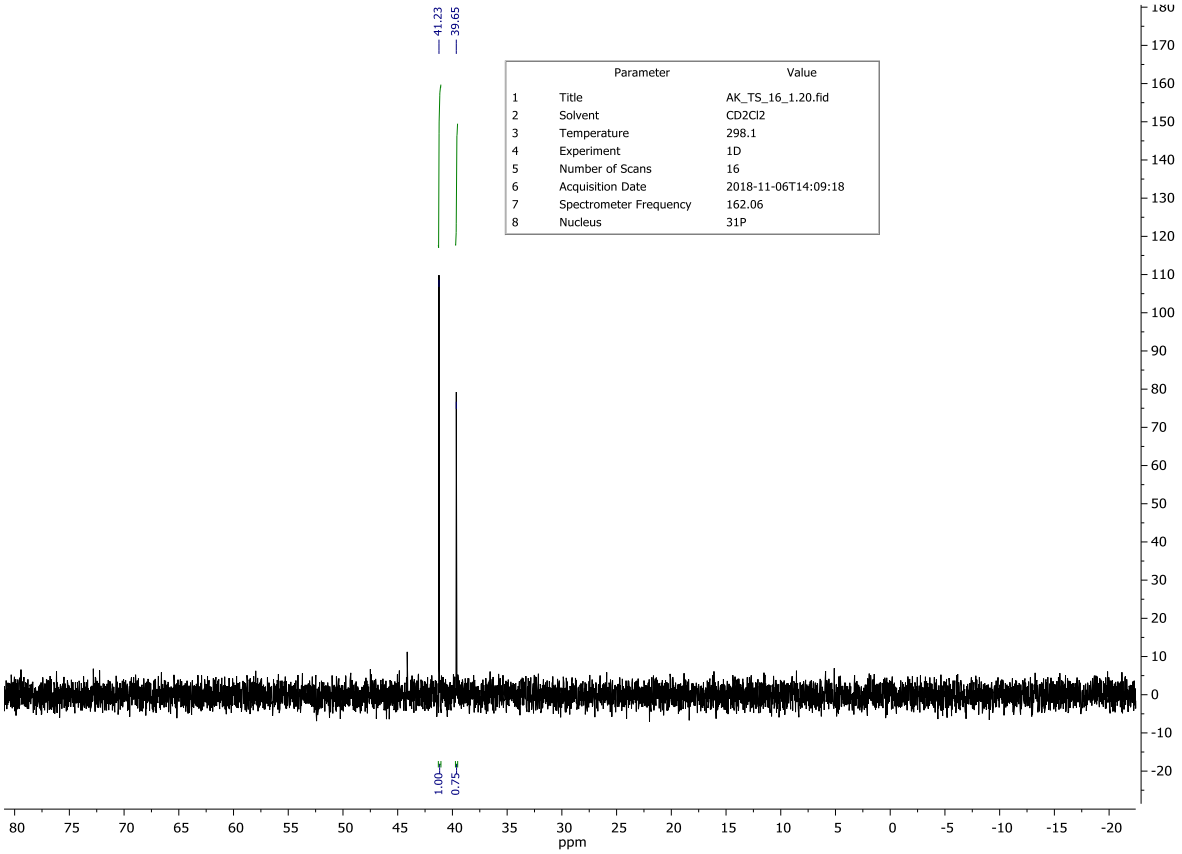


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of compound **1** with $GeCl_2$·Dioxane. The signal at 39.7 ppm corresponds to **1-H**

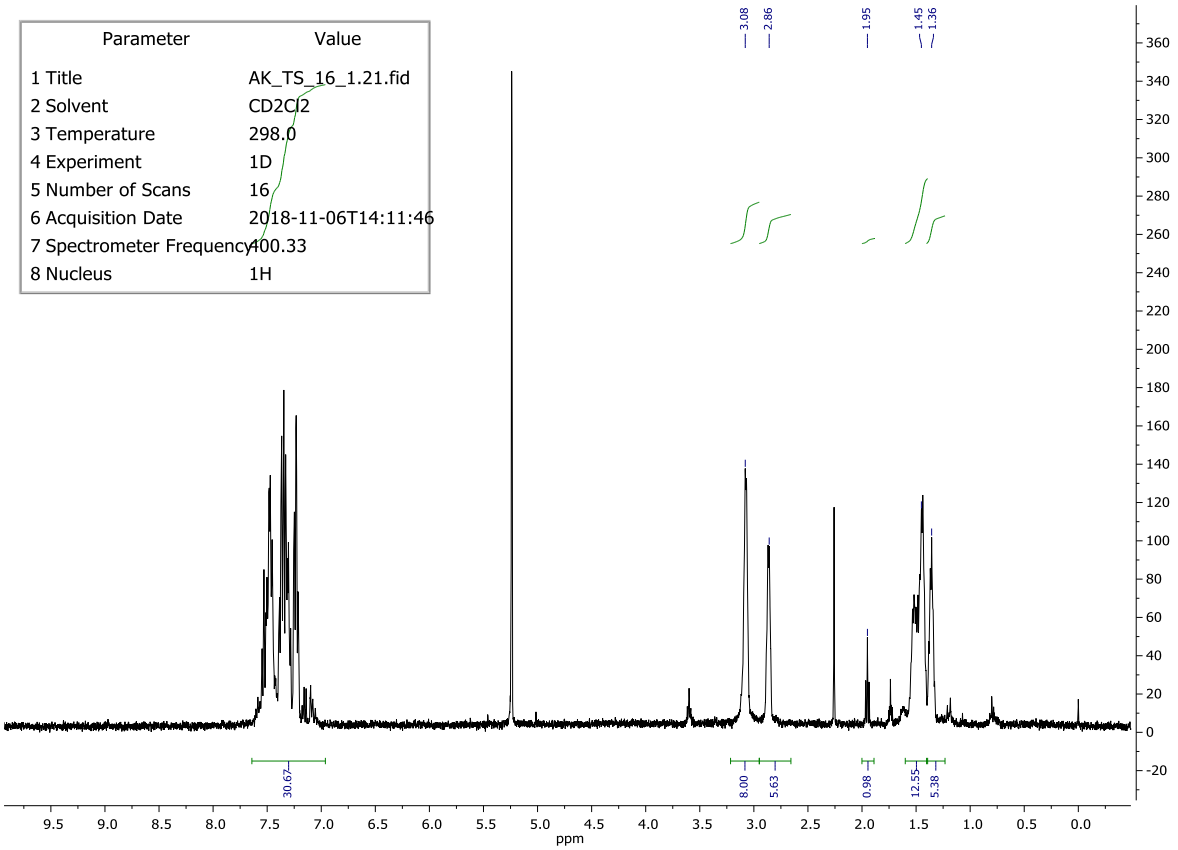


Figure S13. ^{1}H NMR spectrum of the reaction of compound **1** with $GeCl_2$·Dioxane.

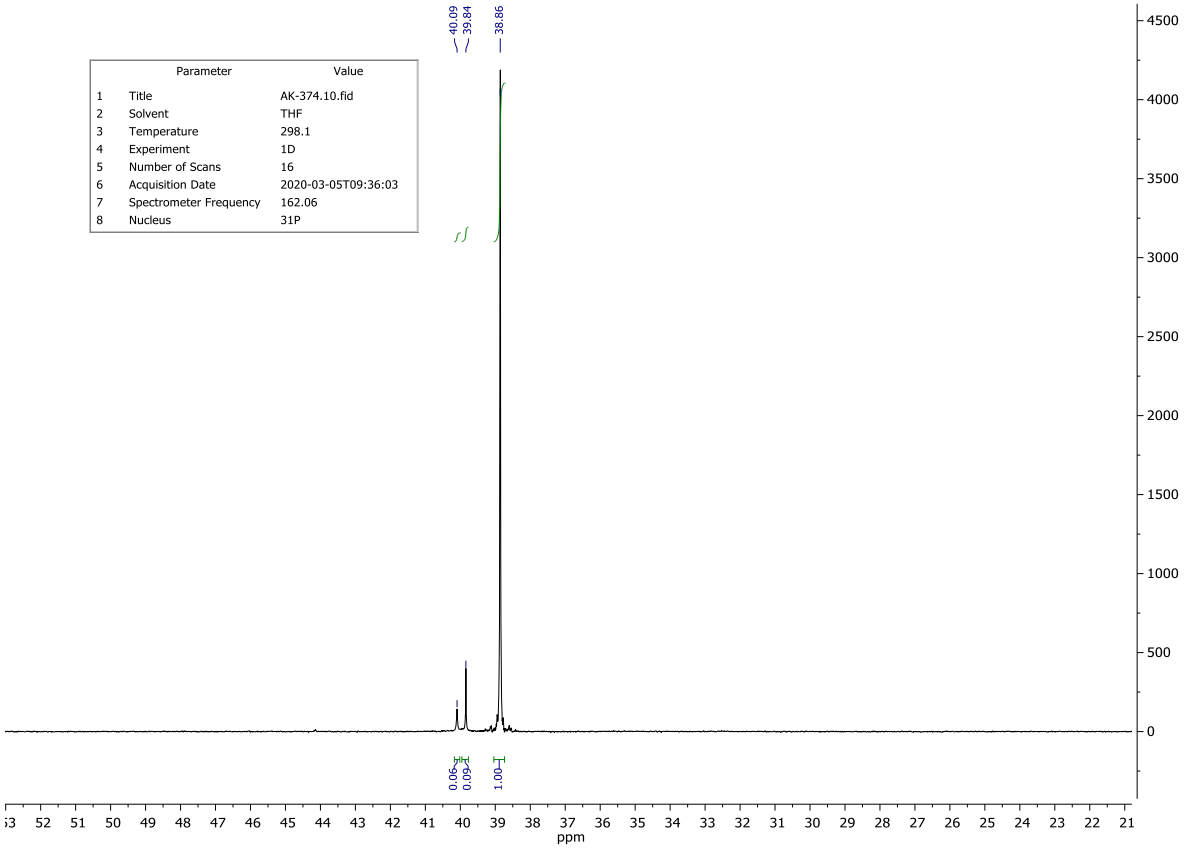


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of compound **1** with $ZnCl_2$. The signal at 39.8 ppm corresponds to **1-H**.

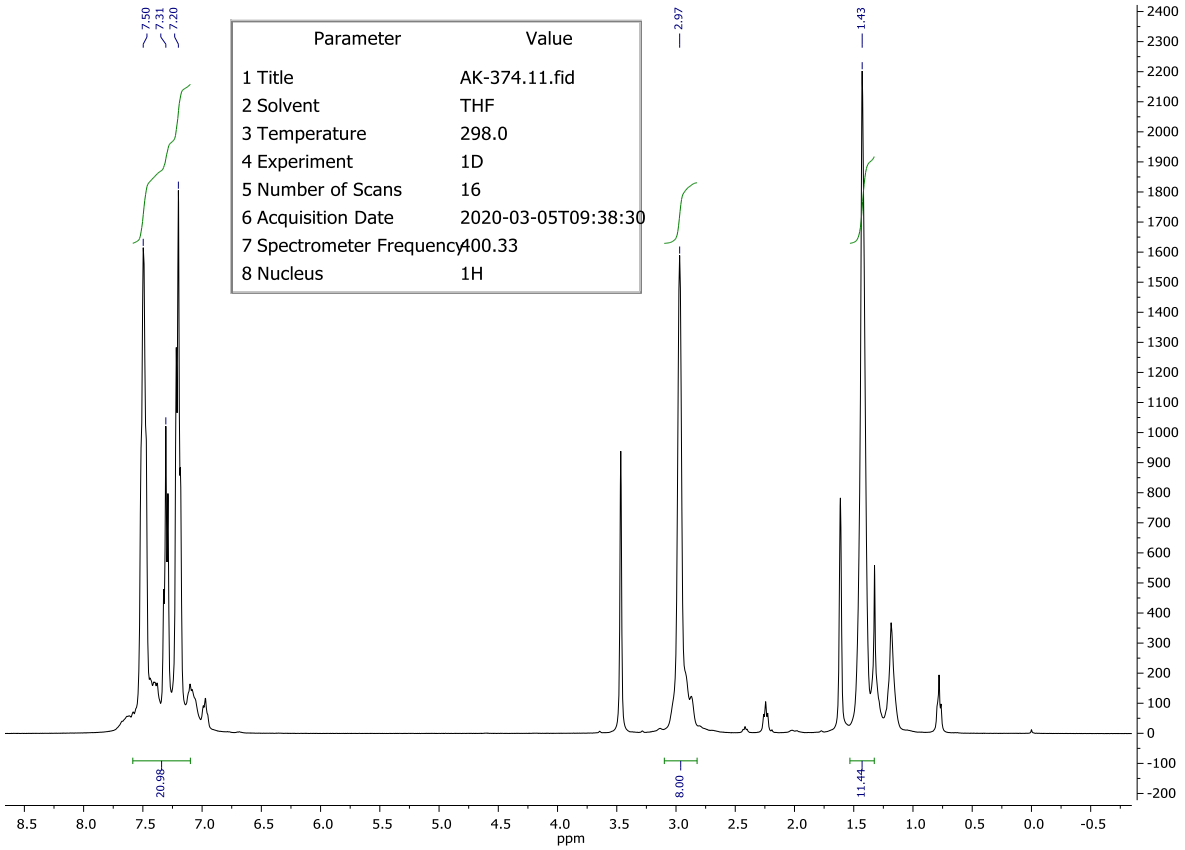


Figure S15. ^{1}H NMR spectrum of the reaction of compound **1** with $ZnCl_2$.

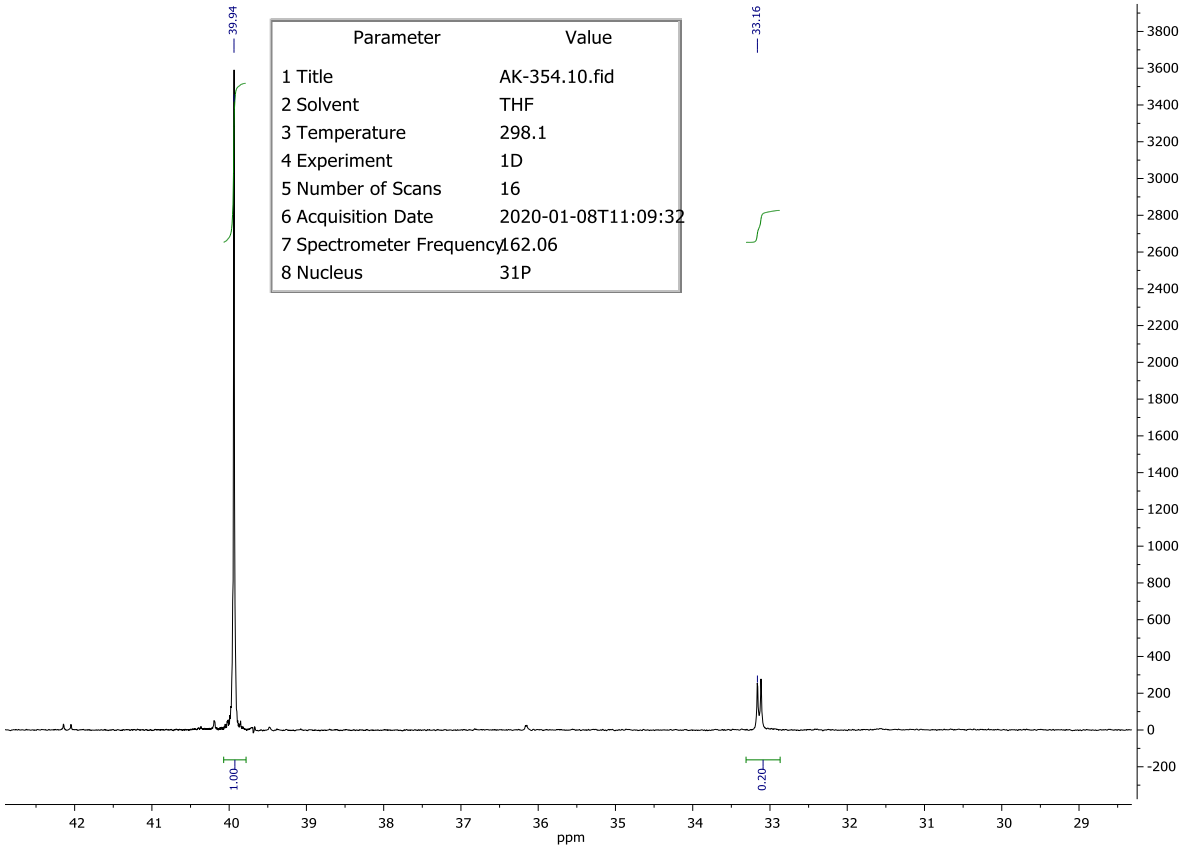


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of compound **1** with $Rh(CO)_2(acac)$.

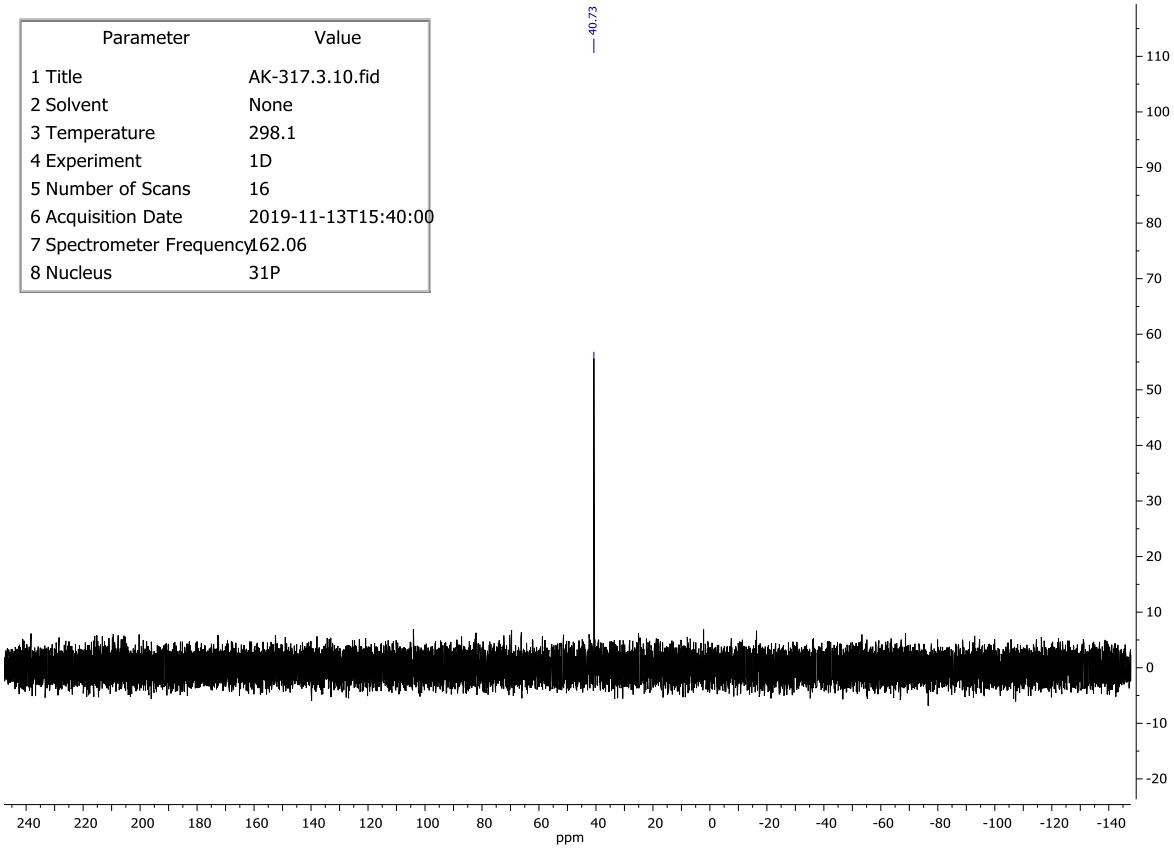


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of compound **1** with $NdCl_3$.

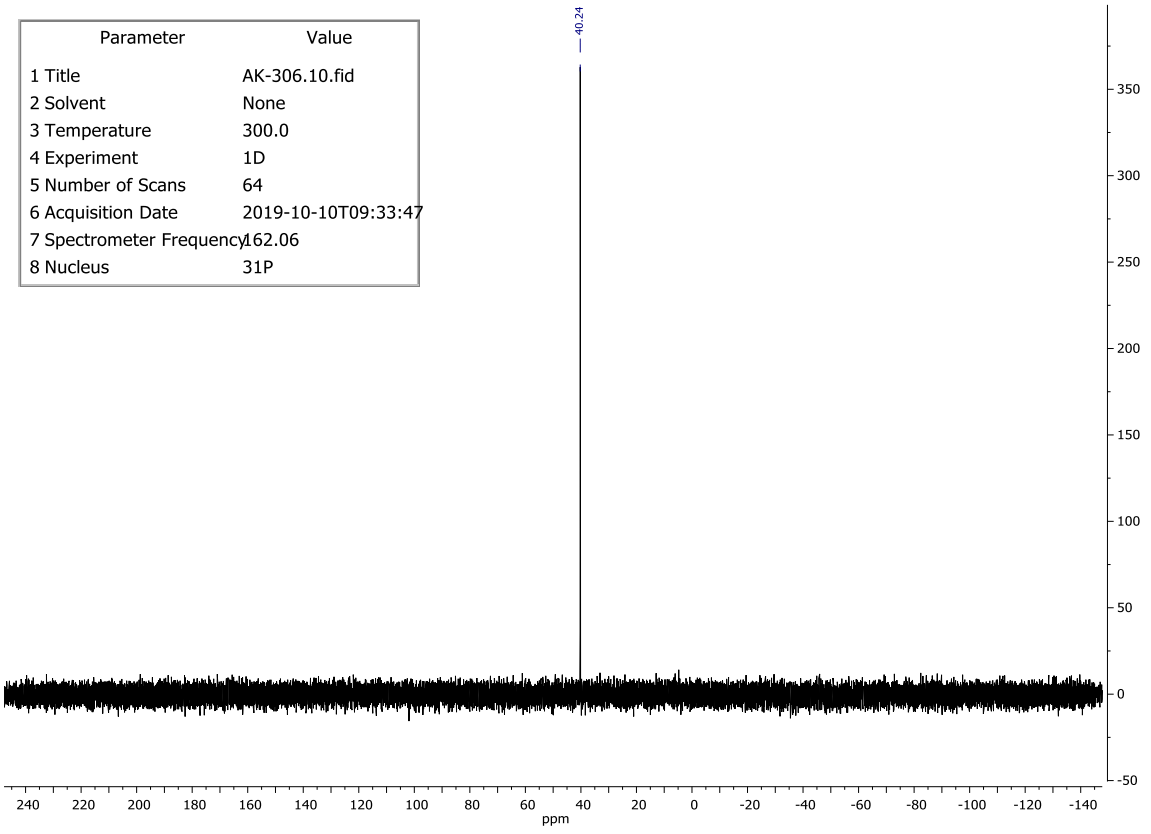


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of compound **1** with YCl_3.

3. Single-Crystal XRD Analyses

3.1. General information

Data collection of all compounds was conducted with a Rigaku Synergy or an Oxford SuperNova. The structures were solved using direct methods, refined with the Shelx software package[3,4] and expanded using Fourier techniques. The crystals of all compounds were mounted in an inert oil (perfluoropolyalkylether). Crystal structure determinations were effected at 100 K. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1812625-1812628. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].

Details on the structure solutions:

The structure of **1-HBr** contained a toluene solvent molecule. This molecule is disordered and was modelled by using the RIGU and SAME restraints.
The structure of **1** contained one piperidyl and one phenyl group that was disordered over the whole six-membered ring with an occupancy of 0.59 an 0.41. This was modelled by using the SADI, RIGU, SIMU and SAME restraints.
The structure of **1-GaCl$_3$** was refined as a two-component twin.
The structure of **1-Rh** was refined as a two-component twin and contained highly disordered solvent molecules which were treated by using the PLATON/SQUEEZE routine.[2,3]
The structure of **1-InCl$_3$** contained a disorder in the piperidyl moiety with an occupancy of 0.61 and 0.39. This was modelled by using the SADI, RIGU und SIMU restraints.

Table S2. Data collection and structure refinement details for compounds **1-HBr, 1** and **1-GaCl$_3$**.

Parameter	**1-HBr**	**1**	**1-GaCl$_3$**
CCDC No.	1993242	1993245	1993247
Formula	$C_{42}H_{49}ClN_2P_2$	$C_{35}H_{40}N_2P_2$	$C_{35}H_{40}Cl_3GaN_2P_2$
Formula weight [g·mol^{-1}]	679.22	550.63	726.70
Temperature [K]	99.95(10)	99.8(2)	293(2)
Wave length [Å]	1.54184	1.54178	1.54184
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	$P2_{1/n}$
a [Å]	23.6941(5)	15.260(2)	10.22942(16)
b [Å]	10.0307(3)	9.5382(11)	18.8800(3)
c [Å]	15.1078(4)	20.529(3)	17.9216(2)
β [°]	93.655(2)	94.766(13)	104.0445(14)

Volume [Å^3]	3583.36(16)	2977.8(7)	3357.77(9)
Z	4	4	4
Calc. density [Mg·m^{-3}]	1.259	1.228	1.438
μ ($Mo_{K\alpha}$) [mm^{-1}]	2.026	1.515	4.430
F(000)	1488	1176	1504
Crystal dimensions [mm]	0.304 x 0.089 x 0.047	0.190 x 0.159 x 0.064	0.086 x 0.072 x 0.014
Theta range [°]	3.739 to 72.121	4.322 to 67.171	3.456 to 67.122
Index ranges	-29 ≤ h ≤ 27	-18 ≤ h ≤ 15	-12 ≤ h ≤ 12
	-12 ≤ k ≤ 10	-11 ≤ k ≤ 11	-22 ≤ k ≤ 22
	-18 ≤ l ≤ 16	-24 ≤ l ≤ 24	-21 ≤ l ≤ 21
Reflections collected	7873	8174	11224
Independent reflections	3532 [R(int) = 0.0244]	2664 [R(int) = 0.0612]	11224 [R(int) = ?]
Data/Restraints/Parameter	3532 / 51 / 246	2664 / 324 / 286	11224 / 0 / 389
Goodness-of-fit on F^2	1.061	1.132	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0344; wR2 = 0.0893	R1 = 0.0618, wR2 = 0.1493	R1 = 0.0325, wR2 = 0.0866
Largest diff. peak and hole hole [e·Å$^-$]	0.363 and -0.581	0.290 and -0.371	0.437 and -0.513

Table S3. Data collection and structure refinement details for compounds **1-Rh, 1-$ZnCl_2$** and **1-$InCl_3$**.

Parameter	**1-Rh**	**1-$ZnCl_2$**	**1-$InCl_3$**
CCDC No.	1993243	1993246	1993244
Formula	$C_{82}H_{94}N_4O_6P_4Rh_2$	$C_{35}H_{40}Cl_2N_2P_2Zn$	$C_{35}H_{40}Cl_3InN_2P_2$
Formula weight [g·mol^{-1}]	1561.31	686.90	771.80
Temperature [K]	100(2)	100(2)	100(2)
Wave length [Å]	1.54184	1.54184	1.54184
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/n$	$P2_1/c$
a [Å]	14.0618(2)	10.10050(10)	10.2163(4)
b [Å]	16.9278(3)	18.2003(2)	32.6718(11)
c [Å]	19.7394(3)	18.2051(2)	10.7854(5)
β [°]	89.7720(10)	96.8830(10)	108.952(5)
Volume [Å^3]	4592.69(13)	3322.56(6)	3404.8(3)
Z	2	4	4
Calc. density [Mg·m^{-3}]	1.129	1.373	1.506
μ ($Mo_{K\alpha}$) [mm^{-1}]	3.922	3.618	8.811
F(000)	1624	1432	1576

Crystal dimensions [mm]	0.090 x 0.050 x 0.010	0.159 x 0.070 x 0.056	0.143 x 0.060 x 0.038
Theta range [°]	3.215 to 77.144	3.446 to 77.390	2.705 to 77.406
Index ranges	-17 ≤ h ≤ 17	-12 ≤ h ≤ 12	-12<=h<=12
	-21 ≤ k ≤ 21	-13 ≤ k ≤ 22	-37<=k<=41
	-24 ≤ l ≤ 24	-20 ≤ l ≤ 22	-13<=l<=13
Reflections collected	29512	25646	25289
Independent reflections	29512 [R(int) = ?]	6879 [R(int) = 0.0295]	7031 [R(int) = 0.0410]
Data/Restraints/Parameter	29512 / 31 / 888	6879 / 0 / 379	7031 / 109 / 443
Goodness-of-fit on F^2	1.054	1.090	1.113
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1172	R1 = 0.0298, wR2 = 0.0788	R1 = 0.0537, wR2 = 0.1546
Largest diff. peak and hole hole [e·Å$^-$]	1.222 and -0.731	0.428 and -0.444	1.011 and -1.731

3.2. Crystal Structure Determination

3.2.1. Crystal structure determination of **1-HBr**

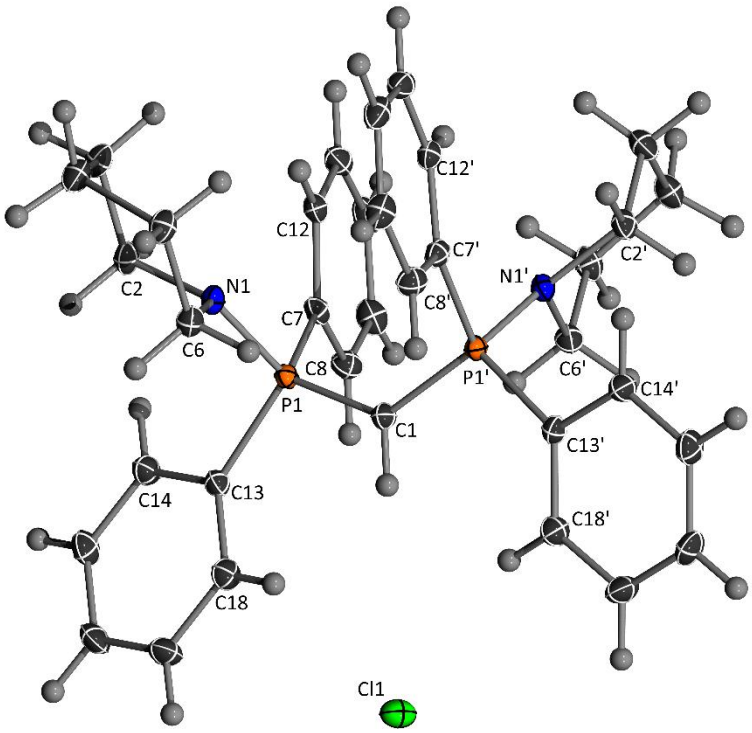


Figure S19. ORTEP Plot of compound **1-HBr**. Ellipsoids are drawn at the 50% probability level.

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1-HBr**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	4100(1)	1767(1)	2902(1)	13(1)
P(1)	4379(1)	824(1)	2133(1)	11(1)
Cl(1)	5000	5986(1)	2500	20(1)
C(1)	5000	82(2)	2500	13(1)
C(2)	3566(1)	2492(1)	2676(1)	16(1)
C(3)	3532(1)	3710(2)	3274(1)	19(1)
C(4)	3562(1)	3285(2)	4248(1)	19(1)
C(5)	4089(1)	2438(2)	4463(1)	18(1)
C(6)	4117(1)	1269(1)	3824(1)	15(1)
C(7)	4419(1)	1929(1)	1196(1)	13(1)
C(8)	4434(1)	1365(2)	351(1)	17(1)
C(9)	4471(1)	2176(2)	-388(1)	19(1)
C(10)	4481(1)	3559(2)	-292(1)	19(1)
C(11)	4476(1)	4121(1)	550(1)	18(1)
C(12)	4456(1)	3312(1)	1296(1)	15(1)
C(13)	3882(1)	-471(1)	1773(1)	14(1)
C(14)	3386(1)	-95(2)	1276(1)	17(1)
C(15)	2971(1)	-1038(2)	1052(1)	20(1)
C(16)	3045(1)	-2355(2)	1319(1)	21(1)
C(17)	3535(1)	-2735(2)	1801(1)	21(1)
C(18)	3952(1)	-1798(1)	2034(1)	17(1)
C11	2554(1)	7858(3)	4626(2)	28(1)
C21	2080(7)	8084(19)	5105(13)	38(3)
C31	1991(2)	7385(5)	5864(3)	43(1)
C41	2368(6)	6410(18)	6183(15)	46(3)
C51	2842(2)	6157(4)	5697(3)	36(1)
C61	2931(6)	6868(15)	4942(13)	29(3)
C71	2662(6)	8647(17)	3831(14)	52(4)

Table S5. Anisotropic displacement parameters ($Å^2$x 10^3) for **1-HBr**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	11(1)	15(1)	14(1)	1(1)	1(1)	2(1)

P(1)	10(1)	11(1)	12(1)	1(1)	0(1)	0(1)
Cl(1)	24(1)	15(1)	21(1)	0	-2(1)	0
C(1)	12(1)	13(1)	15(1)	0	0(1)	0
C(2)	12(1)	19(1)	17(1)	2(1)	0(1)	2(1)
C(3)	17(1)	19(1)	23(1)	0(1)	1(1)	6(1)
C(4)	17(1)	22(1)	20(1)	-3(1)	2(1)	4(1)
C(5)	16(1)	22(1)	15(1)	-2(1)	1(1)	2(1)
C(6)	14(1)	17(1)	14(1)	3(1)	1(1)	2(1)
C(7)	11(1)	15(1)	14(1)	2(1)	-1(1)	-2(1)
C(8)	17(1)	16(1)	17(1)	-1(1)	-1(1)	-2(1)
C(9)	18(1)	25(1)	15(1)	1(1)	0(1)	-3(1)
C(10)	14(1)	24(1)	20(1)	8(1)	-1(1)	-3(1)
C(11)	14(1)	16(1)	25(1)	4(1)	-1(1)	-1(1)
C(12)	11(1)	16(1)	18(1)	-1(1)	1(1)	-1(1)
C(13)	12(1)	14(1)	14(1)	-1(1)	1(1)	-2(1)
C(14)	15(1)	16(1)	21(1)	2(1)	-1(1)	-1(1)
C(15)	13(1)	24(1)	23(1)	0(1)	-2(1)	-2(1)
C(16)	17(1)	20(1)	24(1)	-2(1)	1(1)	-7(1)
C(17)	23(1)	14(1)	24(1)	2(1)	1(1)	-4(1)
C(18)	16(1)	18(1)	17(1)	1(1)	-1(1)	0(1)
C11	21(2)	25(2)	36(2)	-9(1)	-5(1)	-3(1)
C21	20(5)	49(8)	44(5)	-19(4)	-2(4)	3(4)
C31	23(2)	72(3)	35(2)	-20(2)	2(1)	-3(2)
C41	32(4)	61(6)	44(6)	-10(4)	-11(3)	-15(3)
C51	33(2)	27(2)	48(2)	-9(2)	-13(2)	-2(1)
C61	19(5)	22(5)	45(5)	-15(4)	-8(3)	4(3)
C71	57(7)	53(6)	43(6)	11(5)	-7(5)	-22(4)

3.2.2. Crystal structure determination of **1**

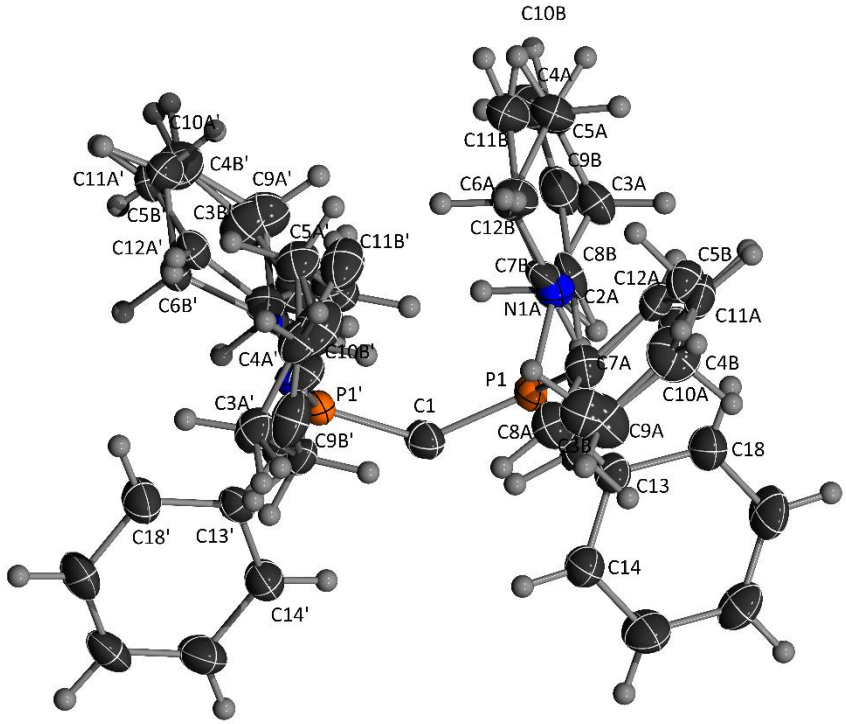


Figure S20. ORTEP Plot of compound **1**. Ellipsoids are drawn at the 50% probability level.

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	5386(1)	1984(1)	3205(1)	27(1)
C(1)	5000	2618(5)	2500	36(1)
N(1A)	4772(10)	933(10)	3662(8)	31(2)
C(2A)	4002(7)	1549(9)	3939(5)	29(2)
C(3A)	3656(6)	643(9)	4466(4)	38(2)
C(4A)	3425(10)	-785(11)	4195(8)	40(2)
C(5A)	4190(5)	-1430(8)	3887(4)	40(2)
C(6A)	4535(11)	-458(13)	3387(8)	32(2)
N(1B)	6366(11)	1120(30)	3217(10)	24(2)
C(2B)	7083(8)	1702(13)	2863(6)	30(2)
C(3B)	7725(15)	600(30)	2663(10)	47(3)
C(4B)	8098(16)	-190(30)	3256(14)	42(3)
C(5B)	7375(13)	-800(19)	3625(11)	36(4)

C(6B)	6753(10)	357(14)	3795(7)	28(3)
C(7A)	6413(11)	950(30)	3214(10)	35(3)
C(8A)	6948(6)	1310(11)	2733(5)	42(2)
C(9A)	7791(10)	730(20)	2763(8)	56(4)
C(10A)	8057(12)	-290(30)	3213(10)	49(4)
C(11A)	7500(9)	-599(15)	3692(8)	36(3)
C(12A)	6664(7)	-13(11)	3689(5)	33(2)
C(7B)	4673(18)	780(17)	3621(14)	33(3)
C(8B)	4134(10)	1312(15)	4064(8)	35(3)
C(9B)	3461(9)	454(17)	4251(6)	48(3)
C(10B)	3395(17)	-935(19)	4065(13)	59(5)
C(11B)	3959(8)	-1408(12)	3619(7)	50(3)
C(12B)	4632(17)	-590(20)	3406(14)	42(4)
C(13)	5638(2)	3407(3)	3768(1)	30(1)
C(14)	5674(2)	4763(3)	3525(2)	40(1)
C(15)	5891(3)	5883(4)	3939(2)	50(1)
C(16)	6151(3)	5648(4)	4596(2)	45(1)
C(17)	6120(3)	4297(4)	4845(2)	48(1)
C(18)	5916(2)	3176(4)	4430(2)	42(1)

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	35(1)	25(1)	22(1)	-2(1)	0(1)	2(1)
C(1)	50(3)	29(2)	28(2)	0	3(2)	0
N(1A)	36(4)	25(3)	31(4)	-1(2)	2(3)	1(2)
C(2A)	35(4)	30(3)	23(4)	5(3)	0(3)	7(3)
C(3A)	43(4)	42(3)	28(4)	8(3)	4(3)	3(3)
C(4A)	45(4)	38(4)	37(5)	12(3)	4(3)	0(3)
C(5A)	48(4)	31(3)	40(4)	9(3)	2(3)	-3(3)
C(6A)	43(5)	26(3)	26(4)	3(3)	0(3)	3(3)
N(1B)	36(4)	16(5)	18(4)	-6(3)	1(4)	-1(3)
C(2B)	35(4)	35(6)	20(5)	-8(4)	1(3)	-8(4)
C(3B)	41(6)	50(6)	50(6)	0(5)	14(4)	4(5)
C(4B)	43(6)	39(7)	46(6)	-11(5)	7(5)	5(5)
C(5B)	35(6)	34(6)	39(7)	-3(5)	-5(6)	5(5)

C(6B)	29(5)	27(6)	25(5)	-3(4)	-5(3)	-2(4)
C(7A)	37(4)	35(7)	32(5)	-3(4)	2(3)	8(4)
C(8A)	43(4)	45(5)	39(5)	-1(4)	6(3)	3(4)
C(9A)	48(5)	66(7)	58(6)	10(5)	18(5)	14(5)
C(10A)	43(5)	51(7)	52(6)	-4(5)	2(4)	8(4)
C(11A)	37(4)	36(4)	32(4)	-9(3)	-12(3)	3(4)
C(12A)	36(3)	31(5)	30(4)	-6(3)	-6(3)	-4(3)
C(7B)	39(6)	28(4)	32(6)	12(4)	2(5)	1(4)
C(8B)	36(5)	43(5)	25(6)	12(4)	-4(4)	11(4)
C(9B)	42(5)	64(5)	38(7)	18(5)	-1(5)	-2(4)
C(10B)	56(7)	57(6)	63(10)	25(5)	1(7)	-4(5)
C(11B)	57(6)	40(4)	51(6)	14(5)	-11(5)	-11(4)
C(12B)	51(7)	29(4)	46(8)	6(4)	-4(6)	0(5)
C(13)	34(2)	31(2)	24(1)	-4(1)	5(1)	3(1)
C(14)	51(2)	34(2)	33(2)	-2(1)	-2(2)	-2(2)
C(15)	71(3)	31(2)	45(2)	-6(2)	3(2)	2(2)
C(16)	53(2)	42(2)	40(2)	-19(2)	4(2)	-3(2)
C(17)	64(2)	53(2)	27(2)	-12(2)	0(2)	2(2)
C(18)	52(2)	41(2)	31(2)	-1(1)	-2(1)	-4(2)

3.2.3. Crystal structure determination of **1-GaCl$_3$**

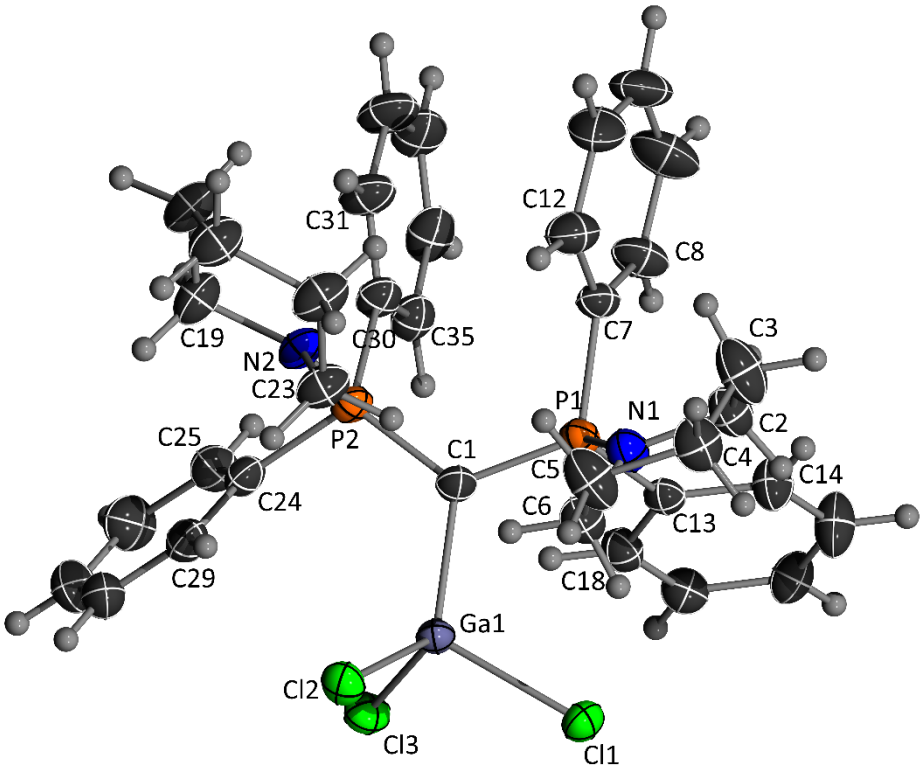


Figure S21. ORTEP Plot of compound **1-GaCl$_3$**. Ellipsoids are drawn at the 50% probability level.

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1-GaCl$_3$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ga(1)	2625(1)	3121(1)	7361(1)	24(1)
Cl(1)	1297(1)	2250(1)	7555(1)	34(1)
N(1)	4774(2)	1478(1)	7919(1)	32(1)
P(1)	4484(1)	1875(1)	7039(1)	26(1)
C(1)	4265(2)	2773(1)	7070(1)	27(1)
Cl(2)	3046(1)	3683(1)	8488(1)	33(1)
C(2)	5021(3)	715(1)	7998(2)	38(1)
N(2)	6725(2)	3532(1)	7604(1)	31(1)
P(2)	5405(1)	3365(1)	6872(1)	26(1)
Cl(3)	1294(1)	3801(1)	6510(1)	33(1)
C(3)	5971(4)	497(2)	8715(2)	54(1)
C(4)	5653(3)	824(2)	9415(2)	42(1)
C(6)	4488(3)	1807(1)	8599(2)	37(1)
C(29)	4391(3)	4646(1)	7203(2)	34(1)
C(24)	4636(2)	4226(1)	6610(1)	31(1)
C(23)	6727(3)	3350(2)	8404(1)	38(1)

C(22)	8138(3)	3175(2)	8846(2)	45(1)
C(21)	9100(3)	3787(2)	8831(2)	45(1)
C(20)	9047(3)	3995(2)	8005(2)	45(1)
C(30)	6135(3)	3104(1)	6085(1)	32(1)
C(35)	5309(3)	2996(1)	5352(2)	35(1)
C(31)	7521(3)	3002(2)	6208(2)	42(1)
C(34)	5889(3)	2814(2)	4749(2)	43(1)
C(25)	4322(3)	4501(2)	5865(2)	39(1)
C(16)	961(3)	894(1)	5229(2)	39(1)
C(15)	1833(3)	463(2)	5735(2)	49(1)
C(14)	2880(3)	748(1)	6295(2)	38(1)
C(13)	3062(2)	1484(1)	6354(1)	26(1)
C(12)	7183(3)	1574(2)	7260(2)	44(1)
C(11)	8275(3)	1262(2)	7071(2)	59(1)
C(10)	8178(3)	991(2)	6343(2)	60(1)
C(9)	6938(4)	998(2)	5805(2)	63(1)
C(8)	5838(3)	1309(2)	5982(2)	42(1)
C(7)	5917(2)	1572(1)	6725(1)	29(1)
C(28)	3837(3)	5312(2)	7052(2)	42(1)
C(18)	2171(3)	1914(1)	5835(2)	34(1)
C(19)	7603(3)	4148(2)	7566(2)	39(1)
C(17)	1122(3)	1623(1)	5281(2)	35(1)
C(33)	7266(3)	2715(2)	4883(2)	49(1)
C(5)	5447(4)	1604(2)	9314(2)	49(1)
C(27)	3540(3)	5576(2)	6313(2)	49(1)
C(32)	8078(3)	2801(2)	5609(2)	51(1)
C(26)	3779(3)	5173(2)	5720(2)	49(1)

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-GaCl₃**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ga(1)	26(1)	25(1)	25(1)	0(1)	11(1)	0(1)
Cl(1)	35(1)	32(1)	40(1)	0(1)	18(1)	-6(1)
N(1)	38(1)	30(1)	30(1)	1(1)	12(1)	2(1)
P(1)	27(1)	27(1)	25(1)	-2(1)	10(1)	2(1)
C(1)	28(1)	28(1)	27(1)	-2(1)	12(1)	-1(1)
Cl(2)	40(1)	33(1)	28(1)	-6(1)	14(1)	-2(1)
C(2)	51(2)	32(1)	34(1)	3(1)	14(1)	6(1)

N(2)	30(1)	37(1)	26(1)	1(1)	10(1)	-6(1)
P(2)	27(1)	31(1)	24(1)	0(1)	11(1)	-2(1)
Cl(3)	31(1)	35(1)	33(1)	5(1)	9(1)	4(1)
C(3)	82(2)	38(2)	39(2)	2(1)	7(2)	15(2)
C(4)	56(2)	39(2)	30(1)	6(1)	10(1)	4(1)
C(6)	49(2)	33(1)	32(1)	2(1)	17(1)	3(1)
C(29)	34(1)	34(1)	36(1)	-1(1)	13(1)	-6(1)
C(24)	28(1)	33(1)	33(1)	1(1)	12(1)	-6(1)
C(23)	35(1)	52(2)	29(1)	3(1)	11(1)	-5(1)
C(22)	38(2)	59(2)	35(2)	9(1)	7(1)	-5(1)
C(21)	36(2)	57(2)	40(2)	3(1)	3(1)	-6(1)
C(20)	35(1)	54(2)	45(2)	3(1)	10(1)	-13(1)
C(30)	34(1)	38(1)	27(1)	0(1)	16(1)	-4(1)
C(35)	40(1)	37(1)	32(1)	0(1)	14(1)	-5(1)
C(31)	36(1)	58(2)	38(2)	-6(1)	18(1)	-4(1)
C(34)	58(2)	47(2)	28(1)	-3(1)	17(1)	-14(1)
C(25)	45(2)	40(1)	35(1)	5(1)	16(1)	2(1)
C(16)	40(1)	39(1)	36(1)	-1(1)	5(1)	-10(1)
C(15)	63(2)	31(1)	49(2)	2(1)	2(2)	-10(1)
C(14)	43(2)	30(1)	36(1)	2(1)	3(1)	-2(1)
C(13)	29(1)	28(1)	25(1)	-2(1)	12(1)	1(1)
C(12)	33(1)	51(2)	49(2)	6(1)	14(1)	4(1)
C(11)	33(2)	55(2)	89(3)	5(2)	12(2)	10(1)
C(10)	44(2)	63(2)	83(3)	7(2)	38(2)	17(2)
C(9)	65(2)	72(2)	59(2)	-8(2)	29(2)	23(2)
C(8)	43(2)	51(2)	37(2)	1(1)	20(1)	12(1)
C(7)	26(1)	32(1)	32(1)	4(1)	13(1)	3(1)
C(28)	44(2)	34(1)	53(2)	-5(1)	19(1)	-4(1)
C(18)	39(1)	31(1)	33(1)	-3(1)	12(1)	2(1)
C(19)	39(1)	44(2)	35(1)	4(1)	7(1)	-12(1)
C(17)	36(1)	37(1)	31(1)	2(1)	7(1)	3(1)
C(33)	56(2)	57(2)	46(2)	-11(1)	35(2)	-11(1)
C(5)	74(2)	44(2)	27(1)	0(1)	10(1)	15(2)
C(27)	51(2)	35(2)	63(2)	7(1)	18(2)	6(1)
C(32)	40(2)	71(2)	50(2)	-10(2)	28(1)	-7(1)
C(26)	56(2)	46(2)	46(2)	14(1)	16(1)	4(1)

3.2.4. Crystal structure determination of **1-Rh**

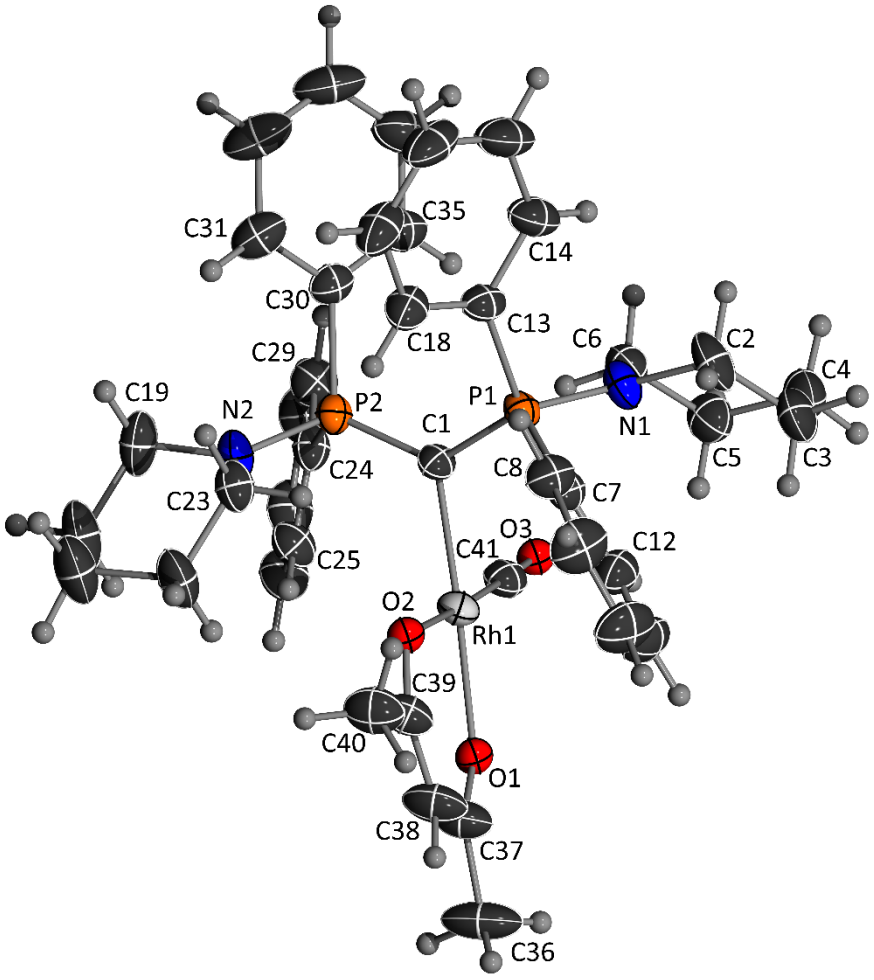


Figure S22. ORTEP Plot of compound **1-Rh**. Ellipsoids are drawn at the 50% probability level.

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1-Rh**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	3382(2)	3683(2)	8058(2)	38(1)
N(2)	-530(2)	3226(2)	7602(2)	38(1)
P(2)	471(1)	3604(1)	7666(1)	29(1)
O(2)	981(2)	2422(1)	10096(1)	41(1)
Rh(2)	4994(1)	2749(1)	4101(1)	30(1)
C(10)	2436(3)	2007(3)	5430(2)	60(1)
C(11)	1740(3)	1775(3)	5848(2)	54(1)
C(41)	1608(2)	3640(2)	9286(2)	35(1)
C(12)	1742(2)	1928(2)	6535(2)	41(1)
C(37)	674(3)	1106(2)	9208(2)	42(1)

C(18)	3043(3)	1350(2)	8770(2)	43(1)
C(35)	253(3)	3825(2)	6264(2)	48(1)
C(32)	1785(3)	4621(2)	6118(2)	55(1)
C(8)	3118(3)	2550(2)	6388(2)	46(1)
C(26)	-187(3)	5944(2)	8355(2)	49(1)
P(1)	2448(1)	2461(1)	7724(1)	28(1)
Rh(1)	1218(1)	2731(1)	9090(1)	30(1)
O(1)	806(2)	1673(1)	8813(1)	37(1)
N(1)	3423(2)	2836(2)	7915(1)	38(1)
C(1)	1405(2)	2977(2)	8061(1)	28(1)
C(22)	-1262(3)	2098(2)	7979(2)	53(1)
C(33)	1265(4)	4480(3)	5559(2)	64(1)
C(30)	776(2)	3962(2)	6834(2)	34(1)
C(13)	2796(2)	1432(2)	8083(2)	32(1)
C(38)	677(3)	1112(2)	9917(2)	53(1)
C(15)	2978(3)	-23(2)	8041(2)	57(1)
C(25)	114(3)	5281(2)	7934(2)	40(1)
C(39)	799(3)	1760(2)	10313(2)	49(1)
C(24)	14(2)	4515(2)	8148(2)	34(1)
C(20)	-2265(3)	3494(3)	7889(3)	62(1)
C(34)	492(4)	4092(3)	5630(2)	65(1)
C(31)	1537(3)	4363(2)	6755(2)	44(1)
C(40)	689(5)	1697(3)	11071(2)	70(1)
C(36)	491(3)	362(2)	8853(2)	54(1)
C(4)	5053(3)	3289(3)	8576(2)	54(1)
O(4)	6003(2)	1712(1)	3842(1)	37(1)
N(4)	2719(2)	2748(2)	2985(1)	35(1)
C(5)	5056(3)	2408(3)	8425(2)	57(1)
O(5)	5413(2)	2509(1)	5106(1)	38(1)
C(7)	2424(2)	2310(2)	6811(2)	34(1)
C(76)	4799(2)	1909(2)	1529(2)	37(1)
C(71)	3933(2)	2269(2)	1855(1)	33(1)
C(65)	4123(2)	1388(2)	3156(2)	34(1)
P(3)	5222(1)	3585(1)	2647(1)	29(1)
C(3)	4009(3)	3763(2)	8668(2)	48(1)
O(3)	1869(2)	4231(1)	9395(1)	43(1)
N(3)	6412(2)	3225(2)	2534(2)	39(1)
C(78)	6494(2)	1195(2)	4254(2)	37(1)
P(4)	3884(1)	2401(1)	2769(1)	29(1)

C(55)	4658(3)	5245(2)	2954(2)	44(1)
C(54)	5216(2)	4495(2)	3129(2)	33(1)
C(6)	4427(3)	2361(3)	7816(2)	54(1)
O(6)	3533(2)	4227(2)	4407(1)	45(1)
C(48)	4690(3)	3949(2)	1830(2)	37(1)
C(42)	4653(2)	2944(2)	3073(1)	28(1)
C(72)	3114(3)	2563(2)	1458(2)	41(1)
C(66)	3900(2)	1326(2)	3842(2)	38(1)
C(14)	2790(3)	740(2)	7717(2)	42(1)
C(82)	4110(2)	3651(2)	4296(2)	36(1)
C(79)	6528(3)	1253(2)	4955(2)	38(1)
C(16)	3184(3)	-90(2)	8717(2)	61(1)
C(80)	6023(3)	1898(2)	5334(2)	38(1)
C(19)	-1490(3)	3730(2)	7440(2)	52(1)
C(74)	3996(3)	2123(2)	451(2)	52(1)
C(47)	6833(2)	2364(2)	2473(2)	38(1)
C(67)	4175(3)	592(2)	4192(2)	47(1)
C(49)	3721(3)	4345(2)	1774(2)	46(1)
C(70)	4589(3)	691(2)	2824(2)	45(1)
C(59)	5761(3)	4423(2)	3724(2)	42(1)
C(58)	5696(3)	5082(2)	4149(2)	47(1)
C(60)	2310(2)	3613(2)	3100(2)	41(1)
C(63)	1286(3)	2347(3)	3490(2)	55(1)
C(50)	3328(4)	4629(3)	1145(2)	65(1)
C(77)	7093(3)	452(2)	3932(2)	52(1)
C(75)	4821(3)	1833(2)	826(2)	45(1)
C(21)	-2281(3)	2597(3)	7829(3)	66(1)
C(64)	1976(3)	2264(2)	2892(2)	47(1)
C(23)	-491(2)	2355(2)	7538(2)	38(1)
C(57)	5113(3)	5817(2)	3974(2)	49(1)
C(27)	-582(3)	5854(2)	8978(2)	48(1)
C(61)	1613(3)	3713(3)	3699(2)	54(1)
C(28)	-711(3)	5099(2)	9188(2)	48(1)
C(62)	824(3)	3227(3)	3618(2)	58(1)
C(29)	-427(2)	4429(2)	8775(2)	40(1)
C(45)	8495(3)	2659(3)	2643(3)	73(1)
C(51)	3894(5)	4515(3)	574(2)	80(1)
C(46)	7782(3)	2132(3)	2864(2)	56(1)
C(43)	7077(3)	3749(2)	2325(3)	63(1)

C(9)	3099(3)	2390(3)	5691(2)	58(1)
C(81)	6214(3)	1897(2)	6092(2)	47(1)
C(52)	4834(5)	4120(3)	621(2)	78(1)
C(44)	8012(3)	3542(3)	2716(3)	82(2)
C(53)	5245(4)	3828(2)	1240(2)	56(1)
C(56)	4603(3)	5901(2)	3379(2)	53(1)
C(73)	3128(3)	2492(2)	763(2)	51(1)
C(17)	3235(3)	604(3)	9083(2)	54(1)
C(68)	4643(3)	-82(2)	3861(2)	54(1)
C(69)	4860(4)	-35(2)	3176(2)	59(1)

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-Rh**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2)	36(2)	44(2)	38(2)	-3(1)	3(1)	-13(1)
N(2)	26(1)	33(1)	52(2)	-4(1)	-3(1)	-4(1)
P(2)	27(1)	27(1)	31(1)	-2(1)	0(1)	-3(1)
O(2)	55(1)	40(1)	29(1)	-1(1)	11(1)	-14(1)
Rh(2)	34(1)	30(1)	26(1)	-4(1)	-2(1)	-6(1)
C(10)	67(3)	72(3)	28(2)	-4(2)	0(2)	15(2)
C(11)	51(2)	63(2)	38(2)	-14(2)	-9(2)	11(2)
C(41)	36(2)	38(2)	29(1)	-2(1)	6(1)	-4(1)
C(12)	38(2)	46(2)	34(2)	-8(1)	1(1)	1(1)
C(37)	47(2)	36(2)	44(2)	-2(1)	11(1)	-14(1)
C(18)	40(2)	49(2)	35(2)	-4(1)	-1(1)	0(2)
C(35)	68(2)	37(2)	38(2)	1(1)	-10(2)	-10(2)
C(32)	65(2)	47(2)	51(2)	12(2)	15(2)	-7(2)
C(8)	50(2)	47(2)	40(2)	3(2)	14(2)	-6(2)
C(26)	48(2)	33(2)	64(2)	-12(2)	-1(2)	-5(2)
P(1)	26(1)	29(1)	27(1)	-4(1)	4(1)	-4(1)
Rh(1)	31(1)	30(1)	28(1)	-2(1)	6(1)	-7(1)
O(1)	41(1)	35(1)	37(1)	-1(1)	3(1)	-13(1)
N(1)	27(1)	42(2)	46(2)	-11(1)	7(1)	-8(1)
C(1)	28(1)	30(1)	26(1)	-3(1)	4(1)	-3(1)
C(22)	33(2)	51(2)	79(3)	-3(2)	3(2)	-15(2)
C(33)	103(4)	53(2)	32(2)	6(2)	12(2)	-9(2)
C(30)	39(2)	27(1)	33(2)	0(1)	0(1)	-1(1)
C(13)	28(1)	33(1)	34(1)	-1(1)	3(1)	0(1)

C(38)	77(3)	42(2)	46(2)	0(2)	18(2)	-27(2)
C(15)	69(3)	32(2)	63(2)	-4(2)	0(2)	4(2)
C(25)	45(2)	32(1)	44(2)	-7(1)	1(1)	-5(1)
C(39)	65(2)	48(2)	37(2)	1(1)	13(2)	-21(2)
C(24)	30(1)	32(1)	38(1)	-6(1)	-1(1)	-2(1)
C(20)	28(2)	60(2)	98(3)	-15(2)	-1(2)	-3(2)
C(34)	107(4)	53(2)	36(2)	4(2)	-13(2)	-19(2)
C(31)	50(2)	41(2)	37(2)	5(1)	4(1)	-5(2)
C(40)	123(4)	60(2)	39(2)	-1(2)	24(2)	-43(3)
C(36)	73(3)	43(2)	52(2)	-1(2)	6(2)	-26(2)
C(4)	38(2)	78(3)	49(2)	-2(2)	-3(2)	-20(2)
O(4)	43(1)	34(1)	31(1)	-5(1)	-1(1)	-3(1)
N(4)	28(1)	44(2)	36(1)	-8(1)	1(1)	-11(1)
C(5)	29(2)	72(3)	69(3)	3(2)	7(2)	-7(2)
O(5)	48(1)	36(1)	28(1)	-5(1)	-5(1)	-2(1)
C(7)	38(2)	33(1)	28(1)	-2(1)	7(1)	1(1)
C(76)	41(2)	42(2)	27(1)	-4(1)	-2(1)	-9(1)
C(71)	40(2)	35(2)	26(1)	-4(1)	-3(1)	-13(1)
C(65)	40(2)	34(2)	31(1)	-1(1)	-2(1)	-15(1)
P(3)	31(1)	26(1)	30(1)	-2(1)	0(1)	-6(1)
C(3)	46(2)	59(2)	44(2)	-10(2)	0(2)	-18(2)
O(3)	49(1)	41(1)	42(1)	-10(1)	7(1)	-17(1)
N(3)	31(1)	30(1)	56(2)	-5(1)	7(1)	-9(1)
C(78)	43(2)	31(2)	37(2)	-3(1)	-1(1)	-6(1)
P(4)	31(1)	33(1)	25(1)	-4(1)	0(1)	-10(1)
C(55)	57(2)	34(2)	40(2)	-4(1)	-3(2)	-7(2)
C(54)	35(2)	30(1)	35(1)	-5(1)	2(1)	-11(1)
C(6)	29(2)	60(2)	72(3)	-16(2)	16(2)	-10(2)
O(6)	42(1)	46(1)	44(1)	-14(1)	-5(1)	2(1)
C(48)	53(2)	29(1)	30(1)	0(1)	-3(1)	-10(1)
C(42)	31(1)	32(1)	22(1)	-2(1)	-4(1)	-9(1)
C(72)	42(2)	44(2)	35(2)	-4(1)	-5(1)	-10(1)
C(66)	44(2)	43(2)	30(2)	-4(1)	2(1)	-16(1)
C(14)	49(2)	35(2)	38(2)	-4(1)	3(1)	-1(1)
C(82)	39(2)	42(2)	28(1)	-6(1)	-3(1)	-10(1)
C(79)	46(2)	34(2)	34(2)	-1(1)	-4(1)	-4(1)
C(16)	72(3)	42(2)	58(2)	10(2)	-1(2)	13(2)
C(80)	49(2)	33(2)	32(2)	-3(1)	-5(1)	-10(1)
C(19)	38(2)	40(2)	75(3)	-6(2)	-16(2)	-1(2)

C(74)	76(3)	59(2)	22(1)	-5(1)	-4(2)	-19(2)
C(47)	32(2)	34(2)	47(2)	-6(1)	4(1)	-6(1)
C(67)	61(2)	49(2)	34(2)	4(1)	3(2)	-20(2)
C(49)	53(2)	43(2)	41(2)	6(1)	-11(2)	-12(2)
C(70)	64(2)	39(2)	37(2)	-7(1)	10(2)	-18(2)
C(59)	42(2)	38(2)	46(2)	-8(1)	-6(1)	-10(1)
C(58)	55(2)	46(2)	46(2)	-12(2)	-3(2)	-19(2)
C(60)	36(2)	48(2)	38(2)	-5(1)	-2(1)	-4(1)
C(63)	40(2)	81(3)	49(2)	10(2)	-5(2)	-25(2)
C(50)	81(3)	51(2)	62(3)	15(2)	-31(2)	-13(2)
C(77)	64(2)	42(2)	41(2)	-7(2)	0(2)	8(2)
C(75)	55(2)	50(2)	31(2)	-7(1)	5(1)	-10(2)
C(21)	34(2)	62(3)	104(4)	-6(2)	3(2)	-13(2)
C(64)	38(2)	57(2)	50(2)	-6(2)	-4(2)	-18(2)
C(23)	32(2)	35(2)	48(2)	-9(1)	-1(1)	-7(1)
C(57)	56(2)	42(2)	54(2)	-19(2)	9(2)	-19(2)
C(27)	40(2)	42(2)	58(2)	-21(2)	0(2)	1(2)
C(61)	43(2)	71(3)	47(2)	-15(2)	10(2)	-11(2)
C(28)	44(2)	50(2)	47(2)	-16(2)	7(2)	-1(2)
C(62)	39(2)	86(3)	50(2)	-7(2)	8(2)	-15(2)
C(29)	36(2)	38(2)	44(1)	-8(1)	8(1)	-2(1)
C(45)	34(2)	78(3)	109(4)	-19(3)	7(2)	-19(2)
C(51)	151(4)	47(2)	36(2)	6(2)	-20(2)	-9(2)
C(46)	34(2)	55(2)	75(3)	-5(2)	-4(2)	-5(2)
C(43)	50(2)	39(2)	104(4)	-10(2)	31(2)	-19(2)
C(9)	65(3)	63(2)	41(2)	9(2)	18(2)	-4(2)
C(81)	64(2)	44(2)	31(2)	-4(1)	-10(2)	-6(2)
C(52)	146(4)	51(2)	34(2)	1(2)	6(2)	-9(2)
C(44)	47(2)	77(3)	132(5)	-42(3)	25(3)	-37(2)
C(53)	90(3)	38(2)	38(2)	1(2)	11(2)	-4(2)
C(56)	68(3)	32(2)	56(2)	-10(2)	2(2)	-6(2)
C(73)	62(2)	60(2)	33(2)	-2(2)	-16(2)	-18(2)
C(17)	52(2)	58(2)	43(2)	12(2)	-5(2)	5(2)
C(68)	73(3)	41(2)	52(2)	7(2)	5(2)	-17(2)
C(69)	86(3)	36(2)	55(2)	-6(2)	18(2)	-16(2)

3.2.5. Crystal structure determination of **1-ZnCl$_2$**

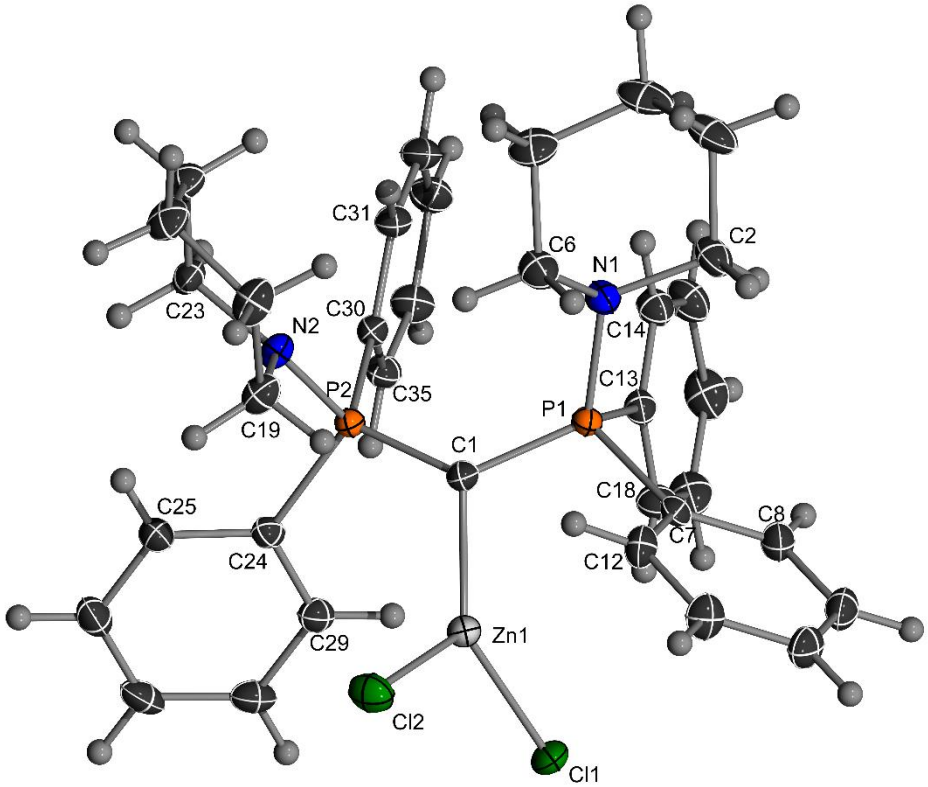


Figure S23. ORTEP Plot of compound **1-ZnCl$_2$**. Ellipsoids are drawn at the 50% probability level.

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1-ZnCl$_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	1045(1)	2466(1)	5266(1)	18(1)
Cl(1)	-163(1)	1894(1)	4334(1)	26(1)
N(1)	5264(2)	1728(1)	5893(1)	20(1)
P(1)	3863(1)	1806(1)	5296(1)	15(1)
C(1)	3013(2)	2602(1)	5319(1)	17(1)
P(2)	3618(1)	3441(1)	5156(1)	15(1)
Cl(2)	-128(1)	2934(1)	6112(1)	28(1)
C(2)	5887(2)	996(1)	5970(1)	26(1)
N(2)	4196(1)	3901(1)	5925(1)	18(1)
C(4)	7504(2)	1466(1)	7009(1)	33(1)
C(3)	7354(2)	1075(1)	6266(1)	33(1)
C(7)	2739(2)	1092(1)	5531(1)	18(1)
C(6)	5306(2)	2095(1)	6615(1)	25(1)
C(5)	6752(2)	2193(1)	6952(1)	30(1)
C(9)	1722(2)	-107(1)	5385(1)	26(1)
C(8)	2587(2)	417(1)	5165(1)	23(1)

C(10)	999(2)	28(1)	5972(1)	26(1)
C(13)	4393(2)	1570(1)	4409(1)	18(1)
C(12)	2036(2)	1216(1)	6137(1)	23(1)
C(11)	1151(2)	694(1)	6346(1)	26(1)
C(14)	5731(2)	1571(1)	4288(1)	22(1)
C(15)	6084(2)	1443(1)	3586(1)	28(1)
C(16)	5108(2)	1314(1)	2997(1)	31(1)
C(17)	3772(2)	1324(1)	3112(1)	30(1)
C(18)	3406(2)	1457(1)	3810(1)	23(1)
C(19)	3417(2)	3887(1)	6562(1)	24(1)
C(20)	4338(2)	3924(1)	7290(1)	27(1)
C(21)	5293(2)	4577(1)	7304(1)	27(1)
C(22)	6035(2)	4578(1)	6623(1)	23(1)
C(23)	5038(2)	4564(1)	5928(1)	20(1)
C(24)	2296(2)	3971(1)	4635(1)	18(1)
C(25)	2077(2)	4708(1)	4806(1)	21(1)
C(26)	1102(2)	5116(1)	4385(1)	26(1)
C(27)	329(2)	4796(1)	3792(1)	28(1)
C(28)	514(2)	4062(1)	3625(1)	26(1)
C(29)	1489(2)	3648(1)	4042(1)	21(1)
C(30)	5003(2)	3433(1)	4608(1)	17(1)
C(31)	6319(2)	3348(1)	4941(1)	21(1)
C(32)	7350(2)	3276(1)	4512(1)	26(1)
C(33)	7091(2)	3271(1)	3746(1)	27(1)
C(34)	5791(2)	3344(1)	3408(1)	25(1)
C(35)	4752(2)	3429(1)	3834(1)	20(1)

Table S13 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-ZnCl₂**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	15(1)	17(1)	22(1)	-1(1)	1(1)	-1(1)
Cl(1)	21(1)	22(1)	32(1)	-7(1)	-4(1)	-2(1)
N(1)	21(1)	21(1)	16(1)	-2(1)	-1(1)	3(1)
P(1)	15(1)	15(1)	16(1)	-1(1)	-1(1)	1(1)
C(1)	15(1)	16(1)	19(1)	0(1)	0(1)	-1(1)
P(2)	15(1)	14(1)	16(1)	0(1)	0(1)	0(1)
Cl(2)	24(1)	35(1)	26(1)	-4(1)	5(1)	4(1)
C(2)	28(1)	26(1)	23(1)	-1(1)	-4(1)	9(1)

N(2)	20(1)	16(1)	16(1)	-2(1)	2(1)	-3(1)
C(4)	23(1)	52(1)	21(1)	-1(1)	-6(1)	7(1)
C(3)	25(1)	47(1)	25(1)	-3(1)	-5(1)	15(1)
C(7)	17(1)	15(1)	21(1)	2(1)	-3(1)	3(1)
C(6)	27(1)	27(1)	20(1)	-3(1)	-2(1)	4(1)
C(5)	29(1)	39(1)	21(1)	-4(1)	-6(1)	-4(1)
C(9)	31(1)	17(1)	29(1)	-1(1)	1(1)	-1(1)
C(8)	25(1)	18(1)	26(1)	-2(1)	2(1)	2(1)
C(10)	29(1)	18(1)	29(1)	6(1)	3(1)	-4(1)
C(13)	21(1)	16(1)	18(1)	-1(1)	0(1)	2(1)
C(12)	30(1)	17(1)	23(1)	0(1)	3(1)	0(1)
C(11)	33(1)	24(1)	24(1)	2(1)	8(1)	-1(1)
C(14)	23(1)	23(1)	20(1)	-1(1)	0(1)	3(1)
C(15)	28(1)	32(1)	26(1)	-2(1)	6(1)	7(1)
C(16)	41(1)	33(1)	18(1)	-2(1)	5(1)	6(1)
C(17)	36(1)	32(1)	20(1)	-4(1)	-5(1)	3(1)
C(18)	22(1)	25(1)	22(1)	-1(1)	-3(1)	1(1)
C(19)	25(1)	26(1)	22(1)	-5(1)	7(1)	-6(1)
C(20)	38(1)	28(1)	17(1)	-4(1)	6(1)	-6(1)
C(21)	31(1)	28(1)	22(1)	-8(1)	0(1)	-4(1)
C(22)	23(1)	24(1)	21(1)	-4(1)	-1(1)	-4(1)
C(23)	22(1)	17(1)	22(1)	-2(1)	0(1)	-4(1)
C(24)	15(1)	18(1)	20(1)	2(1)	3(1)	0(1)
C(25)	18(1)	19(1)	27(1)	0(1)	3(1)	1(1)
C(26)	23(1)	21(1)	36(1)	5(1)	7(1)	5(1)
C(27)	18(1)	32(1)	33(1)	10(1)	2(1)	7(1)
C(28)	18(1)	33(1)	25(1)	4(1)	-2(1)	-1(1)
C(29)	19(1)	21(1)	22(1)	2(1)	1(1)	-1(1)
C(30)	15(1)	15(1)	20(1)	0(1)	1(1)	-1(1)
C(31)	18(1)	22(1)	22(1)	-2(1)	-2(1)	0(1)
C(32)	17(1)	28(1)	32(1)	-4(1)	-1(1)	1(1)
C(33)	19(1)	31(1)	31(1)	-1(1)	8(1)	1(1)
C(34)	24(1)	30(1)	21(1)	2(1)	3(1)	0(1)
C(35)	18(1)	21(1)	20(1)	1(1)	0(1)	1(1)

3.2.6. Crystal structure determination of **1-InCl$_3$**

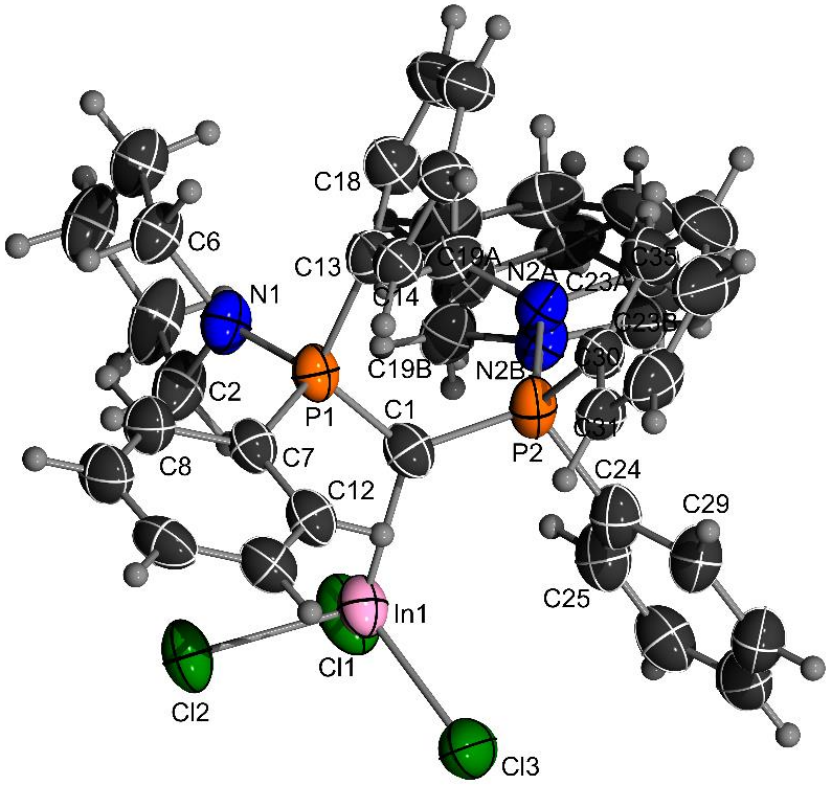


Figure S24. ORTEP Plot of compound **1-InCl$_3$**. Ellipsoids are drawn at the 50% probability level.

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-InCl$_3$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	x	y	z	U(eq)
In(1)	242(1)	3714(1)	1671(1)	50(1)
Cl(1)	-408(2)	3795(1)	-667(1)	73(1)
N(1)	3124(4)	4596(1)	2540(4)	50(1)
P(1)	3134(1)	4185(1)	3471(1)	42(1)
C(1)	2467(5)	3754(1)	2611(4)	46(1)
C(3)	2360(8)	4888(2)	306(5)	75(2)
Cl(3)	-839(1)	3124(1)	2167(2)	69(1)
P(2)	3478(1)	3370(1)	2357(1)	48(1)
Cl(2)	-1015(1)	4268(1)	2186(1)	60(1)
C(2)	1926(6)	4694(2)	1378(5)	62(1)
C(5)	4489(6)	5146(2)	2001(5)	60(1)
C(4)	3297(7)	5258(2)	792(6)	70(2)
C(6)	3966(6)	4966(1)	3049(5)	53(1)
C(7)	2246(4)	4289(1)	4644(4)	43(1)
C(9)	1562(5)	4757(2)	6042(5)	58(1)

C(8)	2108(5)	4686(2)	5042(5)	53(1)
C(10)	1152(5)	4434(2)	6650(5)	57(1)
C(11)	1272(5)	4036(2)	6250(5)	52(1)
C(12)	1800(5)	3965(2)	5245(4)	47(1)
C(13)	4940(5)	4135(1)	4460(4)	45(1)
C(14)	5270(5)	4007(1)	5759(4)	43(1)
C(15)	6644(5)	3943(2)	6508(5)	50(1)
C(16)	7681(5)	4008(2)	5974(6)	59(1)
C(17)	7364(6)	4132(2)	4689(6)	65(1)
C(18)	5996(5)	4192(2)	3920(5)	57(1)
C(24)	2424(6)	2928(2)	1650(5)	53(1)
C(25)	1626(6)	2939(2)	336(5)	62(1)
C(26)	819(6)	2607(2)	-251(6)	66(1)
C(27)	843(6)	2254(2)	444(6)	62(1)
C(28)	1648(6)	2236(2)	1738(6)	63(1)
C(29)	2443(6)	2567(2)	2350(5)	58(1)
C(30)	4722(5)	3178(1)	3872(5)	50(1)
C(31)	4236(5)	3073(1)	4891(5)	47(1)
C(32)	5118(6)	2911(2)	6050(6)	65(1)
C(33)	6488(7)	2855(2)	6194(8)	86(2)
C(34)	6987(6)	2961(2)	5226(10)	99(3)
C(35)	6121(6)	3131(2)	4056(8)	76(2)
N(2A)	4496(9)	3496(3)	1461(8)	43(2)
C(19A)	4532(9)	3892(2)	824(7)	47(2)
C(20A)	4001(11)	3853(3)	-669(9)	57(2)
C(21A)	4839(12)	3531(3)	-1127(10)	58(2)
C(22A)	4836(10)	3134(3)	-434(8)	56(2)
C(23A)	5307(10)	3179(3)	1032(9)	50(2)
N(2B)	4013(16)	3455(5)	1095(12)	46(3)
C(19B)	3502(16)	3819(4)	227(14)	57(3)
C(20B)	4672(19)	3986(5)	-164(16)	66(3)
C(21B)	5280(20)	3673(6)	-821(18)	67(3)
C(22B)	5732(17)	3302(6)	46(16)	71(4)
C(23B)	4562(16)	3137(4)	466(15)	53(3)

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-InCl$_3$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
In(1)	54(1)	49(1)	40(1)	2(1)	8(1)	11(1)
Cl(1)	81(1)	86(1)	40(1)	1(1)	5(1)	29(1)
N(1)	63(2)	44(2)	39(2)	5(2)	11(2)	5(2)
P(1)	49(1)	42(1)	36(1)	4(1)	13(1)	8(1)
C(1)	45(2)	52(2)	40(2)	2(2)	11(2)	8(2)
C(3)	120(5)	44(3)	41(3)	11(2)	-3(3)	4(3)
Cl(3)	57(1)	60(1)	86(1)	11(1)	16(1)	4(1)
P(2)	66(1)	40(1)	48(1)	8(1)	31(1)	11(1)
Cl(2)	70(1)	60(1)	49(1)	7(1)	18(1)	24(1)
C(2)	75(3)	45(3)	52(3)	9(2)	-2(2)	4(2)
C(5)	84(4)	52(3)	46(3)	10(2)	22(2)	0(2)
C(4)	106(5)	46(3)	51(3)	9(2)	18(3)	1(3)
C(6)	67(3)	43(2)	44(2)	6(2)	13(2)	-1(2)
C(7)	41(2)	46(2)	39(2)	-1(2)	9(2)	7(2)
C(9)	57(3)	58(3)	63(3)	-16(2)	24(2)	2(2)
C(8)	54(3)	49(2)	59(3)	-8(2)	21(2)	2(2)
C(10)	42(2)	79(3)	54(3)	-12(2)	19(2)	4(2)
C(11)	46(2)	63(3)	48(2)	4(2)	17(2)	7(2)
C(12)	45(2)	52(2)	41(2)	1(2)	12(2)	10(2)
C(13)	49(2)	43(2)	46(2)	9(2)	20(2)	5(2)
C(14)	45(2)	42(2)	45(2)	4(2)	16(2)	1(2)
C(15)	45(2)	53(3)	50(2)	7(2)	12(2)	-1(2)
C(16)	45(2)	59(3)	73(3)	16(2)	20(2)	3(2)
C(17)	52(3)	75(4)	78(4)	21(3)	34(3)	7(2)
C(18)	59(3)	61(3)	58(3)	17(2)	29(2)	8(2)
C(24)	69(3)	48(2)	49(2)	4(2)	28(2)	9(2)
C(25)	75(3)	61(3)	55(3)	4(2)	25(3)	13(3)
C(26)	64(3)	76(4)	57(3)	-1(3)	20(3)	16(3)
C(27)	59(3)	62(3)	71(3)	-10(3)	28(3)	5(2)
C(28)	75(3)	48(3)	67(3)	0(2)	26(3)	4(2)
C(29)	76(3)	46(3)	52(3)	0(2)	23(2)	5(2)
C(30)	48(2)	40(2)	68(3)	12(2)	27(2)	4(2)
C(31)	47(2)	39(2)	53(2)	9(2)	13(2)	0(2)
C(32)	69(3)	52(3)	63(3)	13(2)	7(3)	-4(2)
C(33)	59(3)	66(4)	111(5)	38(4)	-4(3)	-4(3)

C(34)	43(3)	81(4)	165(8)	38(5)	22(4)	15(3)
C(35)	59(3)	61(3)	120(5)	29(3)	47(3)	12(3)
N(2A)	55(5)	41(3)	36(4)	-2(3)	20(4)	-4(3)
C(19A)	54(4)	50(3)	41(3)	4(3)	21(3)	-10(3)
C(20A)	75(5)	57(4)	40(4)	6(3)	21(4)	-9(4)
C(21A)	72(6)	66(5)	43(4)	-11(3)	29(4)	-23(4)
C(22A)	68(5)	61(4)	49(4)	-9(3)	32(4)	-6(4)
C(23A)	51(4)	53(4)	49(4)	-7(3)	22(3)	-2(3)
N(2B)	61(8)	45(5)	36(6)	-5(4)	18(5)	-4(5)
C(19B)	72(8)	51(6)	51(7)	5(5)	25(6)	-3(5)
C(20B)	82(7)	74(6)	48(6)	6(5)	29(5)	-13(5)
C(21B)	72(8)	84(7)	50(7)	-7(5)	28(6)	-22(6)
C(22B)	60(7)	100(9)	63(8)	1(7)	33(7)	1(6)
C(23B)	52(6)	56(5)	52(6)	-10(5)	21(5)	-2(5)

4. Computational Studies

4.1 General

All computational studies were carried out without symmetry restrictions. If it was not possible to obtain starting coordinates from crystal structures either *GaussView 3.0*[5] or *GaussView 6.0*[6] were used. Calculations were performed either with the *Gaussian09 Revision E.01*[7] or the *Gaussian16 Revision C.01*[8] program packages using Density-Functional Theory (DFT).[9,10] Energy optimizations were carried out with the BP86 functional[11] and def2svp basis set[12] as well as the MWB28[13] ECP as implemented in *Gaussian* for Rh together with GRIMMES D3 dispersion correction with Becke-Johnson damping.[14] To determine the nature of the structure harmonic vibrational frequency analyses were performed on the same level of theory.[15] No imaginary frequencies were observed for the ground states. Single point energies were calculated on BP86[11]/def2tzvp[12] level of theory as with the MWB28[13] ECP as implemented in *Gaussian* for Rh.

NBO Analysis was performed with *NBO Version 7.0*.[16]

Chemcraft 3D[17] and *Gimp*[18] were used for graphical representation.

4.2 Coordinates of the optimized structures

4.2.1 Coordinates of 1-$ZnCl_2$

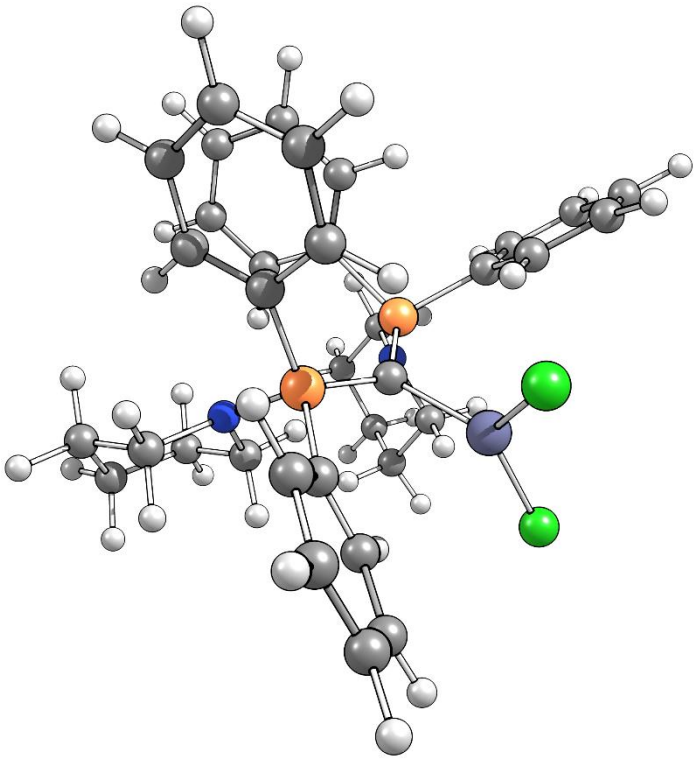


Figure S25. Optimized Structure of **1-$ZnCl_2$**

E = -4851.15022120

Zn -0.961792 -2.313748 -0.476079

C -0.091942 -0.506401 -0.250019

Cl -0.655902 -3.352008 -2.412838

Cl -2.195069 -3.047822 1.245409

N -1.049143 2.153208 -0.936428
C -0.330686 2.045705 -2.213886
C -2.215883 3.048027 -1.007138
P -1.237714 0.715494 -0.008796
C -2.857579 -0.002495 -0.459235
C -1.353229 1.292209 1.718964
P 1.553630 -0.311288 0.092608
N 2.491213 -0.097359 -1.322783
C 1.952129 1.142333 1.121390
C 2.177399 -1.773477 0.998468
C -1.775000 4.460803 -1.407124
H -2.729504 3.056428 -0.024177
H -2.957357 2.658591 -1.750249
C 3.842564 0.467761 -1.359844
C 2.203509 -1.000362 -2.452575
C -0.999860 4.432143 -2.733706
C 0.160256 3.427290 -2.659838
H -0.628883 5.445710 -2.995356
H -1.692533 4.127987 -3.551580
H -2.666193 5.119354 -1.482638
H -1.127965 4.876708 -0.602602
C -3.989889 0.072396 0.373079
C -2.931826 -0.698893 -1.689976
H -0.993459 1.615301 -3.008050
H 0.513683 1.341807 -2.081120
H 0.918588 3.791753 -1.931488
H 0.670941 3.335227 -3.642017
C -5.175346 -0.580017 -0.000487
C -5.236128 -1.306759 -1.201833
H -6.051214 -0.541309 0.665649
H -3.934180 0.609615 1.331687
C -4.115026 -1.363272 -2.047002
H -6.158966 -1.841638 -1.475147
C -1.059412 2.611889 2.108287
C -1.607415 0.299230 2.694111
H -2.048503 -0.779469 -2.344146
H -4.143510 -1.946183 -2.979886
C -1.034552 2.947160 3.472071
H -0.809958 3.361698 1.344083
C -1.301643 1.969104 4.444054

H -0.790157 3.977182 3.775047
C -1.586008 0.646766 4.052887
H -1.279016 2.234574 5.512898
H -1.787765 -0.124497 4.812738
H -1.815165 -0.742055 2.382385
C 2.360322 -0.252223 -3.780801
H 1.180500 -1.417067 -2.346945
H 2.904895 -1.871039 -2.422562
C 3.735838 0.426229 -3.883005
H 1.556647 0.512237 -3.858573
H 2.204894 -0.963958 -4.618595
C 4.020863 1.291035 -2.643518
H 4.523392 -0.358619 -3.959624
H 3.809586 1.034094 -4.809903
H 5.050249 1.707981 -2.679443
H 3.318418 2.154056 -2.612388
H 4.610067 -0.348308 -1.349902
H 4.013614 1.086371 -0.457142
C 3.548771 -2.108244 0.958074
C 1.285452 -2.570526 1.745727
C 4.017306 -3.235502 1.650210
H 4.253071 -1.492344 0.380150
C 3.121432 -4.038588 2.380439
H 5.086586 -3.496159 1.610711
C 1.757429 -3.705968 2.424643
H 3.490520 -4.930359 2.911148
H 1.042077 -4.331805 2.980139
H 0.210777 -2.327278 1.784856
C 2.048464 1.000745 2.521404
C 2.013761 2.426890 0.540783
C 2.198152 3.556246 1.352483
H 1.922025 2.536718 -0.548846
C 2.305209 3.411926 2.746490
H 2.254653 4.555368 0.892518
C 2.221196 2.134954 3.328694
H 2.446082 4.299253 3.383268
H 2.287157 2.020105 4.421309
H 1.981184 0.000810 2.976115

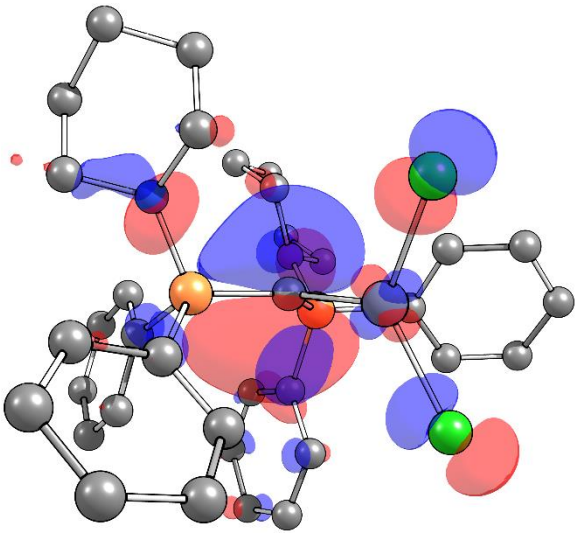


Figure S26. HOMO of **1-ZnCl$_2$** (H-Atoms are omitted for clarity).

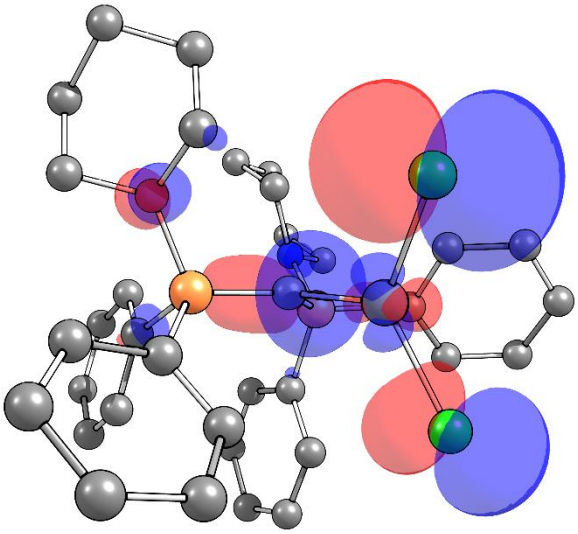


Figure S27. HOMO-1 of **1-ZnCl$_2$** (H-Atoms are omitted for clarity).

4.2.2 Coordinates of 1-$ZnCl_2$-planar

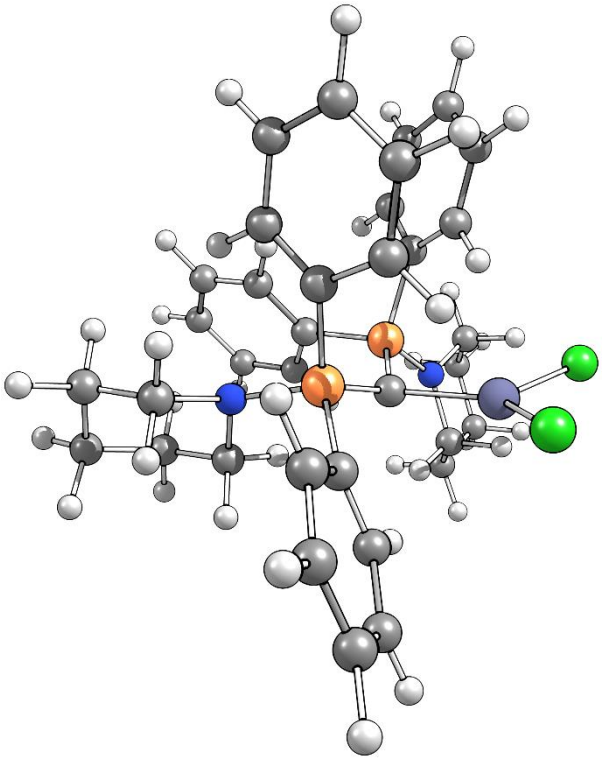


Figure S28. Optimized Structure of **1-ZnCl2-planar**

E = -4851.14338965
Zn -0.274642 -2.402790 -0.631365
C -0.087909 -0.399299 -0.621026
Cl 1.540985 -3.695492 -0.495755
Cl -2.218162 -3.458792 -0.413368
N -1.547585 2.067335 -0.377120
C -1.092043 2.475920 -1.719766
C -2.768142 2.787649 0.027424
P -1.509972 0.371383 -0.086150
C -2.950927 -0.308505 -0.963513
C -1.815820 0.202776 1.708781
P 1.474683 0.061483 -0.094413
N 2.620945 -0.583139 -1.154877
C 1.815904 1.875156 -0.040567
C 1.897080 -0.445891 1.625745
C -2.491359 4.294248 0.081823
H -3.104924 2.412397 1.013676
H -3.598441 2.582594 -0.695527
C 3.911563 -1.117775 -0.699215
C 2.244018 -1.015014 -2.510756
C -1.991451 4.800915 -1.279201

C -0.783906 3.974826 -1.745065
H -1.732636 5.879761 -1.226810
H -2.814989 4.708262 -2.024109
H -3.415856 4.826781 0.391025
H -1.721522 4.488325 0.861374
C -4.232467 -0.300650 -0.378497
C -2.791110 -0.711690 -2.305607
H -1.880040 2.235948 -2.479715
H -0.197393 1.879363 -1.980176
H 0.080836 4.168080 -1.079558
H -0.475715 4.264587 -2.771958
C -5.343179 -0.724707 -1.124924
C -5.180286 -1.140672 -2.457114
H -6.340859 -0.740223 -0.659175
H -4.358978 0.008655 0.670358
C -3.904415 -1.127933 -3.047802
H -6.051826 -1.482938 -3.036812
C -1.431469 1.210273 2.618732
C -2.222783 -1.061664 2.192837
H -1.781203 -0.726831 -2.744358
H -3.773994 -1.462177 -4.088691
C -1.440067 0.954628 3.999232
H -1.121405 2.194221 2.238348
C -1.841458 -0.303369 4.479941
H -1.130148 1.743114 4.702788
C -2.238927 -1.303808 3.575058
H -1.842763 -0.504534 5.562619
H -2.553524 -2.292396 3.944536
H -2.485967 -1.868735 1.484277
C 3.321558 -0.607349 -3.522679
H 1.260342 -0.570624 -2.758833
H 2.114910 -2.123277 -2.507927
C 4.700170 -1.139111 -3.100905
H 3.356522 0.503424 -3.606187
H 3.040111 -0.993862 -4.525646
C 5.031333 -0.707752 -1.663773
H 4.687323 -2.251461 -3.150386
H 5.487526 -0.798124 -3.806617
H 5.988024 -1.161597 -1.327229
H 5.161510 0.397401 -1.622013

H 3.826442 -2.228074 -0.634660
H 4.124502 -0.752118 0.322590
C 2.904521 0.213217 2.366202
C 1.149262 -1.468434 2.240786
C 3.153243 -0.147062 3.699735
H 3.489085 1.023645 1.904216
C 2.394560 -1.162970 4.307610
H 3.940028 0.372905 4.268442
C 1.394374 -1.823077 3.574721
H 2.583461 -1.439120 5.356924
H 0.793115 -2.618085 4.040614
H 0.358567 -1.987233 1.681870
C 1.416793 2.666944 1.055715
C 2.526130 2.471068 -1.100571
C 2.834670 3.841828 -1.066258
H 2.858906 1.841074 -1.939402
C 2.444489 4.623989 0.034472
H 3.392880 4.297741 -1.898803
C 1.733470 4.033363 1.095283
H 2.696039 5.695567 0.067692
H 1.429542 4.640460 1.962470
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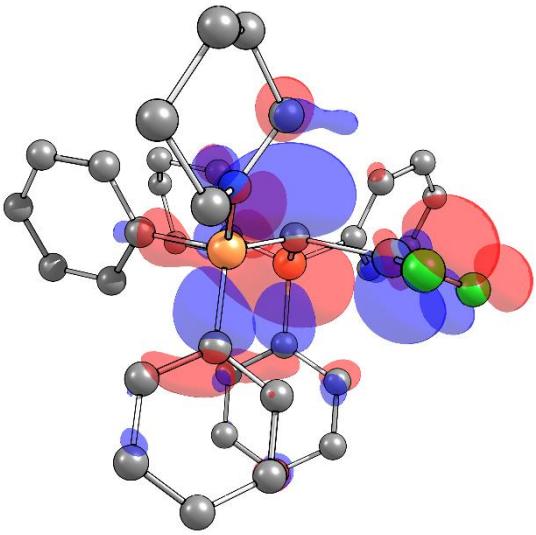

Figure S29. HOMO of 1-$ZnCl_2$-planar (H-Atoms are omitted for clarity).

4.2.3 Coordinates of 1-Rh(acac)CO

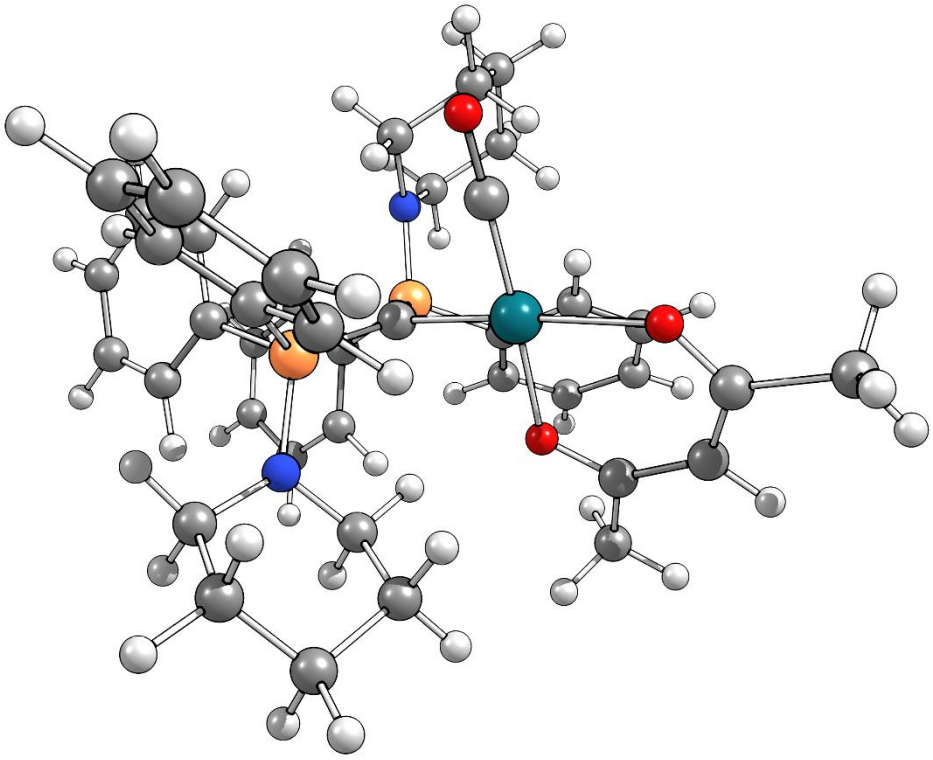

Figure S30. Optimized Structure of **1-Rh(acac)CO**

E = -2720.35354184
Rh -1.682218 0.961464 0.595136
P 1.519632 1.016282 -0.105187
P 0.151290 -1.629897 0.129995
O -0.892330 1.529406 3.409532
O -2.135419 0.489228 -1.383545
O -3.605805 1.748950 0.798301
N 1.568325 1.679233 -1.680603
N 0.368057 -2.415267 1.635560
C 0.143378 0.071512 0.233984
C 1.664954 2.482374 0.994379
C 2.787928 2.721793 1.811962
H 3.638189 2.024277 1.804026
C 2.830589 3.858754 2.638303
H 3.710571 4.034091 3.276957
C 1.757518 4.764963 2.649675
H 1.789452 5.650293 3.304129
C 0.644758 4.541308 1.819127
H -0.200836 5.246659 1.820536
C 0.601838 3.414105 0.986663
H -0.283184 3.217200 0.357030

C 3.104598 0.112576 0.099110
C 3.979985 -0.063423 -0.988777
H 3.701584 0.344984 -1.970983
C 5.171107 -0.787984 -0.823559
H 5.843927 -0.934783 -1.682614
C 5.497570 -1.334799 0.428962
H 6.432723 -1.902568 0.556094
C 4.621724 -1.168015 1.516682
H 4.867846 -1.603740 2.497793
C 3.426983 -0.450995 1.353201
H 2.736106 -0.330892 2.200384
C 2.470190 2.790564 -2.001264
H 3.071851 2.515904 -2.903183
H 3.191040 2.925498 -1.168658
C 1.707633 4.096557 -2.272888
H 1.259479 4.449016 -1.319304
H 2.423700 4.879606 -2.603813
C 0.602558 3.882913 -3.319826
H 1.071900 3.657004 -4.306318
H 0.015640 4.815769 -3.459454
C -0.311065 2.714835 -2.919155
H -1.066533 2.512603 -3.708536
H -0.879181 2.958710 -1.994263
C 0.502128 1.442471 -2.652561
H -0.168808 0.655900 -2.254116
H 0.959757 1.076894 -3.605758
C 1.459087 -2.298299 -0.969308
C 1.461448 -1.930986 -2.332713
H 0.673191 -1.268632 -2.719482
C 2.469586 -2.403744 -3.186042
H 2.467121 -2.113705 -4.248534
C 3.482908 -3.239793 -2.683425
H 4.277495 -3.606270 -3.352285
C 3.487796 -3.596536 -1.324286
H 4.290599 -4.234571 -0.923601
C 2.477451 -3.130023 -0.468314
H 2.487434 -3.379373 0.602504
C -1.413404 -2.351559 -0.527162
C -1.444096 -3.232232 -1.626543
H -0.510275 -3.528251 -2.126500

C -2.671839 -3.738898 -2.092962
H -2.684635 -4.423365 -2.955828
C -3.873166 -3.370616 -1.465568
H -4.833786 -3.757328 -1.840892
C -3.844495 -2.509578 -0.352278
H -4.779702 -2.213841 0.147271
C -2.621852 -2.018322 0.125530
H -2.596730 -1.309561 0.975183
C 0.450270 -1.664565 2.887832
H 0.607210 -0.597723 2.633958
H 1.345878 -2.015645 3.457747
C -0.810726 -1.839951 3.742899
H -0.685054 -1.301216 4.705411
H -1.659366 -1.352917 3.214509
C -1.113511 -3.328541 3.971678
H -0.300246 -3.777392 4.589340
H -2.052312 -3.454899 4.551774
C -1.204402 -4.077374 2.632675
H -1.340956 -5.168589 2.793715
H -2.088002 -3.719838 2.061356
C 0.054909 -3.841213 1.785245
H 0.927838 -4.349078 2.265034
H -0.060808 -4.293650 0.778920
C -1.216601 1.313713 2.301028
C -3.300980 0.517446 -1.925030
C -3.361844 -0.090606 -3.311231
H -4.362338 -0.006107 -3.775999
H -3.083285 -1.163069 -3.239331
H -2.610848 0.398401 -3.966238
C -4.470755 1.040121 -1.334889
H -5.391817 1.006018 -1.933978
C -4.555413 1.646585 -0.053275
C -5.876736 2.247429 0.393321
H -6.688597 2.090919 -0.342271
H -5.747866 3.337521 0.560742
H -6.173694 1.807865 1.368090

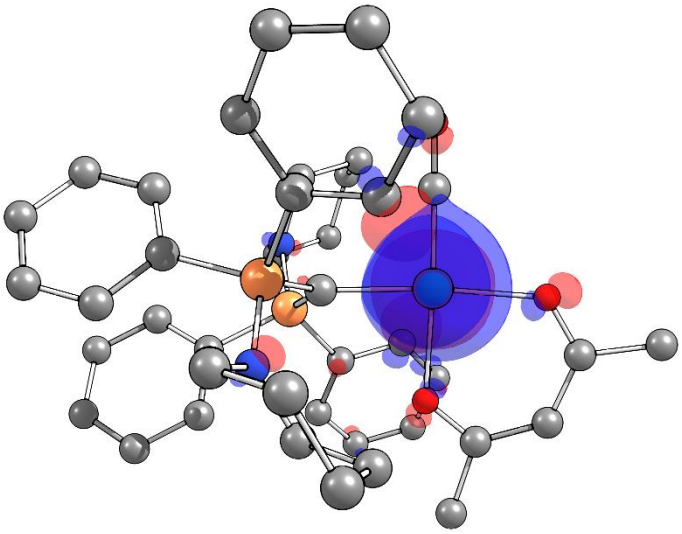

Figure S31. HOMO of **1-Rh(acac)CO** (H-Atoms are omitted for clarity).

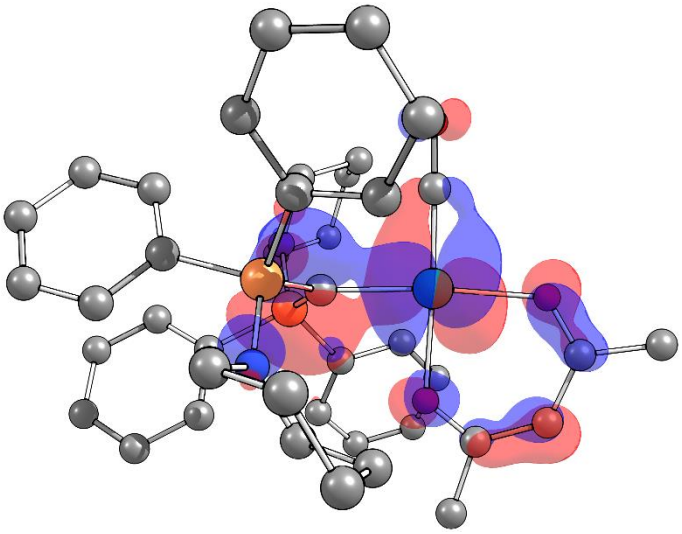

Figure S32. HOMO-1 of **1-Rh(acac)CO** (H-Atoms are omitted for clarity).

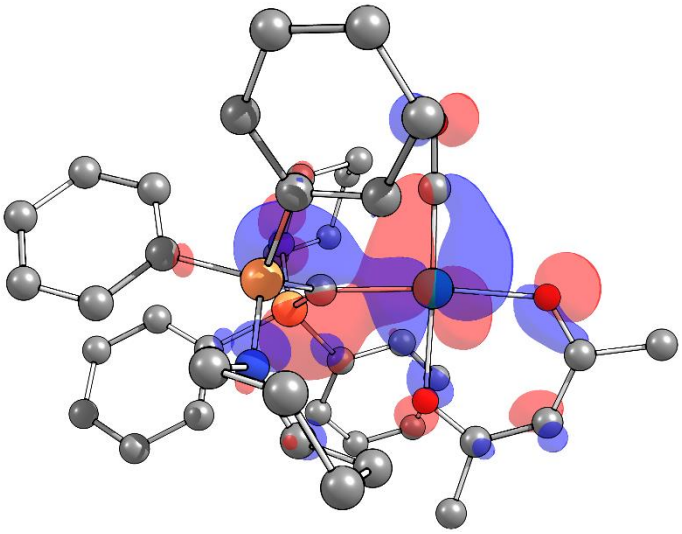

Figure S33. HOMO-2 of **1-Rh(acac)CO** (H-Atoms are omitted for clarity).

4.3 Energetic Comparison of 1-$ZnCl_2$ und 1-$ZnCl_2$-planar

	Corr(H)	Corr(G)	E(SCF)	ΔG in hartree	ΔG in kJ/mol
1-$ZnCl_2$	0.699561	0.578453	-4851.150221	–	–
1-$ZnCl_2$-planar	0.700001	0.580519	-4851.143390	0.00889755	23.360518

4.4 Wiberg Bond Indices and NBO analyses

	1	**CDP A**	**BIPM^{Tol}**	**1-$ZnCl_2$**	**1-Rh**
q_C(NBO)	-1.43594	-1.38110	-1.27821	-1.67303	-1.33601
q_n(NBO)	-0.83021 -0.83021	-	-0.95094 -0.95095	-0.82384 -0.83615	-0.86987 -0.86838
C–M_{exp}	-	-	-	1.994(2)	2.092(3) and 2.009(1)
C–M_{calc}	-	-	-	2.01848 Å	2.06282 Å
$WBI_{C–P}$	1.3677 1.3677	1.3219 1.3219	1.2968 1.2968	1.2086 1.1900	1.2020 1.1984
$WBI_{P–N}$	0.7265 0.7265	-	0.9578 0.9578	0.7684 0.7839	0.7716 0.7713
$WBI_{C–M}$	-	-	-	0.2083	0.5187
NBO_C	2 LP	2 LP	2 LP	2 LP	1 LP
$NBO_{C–P}$	1 BD C1-P1 1 BD C1-P2	1 BD C1-P2 1 BD C1-P2	1 BD C1-P1 1 BD C1-P2	1 BD C1-P2 1 BD C1-P2	1 BD C1-P2 1 BD C1-P2
$NBO_{P–N}$	1 BD P1-N1 1 BD P2-N2	-	1 BD P1-N1 1 BD P2-N2	1 BD P1-N1 1 BD P2-N2	1 BD P1-N1 1 BD P2-N2
$NBO_{C–M}$	-	-	-	-	1 BD C1-Rh1

NBO analysis of **1-$ZnCl_2$** suggests that the two lone pairs remain at the CDP ligand and that the metal ligand interaction is dominated by electrostatic interactions. Since the HOMO-7 shows some bonding interaction between the carbon and zinc atom, the bonding situation can also be interpreted as a single bond, which however is highly polarized towards the carbon atom. This interpretation is also well in line with the low WBI of only 0.21.

In case of the rhodium complex, the NBO analysis suggests the presence of a single bond between C and Rh and a further remaining lone pair at carbon. The molecular orbitals however, suggest that the π-symmetric lone pair at carbon is not completely localized at carbon. Thus, we conclude that this bond can also be interpreted as a double bond, highly polarized towards the carbon atom.

5. References

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