

Supplementary Information for

Catalytic reduction of dinitrogen into tris(trimethylsilyl)amine using rhodium complexes with pyrrole-based PNP-type pincer ligand

Ryosuke Kawakami, Shogo Kuriyama, Hiromasa Tanaka, Kazuya Arashiba, Asuka Konomi, Kazunari Nakajima, Kazunari Yoshizawa,* and Yoshiaki Nishibayashi*

Contents

General Methods.....	2
Preparation of Rhodium Complexes with PNP Ligand.....	3
Electrochemical Study.	6
Protonolysis of Dinitrogen Complex 3.	7
Reduction of N ₂ into NH ₃ or N ₂ H ₄ under N ₂ (1 atm).	8
Catalytic Reduction of N ₂ into N(SiMe ₃) ₃ under N ₂ (1 atm) at room temperature.....	9
Catalytic Reduction of N ₂ into N(SiMe ₃) ₃ under N ₂ (1 atm) at -40 °C.....	10
Mercury Poisoning Test.....	11
X-ray Crystallography.....	12
Computational Details.....	19
¹ H and ³¹ P NMR Spectra.	40
IR Spectra.....	45
References.....	47

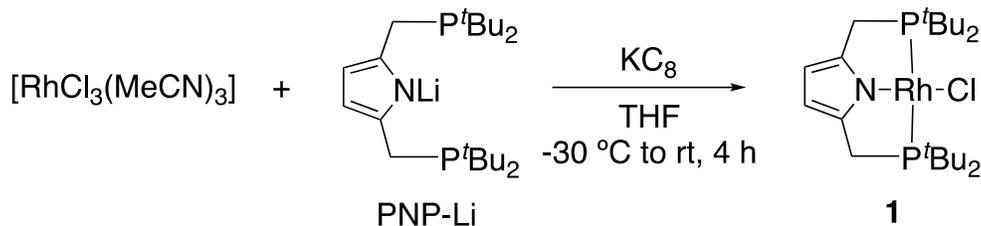
General Methods.

^1H NMR (400 MHz), and $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectra were recorded on a JEOL ECS-400 spectrometer in suitable solvent, and spectra were referenced to residual solvent (^1H) or external standard ($^{31}\text{P}\{^1\text{H}\}$: H_3PO_4). IR spectra were recorded on a JASCO FT/IR 4100 Fourier Transform infrared spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-1850. Gas chromatography (GC) analyses for the quantification of $\text{N}(\text{SiMe}_3)_3$ and byproducts were carried out on a Shimadzu GC-2014 instrument equipped with a flame-ionization detector using CBP 10 fused silica capillary column (25 m \times 0.25 mm). Evolved dihydrogen was quantified by GC using a Shimadzu GC-8A equipped with a TCD detector and a SHINCARBON ST (6 m \times 3 mm). Magnetic susceptibility was measured in C_6D_6 using the Evans method.^{S1} Elemental analyses were performed at Microanalytical Center of The University of Tokyo.

All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques or glovebox techniques unless otherwise stated. Solvents were dried by general methods, and degassed before use. Me_3SiCl was distilled prior to use. PNP-Li (PNP = 2,5-bis(di-*tert*-butylphosphinomethyl)pyrrolide),^{S2} $[\text{RhCl}_3(\text{MeCN})_3]$,^{S3} $[\text{Rh}(\text{CH}_2\text{CH}_2)(\text{PNP})]$,^{S4} $\text{NaBAr}^{\text{F}}_4$ (Ar^{F} = 3,5-bis(trifluoromethyl)phenyl),^{S5} KC_8 ,^{S6} $[\text{H}(\text{OEt}_2)_2]\text{BAr}^{\text{F}}_4$,^{S7} $[\text{CoI}]\text{OTf}$ (Col = 2,4,6-trimethylpyridine),^{S8} CoCp^*_2 (Cp^* = $\eta^5\text{-C}_5\text{Me}_5$),^{S9} and $\text{SmI}_2(\text{thf})_2$ ^{S10} were prepared according to the literature. Other reagents were purchased commercially and used as received.

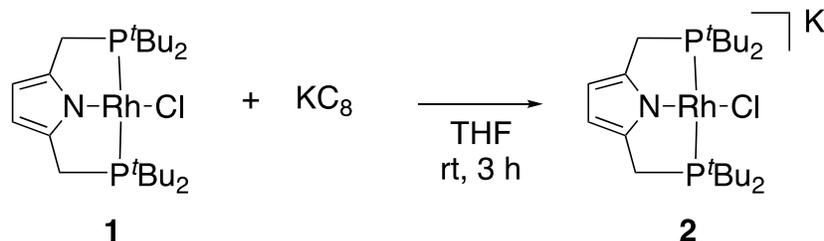
Preparation of Rhodium Complexes with PNP Ligand.

Preparation of [RhCl(PNP)] (1)



A mixture of $[\text{RhCl}_3(\text{MeCN})_3]$ (664 mg, 2.00 mmol), PNP-Li (778 mg, 2.00 mmol) and KC_8 (269 mg, 1.99 mmol) was precooled at $-30\text{ }^\circ\text{C}$. Cold THF (20 mL, $-30\text{ }^\circ\text{C}$) was added to the mixture, then the mixture was stirred at room temperature for 4 h. The reaction mixture was filtered through Celite, and the filter cake was washed with THF (3 mL, 4 times). The combined filtrate was dried *in vacuo*. After the addition of hexane (50 mL) to the brown residue, the solution was filtered through Celite, and the filter cake was washed with hexane (3 mL, 8 times). The combined filtrate was dried *in vacuo*. The obtained brown solid was washed with a small amount of cold pentane, and dried *in vacuo* to afford **1** as a brown solid. (333 mg, 0.639 mmol, 32%). Single crystals of **1** suitable for X-ray crystallography were obtained as yellow crystals from pentane at $-30\text{ }^\circ\text{C}$. Magnetic susceptibility (Evans' Method): $\mu_{\text{eff}} = 2.0\ \mu_{\text{B}}$ in C_6D_6 at 298 K. Anal. Calcd. for $\text{C}_{22}\text{H}_{42}\text{ClNP}_2\text{Rh}$: C, 50.73; H, 8.13; N, 2.69. Found: C, 50.55; H, 7.84; N, 2.83.

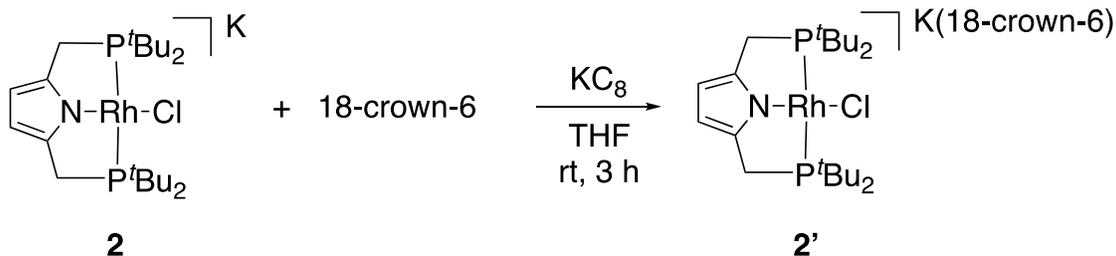
Preparation of $\text{K}[\text{RhCl}(\text{PNP})]$ (2)



To a mixture of **1** (50.2 mg, 0.096 mmol) and KC_8 (14.3 mg, 0.106 mmol) was added THF (3 mL). After stirring at room temperature for 3 h, the reaction mixture was dried *in vacuo*. THF/ Et_2O ($v/v = 1:1$, 3 mL) was added, then the suspension was filtered through Celite, and the filter cake was washed with THF/ Et_2O ($v/v = 1:1$, 2 mL, 3 times). The obtained orange filtrate was concentrated to *ca.* 2 mL and Et_2O (15 mL) was added. After orange supernatant was removed by decantation, the residue was washed with Et_2O (2 mL, 2 times), and dried *in vacuo* to afford **2** as a yellow solid (35.6 mg, 0.064 mmol, 66%). Anal. Calcd. for $\text{C}_{22}\text{H}_{42}\text{ClKNP}_2\text{Rh}$: C, 47.19; H, 7.56;

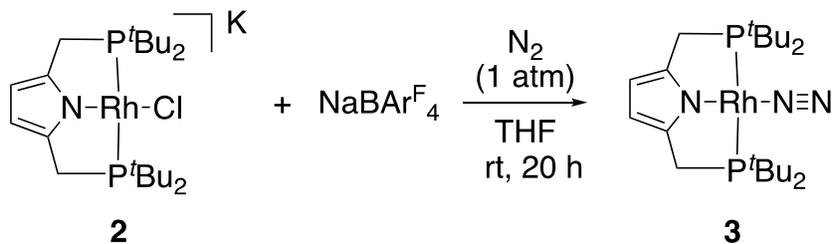
N, 2.50. Found: C, 47.12; H, 7.67; N, 2.30. NMR spectra of **2** are too broad to identify peaks derived from **2**.

Preparation of [K(18-crown-6)][RhCl(PNP)] (**2'**)



To a mixture of **2** (14.6 mg, 0.026 mmol) and 18-crown-6 (7.0 mg, 0.026 mmol) was added THF (1 mL). After stirring at room temperature for 3 h, the solvent was removed *in vacuo*. The obtained yellow solid was washed with pentane (1 mL, 3 times) and dried *in vacuo* to afford **2'** (9.7 mg, 0.012 mmol, 45%). Single crystals of **2'** (thf)₂ suitable for X-ray crystallography were obtained as yellow crystals from THF-Et₂O at -30 °C. ¹H NMR (CD₃CN): δ 5.54 (s, ArH, 2H), 3.57 (s, OCH₂, 24H), 2.83 (pseudo t, *J* = 4.0 Hz, PCH₂, 4H), 1.33 (pseudo t, *J* = 6.2 Hz, P^tBu₂, 36H). ³¹P{¹H} NMR (CD₃CN): δ 80.7 (d, ²*J*_{Rh-P} = 153 Hz). Anal. Calcd. for C₃₄H₆₆ClKNO₆P₂Rh: C, 49.54; H, 8.07; N, 1.70. Found: C, 49.94; H, 8.00; N, 1.56.

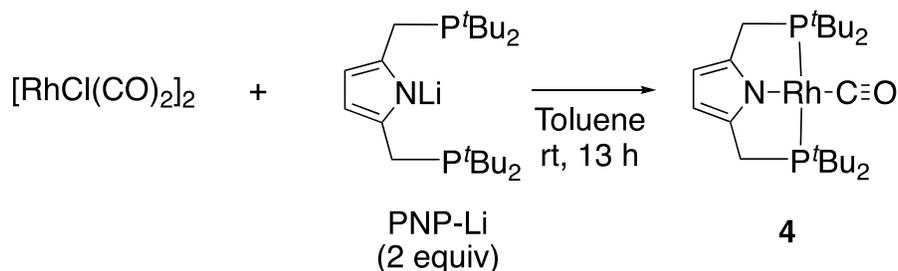
Preparation of [Rh(N₂)(PNP)] (**3**)



A solution of **2** (126 mg, 0.224 mmol) and NaBAR₄^{F₄} (198 mg, 0.224 mmol) in THF (4 mL) was stirred at room temperature for 20 h under N₂ (1 atm). The solvent was removed *in vacuo*. After the addition of toluene (6 mL) to the brown residue, the solution was filtered through Celite, the filter cake was washed with toluene (2 mL, 3 times). After the combined filtrate was dried *in vacuo*, the obtained brown solid was washed with Et₂O (3 mL, 3 times) to afford **3** as a yellow solid (75.8

mg, 0.148 mmol, 66%). Single crystals of **3** suitable for X-ray crystallography were obtained yellow crystals from THF–Et₂O at –30 °C. ¹H NMR (C₆D₆): δ 6.40 (s, ArH, 2H), 2.95 (pseudo t, *J* = 4.2 Hz, PCH₂, 4H), 1.22 (pseudo t, *J* = 6.6 Hz, P^tBu₂, 36H). ³¹P{¹H} NMR (C₆D₆): δ 86.0 (d, ²*J*_{Rh-P} = 139 Hz). IR(KBr, cm⁻¹) 2110 cm⁻¹, IR(THF, cm⁻¹) 2112 cm⁻¹, IR(C₆D₆, cm⁻¹) 2112cm⁻¹, Anal. Calcd. for C₂₂H₄₂N₃P₂Rh: C, 51.46; H, 8.25; N, 8.18. Found: C, 51.72; H, 8.12; N, 7.82.

Preparation of [Rh(CO)(PNP)] (**4**)



To a mixture of [RhCl(CO)₂]₂ (194 mg, 0.499 mmol) and PNP-Li (386 mg, 0.991 mmol) was added toluene (4 mL). After stirring at room temperature for 13 h, the solvent was removed *in vacuo*. After Et₂O (5 mL) was added to the residue, the solution was filtered through Celite, and the filter cake was washed with Et₂O (2 mL, 3 times). After the combined filtrate was dried *in vacuo*, the obtained orange solid was washed with a small amount of cold pentane and dried *in vacuo* to afford **4** as a yellow solid (214 mg, 0.417 mmol, 42%). Single crystals of **4** suitable for X-ray crystallography were obtained as pale yellow crystals from Et₂O at –30 °C. ¹H NMR (C₆D₆): δ 6.43 (s, ArH, 2H), 3.09 (pseudo t, *J* = 4.2 Hz, PCH₂, 4H), 1.19 (pseudo t, *J* = 6.8 Hz, P^tBu₂, 36H). ³¹P{¹H} NMR (C₆D₆): δ 96.3 (d, ²*J*_{Rh-P} = 131 Hz). IR(KBr, cm⁻¹) 1941 cm⁻¹ Anal. Calcd. for C₂₃H₄₂NOP₂Rh: C, 53.80; H, 8.25; N, 2.73. Found: C, 54.38; H, 8.42; N, 2.94.

Electrochemical Study.

Cyclic voltammogram (CV) was recorded on an ALS/Chi model 610C electrochemical analyzer with platinum working electrode in THF containing 1 mM of sample and 0.1 M of $[N^+Bu_4]PF_6$ as a supporting electrolyte at a scan rate 0.1V/s at room temperature. All potentials were measured against an $Ag^{0/+}$ electrode and converted to the values vs ferrocene.

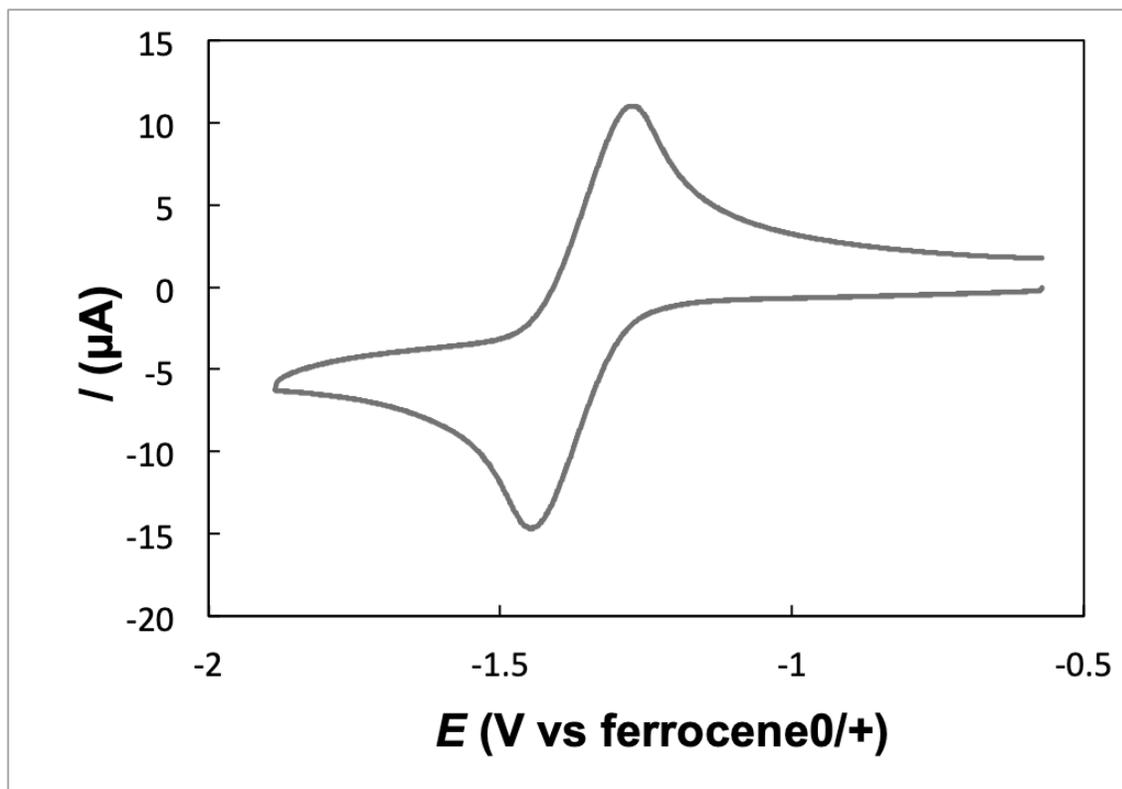


Fig. S1. CV of **1** under 1 atm of N_2 . The CV of **1** revealed a reversible reduction at $E_{1/2} = -1.36$ V vs ferrocene^{0/+}.

Protonolysis of Dinitrogen Complex 3.

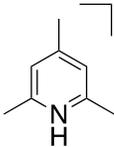
To a solution of **3** (10.1 mg, 0.02 mmol) in THF (3 mL) was added concentrated sulfuric acid (30 μ L). After the mixture was stirred at room temperature for 24 h at room temperature, the solvent was removed *in vacuo*. Aqueous solution of potassium hydroxide (30 wt%, 5 mL) was added to the residue, and the mixture was distilled into dilute H₂SO₄ solution (0.25 M, 10 mL). The amount of NH₃ and N₂H₄ was determined by the indophenol method^{S11} and the *p* – (dimethylamino)benzaldehyde method,^{S12} respectively. However, no formation of the NH₃ and N₂H₄ was observed.

Reduction of N₂ into NH₃ or N₂H₄ under N₂ (1 atm).

Reductions of molecular dinitrogen into NH₃ or N₂H₄ by using **3** as a catalyst were carried out under the reported conditions.^{S13} However, no formation of NH₃ or N₂H₄ was observed and only H₂ formation occurred. The detailed conditions and the results are shown in Table S1.

Table S1 Reductions of molecular dinitrogen into NH₃ or N₂H₄ by using **3**.
$$\text{N}_2 + \text{reductant} + \text{proton source} \xrightarrow[\text{Solvent, T, Time}]{\text{cat. 3}} \text{NH}_3 + \text{N}_2\text{H}_4 + \text{H}_2$$

(1 atm) $\left(\begin{array}{c} \text{X} \\ \text{equiv./Rh} \end{array} \right) \left(\begin{array}{c} \text{Y} \\ \text{equiv./Rh} \end{array} \right)$

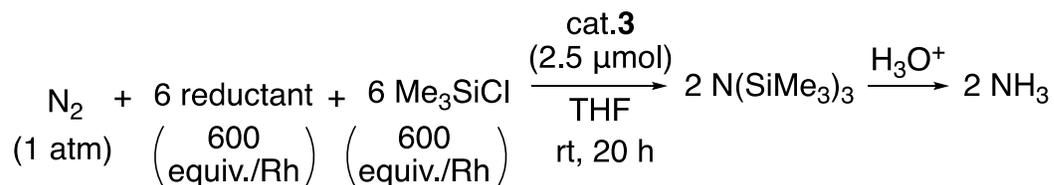
Entry	reductant (X)	proton source (Y)	T	time	Solvent	NH ₃ (equiv./Rh)	N ₂ H ₄ (equiv./Rh)	H ₂ (equiv./Rh)
1	KC ₈ (40)	[H(OEt ₂)] [BAR ^F ₄] (38)	-78 °C	1 h	Et ₂ O	0	0	4.2
2	Sml ₂ (36)	HOCH ₂ CH ₂ OH (36)	rt	20 h	THF	0	0	15.1
3	Cp* ₂ Co (36)	 (48)	rt	20 h	toluene	0	0	7.8

Catalytic Reduction of N₂ into N(SiMe₃)₃ under N₂ (1 atm) at room temperature.

A typical experimental procedure using **3** is described below. In a 50 mL Schlenk flask were placed **3** (1.3 mg, 2.5 μmol), KC₈ (203 mg, 1.5 mmol), THF (3 mL) and Me₃SiCl (163 mg, 1.5 mmol) and the mixture was stirred at room temperature for 20 h under N₂ (1 atm). After dilute H₂SO₄ solution (0.5 M, 3 mL) was added to the mixture, the mixture was stirred at room temperature for 1 h. Aqueous solution of potassium hydroxide (30 wt%, 5 mL) was added to the reaction mixture, and the mixture was distilled into another dilute H₂SO₄ solution (0.25 M, 10 mL). The amount of NH₃ was determined by the indophenol method.^{S11}

Separately, the amount of N(SiMe₃)₃ and byproducts were determined by GC analysis. A typical experimental procedure is described below. In a 50 mL Schlenk flask were placed **3** (1.3 mg, 2.5 μmol), KC₈ (203 mg, 1.5 mmol), THF (3 mL) and Me₃SiCl (163 mg, 1.5 mmol) were added, and the mixture was stirred at room temperature for 20 h under N₂ (1 atm). To the reaction mixture were added 1,2,4,5-tetramethylbenzene (50.2 mg, 0.374 mmol) and THF solution of cyclododecane (0.012 mM, 1.0 mL, 0.012 mmol) as internal standards for GC analysis. After the mixture was stirred at room temperature for 10 min, an aliquot of the mixture was filtered. The filtrate was subjected to GC analysis.

Table S2 Effect of reductants.



Entry	reductant	NH ₃ (equiv./Rh)
1	KC ₈	6.9
2	Na	0

Table S3. Effect of solvents.
$$\text{N}_2 + 6 \text{KC}_8 + 6 \text{Me}_3\text{SiCl} \xrightarrow[\text{Solvent, rt, 3 h}]{\text{cat. 3 (2.5 } \mu\text{mol)}} 2 \text{N}(\text{SiMe}_3)_3 \xrightarrow{\text{H}_3\text{O}^+} 2 \text{NH}_3$$

(1 atm) (600 equiv./Rh) (600 equiv./Rh)

Entry	Solvent	NH ₃ (equiv./Rh)
1	THF	3.7
2	Et ₂ O	1.0
3	DME	2.5
4	Toluene	0.4

Catalytic Reduction of N₂ into N(SiMe₃)₃ under N₂ (1 atm) at –40 °C.

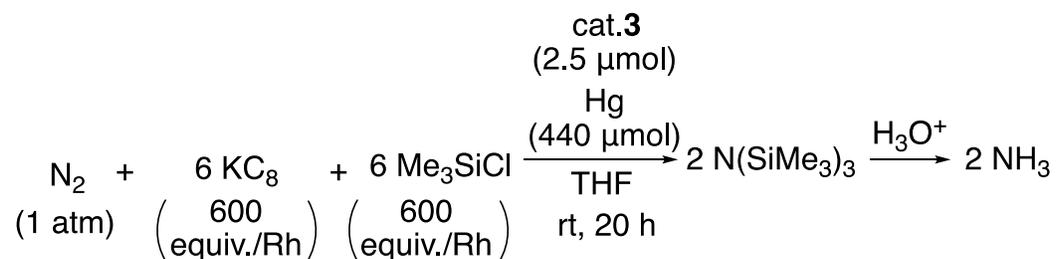
A typical experimental procedure using **3** at –40 °C is described below. In a 50 mL Schlenk flask were placed **3** (1.3 mg, 2.5 μmol), KC₈ (203 mg, 1.5 mmol). THF (3 mL) was added and the mixture was stirred at –40 °C for 40 min under N₂ (1 atm). After the addition of Me₃SiCl (163 mg, 1.5 mmol) to the mixture at –40 °C, the resultant suspension was stirred at –40 °C for 20 h under N₂ (1 atm). The reaction mixture was warmed up and stirred at room temperature for 1 h. After dilute H₂SO₄ solution (0.5 M, 3 mL) was added to the mixture, the mixture was stirred at room temperature for 1 h. Aqueous solution of potassium hydroxide (30 wt%, 5 mL) was added to the reaction mixture, and the mixture was distilled into another dilute H₂SO₄ solution (0.5 M, 10 mL). The amount of NH₃ was determined by the indophenol method.^{S11}

Separately, GC analysis was carried out to determine the yields of N(SiMe₃)₃ and byproducts in the same manner as described above.

Mercury Poisoning Test.

To a mixture of **3** (1.3 mg, 2.5 μmol) and KC_8 (203 mg, 1.5 mmol) were added THF (3 mL) and mercury (87.4 mg, 0.44 mmol) at room temperature. After stirring 5 min at room temperature, Me_3SiCl (163 mg, 1.5 mmol) was added. The mixture was stirred at room temperature for 20 h under N_2 (1 atm). After the mixture was filtered through Celite, dilute H_2SO_4 solution (0.5 M, 3 mL) was added to the filtrate, and the mixture was stirred at room temperature for 1 h. Aqueous solution of potassium hydroxide (30 wt%, 5 mL) was added to the mixture, and the mixture was distilled into another dilute H_2SO_4 solution (0.25 M, 10 mL). The amount of NH_3 was determined by the indophenol method.^{S11} Formation of NH_3 (13.6 μmol , 5.4 equiv. based on the Rh atom) was observed.

Scheme S1. Mercury poisoning test.



X-ray Crystallography.

Crystallographic data of **1**, **2'** (thf)₂, **3** and **4** are summarized in Tables S4-5. Selected bond lengths and angles are summarized in Tables S6-9 and their ORTEP drawings are shown in Fig. S2-5. Diffraction data for **1**, **2'** (thf)₂, **3** and **4** were collected for the 2θ range of 4° to 55° at –100 °C on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo-K α ($\lambda = 0.71075$ Å) radiation with VariMax optics. Intensity data were corrected for Lorentz and polarization effects and for empirical absorptions (ABSCOR),^{S14} while structure solutions and refinements were carried out by using CrystalStructure package.^{S15} The positions of non-hydrogen atoms were determined by direct methods (SIR97^{S16} for, **2'** (thf)₂, **3**, **4** and DIRDIF99–PATTY^{S17} for **1**) and subsequent Fourier syntheses (SHELXL^{S18} version 2016/6) and were refined on F_o^2 using all unique reflections by full-matrix least-squares with anisotropic thermal parameters.

Table S4. X-ray crystallographic data for 1, 2' (thf)₂.

compound	1	2' (thf)₂
chemical formula	C ₂₂ H ₄₂ ClNP ₂ Rh	C ₄₂ H ₈₂ ClKNO ₈ P ₂ Rh
CCDC number	1950030	1950033
formula weight	520.89	968.52
dimensions of crystals,	0.20 × 0.20 × 0.20	0.60 × 0.07 × 0.06
crystal color, habit	yellow, block	yellow, needle
crystal system	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	11.5932(3)	30.3543(9)
<i>b</i> , Å	14.5110(3)	10.6969(4)
<i>c</i> , Å	15.1619(4)	31.0098(10)
α , deg	90	90
β , deg	90	92.302(7)
γ , deg	90	90
<i>V</i> , Å ³	2550.67(11)	10060.6(6)
<i>Z</i>	4	8
ρ_{calcd} , g cm ⁻³	1.356	1.279
<i>F</i> (000)	1092.0	4128
μ , cm ⁻¹	9.06	5.84
temperature, °C	-100	-100
trans. factors range	0.636 – 0.834	0.652 – 0.966
no. reflections measured	24445	47442
no. unique reflections	5810 (<i>R</i> _{int} = 0.0470)	11455 (<i>R</i> _{int} = 0.0521)
no. parameters refined	257	505
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0257	0.0374
<i>wR</i> 2 (all data) ^b	0.0583	0.0837
GOF ^c	1.056	0.990
Flack parameter	0	
max diff peak / hole, e Å ⁻³	+0.400 / -0.582	+0.57 / -0.44

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (qP)^2 + rP]$, $P = (\text{Max}(F_o^2, 0) + 2 F_c^2) / 3$ [$q = 0.0281$ (**1**), 0.0384 (**2' (thf)₂**); $r = 0.2197$ (**1**), 10.1561 (**2' (thf)₂**)]. ^c $\text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (N_o - N_{\text{params}})]^{1/2}$

Table S5. X-ray crystallographic data for 3, 4.

compound	3	4
chemical formula	C ₂₂ H ₄₂ N ₃ P ₂ Rh	C ₂₃ H ₄₂ NOP ₂ Rh
CCDC number	1950031	1950032
formula weight	513.45	513.44
dimensions of crystals,	0.40 × 0.40 × 0.30	0.17 × 0.16 × 0.09
crystal color, habit	yellow, block	pale yellow, block
crystal system	monoclinic	monoclinic
space group	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> , Å	15.2008(5)	15.2192(4)
<i>b</i> , Å	13.0723(4)	13.0419(4)
<i>c</i> , Å	14.5495(4)	14.5491(5)
α , deg	90	90
β , deg	118.509(8)	118.510(8)
γ , deg	90	90
<i>V</i> , Å ³	2540.6(2)	2537.6(2)
<i>Z</i>	4	4
ρ_{calcd} , g cm ⁻³	1.342	1.344
<i>F</i> (000)	1080	1080
μ , cm ⁻¹	8.09	8.11
temperature, °C	-100	-100
trans. factors range	0.713 – 0.976	0.663 – 0.930
no. reflections measured	24186	23347
no. unique reflections	5812 (<i>R</i> _{int} = 0.0672)	5799 (<i>R</i> _{int} = 0.0533)
no. parameters refined	265	265
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0526	0.0459
<i>wR</i> 2 (all data) ^b	0.1102	0.1087
GOF ^c	1.145	1.097
max diff peak / hole, e Å ⁻³	+1.07 / -0.71	+2.13 / -0.87

^a *R*1 = $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^b *wR*2 = $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (qP)^2 + rP]$, $P = (\text{Max}(F_o^2, 0) + 2 F_c^2) / 3$ [$q = 0.0533$ (**3**), 0.0507 (**4**); $r = 0$ (**3**), 2.3195 (**4**)]. ^c GOF = $[\Sigma w(F_o^2 - F_c^2)^2 / (N_o - N_{\text{params}})]^{1/2}$.

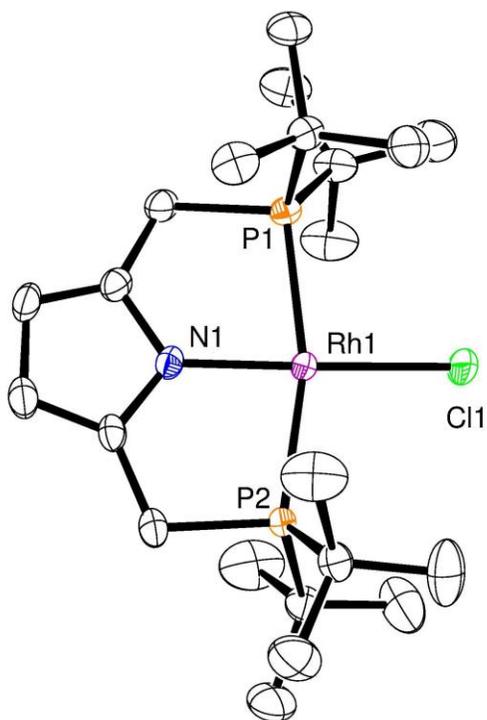


Fig. S2. Molecular structure of **1**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table S6. Selected Bond Lengths (Å) and Angles (deg) for **2**.

Rh(1)–P(1)	2.3219(8)	Rh(1)–P(2)	2.3366(8)
Rh(1)–N(1)	1.952(2)	Rh(1)–Cl(1)	2.3218(8)
P(1)–Rh(1)–P(2)	164.37(3)	N(1)–Rh(1)–Cl(1)	178.68(7)

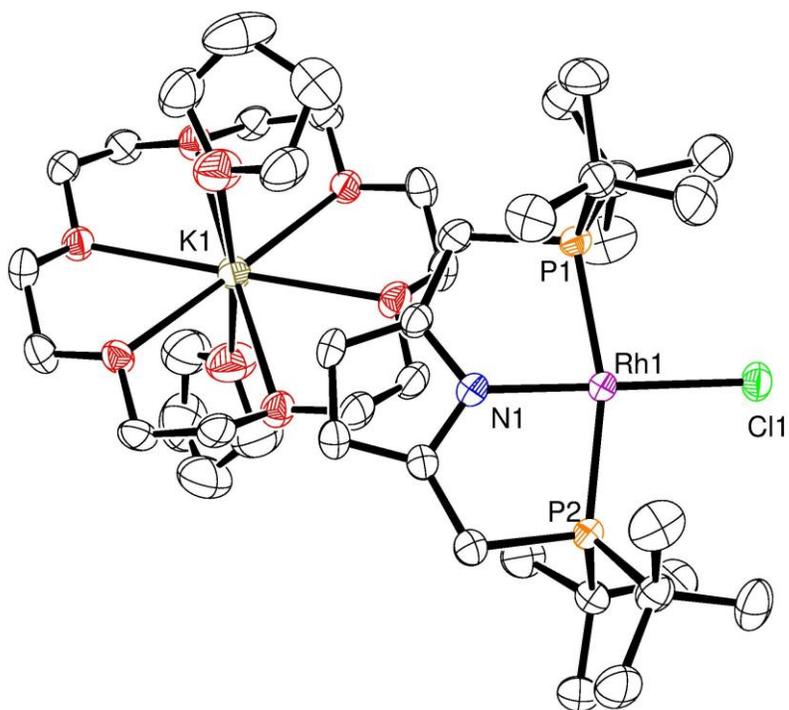


Fig. S3. Molecular structure of **2'** ·(thf)₂. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table S7. Selected Bond Lengths (Å) and Angles (deg) for **2'** ·(thf)₂.

Rh(1)–P(1)	2.2705(6)	Rh(1)–P(2)	2.2721(6)
Rh(1)–N(1)	2.0036(18)	Rh(1)–Cl(1)	2.4143(6)
P(1)–Rh(1)–P(2)	162.42(2)	N(1)–Rh(1)–Cl(1)	177.45(6)

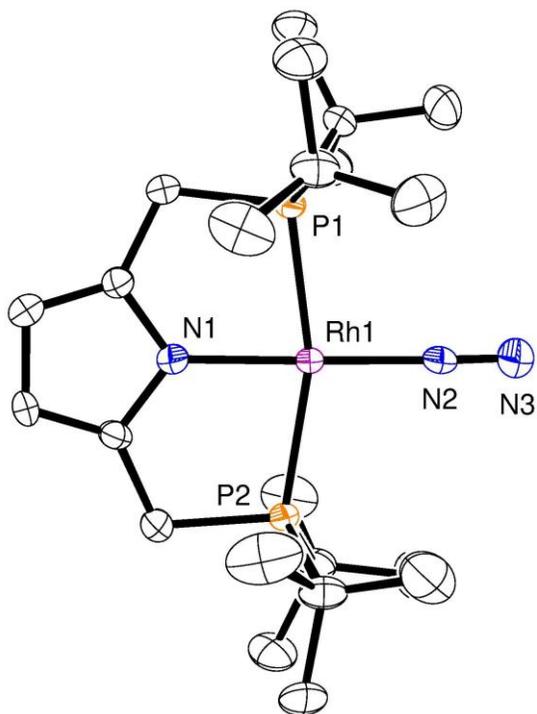


Fig. S4. Molecular structure of **3**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table S8. Selected Bond Lengths (Å) and Angles (deg) for **3**.

Rh(1)–P(1)	2.3194(9)	Rh(1)–P(2)	2.3247(9)
Rh(1)–N(1)	1.989(3)	Rh(1)–N(2)	1.899(3)
N(2)–N(3)	1.109(5)		
P(1)–Rh(1)–P(2)	161.98(3)	N(1)–Rh(1)–N(2)	179.01(12)
Rh(1)–N(2)–N(3)	178.7(3)		

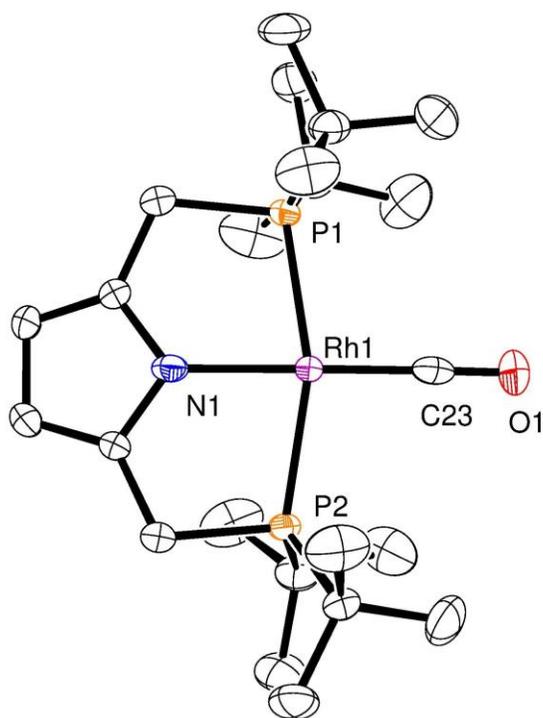


Fig. S5. Molecular structure of **4**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table S9. Selected Bond Lengths (Å) and Angles (deg) for **4**.

Rh(1)–P(1)	2.3234(8)	Rh(1)–P(2)	2.3210(9)
Rh(1)–N(1)	2.018(3)	Rh(1)–C(23)	1.803(4)
C(23)–O(1)	1.174(5)		
P(1)–Rh(1)–P(2)	161.44(3)	N(1)–Rh(1)–C(23)	179.22(13)
Rh(1)–C(23)–O(1)	178.4(4)		

Computational Details.

Density-functional-theory (DFT) calculations were performed with the Gaussian 09 program (Rev. E01).^{S19} All geometry optimizations were carried out with the B3LYP functional with the Grimme's dispersion correction (B3LYP-D3).^{S20-24} We employed the SDD (Stuttgart/Dresden pseudopotentials) basis set^{S25,26} for Rh and the 6-31G(d) basis set^{S27-30} for the others. Solvation effects of THF were taken into account by using the polarizable continuum model (PCM)^{S31} for all calculations. Optimized structures were confirmed to have no imaginary frequencies by vibrational analysis. Calculated vibrational frequencies were corrected with a scaling factor of 0.960.^{S32} To discuss the energetics, single-point energy calculations were performed for all optimized structures at the B3LYP-D3/def2-TZVP^{S33,34} level of theory. Energy profiles calculated for silylation of the Rh–dinitrogen complex **3** are described by the Gibbs free energy changes (ΔG) at 233 K (–40 °C). Fig. S6 presents the optimized structure and selected geometric parameters of **3** in the closed-shell singlet state. The triplet and quintet states lie 40.4 and 106.1 kcal/mol above the closed-shell singlet, respectively. Bond dissociation free energy (BDFE) of the Rh–N₂ bond in **3** is calculated as the free energy changes at 233 K (ΔG_{233}) for reaction $[\mathbf{Rh}](\text{N}_2) \rightarrow [\mathbf{Rh}] + \text{N}_2$, where $[\mathbf{Rh}]$ represents Rh(PNP). Electron affinity of **3** was obtained as an energy difference between optimized structures of **3** and its anion $[\mathbf{3}]^-$. Optimized structures and selected geometric parameters of three silylated complexes of **3**, $[\mathbf{Rh}](\text{NN}(\text{SiMe}_3)_x)$ ($x = 1-3$), are shown in Fig. S7. The values of BDFE for the silylation reactions are calculated as ΔG_{233} for reaction of $[\mathbf{Rh}](\text{NN}(\text{SiMe}_3)_x) \rightarrow [\mathbf{Rh}](\text{NN}(\text{SiMe}_3)_{x-1}) + \bullet\text{SiMe}_3$, where $\bullet\text{SiMe}_3$ represents the trimethylsilyl radical. For the silylated complex with $x = 3$, we were able to optimize only a “hydrazide(1–)” complex $[\mathbf{Rh}](\text{Me}_3\text{SiNN}(\text{SiMe}_3)_2)$. Formation of a “hydrazidium” complex $[\mathbf{Rh}](\text{NN}(\text{SiMe}_3)_3)$ was not allowed due to the bulkiness of the SiMe₃ groups. Cartesian coordinates of **3**, $[\mathbf{3}]^-$, $[\mathbf{Rh}]$, and $[\mathbf{Rh}](\text{NN}(\text{SiMe}_3)_x)$ ($x = 1-3$) are listed in Tables S10-S15.

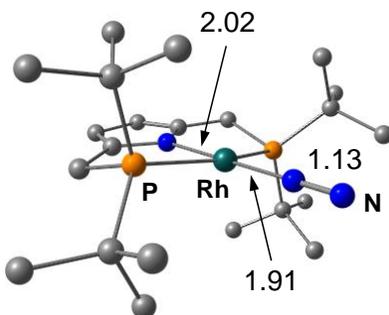


Fig. S6. Optimized structure and selected geometric parameters of $[\text{Rh}](\text{N}_2)$ **3** in the closed-shell singlet state. Bond distances are presented in Å. Hydrogen atoms are omitted for clarity.

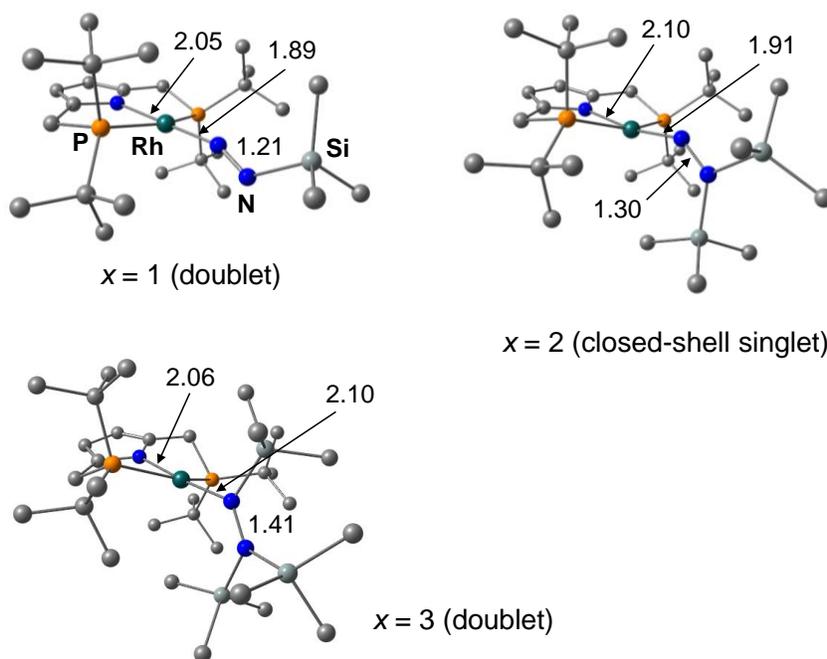


Fig. S7. Optimized structures and selected geometric parameters of silylated complexes of **3**, $[\text{Rh}](\text{NN}(\text{SiMe}_3)_x)$ ($x = 1-3$). Bond distances are presented in Å. Hydrogen atoms are omitted for clarity.

Table S10. Cartesian coordinate of [Rh](N₂) **3** in the closed-shell singlet state. Units are presented in Å.

SCF Energy (opt) = -1821.40226125 hartree
thermal correction (233.15 K) = 0.572886 hartree
SCF Energy (single point) = -1821.89873034 hartree

```
-----  
Atom      Coordinates (Angstroms)  
          X           Y           Z  
-----  
Rh    -0.000001    0.337259    0.000002  
P      2.315445   -0.040003   -0.085317  
N     -0.000002   -1.686296   -0.000001  
N     -0.000000    2.243544   -0.000012  
C      1.090915   -2.494225   -0.248248  
C      0.697131   -3.823123   -0.156278  
H      1.330048   -4.690341   -0.306913  
C      2.398577   -1.844677   -0.595050  
H      2.576475   -1.858957   -1.677431  
H      3.256025   -2.347149   -0.132837  
C      3.336789    0.862348   -1.412390  
C      4.656643    0.152320   -1.774545  
H      4.492802   -0.871090   -2.125812  
H      5.142153    0.704941   -2.589833  
H      5.356321    0.118816   -0.937194  
C      3.633216    2.307327   -0.967900  
H      2.725465    2.832151   -0.653476  
H      4.356686    2.343438   -0.148380  
H      4.064589    2.860086   -1.812624  
C      2.434862    0.911029   -2.667612  
H      2.160969   -0.089729   -3.019964  
H      1.510252    1.463598   -2.473241  
H      2.977638    1.413648   -3.478803  
C      3.126029    0.022396    1.637307  
C      4.642147   -0.233930    1.623291  
H      4.896537   -1.171371    1.116958
```

H	5.189098	0.580828	1.140719
H	5.003800	-0.306723	2.657411
C	2.829694	1.391139	2.285530
H	1.751684	1.577883	2.335031
H	3.224752	1.394397	3.309992
H	3.296460	2.219948	1.747211
C	2.434988	-1.067174	2.489546
H	1.350254	-0.921877	2.524103
H	2.628961	-2.076995	2.115270
H	2.823086	-1.008299	3.514767
P	-2.315447	-0.040000	0.085319
C	-1.090920	-2.494224	0.248247
C	-0.697138	-3.823122	0.156276
H	-1.330056	-4.690340	0.306911
C	-2.398580	-1.844674	0.595053
H	-2.576476	-1.858954	1.677435
H	-3.256030	-2.347145	0.132841
C	-3.336790	0.862352	1.412393
C	-4.656647	0.152328	1.774549
H	-4.492810	-0.871084	2.125809
H	-5.142151	0.704947	2.589841
H	-5.356328	0.118833	0.937200
C	-3.633210	2.307334	0.967909
H	-2.725458	2.832153	0.653481
H	-4.356687	2.343454	0.148395
H	-4.064573	2.860094	1.812639
C	-2.434863	0.911026	2.667616
H	-2.160975	-0.089735	3.019965
H	-1.510251	1.463590	2.473247
H	-2.977637	1.413644	3.478808
C	-3.126026	0.022395	-1.637308
C	-4.642143	-0.233935	-1.623300
H	-4.896534	-1.171374	-1.116963
H	-5.189100	0.580824	-1.140738
H	-5.003789	-0.306735	-2.657422
C	-2.829689	1.391136	-2.285534

H	-1.751679	1.577882	-2.335028
H	-3.224739	1.394389	-3.309999
H	-3.296461	2.219946	-1.747223
C	-2.434979	-1.067176	-2.489540
H	-1.350245	-0.921877	-2.524093
H	-2.628951	-2.076997	-2.115262
H	-2.823072	-1.008305	-3.514764
N	-0.000001	3.369579	-0.000019

Table S11. Cartesian coordinate of [3]⁻ in the doublet state. Units are presented in Å.

SCF Energy (opt) = -1821.44071919 hartree

thermal correction (233.15 K) = 0.569424 hartree

SCF Energy (single point) = -1821.94030772 hartree

```
-----  
Atom      Coordinates (Angstroms)  
          X           Y           Z  
-----  
Rh      -0.003403    0.387813   -0.146535  
P        2.294697   -0.017840   -0.090138  
N        0.001481   -1.704339   -0.176673  
N       -0.005835    2.389584   -0.330284  
C        1.104499   -2.492750   -0.382402  
C        0.743496   -3.833585   -0.233448  
H        1.396536   -4.693595   -0.343688  
C        2.409759   -1.809170   -0.680729  
H        2.607275   -1.761828   -1.760206  
H        3.265686   -2.328404   -0.231749  
C        3.476853    0.890014   -1.289016  
C        4.792973    0.148618   -1.597711  
H        4.615255   -0.848992   -2.012057  
H        5.358663    0.718684   -2.348237  
H        5.431057    0.042303   -0.718233  
C        3.792172    2.298514   -0.750241  
H        2.880742    2.836505   -0.469061  
H        4.456119    2.263990    0.118926  
H        4.301704    2.881208   -1.530057  
C        2.682037    1.043879   -2.606502  
H        2.404584    0.073832   -3.035262  
H        1.761697    1.615134   -2.452082  
H        3.302853    1.570648   -3.344863  
C        3.028934   -0.073512    1.678870  
C        4.531454   -0.390713    1.752802  
H        4.783793   -1.311757    1.215757  
H        5.143031    0.421833    1.349616
```

H	4.824704	-0.529694	2.802946
C	2.740776	1.271801	2.377715
H	1.672072	1.506671	2.338732
H	3.044604	1.206369	3.432062
H	3.286268	2.105312	1.927512
C	2.248581	-1.168976	2.441107
H	1.171345	-0.972769	2.417413
H	2.416636	-2.168194	2.027365
H	2.577751	-1.175786	3.489416
P	-2.291708	-0.025920	0.079350
C	-1.065358	-2.515081	0.114347
C	-0.649461	-3.848255	0.080049
H	-1.264839	-4.721310	0.273298
C	-2.367587	-1.865683	0.498980
H	-2.531006	-1.935223	1.582146
H	-3.237790	-2.341032	0.029109
C	-3.289869	0.776932	1.499442
C	-4.583717	0.040329	1.898137
H	-4.394514	-0.998166	2.188460
H	-5.031999	0.545059	2.765707
H	-5.328681	0.039367	1.099664
C	-3.617994	2.237657	1.137552
H	-2.727830	2.777683	0.798724
H	-4.382596	2.302461	0.357410
H	-4.009144	2.753855	2.025127
C	-2.331479	0.784412	2.712956
H	-2.051113	-0.229259	3.021374
H	-1.410771	1.331298	2.486118
H	-2.829766	1.267333	3.565380
C	-3.247278	0.082006	-1.578134
C	-4.748769	-0.238855	-1.493062
H	-4.939294	-1.205677	-1.013650
H	-5.299686	0.531587	-0.945231
H	-5.170785	-0.284452	-2.506991
C	-3.051986	1.487252	-2.184521
H	-1.989138	1.741176	-2.255744

H	-3.481075	1.508470	-3.196103
H	-3.546296	2.266959	-1.599119
C	-2.567903	-0.934279	-2.524817
H	-1.492744	-0.739804	-2.603288
H	-2.699829	-1.968837	-2.191882
H	-3.012100	-0.843301	-3.525646
N	0.012375	3.402158	0.263890

Table S12. Cartesian coordinate of [Rh] in the closed-shell singlet state. Units are presented in Å.

SCF Energy (opt) = -1711.82207061 hartree

thermal correction (233.15 K) = 0.565607 hartree

SCF Energy (single point) = -1712.27255363 hartree

```
-----
```

Atom	Coordinates (Angstroms)		
	X	Y	Z
Rh	0.000002	0.454012	-0.000026
P	2.305783	0.124258	-0.086518
N	-0.000003	-1.525855	0.000093
C	1.091561	-2.328541	-0.256500
C	0.694714	-3.658773	-0.160907
H	1.328347	-4.525242	-0.313395
C	2.399953	-1.679956	-0.602985
H	2.576529	-1.690126	-1.685797
H	3.256165	-2.187678	-0.143834
C	3.331945	1.028420	-1.415211
C	4.663400	0.339841	-1.773487
H	4.515586	-0.692348	-2.106433
H	5.136260	0.886541	-2.600547
H	5.367968	0.331747	-0.939955
C	3.599648	2.479691	-0.973916
H	2.677335	2.986645	-0.664632
H	4.315185	2.532404	-0.148187
H	4.024506	3.042673	-1.815408
C	2.437258	1.060875	-2.676228
H	2.188953	0.055436	-3.033549
H	1.495769	1.587768	-2.485712
H	2.970627	1.580625	-3.483308
C	3.147862	0.174101	1.626315
C	4.666761	-0.060850	1.601071
H	4.930493	-0.987982	1.080504
H	5.200323	0.767121	1.125700
H	5.037380	-0.142503	2.631705

```
-----
```

C	2.838211	1.531727	2.291653
H	1.756490	1.702269	2.346666
H	3.235271	1.532330	3.315683
H	3.292258	2.372119	1.759616
C	2.480451	-0.932181	2.475490
H	1.393222	-0.807828	2.511555
H	2.692531	-1.935980	2.094972
H	2.869415	-0.872804	3.500653
P	-2.305780	0.124279	0.086503
C	-1.091569	-2.328505	0.256787
C	-0.694729	-3.658750	0.161358
H	-1.328366	-4.525197	0.313954
C	-2.399957	-1.679870	0.603196
H	-2.576531	-1.689904	1.686010
H	-3.256172	-2.187645	0.144109
C	-3.331947	1.028608	1.415079
C	-4.663435	0.340108	1.773384
H	-4.515664	-0.692050	2.106447
H	-5.136307	0.886911	2.600369
H	-5.367974	0.331944	0.939828
C	-3.599594	2.479845	0.973638
H	-2.677258	2.986737	0.664318
H	-4.315117	2.532502	0.147895
H	-4.024443	3.042923	1.815069
C	-2.437294	1.061156	2.676118
H	-2.189029	0.055744	3.033540
H	-1.495784	1.588002	2.485577
H	-2.970669	1.580998	3.483134
C	-3.147855	0.173897	-1.626337
C	-4.666773	-0.060927	-1.601048
H	-4.930579	-0.987944	-1.080315
H	-5.200265	0.767174	-1.125823
H	-5.037402	-0.142733	-2.631666
C	-2.838092	1.531379	-2.291917
H	-1.756358	1.701831	-2.346943
H	-3.235135	1.531825	-3.315953

H	-3.292085	2.371902	-1.760042
C	-2.480535	-0.932593	-2.475314
H	-1.393297	-0.808326	-2.511417
H	-2.692683	-1.936305	-2.094602
H	-2.869509	-0.873381	-3.500482

Table S13. Cartesian coordinate of [Rh](NNSiMe₃) in the doublet state. Units are presented in Å.

SCF Energy (opt) = -2230.63919672 hartree

thermal correction (233.15 K) = 0.678284 hartree

SCF Energy (single point) = -2231.21748765 hartree

Atom	Coordinates (Angstroms)		
	X	Y	Z
Rh	-0.008397	0.348468	0.033867
P	2.297394	0.766445	0.097547
N	-0.028795	2.380642	-0.196717
N	0.007300	-1.534502	0.232769
C	1.050513	3.220243	-0.029773
C	0.635905	4.533235	-0.227026
H	1.256960	5.419483	-0.158067
C	2.366525	2.621607	0.379286
H	2.550176	2.770666	1.450729
H	3.218876	3.066795	-0.147095
C	3.310567	0.034519	1.531335
C	4.619530	0.792669	1.832277
H	4.440116	1.843477	2.080689
H	5.103716	0.329485	2.702378
H	5.327719	0.754016	1.002126
C	3.623607	-1.448696	1.254665
H	2.723429	-2.010920	0.989969
H	4.358732	-1.569696	0.453568
H	4.046437	-1.900994	2.161333
C	2.392305	0.116470	2.772890
H	2.104754	1.147915	3.005956
H	1.476352	-0.464985	2.630698
H	2.929966	-0.285293	3.642062
C	3.134699	0.496783	-1.594601
C	4.649306	0.762045	-1.595090
H	4.893414	1.755783	-1.203819
H	5.194140	0.014780	-1.011084

H	5.023169	0.710805	-2.626318
C	2.852728	-0.942174	-2.075065
H	1.776855	-1.139740	-2.108592
H	3.257180	-1.068121	-3.088390
H	3.318658	-1.697333	-1.436857
C	2.448938	1.467223	-2.583422
H	1.364898	1.314903	-2.605678
H	2.638813	2.517017	-2.340245
H	2.844020	1.279777	-3.590489
P	-2.322262	0.700630	-0.069933
C	-1.136038	3.147751	-0.488754
C	-0.762435	4.487170	-0.515939
H	-1.411035	5.329919	-0.728071
C	-2.442182	2.449611	-0.742969
H	-2.646908	2.362512	-1.817520
H	-3.296067	2.980767	-0.306292
C	-3.328351	-0.345907	-1.300253
C	-4.674949	0.284345	-1.708577
H	-4.547116	1.274073	-2.158384
H	-5.151908	-0.358222	-2.460684
H	-5.365270	0.376280	-0.868109
C	-3.570935	-1.753079	-0.721009
H	-2.645751	-2.207202	-0.352986
H	-4.298329	-1.738430	0.095881
H	-3.973861	-2.401641	-1.509982
C	-2.441431	-0.479231	-2.559890
H	-2.211635	0.494366	-3.007546
H	-1.493968	-0.975503	-2.331260
H	-2.976116	-1.075135	-3.311621
C	-3.129334	0.773525	1.654369
C	-4.650666	0.994598	1.630609
H	-4.930818	1.873576	1.039851
H	-5.182671	0.126081	1.232013
H	-5.007227	1.156372	2.656621
C	-2.796415	-0.523561	2.421585
H	-1.714807	-0.685626	2.468117

H	-3.177046	-0.439288	3.448231
H	-3.253356	-1.407804	1.970404
C	-2.456031	1.948296	2.400440
H	-1.367829	1.830092	2.429067
H	-2.680363	2.917803	1.945312
H	-2.827980	1.967758	3.433198
N	0.037547	-2.581687	0.839417
Si	0.061362	-4.192275	-0.038860
C	-0.202695	-3.903351	-1.877773
H	-0.176656	-4.852137	-2.427405
H	-1.171632	-3.426520	-2.061289
H	0.577177	-3.249730	-2.284099
C	-1.338779	-5.171894	0.743477
H	-1.386964	-6.185271	0.326847
H	-1.200187	-5.254293	1.827571
H	-2.301589	-4.680933	0.558292
C	1.752793	-4.922887	0.337237
H	1.838573	-5.934340	-0.078267
H	2.546551	-4.305778	-0.099754
H	1.922835	-4.981931	1.418318

Table S14. Cartesian coordinate of [Rh](NN(SiMe₃)₂) in the closed-shell singlet state. Units are presented in Å.

SCF Energy (opt) = -2639.91724789 hartree
thermal correction (233.15 K) = 0.79128 hartree
SCF Energy (single point) = -2640.57668832 hartree

```
-----  
Atom      Coordinates (Angstroms)  
          X           Y           Z  
-----  
Rh      0.203317    -0.546186    0.076252  
P       1.544118    -0.242666   -0.184683  
N       0.891433    -2.514696    0.346858  
N      -0.461509     1.142979   -0.511781  
C       2.162183    -2.961875    0.083792  
C       2.230756    -4.333819    0.323079  
H       3.104693    -4.964588    0.200614  
C       3.147603    -1.993483   -0.496074  
H       3.216002    -2.112174   -1.584917  
H       4.161985    -2.134433   -0.107225  
C       3.077446     0.690272   -1.762540  
C       4.512668     0.379473   -2.232202  
H       4.667506    -0.689693   -2.407742  
H       4.692832     0.897096   -3.184119  
H       5.269931     0.722369   -1.525032  
C       2.927959     2.208156   -1.544048  
H       1.966465     2.462492   -1.086761  
H       3.728264     2.604195   -0.912805  
H       2.987642     2.722498   -2.512256  
C       2.097267     0.246431   -2.873013  
H       2.153837    -0.831094   -3.064552  
H       1.063639     0.489430   -2.618194  
H       2.358981     0.764555   -3.805600  
C       3.579530     0.290156    1.331542  
C       5.104934     0.256651    1.127685  
H       5.460173    -0.699638    0.731050
```

H	5.441181	1.054570	0.460088
H	5.595818	0.413641	2.097605
C	3.171459	1.704894	1.779250
H	2.088749	1.814204	1.803007
H	3.553542	1.894716	2.791128
H	3.577359	2.478922	1.124162
C	3.196328	-0.709977	2.446883
H	2.116365	-0.717717	2.621191
H	3.503685	-1.733167	2.208579
H	3.697177	-0.414720	3.378308
P	-1.829718	-1.779299	0.133905
C	0.133378	-3.594181	0.728882
C	0.926415	-4.740719	0.730404
H	0.604819	-5.743442	0.990826
C	-1.328981	-3.378858	0.973667
H	-1.562562	-3.253833	2.038972
H	-1.937585	-4.216961	0.613834
C	-3.391215	-1.283283	1.119701
C	-4.335128	-2.459176	1.445653
H	-3.829714	-3.245231	2.015350
H	-5.159590	-2.082872	2.066137
H	-4.774815	-2.911678	0.555984
C	-4.165077	-0.174371	0.385124
H	-3.504546	0.651998	0.107750
H	-4.662904	-0.538812	-0.518042
H	-4.942832	0.225770	1.049637
C	-2.875767	-0.692546	2.446089
H	-2.237391	-1.387412	3.002328
H	-2.302458	0.213655	2.261677
H	-3.730185	-0.434345	3.085969
C	-2.295364	-2.286049	-1.656821
C	-3.563648	-3.150878	-1.760121
H	-3.504886	-4.046816	-1.132847
H	-4.465605	-2.595275	-1.490039
H	-3.684451	-3.483736	-2.799755
C	-2.467705	-1.014506	-2.513487

H	-1.579885	-0.378137	-2.460589
H	-2.623672	-1.307638	-3.560681
H	-3.330726	-0.417787	-2.206925
C	-1.108313	-3.087106	-2.239287
H	-0.183986	-2.502929	-2.220354
H	-0.927420	-4.020350	-1.697690
H	-1.338370	-3.338582	-3.283474
N	-0.770898	2.294959	-0.003306
Si	-1.467413	3.356716	-1.344712
C	-1.232705	5.186022	-0.941921
H	-1.640431	5.765744	-1.780330
H	-1.753358	5.507817	-0.034685
H	-0.173204	5.445770	-0.842410
C	-3.301690	2.960761	-1.498375
H	-3.760106	3.627102	-2.240113
H	-3.447187	1.929539	-1.835511
H	-3.833196	3.091040	-0.549666
C	-0.583023	2.975530	-2.957009
H	-0.923368	3.686068	-3.721660
H	0.501675	3.076361	-2.857294
H	-0.800125	1.961397	-3.303543
Si	-0.716265	2.832382	1.778266
C	0.488430	4.283540	1.883616
H	0.784970	4.421984	2.930874
H	1.397834	4.087618	1.304553
H	0.052429	5.220949	1.528602
C	-2.482901	3.366701	2.173824
H	-2.539674	3.693241	3.219975
H	-2.831003	4.192461	1.544848
H	-3.175183	2.526639	2.046074
C	-0.173416	1.455883	2.940973
H	-0.962311	1.237061	3.668052
H	0.049104	0.535181	2.378636
H	0.724577	1.753328	3.491276

Table S15. Cartesian coordinate of [Rh](Me₃SiNN(SiMe₃)₂) in the doublet state. Units are presented in Å.

SCF Energy (opt) = -3049.16913774 hartree
thermal correction (233.15 K) = 0.910106 hartree
SCF Energy (single point) = -3049.9127114 hartree

```

-----
Atom      Coordinates (Angstroms)
          X           Y           Z
-----
Rh      0.635110    0.202814    0.084722
P       2.074658   -1.770351    0.267150
N       2.553301    0.899760   -0.196170
N      -1.325802   -0.434332    0.523985
C       3.703875    0.343390    0.301505
C       4.800127    1.065082   -0.167268
H       5.843523    0.854429    0.039270
C       3.529649   -0.915492    1.092366
H       3.233742   -0.707572    2.127118
H       4.428252   -1.538332    1.121199
C       1.683130   -3.272419    1.400667
C       2.712637   -4.416501    1.398471
H       3.715870   -4.059299    1.653854
H       2.419324   -5.150438    2.161702
H       2.762661   -4.945443    0.444295
C       0.296305   -3.819242    1.010500
H      -0.448419   -3.020439    0.959858
H       0.318690   -4.327487    0.044058
H      -0.035723   -4.550470    1.759775
C       1.610867   -2.735152    2.842830
H       2.602045   -2.492774    3.239279
H       0.990516   -1.845481    2.910413
H       1.173220   -3.504005    3.492972
C       2.887339   -2.430234   -1.367240
C       4.305814   -3.008435   -1.165179
H       5.009546   -2.234866   -0.843702

```

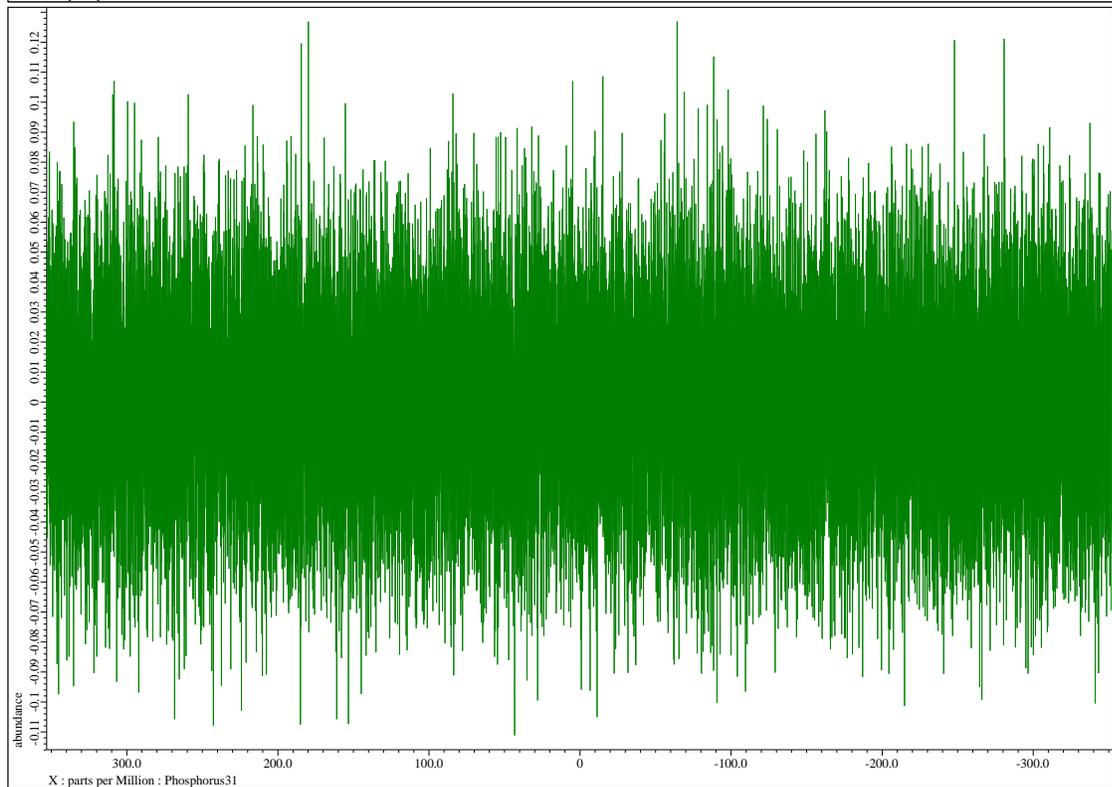
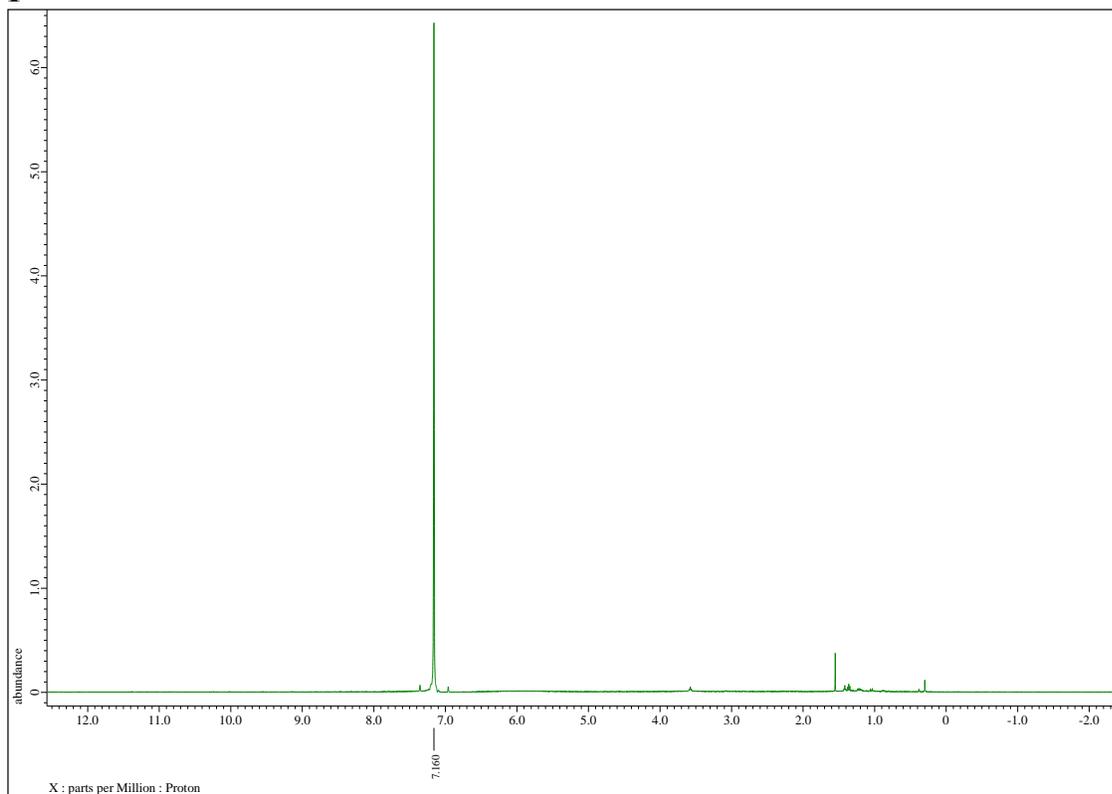
H	4.349894	-3.833914	-0.455569
H	4.663001	-3.387440	-2.132465
C	1.976666	-3.513465	-1.977217
H	0.941790	-3.177317	-2.061487
H	2.332416	-3.759809	-2.986429
H	1.984240	-4.438647	-1.395573
C	3.044711	-1.274292	-2.384329
H	2.121275	-0.727255	-2.553359
H	3.800473	-0.556351	-2.059798
H	3.370210	-1.703789	-3.342484
P	0.331538	2.584563	-0.289141
C	2.890410	1.975385	-0.972242
C	4.277403	2.117137	-0.980429
H	4.841183	2.891940	-1.488116
C	1.756785	2.793842	-1.505003
H	1.386197	2.417898	-2.468707
H	2.028462	3.843710	-1.648634
C	-1.145228	3.346159	-1.263132
C	-0.741951	4.519986	-2.180291
H	-0.026551	4.210524	-2.948091
H	-1.639790	4.884236	-2.698062
H	-0.312851	5.361247	-1.633620
C	-2.284848	3.797189	-0.330978
H	-2.549341	3.022598	0.395506
H	-2.039126	4.714824	0.209816
H	-3.177447	4.003467	-0.936490
C	-1.689384	2.216402	-2.151989
H	-0.933507	1.847879	-2.848548
H	-2.044873	1.377125	-1.551950
H	-2.533956	2.594396	-2.744454
C	0.829084	3.800044	1.136517
C	1.016700	5.254489	0.664213
H	1.732467	5.342992	-0.159082
H	0.073609	5.714050	0.356670
H	1.408788	5.847420	1.501667
C	-0.216773	3.782003	2.265481

H	-0.365754	2.771432	2.639212
H	0.152652	4.393415	3.099901
H	-1.183644	4.187655	1.967652
C	2.159226	3.312128	1.754026
H	2.090459	2.273517	2.086213
H	2.996088	3.384336	1.056635
H	2.384948	3.939504	2.627258
N	-2.348492	-0.935627	-0.307876
Si	-4.157928	-0.964872	0.029278
C	-4.953915	-2.471253	-0.812188
H	-6.030912	-2.376492	-0.618806
H	-4.824175	-2.607862	-1.883823
H	-4.616710	-3.383108	-0.305545
C	-4.881545	0.663235	-0.608682
H	-5.952123	0.708643	-0.372958
H	-4.394784	1.524120	-0.138769
H	-4.764516	0.773234	-1.689551
C	-4.884905	-1.270095	1.758925
H	-5.957892	-1.089020	1.602372
H	-4.774505	-2.319813	2.045061
H	-4.571337	-0.649960	2.594214
Si	-1.982932	-1.479382	-2.027920
C	-1.911662	-3.368710	-2.047367
H	-1.577116	-3.698709	-3.039484
H	-1.190704	-3.734390	-1.312157
H	-2.873233	-3.843497	-1.838353
C	-3.291759	-0.868365	-3.267509
H	-3.001162	-1.327627	-4.223004
H	-4.341158	-1.105397	-3.095535
H	-3.200412	0.215374	-3.395035
C	-0.414049	-0.807564	-2.813724
H	-0.679802	-0.152584	-3.649308
H	0.196773	-0.238964	-2.095843
H	0.186761	-1.629757	-3.208024
Si	-1.621156	-0.244671	2.300566
C	-2.872687	1.155109	2.612783

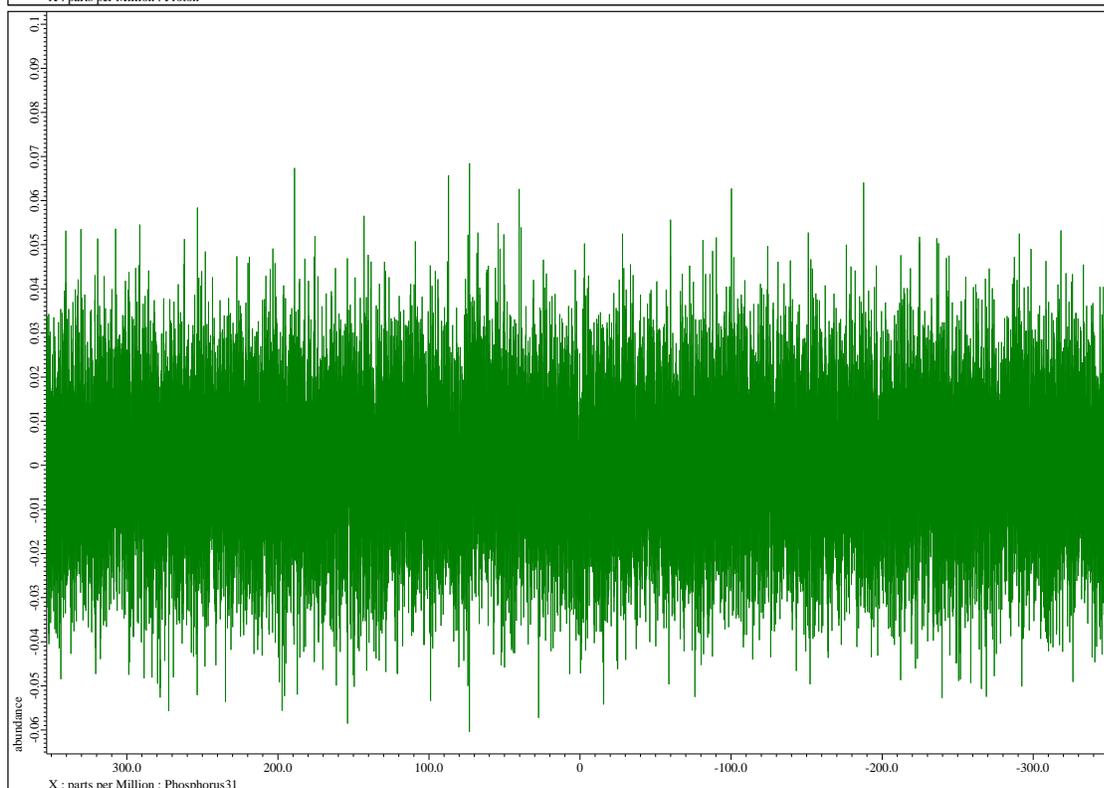
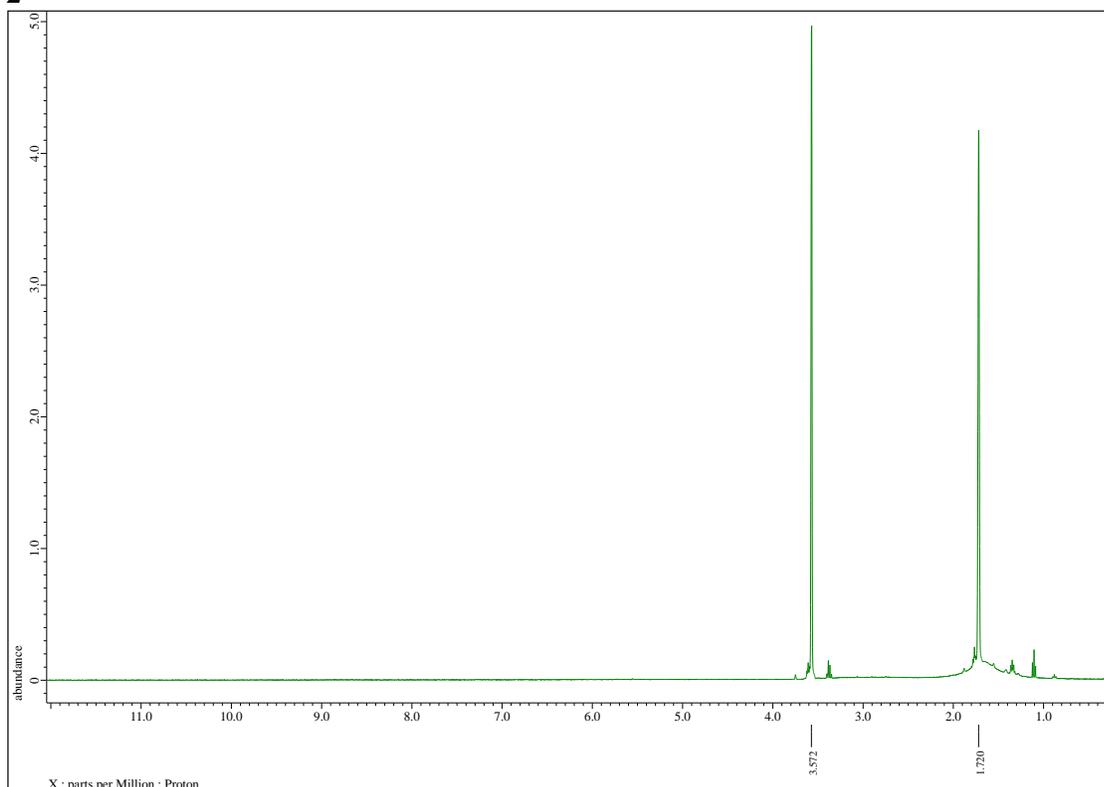
H	-2.335599	2.105773	2.577669
H	-3.708160	1.227159	1.917437
H	-3.283203	1.049824	3.626265
C	-0.124407	0.293542	3.346862
H	0.775982	0.463959	2.749543
H	-0.365345	1.219370	3.879225
H	0.094132	-0.466719	4.104511
C	-2.109995	-1.945789	2.997051
H	-2.799071	-1.845472	3.843795
H	-2.573942	-2.601710	2.257240
H	-1.205797	-2.445967	3.357427

^1H and ^{31}P NMR Spectra.

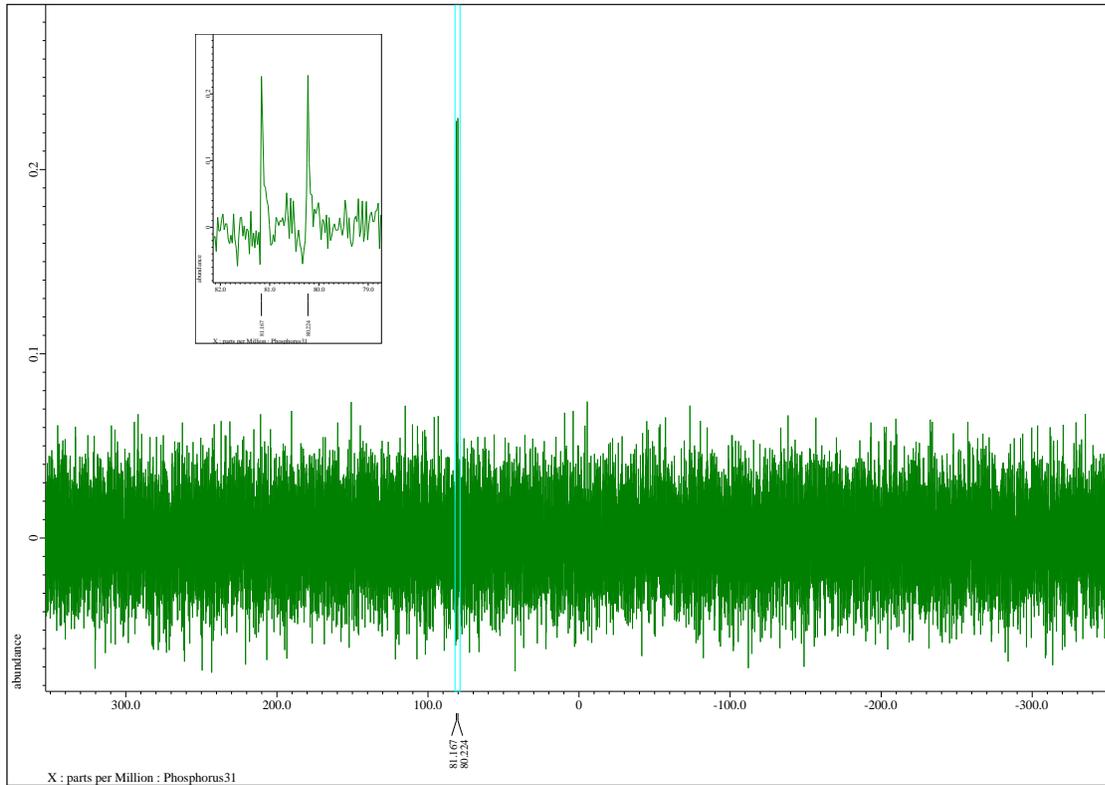
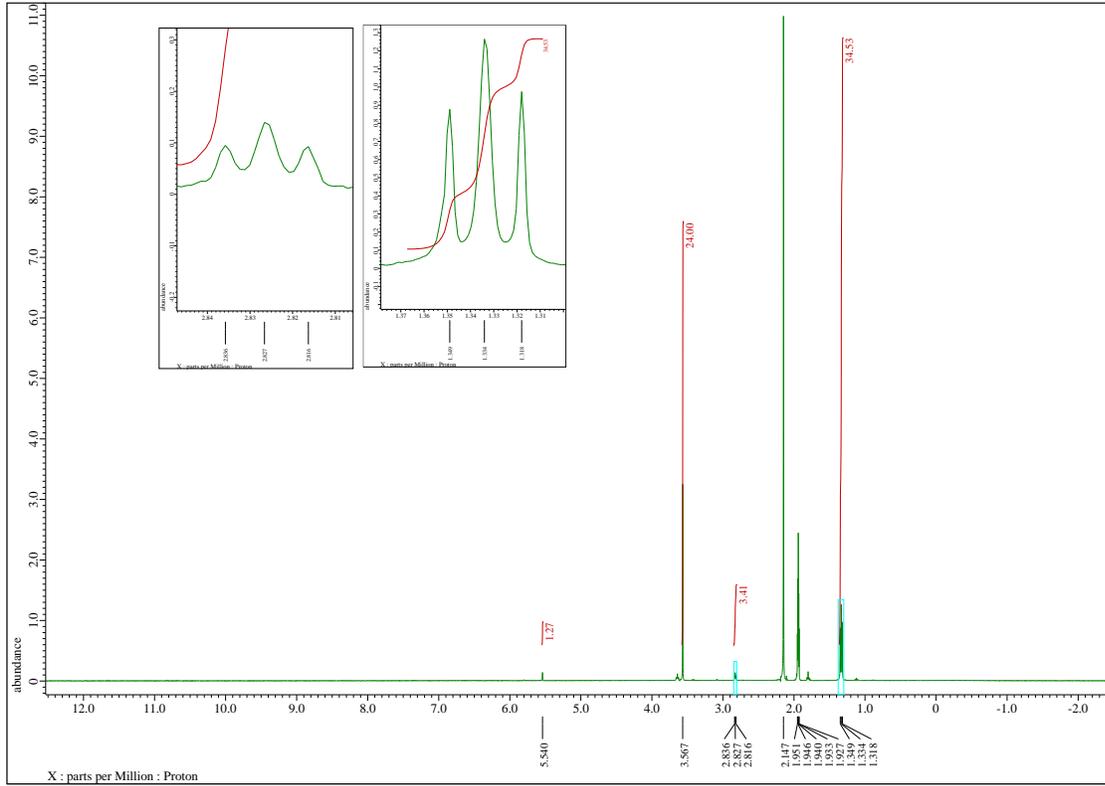
1



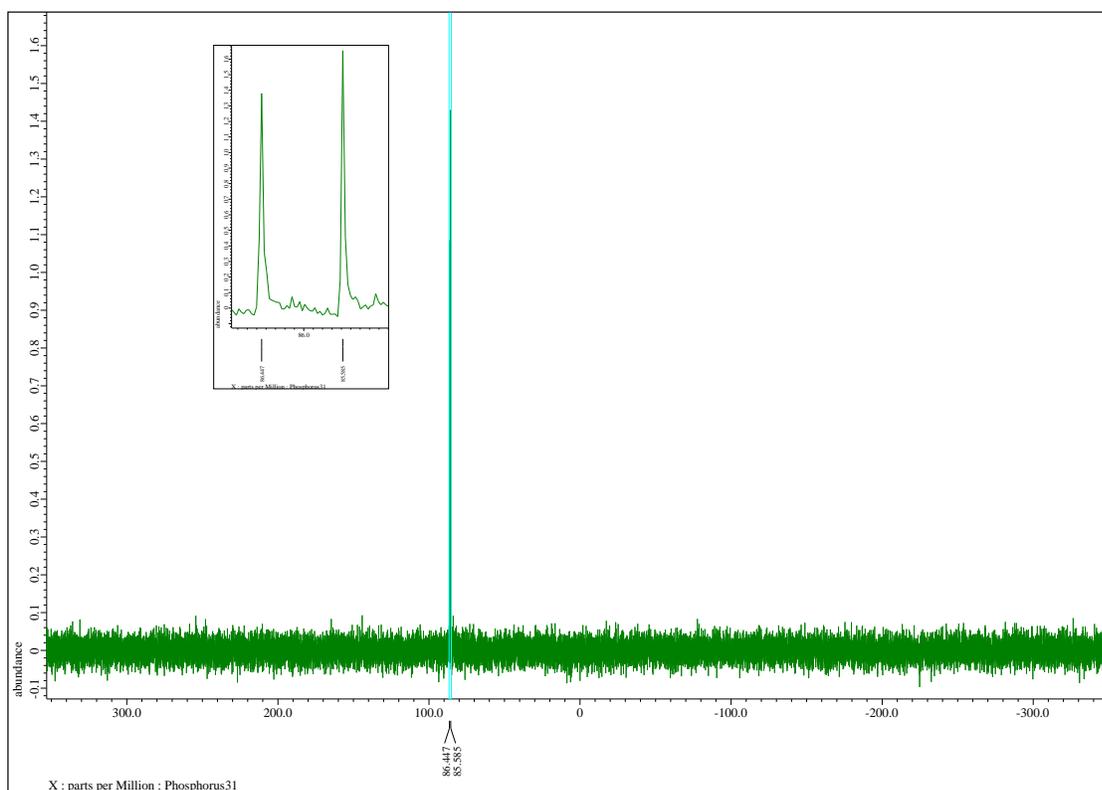
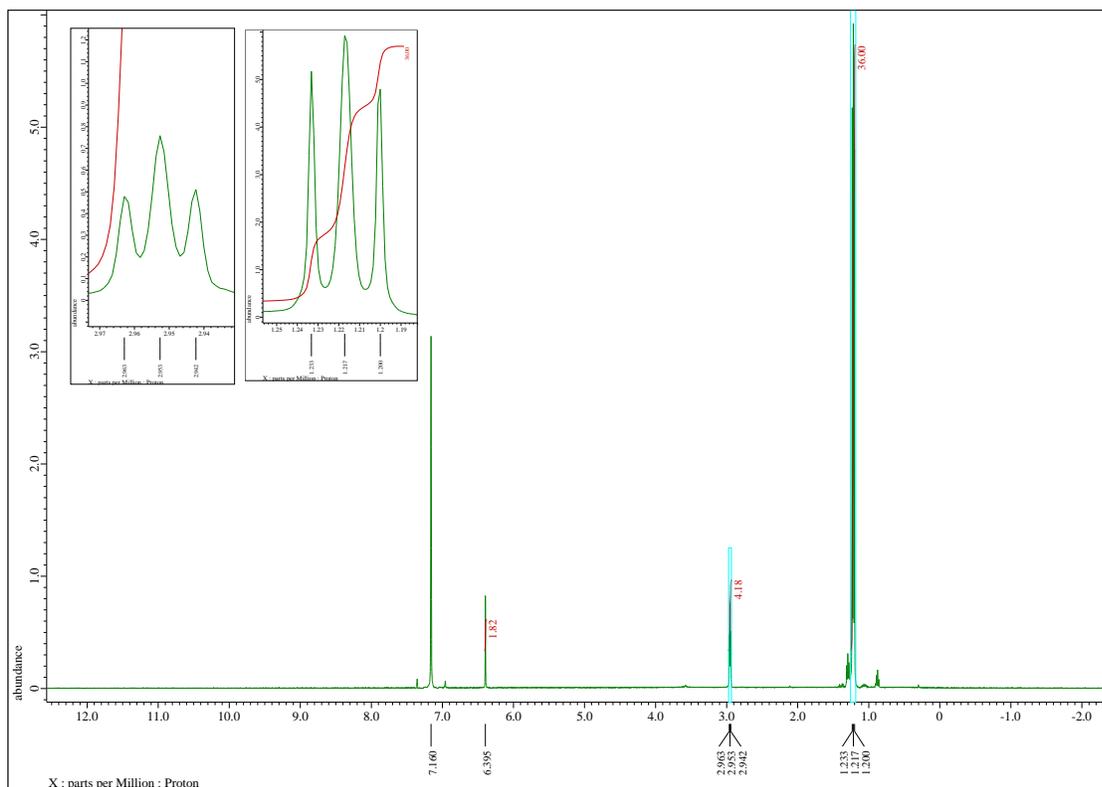
2

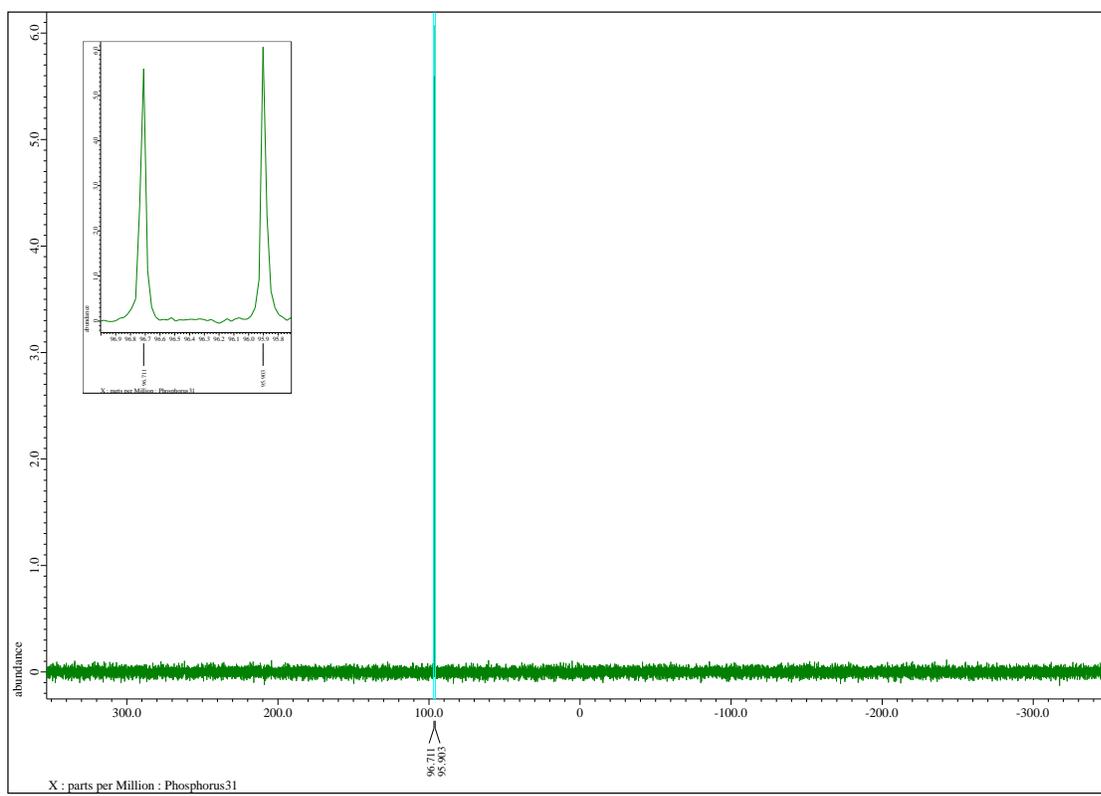
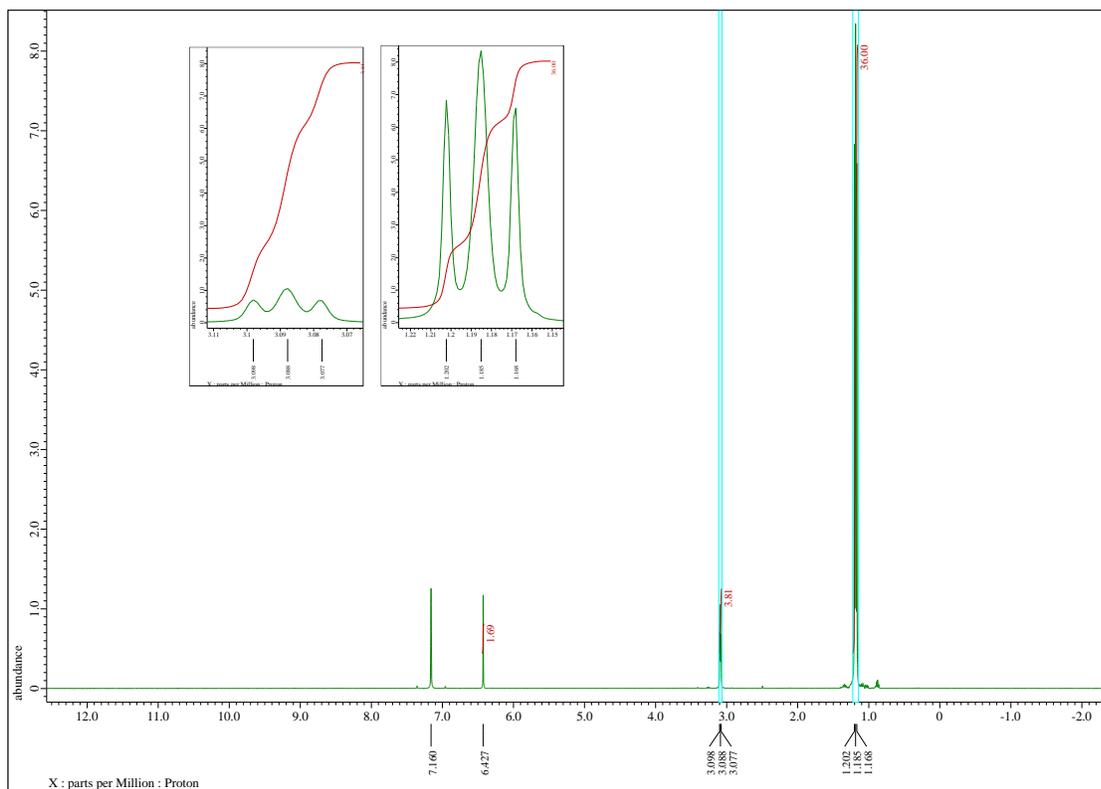


2'

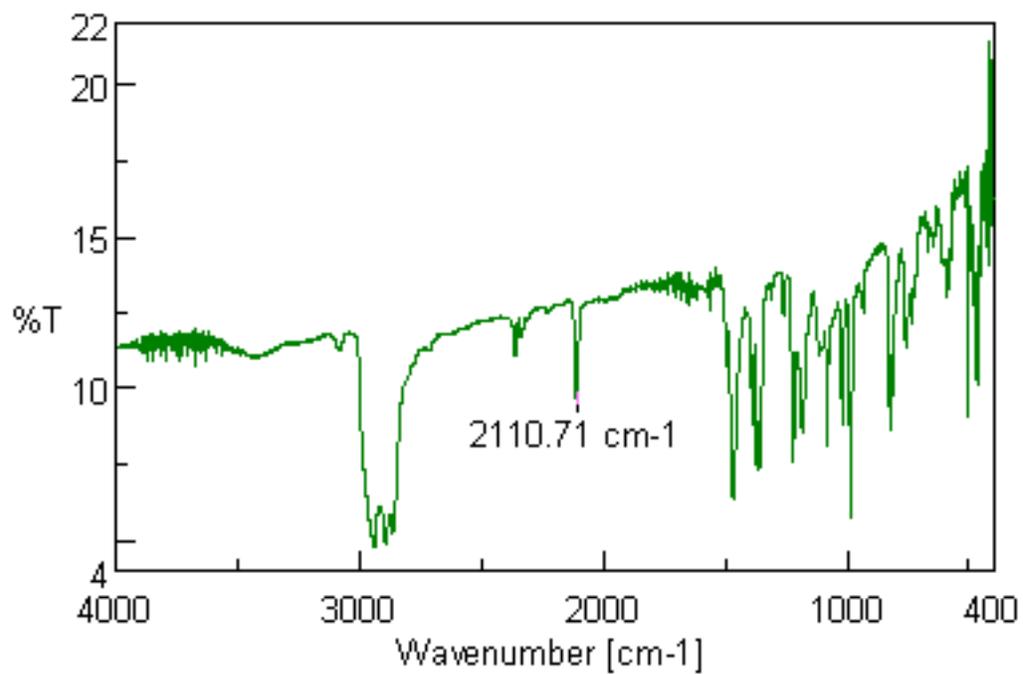


3

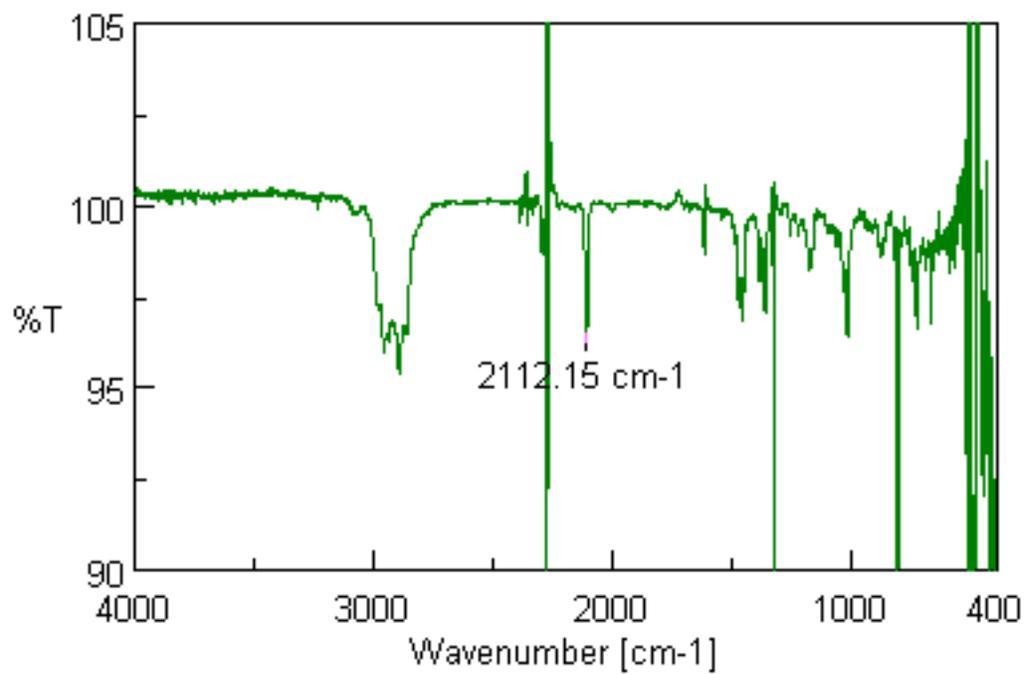




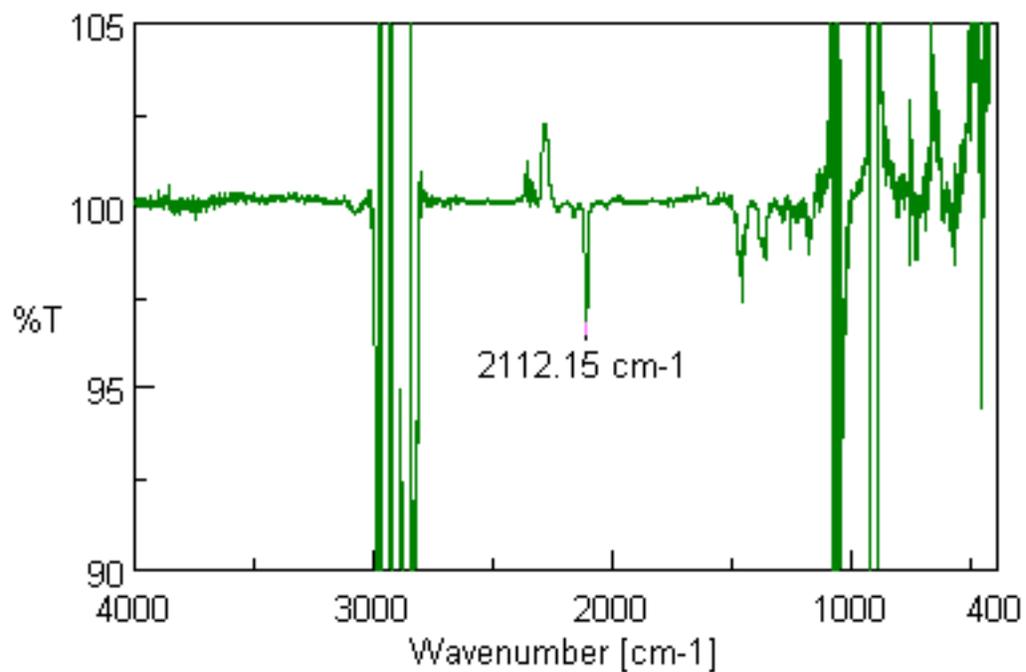
IR Spectra.
3 (KBr)



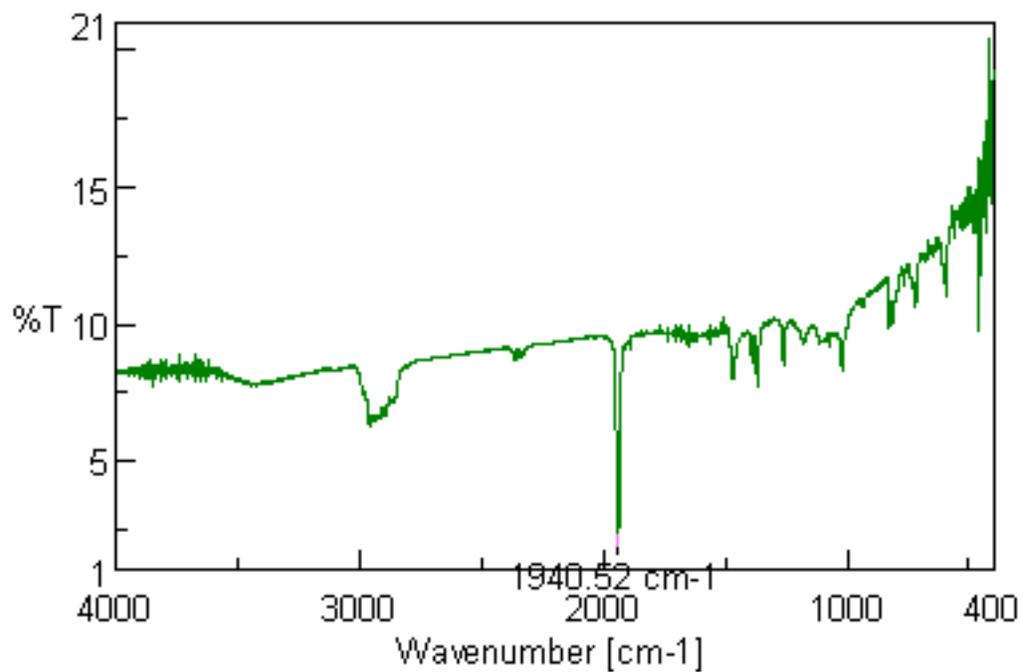
3 (C₆D₆)



3 (THF)



4 (KBr)



References.

- S1 (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791. (c) Bain, G. A.; Berry, J. F. *J. Chem. Educ.* **2008**, *85*, 532.
- S2 Kuriyama, S.; Arashiba, K.; Nakajima, K.; Matsuo, Y.; Tanaka, H.; Ishii, K.; Yoshizawa, K.; Nishibayashi, Y. *Nat. Commun.* **2016**, *7*, 12181.
- S3 Catsikis, B.; Good, M. L. *J. Inorg. Nucl. Chem.* **1968**, *4*, 529.
- S4 Nakayama S.; Morisako, S.; Yamashita, M. *Organometallics*, **2018**, *37*, 1304.
- S5 Reger, D. L.; Little, C. A.; Lamba, J. J. S.; Brown, K. J. *Inorg. Synth.* **2004**, *34*,5.
- S6 Weitz, I. S.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 117.
- S7 Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.
- S8 Arashiba, K.; Kinoshita, E.; Kuriyama, S.; Eizawa, A.; Nakajima, K.; Tanaka, H.; Yoshizawa, K.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2015**, *137*, 5666.
- S9 Yandulov, D. V.; Schrock, R. R. *Can. J. Chem.* **2005**, *83*, 341.
- S10 Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, .
- S11 Weatherburn, M. W. *Anal. Chem.* **1967**, *39*, 971.
- S12 Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006.
- S13 (a) Anderson, J. S.; Rittle, J.; Peters, J. C. *Nature* **2013**, *501*, 84. (b) Ashida, Y.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. *Nature* **2019**, *568*, 536. (c) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120.
- S14 Higashi, T. *ABSCOR*: Program for Absorption Correction; Rigaku Corporation: Tokyo, Japan, 1995.
- S15 *CrystalStructure* 4.3: Crystal Structure Analysis Package; Rigaku Corporation: Tokyo, Japan, 2000-2018.
- S16 Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97: a new tool for crystal structure determination and refinement, *J. Appl. Crystallogr.* **1999**, *32*, 115.
- S17 Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *PATY: The DIRDIF Program System*; Technical Report of the Crystallography Laboratory; University of Nijimegen: Nijimegen, The Netherlands, 1992.
- S18 Sheldrick, G. M. Crystal structure refinement with SHELXL, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *C71*, 3.

- S19 Frisch, M. J. *et al.* *Gaussian 09*, Revision E.01; Gaussian, Inc.: Wallingford CT, 2013.
- S20 Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- S21 Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- S22 Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- S23 Vosko, S. H.; Wilk, L.; Nusair, M. J. *Can. J. Phys.* **1980**, *58*, 1200.
- S24 Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
- S25 Dolg, M.; Wedig, U.; Stoll, H.; Preuß, H. *J. Chem. Phys.* **1987**, *86*, 866.
- S26 Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. *Theor. Chim. Acta.* **1990**, *77*, 123.
- S27 Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728.
- S28 Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.
- S29 Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acc.* **1973**, *28*, 213–222.
- S30 Francl, M. M.; Pietro, W. J.; Hehre, W. J. *J. Chem. Phys.* **1982**, *77*, 3654–3665.
- S31 Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999–3094.
- S32 Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.
- S33 Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- S34 Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.