Supporting Information

N_2 Provides Insight into the Mechanism of H-C(sp^3) Bond Cleavage

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Experimental.

General Considerations: All manipulations were performed using standard Schlenk or glovebox techniques in inert (Argon) atmosphere. All solvents, including deuterated NMR solvents, were dried over and distilled from Na/benzophenone, CaH_2, or 4Å molecular sieves, then degassed and stored in air tight vessels. All other reagents were degassed and / or used as received from commercial vendors. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on either a Varian Unity I400 (400 MHz ^1H, 101 MHz ^{13}C, 162 MHz ^{31}P, 376 MHz ^{19}F) instrument, or a Varian Gemini 2000 (300 MHz ^1H, 75 MHz ^{13}C, 121 MHz ^{31}P, 282 MHz ^{19}F) instrument, with chemical shifts reported in ppm, referenced to protio impurities in each stated solvent, with the exception of $^{31}P\{^1H\}$and $^{19}F\{^1H\}$ spectra which were externally referenced to 85% H_3PO_4 (0 ppm), and neat CF_3CO_2H (-78.5 ppm), respectively. All FT-IR spectra were recorded on a Nicolet 510P spectrophotometer.

Reaction of PNPRuCl with Tetramethylammonium Fluoride (Me_4NF):

To 300 mg (0.513 mmol) of PNPRuCl in THF, 140 mg (3 eq.) of very dry Me_4NF (and 78 mg of CsF as an HF scavenger) were added, and the mixture stirred at ambient temperature for 90 minutes. The mixture was then filtered and stripped to dryness. The green residue was then redissolved in 5 mL of pentane and placed in a freezer, overnight at -40 C^o. Bright pea green crystals of (PNP)RuF were collected (185 mg) and the amount of solvent reduced and the solution placed back in the freezer overnight. A second crop (60 mg) of comparable purity was then isolated; total percent yield is 85%. Minor impurities include (PNP)RuCl and a (PNP)Ru complex where the ligand has been hydrolyzed, presumably by water from Me_4NF. ^1H NMR (400 MHz, THF-D_8): δ 24.68 (s, 12H, SiMe_2), -7.52 (s, 36H, PCMe_3), -37.43 (s, 4H, Si-CH_2-P). $^{31}P\{^1H\}$ NMR(161.2 MHz, THF-D_8): No signal from -500 to +500 ppm. $^{19}F\{^1H\}$ NMR (376 MHz, THF-D_8): No signal from +100 to -500 ppm.

Reaction of PNPRuF and trifluoromethanesulfonatotrimethylsilane (TMSOTf):

To 9.98 mg (0.0171 mmol) of PNPRuF in C_6D_6, 3.2 μL of TMSOTf was added. Upon addition of TMSOTf at 22 C, there was a rapid, distinct color change of the solution from pea green to yellow-orange, quantitatively yielding (PNP)Ru(OTf): ^1H NMR (400 MHz, C_6D_6): δ 32.42 (s, 12H, SiMe_2), -12.26 (s, 36H, PCMe_3), -38.18 (s, 4H, Si-CH_2-P). $^{19}F\{^1H\}$ NMR (376

MHz, C_6D_6): δ -24.00 (s, CF_3 of PNPRuOTf). $^{31}P\{^1H\}$ NMR (161.2 MHz, C_6D_6): no signal in -500 – +500 ppm.

Reaction of PNPRuOTf with excess N_2: Product **2**

To 10.4 mg (0.0171 mmol) of PNPRuF in C_6H_6, 3.2 μL of TMSOTf was added, in a J-Young tube. Upon addition of TMSOTf at 22 C, there was a rapid, distinct color change of the solution from pea green to yellow-orange. Volatiles were stripped by vacuum and the resultant oily residue was redissolved in C_6D_6, and immediately frozen in liquid N_2. The headspace of the tube was then charged with 1 atm of N_2, and the tube was then allowed to thaw, and mixed vigorously to ensure homogeneity. Conversion to **2** was quantitative.

^1H NMR (400 MHz, C_6D_6): Selected resonances - δ 3.41 (bs, 1H, N-H backbone), 1.38 (d, J_{P-H} = 18.4 Hz, 9H, PC*Me₃*), 1.30 (d, J_{P-H} = 16.0 Hz, 9H, PC*Me₃*), 0.97 (d, J_{P-H} = 14.4 Hz, 9H, PC*Me₃*), 0.44 (s, 3H, Si*Me*), 0.38 (s, 3H, Si*Me*), 0.18 (s, 3H, Si*Me*), 0.01 (s, 3H, Si*Me*). $^{31}P\{^1H\}$ NMR (161.2 MHz, C_6D_6) δ 55.10 (d, J_{P-P}= 283 Hz, A of AX), 15.29 (d, J_{P-P}=285 Hz, X of AX). $^{19}F\{^1H\}$NMR (376 MHz, C_6D_6) δ -81.23 ppm. After approximately 30 minutes, bright orange crystals began to precipitate. FT-IR: KBr – 2079 cm^{-1}.

Variable Temperature study:

To 10.2 mg (0.0171 mmol) of PNPRuF in C_6H_6, 3.2 μL of TMSOTf was added, in a J-Young tube, stripped to dryness, and solid (PNP)Ru(OTf) redissolved in C_7D_8 under N_2. The dark orange mixture was kept frozen until it was placed into a precooled NMR probe, where spectra were obtained at -60 ^oC up to 20 ^oC in 10 or 20 degree increments. The spectra are as follows:

^1H NMR (400 MHz, C_7D_8, -60 ^oC): δ 3.23 (bs, N-H of **2**), 1.21 (br), 0.38 (br s). $^{31}P\{^1H\}$ NMR (161.2 MHz, C_7D_8, -60 ^oC): δ 93.3 (s, A of AX pattern for **X**), 59.8 (s, X of AX pattern for **X**), 50.1 (d, J_{P-P}=277 Hz, A of AX pattern for **2**), 17.1 (d, J_{P-P}=277 Hz, X of AX pattern for **2**). $^{19}F\{^1H\}$ NMR (376.4 MHz, C_7D_8, -60^oC): δ -80.24 (s, **X**), -81.13 (bs, **2**).

^1H NMR (400 MHz, C_7D_8, -50 ^oC): δ 3.25 (bs, N-H of **2**), 1.31 (br), 1.10 (br), 0.93 (br), 0.72 (br), 0.33 (br), 0.21 (br), 0.14 (br). $^{31}P\{^1H\}$ NMR (161.2 MHz, C_7D_8, -50 ^oC): δ 93.1 (s, A of AX pattern for species **X**), 59.8 (s, X of AX pattern for species **X**), 50.1 (d, J_{P-P}=270 Hz, A of AX pattern for **2**), 17.0 (d, J_{P-P}=270 Hz, X of AX pattern for **2**) $^{19}F\{^1H\}$ NMR (376.4 MHz, C_7D_8, -50^oC): δ -80.22 (s, **X**), -81.21 (bs, **2**).

^1H NMR (400 MHz, C_7D_8, -40 ^oC): δ 3.25 (bs, N-H of **2**), 1.49 (br s), 1.36 (br s), 1.11 (br s), 0.92 (br s), 0.72 (br s), 0.36 (br s), 0.20 (br s), 0.15 (br s) $^{31}P\{^1H\}$ NMR (161.2 MHz, C_7D_8, -40 ^oC): δ 50.2 (d, J_{P-P}=270 Hz, A of AX pattern for **2**), 17.1 (d, J_{P-P}=270 Hz, X of AX pattern for **2**). $^{19}F\{^1H\}$ NMR (376.4 MHz, C_7D_8, -40^oC): δ -81.21 (bs, **2**).

^1H NMR (400 MHz, C_7D_8, -30 ^oC): δ 3.25 (bs, N-H of **2**), 1.46 (br s), 1.35 (br s), 1.08 (bd, J_{P-H} = 1.0 Hz), 0.91 (bd, J_{P-H} = 1.2 Hz), 0.17 (s), 0.13 (s). $^{31}P\{^1H\}$ NMR (161.2 MHz, C_7D_8, -30 ^oC): δ 51.4 (d, J_{P-P}=270 Hz, A of AX pattern for **2**), 17.1 (d, J_{P-P}=272 Hz, X of AX pattern for **2**). $^{19}F\{^1H\}$ NMR (376.4 MHz, C_7D_8, -30^oC): δ -81.17 (bs, **2**).

^1H NMR (400 MHz, C_7D_8, -20 ^oC): δ 3.27 (bs, N-H of **2**), 1.42 (bd, J_{P-H} = 10.8 Hz, PC*Me₃*), 1.30 (bd, J_{P-H} = 10.6 Hz, PC*Me₃*), 1.00 (bd, J_{P-H} = 4.2 Hz, PC*Me₃*), 0.32 (s, Si*Me*), 0.23 (s, Si*Me*), 0.15 (s, Si*Me*), -0.06 (s, Si*Me*). $^{31}P\{^1H\}$ NMR (161.2 MHz, C_7D_8, -20 ^oC): δ 52.14 (d,

J_{P-P}= 276 Hz, A of AX pattern for **2**), 16.37 (d, J_{P-P}=278 Hz, X of AX pattern for **2**). $^{19}F\{^{1}H\}$ NMR (376.4 MHz, C_7D_8, -20^{o}C): δ -81.18 (bs, **2**).

^{1}H NMR (400 MHz, C_7D_8, 0 ^{o}C): δ 3.36 (bs, 1H, N-H of **2**), 1.37 (d, J_{P-H} = 17.6 Hz, 9H, PC*Me₃*), 1.28 (d, J_{P-H} = 16.8 Hz, 9H, PC*Me₃*), 0.98 (d, J_{P-H} = 12.4 Hz, 9H, PC*Me₃*), 0.41 (s, 3H, Si*Me*), 0.38 (s, 3H, Si*Me*), 0.14 (s, 3H, Si*Me*), 0.00 (s, 3H, Si*Me*). $^{31}P\{^{1}H\}$ NMR (161.2 MHz, C_7D_8, 0 ^{o}C): δ 54.14 (d, J_{P-P}= 280 Hz, A of AX pattern for **2**), 15.35 (d, J_{P-P}=280 Hz, X of AX pattern for **2**). $^{19}F\{^{1}H\}$ NMR (376.4 MHz, C_7D_8, 0^{o}C): δ -81.18 (bs, **2**).

^{1}H NMR (400 MHz, C_7D_8, 20 ^{o}C): δ 3.40 (bs, 1H, N-H of **2**), 1.37 (d, J_{P-H} = 17.8 Hz, 9H, PC*Me₃*), 1.29 (d, J_{P-H} = 17.6 Hz, 9H, PC*Me₃*), 0.98 (d, J_{P-H} = 14.0 Hz, 9H, PC*Me₃*), 0.40 (s, 3H, Si*Me*), 0.38 (s, 3H, Si*Me*), 0.15 (s, 3H, Si*Me*), 0.00 (s, 3H, Si*Me*). $^{31}P\{^{1}H\}$ NMR (161.2 MHz, C_7D_8, 20^{o}C) δ 55.14 (d, J_{P-P}= 282 Hz, A of AX pattern for **2**), 15.37 (d, J_{P-P}=282 Hz, X of AX pattern for **2**). $^{19}F\{^{1}H\}$ NMR (376.4 MHz, C_7D_8, 20^{o}C): δ -81.23 (bs, **2**).

X-Ray Structure Determination

Data collection

A orange crystal (approximate dimensions 0.30 × 0.28 × 0.25 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a SMART6000 (Bruker) at 130(2) K. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 2 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of a sphere. Four major sections of frames were collected with 0.30º steps in ω at different ϕ settings and a detector position of –43° in 2θ. An additional set of 50 frames was collected in order to model decay. Data to a resolution of 0.80 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 4009 strong reflections from the actual data collection after integration (SAINT).[1] The intensity data were corrected for absorption (SADABS).[2]

Structure solution and refinement

The space group $P2_1/n$ was determined based on intensity statistics and systematic absences. The structure was solved using SIR-92[3] and refined with SHELXL-97.[4] A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters; the exception is H1n, which was refined for all parameters. The final full matrix least squares refinement converged to R1 = 0.0478 and wR2 = 0.1162 (F^2, all data). The remaining electron density is located near the metal.

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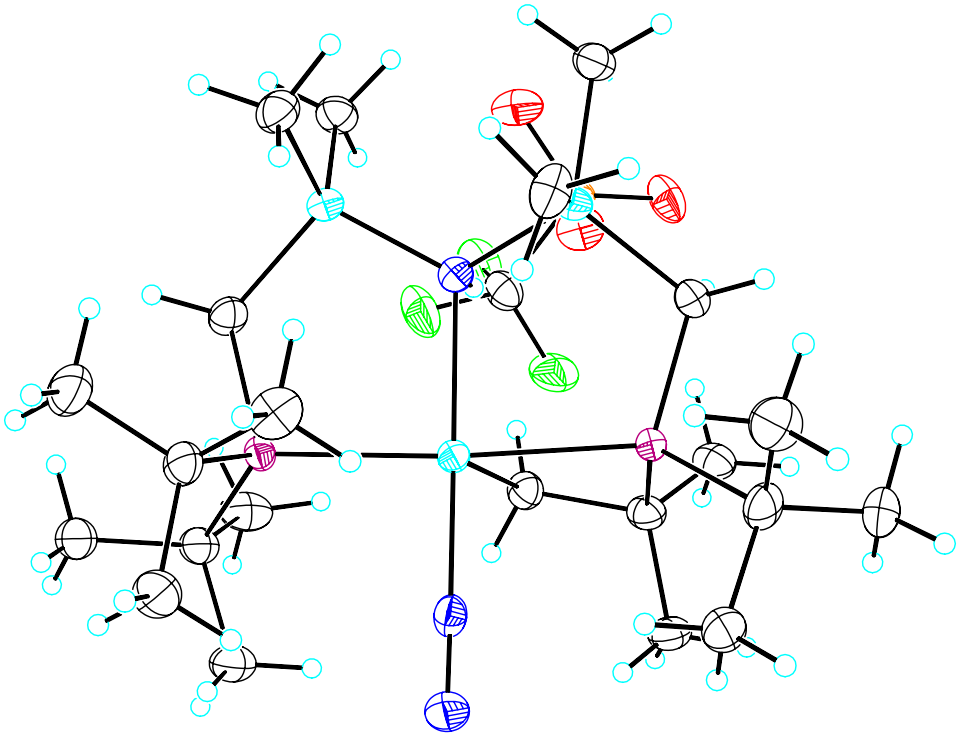
[1] SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.

[2] An empirical correction for absorption anisotropy, R. Blessing, Acta Cryst. A51, 33 - 38 (1995).

[3] SIR-92, A. Altomare, G. Cascarno, C. Giacovazzo, A. Gualardi, J. Appl. Cryst. 26, 343-350 (1993).

[4] SHELXTL-Plus, Bruker Analytical X-Ray Systems, Madison, WI, current version.



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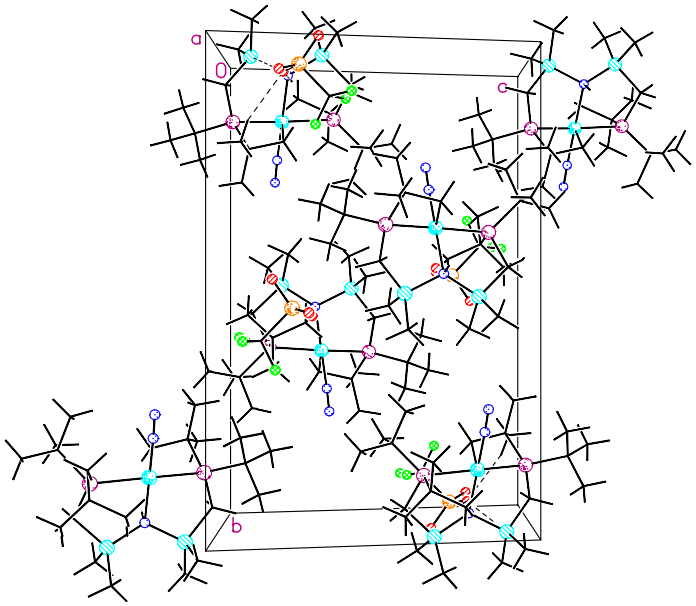


Cell plot, view along *a*.

Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 5.5 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[2-5] functional and the 6-31G** basis set. The transition metals were represented using the Los Alamos LACVP** basis[6-8] that includes relativistic effective core potentials. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ζ basis set[9] ccpVTZ(-f) that includes a double set of polarization functions. For all transition metals, we used a modified version of LACVP**, designated as LACV3P**, in which the exponents were decontracted to match the effective core potential with the triple-ξ.

References

(1) Jaguar. *5.5 ed, Schrödinger, L.L.C, Portland, OR, 1991-2003*.
(2) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(3) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(4) Lee, C. T.; Yang, W. T.; Parr, R. G. *1988* **Phys. Rev. B**, *37*, 785.
(5) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(6) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
(7) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(8) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
(9) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

S1. Energy profile.

E(SCF) of N_2: -109.56463 Hartree.

Reactant (PNP)Ru(OTf) (**1**) —(+ N_2, -1.4 kcal/mol)→ (PNP)Ru(N_2)(OTf) (**3**)

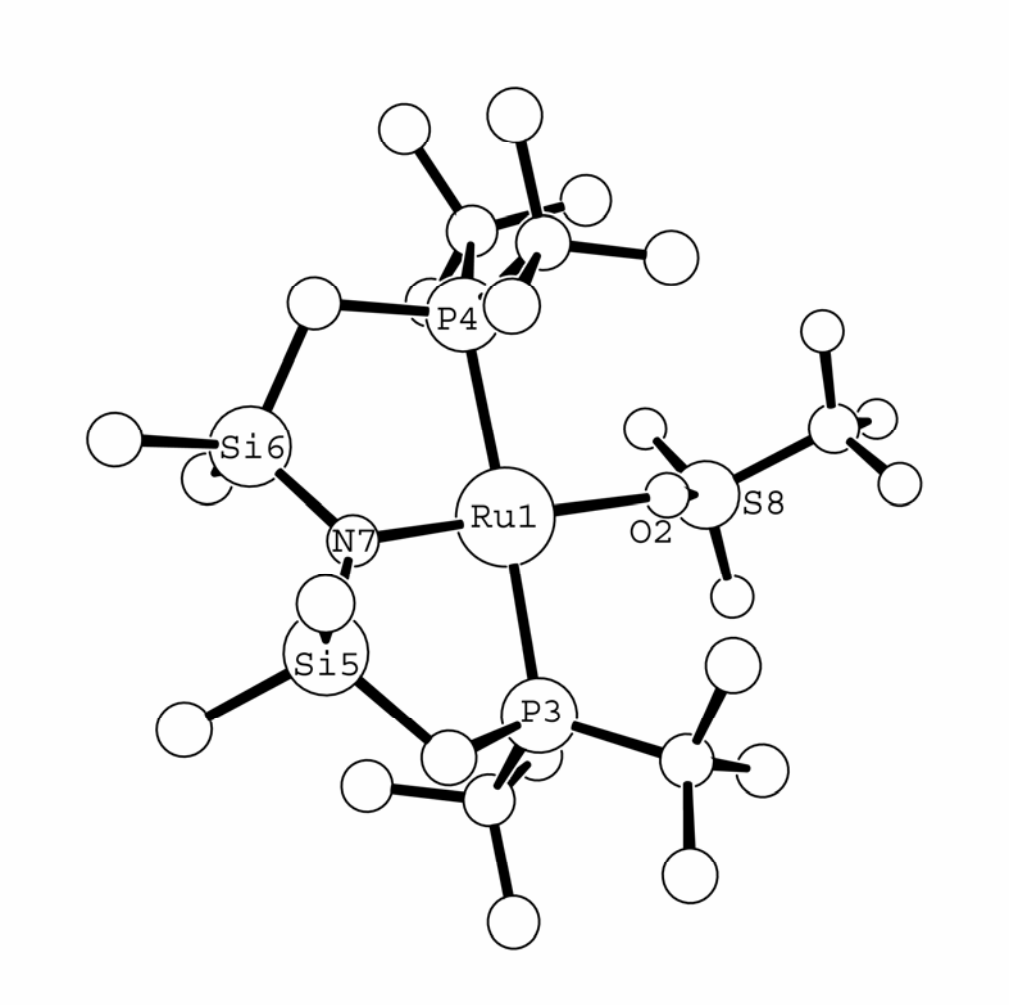
Reactant (PNP)Ru(OTf) (**1**) —(+29.4 kcal/mol)→ (PNP')Ru(H)(OTf) (**4**)

Reactant (PNP)Ru(OTf) (**1**) —(+11.4 kcal/mol)→ (PNHP')Ru(OTf) (**5**)

Reactant (PNP)Ru(OTf) (**1**) —(+ N_2, -0.0 kcal/mol)→ (PNHP')Ru(N_2)(OTf) (**X**) —(-7.1kcal/mol)→ Product (**2**)

S2. Optimized Structure and energy of the reactant (PNP)Ru(OTf), **1**.

Triplet ground state, E(SCF) = -3242.31666 Hatree.



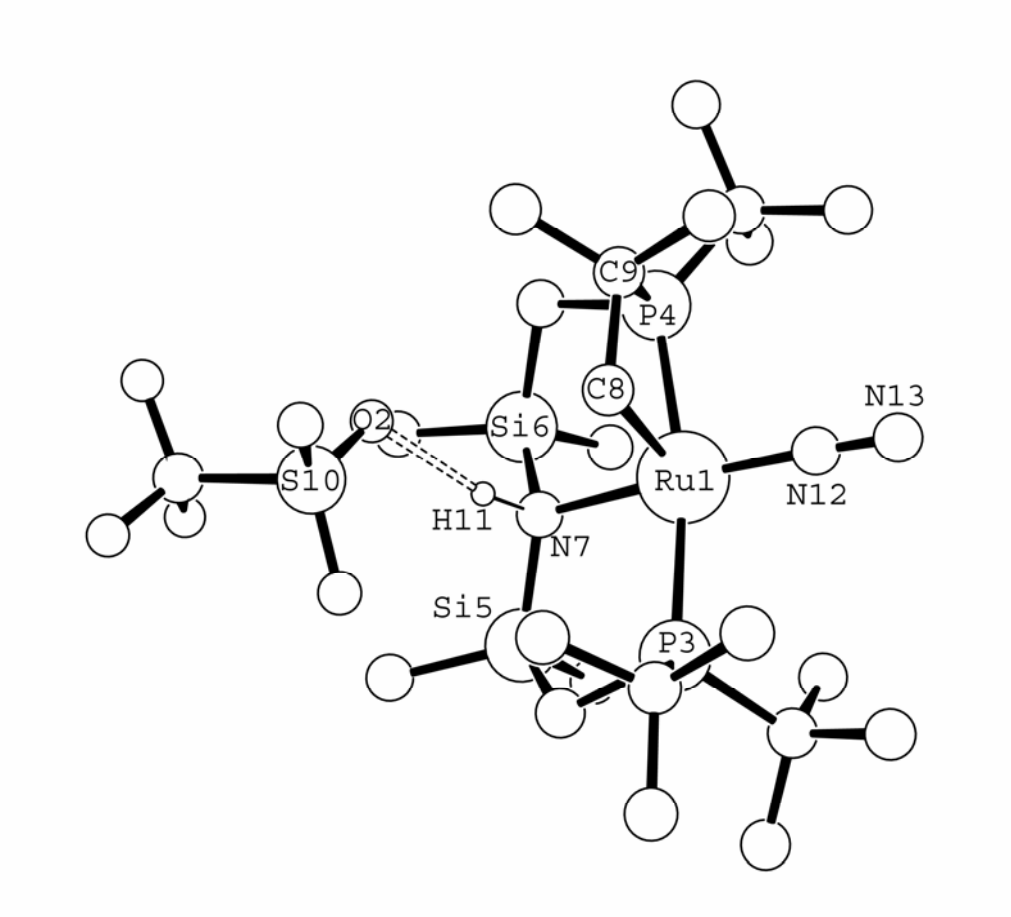
Select bond lengths (in Å) and bond angles (in ˚):

Ru1–O2:	2.19	O2-Ru1-P4:	93.8
Ru1-N7:	2.05	O2-Ru1-N7:	175.9
Ru1-P4:	2.53	P4-Ru1-P3:	171.1
O2-S8 :	1.52	P4-Ru1-N7:	87.3
N7-Si6:	1.76	S8-O2-Ru1:	133.3
Ru1-P3:	2.47	Si5-N7-Ru1:	121.3
		Si6-N7-Ru1:	116.1
		Si6-N7-Si5:	122.5

Coordinates:

Ru	14.620341954	1.716547164	18.955706267
O	15.696033918	1.528146308	17.054471446
P	16.021036618	-0.038778898	19.987104844
P	13.298186519	3.739695780	18.198525481
Si	14.588012036	1.529195259	22.268259415
Si	12.104893169	2.588214926	20.786922298
N	13.739646284	1.946186529	20.789477528
C	15.320157036	3.062134351	23.117708426
H	14.541822588	3.765584271	23.433164488
H	16.000329588	3.602012567	22.448751896
H	15.887974247	2.779856604	24.013338622
C	13.529769697	0.634172554	23.571884094
H	12.949174781	1.339387093	24.174664243
H	14.181823924	0.084616505	24.262612230
H	12.832122485	-0.086898170	23.134105052
C	16.060451717	0.423276148	21.782672146
H	16.962682569	1.025898482	21.931223243
H	16.167916942	-0.453987951	22.429920347
C	15.267254152	-1.801019721	19.946368193
C	13.955367367	-1.756491824	20.758317270
H	13.426467269	-2.708735445	20.627839031
H	13.290943780	-0.955539299	20.421337971
H	14.134849628	-1.627442785	21.829168803
C	16.178985115	-2.881468981	20.558208676
H	15.626790243	-3.828714793	20.605464183
H	16.488650814	-2.637214236	21.580012643
H	17.074828615	-3.059740823	19.959120075
C	14.915377355	-2.169250911	18.491529395
H	14.454812217	-3.165267618	18.476755989
H	15.777473494	-2.186259161	17.825057718
H	14.193454367	-1.466107191	18.065056293
C	17.891570733	-0.064979252	19.516866773
C	18.789609299	-0.617267945	20.644591962
H	19.832515370	-0.583362340	20.305263268
H	18.562373633	-1.656055730	20.893141960
H	18.732052443	-0.028229905	21.563565804
C	18.161723746	-0.870661517	18.232354571
H	19.204944626	-0.708782537	17.931596042
H	17.524217033	-0.574261368	17.399570399
H	18.039328160	-1.946374908	18.389026581
C	18.267555865	1.412316456	19.260384985
H	19.344652969	1.482376886	19.062651822
H	18.055836320	2.053580418	20.124679686
H	17.737305722	1.807255800	18.390533425
C	11.486186463	3.260482487	22.453533173
H	12.178602258	3.979992950	22.904108476
H	11.290278100	2.472695436	23.186705488
H	10.537647381	3.786361829	22.285435052
C	10.863131703	1.269081503	20.228981497
H	11.150001984	0.810649367	19.277021170
H	9.852740120	1.680580210	20.113347822
H	10.805172896	0.465487012	20.972740282
C	12.093546402	4.055780128	19.581451810
H	11.088013065	4.222585743	19.187740080
H	12.369377602	4.967718341	20.122121805
C	14.501184297	5.241237366	18.239137608
C	13.819856424	6.596751915	17.982178810
H	14.541175510	7.405671535	18.156694581
H	12.969838058	6.768577390	18.650073635
H	13.472138003	6.692460598	16.951184267
C	15.137280714	5.265988511	19.646337283
H	15.886726798	6.066213035	19.683335994
H	15.643504234	4.324505755	19.880741119
H	14.412030051	5.460001924	20.441028365
C	15.638664767	5.023709036	17.219268730
C	12.170266618	3.799636109	16.628927393
C	11.466123689	2.426341814	16.568729427
H	10.788942572	2.410136882	15.705424111
H	10.857438904	2.240864533	17.459612492
H	12.182433270	1.612372639	16.440988828
C	12.995774373	4.005558915	15.344698018
H	12.342963217	3.836627220	14.479215944
H	13.824048526	3.305121963	15.260172472
H	13.374866430	5.028914263	15.265359992
C	11.085213460	4.897856021	16.679645797
H	10.541306324	4.881807791	15.727209982
H	11.494170821	5.902001985	16.804561031
H	10.343737416	4.732054999	17.465556493
S	15.428666778	0.744339681	15.776220346
C	16.545577610	1.672510469	14.613219410
O	14.066513117	0.918503305	15.255129991
O	15.973135365	-0.618607011	15.799001252
F	16.442885689	1.160969403	13.383259690
F	17.818694410	1.581859734	15.018855192
F	16.208143037	2.972634251	14.565276170
H	16.128001486	4.056001487	17.354176782
H	15.293975187	5.073135768	16.186558635
H	16.393814366	5.808694274	17.354282944

S3. Optimized Structure and energy of the product (Compound **2**) $[(PNHP')Ru(N_2)]^+[OTf]^-$, **2**. Singlet ground state, E(SCF) = -3351.89266 Hartree.



Select bond lengths (in Å) and bond angles (in ˚):

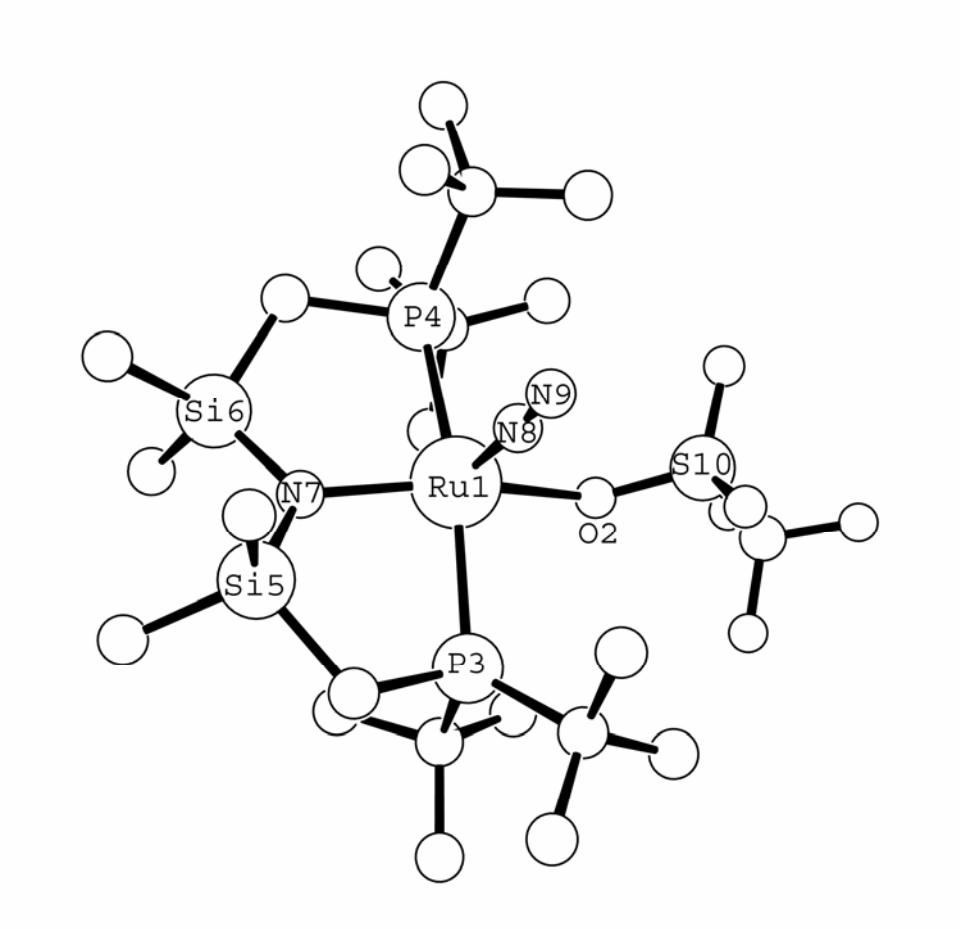
N12-N13:	1.13	N13-N12-Ru1:	77.7
Ru1-N12:	1.91	N12-Ru1-P4:	94.5
Ru1-C8:	2.12	N12-Ru1-C8:	89.4
Ru1-P4:	2.40	P4-Ru1-C8:	68.6
Ru1-P3:	2.48	P4-Ru1-N7:	87.1
Ru1-N7:	2.30	C8-Ru1-N7:	96.0
N7-H11:	1.04	H11-N7-Ru1:	100.4
N7-Si6:	1.81	Si6-N7-Ru1:	111.2
O2-H11:	1.85	Si6-N7-Si5:	121.1
O2-N7:	2.85	Si5-N7-Ru1:	114.0
		O2-H11-N7:	158.5

Coordinates:

Ru	14.574116953	3.597362797	17.083253802	C	13.405545764	7.662133113	17.470245071
N	15.391248372	3.690343286	15.356638936	C	14.430129734	6.983418674	15.289556949
P	16.599236869	2.574491224	18.077161422	N	15.876408131	3.700213214	14.339266762
P	12.706901051	4.982341758	16.483356793	H	13.800254866	4.168041843	19.596706098
Si	14.265799020	1.954297147	20.113693849	O	13.577987763	5.817214560	20.412879184
Si	11.741649318	3.469485182	18.968878549	S	14.764336855	6.181477336	21.259278402
C	13.953337660	2.159240577	21.958580153	C	13.955842883	6.543881699	22.891457734
H	12.895180552	2.050021398	22.215814727	O	15.439736626	7.426500452	20.871905942
H	14.301184518	3.134202410	22.308967035	O	15.631950880	5.010630713	21.544976107
H	14.504805902	1.382963032	22.504070179	F	14.873518912	6.805955689	23.829408989
C	13.542849042	0.271740336	19.621425914	F	13.227809713	5.480613783	23.291955724
H	12.628611030	0.081203478	20.194340412	F	13.135102935	7.597877176	22.788125124
H	14.251015016	-0.523389525	19.884329371	H	17.751721008	-1.099266330	17.555069290
H	13.294017708	0.159967518	18.563969935	H	16.780787504	-0.489464192	18.892249470
C	16.128171275	2.121930850	19.814787458	H	18.431771944	0.105226719	18.653713904
H	16.376641006	2.991751360	20.433952116	H	18.004301570	0.123516536	15.447240122
H	16.700769748	1.278213891	20.209495103	H	18.981415287	1.279605457	16.348129729
C	16.978085515	0.889146742	17.187447146	H	17.653142929	1.847444751	15.318557961
C	18.230272597	3.588615857	18.297450822	H	15.802571963	-0.577288341	16.096485087
C	10.923117521	3.703273569	20.651048434	H	15.251026043	1.081131622	15.834102324
H	11.489591534	4.418540875	21.254774834	H	14.878913140	0.242620810	17.353194726
H	10.843972630	2.764069719	21.208989894	H	19.529608503	4.866340232	17.136243685
H	9.906097421	4.094213582	20.526546771	H	17.917553599	4.713265420	16.435933850
C	10.984107003	1.976838687	18.093060839	H	19.090754154	3.400089862	16.262118970
H	11.521760674	1.705673310	17.179355627	H	18.870866301	5.336546213	19.382131654
H	9.948450952	2.202462963	17.813139498	H	17.537064070	4.525517254	20.202241174
H	10.957535498	1.096745609	18.741960445	H	17.226008202	5.492686418	18.772750710
C	11.546303479	5.044361267	17.935870028	H	20.217823799	3.386845428	19.128654013
C	11.574078930	5.038998576	14.941770127	H	19.677774622	1.918758540	18.314459036
C	17.517323750	-0.198764846	18.137753942	H	19.037882694	2.339654630	19.916742820
C	17.964277526	1.063178679	16.013935287	H	9.935993388	3.869683333	14.145930771
C	15.643528332	0.391627053	16.589114831	H	9.920333014	3.933969942	15.908586574
C	19.345289530	2.745979962	18.947393376	H	11.092007352	2.899899821	15.070105343
C	17.931702347	4.791964661	19.220545723	H	10.115563359	6.359485383	14.023952321
C	18.711481132	4.160169152	16.946315139	H	11.462114187	7.229521408	14.768760609
C	10.797326204	6.369140717	14.884646612	H	10.188988753	6.531480470	15.780673565
C	10.577041695	3.865447347	15.036807597	H	11.716000879	4.769024859	12.798957172
C	12.400036678	4.845528656	13.654068783	H	12.990257538	3.924497675	13.688576277
N	13.539681862	3.282383491	19.112415309	H	13.077241494	5.677769052	13.456661608
H	11.825725289	5.882599927	18.579458971	H	14.202532082	8.414160571	17.523725023
H	10.511112095	5.206676314	17.620666327	H	13.172365596	7.389771190	18.501311738
C	15.008977568	5.654236676	17.373169664	H	12.530677692	8.136631483	17.008979406
C	13.908811524	6.466122003	16.642572105	H	15.249668756	7.686025646	15.486106353
H	14.977672559	5.827264240	18.447277209	H	13.665337477	7.531153526	14.729092828
H	16.004561365	5.883967952	16.984970618	H	14.829342934	6.191851546	14.651627638

S4. Optimized Structure and energy of the structure **3** (PNP)Ru(N_2)(OTf) in Scheme 1.

Singlet ground state, E(SCF) = -3351.88348 Hartree



Select bond lengths (in Å) and bond angles (in ˚):

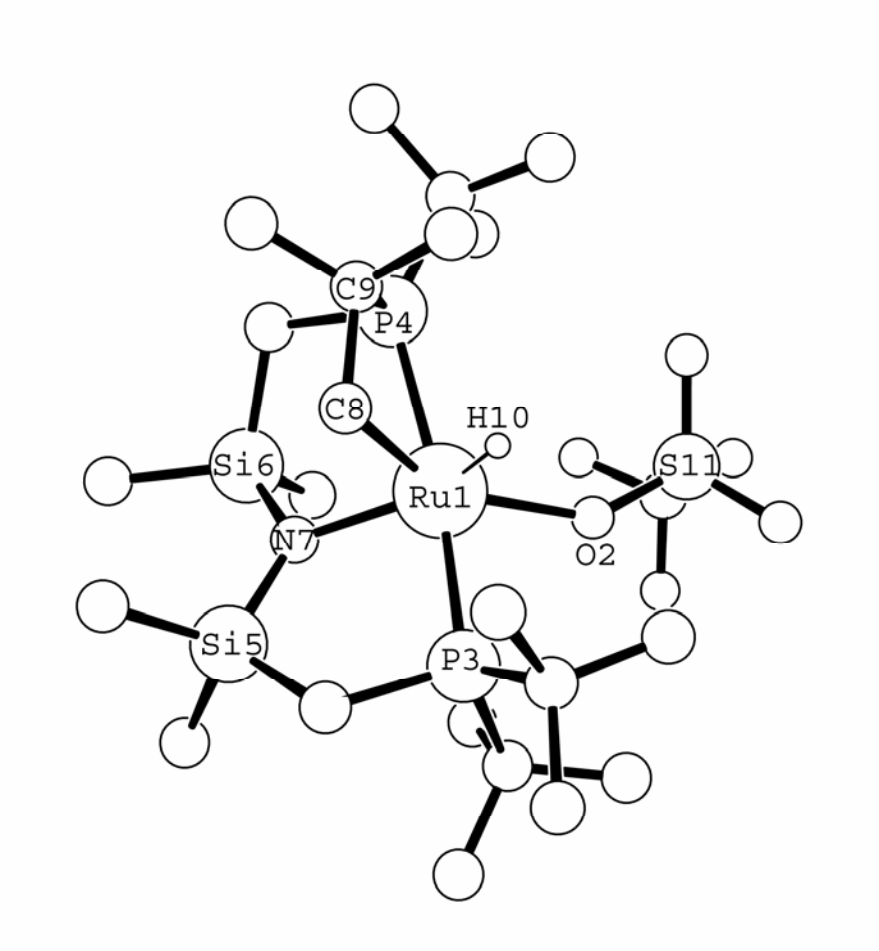
Ru1-N8:	1.88	N9-N8-Ru1:	175.6
N8-N9:	1.12	N8-Ru1-O2:	95.9
Ru1-O2:	2.22	N8-Ru1-N7:	105.3
Ru1-P4:	2.52	O2-Ru1-N7:	158.7
Ru1-P3:	2.53	O2-Ru1-P4:	91.8
Ru1-N7:	2.09	P4-Ru1-N7:	88.1
O2-S10:	1.52	P4-Ru1-P3:	168.5
N7-Si6:	1.75	S10-O2-Ru1:	131.2
		Si6-N7-Ru1:	122.1
		Si6-N7-Si5:	118.9
		Si5-N7-Ru1:	118.3

Coordinates:

Ru	15.440415996	2.281092408	18.737435686
O	15.938458253	1.878855135	16.607070215
P	16.534113080	0.102262351	19.399010045
P	13.924206921	4.185764487	18.107035082
Si	15.221540863	1.394708582	21.908744046
Si	12.912244994	3.009987005	20.831608728
N	14.417127429	2.158528020	20.552291499
C	16.272229288	2.627625542	22.896028467
H	15.659938306	3.413549204	23.350539041
H	17.007654630	3.117767112	22.247296691
H	16.820151271	2.126857173	23.704075821
C	14.043375497	0.512490861	23.114145912
H	13.365062607	1.188185550	23.641522012
H	14.634655882	-0.008150147	23.877220909
H	13.431357202	-0.239195472	22.605321220
C	16.419175396	0.070361230	21.244187998
H	17.412729601	0.311024865	21.634154821
H	16.177774583	-0.932557830	21.611516042
C	15.405181739	-1.345399024	18.810708619
C	18.394990949	-0.327880478	19.084980877
C	12.790049237	3.919289229	22.499916386
H	13.608575482	4.638145426	22.619693245
H	12.799015223	3.258812720	23.371960244
H	11.850014898	4.484923786	22.534933781
C	11.415840489	1.849224959	20.721945351
H	11.344884849	1.355802042	19.746631722
H	10.481358458	2.400123922	20.885510715
H	11.469445303	1.062067015	21.481874406
C	12.752855671	4.383519395	19.531260878
H	11.723129536	4.497514559	19.189033867
H	13.003573757	5.314034046	20.044710067
C	14.605808929	5.980743753	17.889570778
C	13.501781037	6.974063273	17.468679085
H	13.912187662	7.990923197	17.499637476
H	12.640269618	6.953142890	18.144770965
H	13.148589052	6.801386249	16.448830979
C	12.791067403	3.681689299	16.620414784
S	17.061304778	2.407307064	15.720530408
C	16.972683665	1.191756829	14.311276035
O	18.403327538	2.254316272	16.306504249
O	16.755297677	3.689420899	15.086965728
F	17.191872151	-0.061462110	14.733371219
F	17.905569410	1.493530769	13.402242355
F	15.763208652	1.227742530	13.733306378
C	15.929571415	-2.740174484	19.203829718
C	15.223418098	-1.279157570	17.280358204
C	14.019214266	-1.161362985	19.464402299
C	18.934144632	-1.380226849	20.079423471
C	19.188805088	0.979002714	19.289988914
C	18.647754325	-0.830524389	17.653016208
C	11.379345582	4.303373184	16.677940808
C	12.647479652	2.146162116	16.702486987
C	13.432444769	4.038916650	15.265100145
C	15.166891145	6.444570604	19.259127756
C	15.755174904	6.023300893	16.863856941
N	16.942304972	3.360908478	19.086172694
N	17.806753272	4.017186558	19.374295528
H	20.260402699	0.748122251	19.251301917
H	18.995263270	1.440814070	20.264332308
H	18.976685742	1.699929871	18.500852161
H	19.730677461	-0.927634669	17.506249201
H	18.284928452	-0.132256100	16.901477837
H	18.211438529	-1.816530995	17.473894334
H	19.988156457	-1.562304713	19.836594073
H	18.417510213	-2.338369971	20.018707874
H	18.899918394	-1.040269350	21.117293871
H	13.332882630	-1.909431778	19.049121537
H	13.594510702	-0.172418110	19.277194626
H	14.047888054	-1.310261549	20.547067519
H	14.542811459	-2.082264231	16.970535748
H	16.157210454	-1.407701231	16.734916150
H	14.793347094	-0.327626596	16.961497746
H	15.171055010	-3.488569289	18.941584561
H	16.114663380	-2.832758280	20.278625264
H	16.843636681	-3.008092382	18.670722118
H	12.849742248	3.560623929	14.467326648
H	14.463170896	3.695966732	15.177958507
H	13.409333809	5.114346543	15.071923448
H	10.853787901	4.046683272	15.750151180
H	11.389325297	5.391632920	16.754247802
H	10.777706458	3.905954021	17.500437278
H	11.929245023	1.810416293	15.943119505
H	12.264749622	1.816496041	17.675899526
H	13.600694567	1.649898321	16.502923689
H	16.109503439	7.059203471	16.784524598
H	15.461768199	5.691583081	15.867340263
H	16.604986413	5.408200882	17.167580206
H	15.743690153	7.356738233	19.104241155
H	15.833774545	5.720202014	19.717543279
H	14.386436736	6.687236092	19.978107422

S5. Optimized Structure and energy of the structure **4** (PNP')Ru(H)(OTf) in Scheme 1.

Singlet ground state, E(SCF) = -3242.26972 Hartree



Select bond lengths (in Å) and bond angles (in ˚):

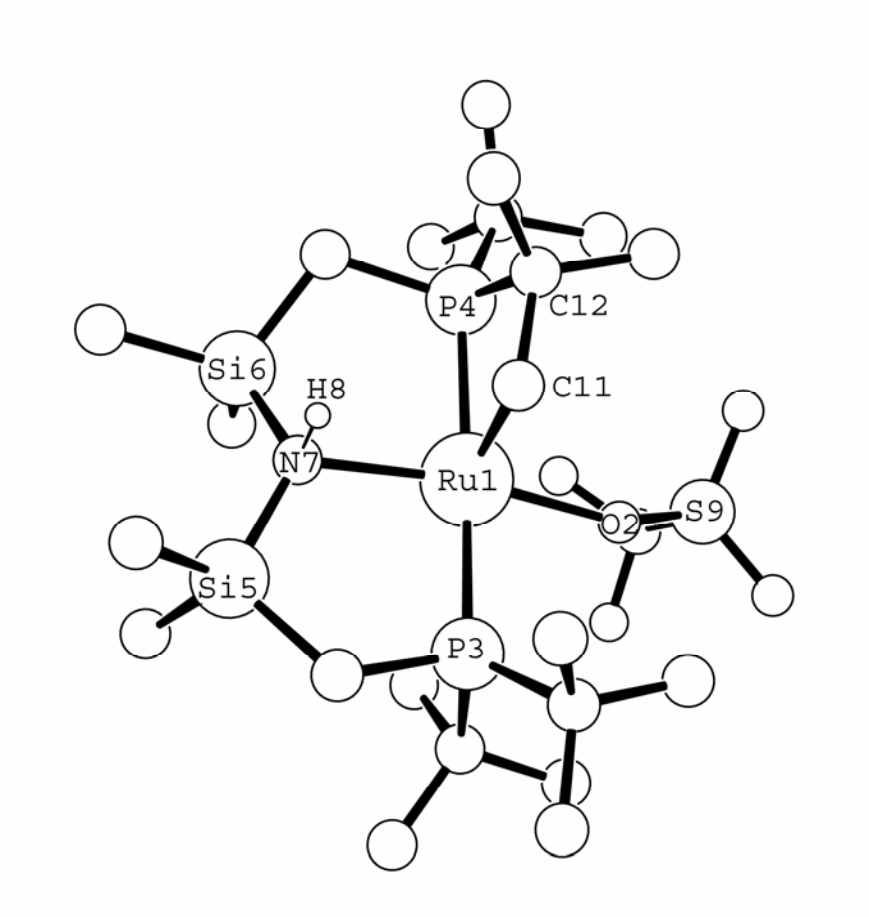
Ru1-H10:	1.56	H10-Ru1-P4:	87.4
Ru1-O2:	2.12	H10-Ru1-O2:	81.5
Ru1-C8:	2.20	H10-Ru1-C8:	61.7
Ru1-P4:	2.48	O2-Ru1-P4:	108.5
Ru1-P3:	2.33	O2-Ru1-C8:	142.7
Ru1-N7:	2.08	C8-Ru1-P4:	66.0
O2-S11:	1.53	C8-Ru1-N7:	81.2
N7-Si6:	1.76	P4-Ru1-N7:	89.5
		Si6-N7-Ru1:	113.2
		Si6-N7-Si5:	125.3
		Si5-N7-Ru1:	121.5
		N7-Ru1-O2:	136.1

Coordinates:

Ru	14.799015087	3.329650465	16.785780796	C	11.326974220	4.272853972	14.003095987
O	15.434621696	2.272486425	15.058434710	C	13.035170803	6.012396404	13.455189884
P	16.674845513	2.158886243	17.797873518	C	14.095119266	6.261039421	16.921598831
P	13.007349008	4.915628558	16.123312437	H	14.454794085	5.128828988	18.750826966
Si	14.552767316	2.496961640	20.017350479	H	15.950483206	5.618609297	17.930133824
Si	11.995367627	3.003745466	18.304405554	N	13.736304319	2.875251180	18.510935586
C	14.374283753	3.828592192	21.363037806	C	14.995703173	6.968284071	15.891133713
H	13.339916296	3.926000195	21.709038729	C	13.407170840	7.330499074	17.786952459
H	14.703223718	4.814416249	21.016474170	H	15.826902278	4.375437791	16.241120368
H	14.985334118	3.567575715	22.236576580	H	11.478927301	5.454174236	18.006302339
C	13.960899457	0.880739658	20.822706836	H	10.699429826	4.463258247	16.787078750
H	12.922601507	0.961271668	21.161074455	H	15.816292531	7.465380383	16.423718722
H	14.570856666	0.672377634	21.710711789	H	14.452642016	7.740231253	15.340397774
H	14.025409538	0.009839834	20.164833627	H	15.436114948	6.276957395	15.168108797
C	16.416634102	2.405748087	19.610400393	H	14.171850008	7.963540518	18.255478792
H	16.810131248	3.401696610	19.840295279	H	12.808847929	6.900740498	18.595143407
H	16.965271692	1.696582968	20.236707220	H	12.759993658	7.984656980	17.193084606
C	16.623132686	0.237774591	17.536789028	H	12.477126086	6.099546685	12.515941556
C	18.447709557	2.818437118	17.434364995	H	13.858747302	5.322383346	13.287217775
C	11.002889231	3.082865850	19.922453323	H	13.431753815	7.000512879	13.683696553
H	11.275498196	3.948599705	20.535007700	H	10.529722264	6.908381105	13.984900711
H	11.113482284	2.185154414	20.539101178	H	11.574758710	7.522164152	15.267538887
H	9.936507129	3.174595356	19.681740090	H	10.329661210	6.317348202	15.636587778
C	11.331183606	1.542623349	17.300970581	H	10.737744816	4.572912498	13.127777268
H	11.794379841	1.489653137	16.309950341	H	10.630764563	3.840226434	14.728712474
H	10.244450370	1.606049102	17.163842343	H	12.024356710	3.495673180	13.687320062
H	11.543998570	0.595153173	17.809845137	H	19.679080725	3.330140374	15.731980627
C	11.634187029	4.601548467	17.339266972	H	17.945069765	3.357165416	15.366882764
C	14.922575069	5.283029372	17.781498615	H	18.797459053	1.823513313	15.486224714
C	12.076213181	5.506191291	14.549259043	H	19.525568473	4.673246843	17.681569585
S	15.343981010	2.212456280	13.532217633	H	18.376336785	4.398696955	18.988121332
C	14.070128455	0.866326231	13.327632609	H	17.803051927	4.916041117	17.387199175
O	16.575770656	1.660621511	12.964476524	H	20.509474922	2.491523906	18.011194554
O	14.745500674	3.400631599	12.913879624	H	19.611406796	0.986513647	17.832745413
F	14.500812520	-0.278497307	13.879678008	H	19.363037165	2.005277557	19.262994637
F	13.821752243	0.655760837	12.032894902	H	17.218074096	-1.273523885	16.123646295
F	12.916703393	1.214524116	13.932832088	H	18.497558849	-0.105174254	16.421531082
C	17.153365064	-0.522199509	18.771208053	H	17.116620212	0.330390923	15.392647563
C	17.417919857	-0.207892909	16.292279100	H	17.161259822	-1.595531611	18.544241124
C	15.149962437	-0.165580590	17.303610097	H	16.515816206	-0.384004414	19.648231372
C	19.533859560	2.018400324	18.181161595	H	18.173749889	-0.238821865	19.041999318
C	18.525308823	4.285668767	17.910033927	H	15.084815576	-1.261137393	17.275209030
C	18.723840840	2.821941992	15.915023770	H	14.785190410	0.212127906	16.348001110
C	11.072826070	6.623966947	14.895442347	H	14.480972099	0.189993283	18.087344583

S6. Optimized Structure and energy of the structure **5** (PNHP')Ru(OTf) in Scheme 1.

Singlet ground state, E(SCF) = -3242.29849 Hartree



Select bond lengths (in Å) and bond angles (in ˚):

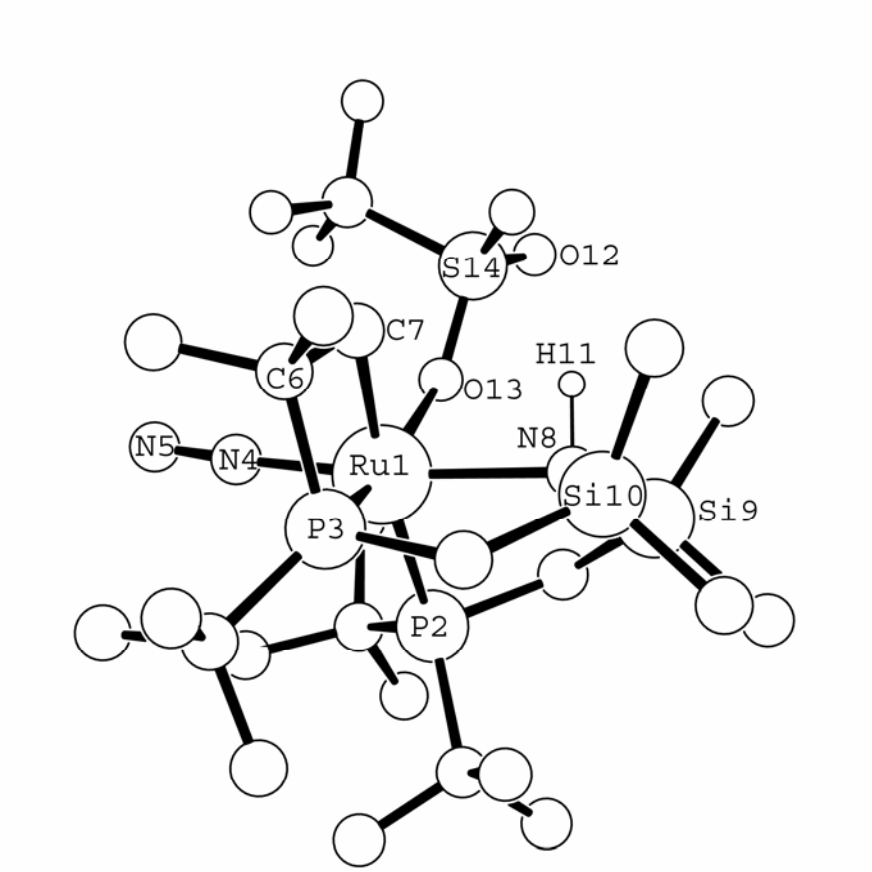
Ru1-O2:	2.19	P4-Ru1-C11:	69.3
Ru1-N7:	2.29	O2-Ru1-P4:	101.9
Ru1-P4:	2.42	O2-Ru1-C11:	95.5
Ru1-P3:	2.42	C11-Ru1-N7:	88.0
Ru1-C11:	2.10	P4-Ru1-N7:	86.7
O2-S9 :	1.51	S9-O2-Ru1:	151.6
N7-Si6:	1.81	Si6-N7-Ru1:	108.0
N7-H8:	1.07	Si5-N7-Ru1:	116.9
		Si6-N7-Si5:	122.5
		H8-N7-Ru1:	94.1

Coordinates:

Ru	14.433108632	3.542183761	16.880086337
O	15.501476440	3.263932498	14.990661019
P	16.447167913	2.604951381	17.853053381
P	12.525061539	4.862850903	16.186622719
Si	14.455924145	2.736144369	20.292343417
Si	11.755059166	3.580627461	18.860308253
C	14.422900887	3.781249870	21.870329205
H	13.411484356	3.890252067	22.275005805
H	14.823569610	4.787276475	21.697255538
H	15.040857484	3.316871319	22.648012234
C	13.669759636	1.064156905	20.676482364
H	12.675589590	1.176783004	21.121510856
H	14.294538159	0.546938231	21.414702476
H	13.576957321	0.405576176	19.809878775
C	16.246344129	2.609777973	19.713817284
H	16.714795766	3.535822862	20.062867527
H	16.784142428	1.795264756	20.208546365
C	16.518815978	0.724633364	17.383193601
C	18.195096598	3.402367339	17.648869377
C	10.909808665	3.892535032	20.527975282
H	11.233178022	4.835128336	20.983444436
H	11.092105267	3.090723771	21.251843310
H	9.823967915	3.955757124	20.385817688
C	11.188796038	1.919248108	18.180012342
H	11.686357303	1.680439179	17.235873408
H	10.108893100	1.947366716	17.991605950
H	11.374190067	1.100250325	18.881388936
C	11.389043272	4.999542038	17.682342847
C	11.231960592	4.965296992	14.758107903
S	15.523295002	3.070066328	13.494956414
C	14.420896856	1.582926938	13.246833806
O	16.837419617	2.608151147	13.033876587
O	14.858815108	4.140840098	12.738437657
F	15.000063360	0.469125225	13.729565450
F	14.161345289	1.399191542	11.950068325
F	13.242690222	1.738158096	13.894531758
C	17.050000870	-0.182558914	18.510303096
C	17.351108356	0.482349401	16.106670538
C	15.058229180	0.327143974	17.070629941
C	19.318245506	2.562715494	18.288807953
C	18.173982097	4.780001459	18.353744011
C	18.494399972	3.654547409	16.155740660
C	10.392078449	6.254402456	14.859417621
C	10.319230821	3.725574464	14.895122791
C	11.882366260	4.900324846	13.364629066
N	13.556630492	3.627485373	18.999051456
H	11.520668123	5.960112498	18.190599410
H	10.341169697	4.965398305	17.372301501
C	14.848974323	5.589772934	17.047757598
C	13.721805332	6.357152410	16.296173925
H	14.909910093	5.924579327	18.098998079
H	15.822531380	5.780243904	16.583808438
C	13.221420872	7.594322416	17.057219767
C	14.212575838	6.790552572	14.903038195
H	13.804132608	4.612344240	19.141492250
H	19.448040331	4.191939935	16.073840131
H	17.716305844	4.258730232	15.686603172
H	18.581409150	2.738930396	15.571689321
H	19.090776457	5.319878914	18.088706640
H	18.162332751	4.700331320	19.445395070
H	17.327655237	5.395144317	18.041089371
H	20.261249770	3.121775252	18.231635209
H	19.477615627	1.611107143	17.777022351
H	19.128750852	2.356821083	19.348091926
H	17.199022551	-0.555443155	15.783328908
H	18.422485418	0.607965635	16.279459815
H	17.054507133	1.129498351	15.280611144
H	17.099206589	-1.215832858	18.143786998
H	16.396001939	-0.186941077	19.387867063
H	18.056324055	0.095019044	18.835664993
H	15.012841231	-0.738550783	16.809723413
H	14.666324100	0.882820628	16.213524878
H	14.392207117	0.482752192	17.922869530
H	9.628343867	6.249671121	14.070834510
H	11.005794093	7.148258230	14.712210853
H	9.869842264	6.355064922	15.815989687
H	9.576308267	3.738035169	14.088004019
H	9.766367471	3.692410540	15.838952159
H	10.894384715	2.799543172	14.800291491
H	11.083638178	4.842802639	12.613480967
H	12.522350778	4.029065778	13.239313752
H	12.483275301	5.779913118	13.135570319
H	14.017956786	8.348641231	17.079987294
H	12.963627935	7.378042502	18.099572132
H	12.347650647	8.050978940	16.579017267
H	15.069506728	7.464015151	15.031712613
H	13.444994445	7.345734072	14.353554408
H	14.539791431	5.947192834	14.290901565

S7. Optimized Structure and energy of the intermediate **X** (PNHP')Ru(N_2)(OTf) in Scheme 1.

Singlet ground state, E(SCF) = -3351.88130 Hartree



Select bond lengths (in Å) and bond angles (in ˚):

Ru1 – P2:	2.65	P2 – Ru1 – P3:	117.8
Ru1 – P3:	2.33	P3 – Ru1 – O13:	161.6
Ru1 – N4:	1.91	P2 – Ru1 – C7:	172.8
N4 – N5:	1.12	N8 – Ru1 – N4:	171.9
Ru1 – C7:	2.17	C7 – Ru1 – P3:	67.3
Ru1 – O13:	2.23	C7 – Ru1 – O13:	94.9
Ru1 – N8:	2.35	N4 – Ru1 –P3:	93.8
N8 – H11:	1.03	O13 – Ru1 – N8:	81.8
N8 – O12:	3.48	N5 – N4 – Ru1:	176.3
H11 – O12:	2.51	S14 – O13 – Ru1:	132.1
S14 – O13:	1.52	S10 – N8 – Ru1:	111.2
S14 – O12:	1.47	S9 – N8 – Ru1:	113.2
N8 – Si10:	1.81	Si10 – N8 – Si9:	127.2
N8 – Si9:	1.84	H11 – N8 – Ru1:	89.0

Coordinates:

Ru	14.958795590	2.447492525	17.108354657	O	12.642699659	-0.351106188	17.592752559
P	13.891438142	4.876994642	17.159729518	O	10.607205598	0.887186030	16.780331167
Si	15.562047748	1.820741863	20.442230724	C	12.286360182	0.004811419	14.958272296
Si	12.737022414	3.284373878	19.686446667	C	17.229855349	2.201722079	19.590135667
C	12.831378019	4.263629653	21.310136515	H	17.479271547	3.219209454	19.910491735
H	13.677239205	4.938885051	21.444944936	P	17.195811747	2.227236467	17.737321140
H	12.789629111	3.597732019	22.177495121	H	18.022660279	1.551432553	19.978311695
H	11.920745652	4.875965446	21.340716030	C	18.810349048	3.126066061	17.211838169
C	11.248837605	2.156846396	19.938203718	C	20.035593991	2.272448642	17.595371006
H	10.886945526	1.677210035	19.026018484	C	18.926115237	4.495190817	17.908704457
H	10.423523365	2.754586390	20.344350945	H	19.852360978	4.982621473	17.579488334
H	11.467415236	1.369998284	20.669661029	H	18.975630355	4.415919632	18.998903476
C	12.427594319	4.478557326	18.238859832	H	18.098545297	5.157763532	17.645104620
C	13.084455340	5.571939975	15.536688483	H	20.954354259	2.802991808	17.314628099
C	12.285258181	6.874058747	15.736659911	H	20.045442756	1.306671218	17.085248543
C	12.114285853	4.503615927	14.982222340	H	20.083053400	2.088099953	18.673828282
C	14.175254644	5.798770294	14.464990881	C	15.635692935	2.819529931	22.046818768
H	11.892132089	5.369279827	18.584451225	H	16.537079613	2.495369876	22.583048400
H	11.750759252	3.918545040	17.587749015	H	14.783877672	2.637027583	22.707304531
C	14.742245261	6.344697252	18.094812543	H	15.724442839	3.898364118	21.892707983
H	11.766527092	4.834524154	13.995504133	C	15.356600807	0.017106206	20.961736374
H	11.228489018	4.375288807	15.609856687	H	16.211126504	-0.310736419	21.565505796
H	12.580391168	3.525290900	14.868200957	H	15.245910978	-0.679284931	20.127332218
H	11.753738970	7.113686269	14.806400241	H	14.461754511	-0.079041960	21.588357689
H	12.923412986	7.730614764	15.969480624	C	18.780505793	3.377777955	15.690202721
H	11.530106736	6.779246180	16.523750098	H	19.673876953	3.944899464	15.399793814
H	13.690977517	6.102148121	13.527945784	H	17.904633611	3.966825662	15.401745089
H	14.738756332	4.887640978	14.256787139	H	18.774581075	2.455202993	15.108321394
H	14.882924743	6.585189858	14.729957507	C	17.160272745	0.407132263	17.204539250
C	13.772965404	7.337515349	18.768941224	C	15.604196827	0.381372063	17.190192516
C	15.689172998	7.119663671	17.156402061	H	15.216239271	-0.154479876	16.323008034
C	15.604567131	5.709469644	19.202158766	H	15.198479719	-0.110159806	18.075705593
H	16.332899894	7.777261812	17.754587699	C	17.710432376	0.131981249	15.792387482
H	15.148940738	7.754899648	16.450621474	C	17.799250383	-0.608715775	18.166412342
H	16.340983782	6.451033512	16.584463815	H	17.425882708	-0.890449910	15.514599252
H	16.148483906	6.494465752	19.743794463	H	18.802951761	0.188001460	15.744078083
H	16.329961573	5.010565484	18.787848484	H	17.295043002	0.793567702	15.031964451
H	14.999185608	5.170534525	19.931521858	H	17.545030682	-1.621635594	17.829108620
H	14.356234706	8.125944558	19.262518161	H	17.435499710	-0.513179906	19.191239632
H	13.167158861	6.858155819	19.542534309	H	18.893013489	-0.532894729	18.184634715
H	13.098082888	7.824763624	18.064259729	N	15.355807468	2.479072341	15.240505973
N	14.199957997	2.235063414	19.319330873	N	15.523470022	2.471806032	14.128715892
H	13.777615698	1.331844361	19.068137430	F	11.670675282	-1.173428231	14.824783994
O	12.824689095	1.961479922	16.669082638	F	13.587559605	-0.158740166	14.660717560
S	12.053245555	0.653155845	16.691124226	F	11.766803569	0.869799282	14.076326910