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Supporting Information

Reactivity of NO with an Osmium Polyhydride: Reductive Elimination and Reductive Nitrosylation on the Path from Odd- to Even-Electron Molecules

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General Considerations. All manipulations were performed using standard Schlenk techniques or in an argon filled glovebox unless otherwise noted. Solvents were distilled from Na, Na/benzophenone, or CaH_2, degassed prior to use, and stored over 4Å molecular sieves in air-tight vessels. All NMR solvents were also dried, vacuum transferred and stored in the glovebox under argon. All other reagents were used as received from commercial vendors. $[LiPNP(12\text{-crown-}4)]_2LiCl$ was synthesized according to a published procedure[1] using HP^tBu_2 instead of HP^iPr_2. and using 12-crown-4 for crystallization. $[CymOsCl_2]_2$ (Cym = cymene)was synthesized according to a published procedure[2]. NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. ^{31}P NMR spectra are referenced to external standards of H_3PO_4. NMR spectra were recorded with a Varian Gemini 2000 (300 MHz ^1H; 121 MHz ^{31}P; 75 MHz ^{13}C) or a Varian Unity INOVA instrument (400 MHz ^1H; 162 MHz ^{31}P; 101 MHz ^{13}C). Infrared spectra were recoded on a Nicolet 510P FT-IR spectrometer. Below "Ar" is $C_6H_4{}^iPr$.

The purity of NO(with respect to trace impurities of NO_2) was assayed by observing the absence of green or blue coloration of N_2O_3, or by contact of the NO gas with Ascarite(supported KOH). Stoichiometric control of NO, using PVT methods, is necessary since excess of NO reacts further over a time of hours at 22 C with both $(PNP)OsH(NO)_2$ and (PNP)OsNO, to give uncharacterized paramagnetic products.

$(PNP)Os(H)_2(CAr)$

[1] Fryzuk. M. D., Giesbrecht. G. R., Tettig, S. J. *Organometallics* **1997**, 16, 725.
[2] Werner, H., Zenkert, K. *J. Organomet. Chem.* **1988**, 345, 151.

0.35 g of $[LiPNP(12\text{-crown-}4)]_2LiCl$ (0.27 mmol) was added into the solution of 0.1 g of $[CymOsCl_2]_2$ (0.25 mmol) (in 30 mL of benzene) in a 50 mL flask. After 4 hours, the volatiles were removed in *vacuo*. Pentane was added to the reaction flask. The precipitate was removed by the filtration and the solution was dried by vacuum. 20 mL of acetonitrile with 0.018 mL of NEt_3 was added to the reaction mixture. It was stirred 2 hours and stored at -20 ^oC over 12 hours. The orange precipitate was collected by filtration and wash with acetonitrile (10 mL × 3). After drying in *vacuo* overnight, 0.16 g of orange solid was collected (yield: 81 %). ^1H NMR (C_6D_6, 25 ^oC): -1.02 ppm (t, J_{PH} = 14.7 Hz, 2H, Os*H*$_2$), 0.42 (s, 12H, Si*Me*), 0.92 (d, J_{HH} = 6.9 Hz, 6H, CH*Me*$_2$), 1.28 (vt, J = 6.9 Hz, 4H, SiC*H*$_2$), 1.36 (vt, J = 6.3 Hz, 36H, P^t*Bu*$_2$), 2.41 (m, 1H, C*H*Me$_2$), 6.79 (d, J_{HH} = 7.8 Hz, 2H, *Ar*), 7.57 (d, J_{HH} = 7.8 Hz, 2H, *Ar*). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 ^oC): 58.4 ppm (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 ^oC): 259 ppm (t, J_{CP} = 11 Hz, Os*C*).

(PNP)Os(H)$_3$, 1

0.1 g of $(PNP)Os(H)_2(CAr)$ (0.13 mmol) in 100 mL flask was dissolved in 20 mL of pentane and was degassed through 3 freeze-pump-thaw cycles using liquid N_2. 1 atm of H_2 was added to the evacuated head space of the frozen solution in the tube and the solution was thawed and stirred for 1 h. The volatiles were removed in *vacuo*. 0.075g of brown solid was obtained (yield: 90 %). ^1H NMR (C_6D_6, 25 ^oC): -16.56 ppm (t, J_{PH} = 11.1 Hz, 3H, Os*H*$_3$), 0.41 (s, 12H, Si*Me*$_2$), 0.94 (vt, J = 4.5Hz, 4H, SiC*H*$_2$), 1.19 (vt, J = 6Hz, 36H, P^t*Bu*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 ^oC): 69.8 ppm (s).

(PNP)Os(NO), 8

$(PNP)Os(H)_3$ (10 μmol) in a J-Young tube was dissolved in 0.5 mL of C_6D_6 and was degassed through 3 freeze-pump-thaw cycles using liquid N_2. 0.13 atm of NO was added to the evacuated head space of the frozen solution in the tube. On thawing, there is an immediate color change from brown to pale yellow. During 19 hours of mixing at 22 C, the solution color changes to brown again. ^1H NMR (C_6D_6, 25 ^oC): 0.20 (s, 12H, Si*Me*), 1.41 (vt, J = 6 Hz, 36H, P^t*Bu*),. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 ^oC): 59.3 ppm (s). IR (pentane

solution): *v*(NO) 1682 cm^{-1}. Repeating this experiment with 0.26 atm of NO in the reaction tube, a small amount of (PNP)Os$(H)_2$(NO) was detected by NMR spectra. Compared to the reaction with 0.13 atm of NO, its concentration is higher. Vacuum transfer of the volatiles from the 0.26 atm experiment showed water(broad ^{1}H NMR signal at 0.4 ppm). Identity of this chemical shift was confirmed by comparison to an authentic sample of water in d_6-benzene. Loss of hydride ligands as H_2 was detected during reaction by its coordination to (PNP)Os$(H)_3$ to give (PNP)OsH_5, and after reaction by a ^{1}H NMR signal due to free H_2. IR spectra from the reaction of (PNP)OsH_3 and NO (more than 1eq.) in pentane (one day or 30 min reaction period) shows a signal at 2216 cm^{-1} which corresponds to N_2O.

(PNP)OsH$(NO)_2$, 6

(PNP)Os$(H)_3$ (10 μmol) was dissolved in 0.5 mL of pentane in a J-Young tube and was degassed through 3 freeze-pump-thaw cycles using liquid N_2. 0.13 atm of NO was added to the evacuated head space of the frozen solution in the tube. There is immediate color change from brown to pale yellow. After 10 minutes reaction period, pale yellow precipitate was collected and washed with pentane. The solid was dried in vacuum. ^{1}H NMR (C_6D_6, 25 ^{o}C): -8.58 ppm (t, J_{HP} = 15.6 Hz, H, Os*H*), 0.25 (s, 6H, Si*Me*), 0.60 (s, 6H, Si*Me*), 1.12 (vt, J = 6.8 Hz, 18H, P^t*Bu*), 1.16 (vt, J = 6.8 Hz, 18H, P^t*Bu*). The ^{31}P signal is a doublet with selective proton coupling to only the hydride hydrogen, confirming the monohydride character. ^{31}P{^{1}H} NMR (C_6D_6, 25 ^{o}C): 47.4 ppm (s). IR (pentane solution): *v*(NO) 1775 cm^{-1}. This frequency is unchanged in the deuteride (PNP)OsD$(NO)_2$, synthesized from (PNP)Os$(D)_3$, showing the lack of vibrational mixing of NO and Os-H stretching vibrations. IR(Nujol; CsBr windows): 1763, 1586 cm^{-1}; relative intensity 4:1. The lower energy stretch, attributed to bent NO, is eliminated by any oxidizing condition(conversion to nitrite ligand) and apparently also by reaction with salt plates for IR cells. It was gone completely when a Nujol-sealed sample was held between CsBr plates for 12 h. DFT calculation of IR gave 1778 and

1606 cm^{-1}, with relative intensity 4:2.8; the Os-H stretch is calculated to be very weak(12% of the linear NO stretch).

The crystal structure of crystals grown by reaction in pentane revealed the selected crystal to be a mixture of (PNP)OsH(NO)X where X is NO or ONO (the O-bound nitrito linkage isomer). We suspect that the nitrito isomer is formed from HONO released in the decay of HNO. In the structure refinement, the site occupancies of NO and ONO were set to 50%. Geometrical parameters for the disordered NO/ONO moieties were constrained to chemically reasonable values and displacement parameters of atoms that are practically superimposed were constrained to the same value. Moreover, rigid-bond restraints were applied to the ONO moiety. See CIF for details of the refinement model. A full structure determination of a crystal from a different reaction of $(PNP)Os(H)_3$ with NO showed this same co-crystallization (compositional disorder). This disorder of ONO with bent NO causes a systematic error in the Os-N3D distance. The nitrite species (PNP)OsH(NO)(ONO) is detected by its most diagnostic NMR "signatures:" ^1H NMR: Os-H -8.13ppm, t, J=14.8Hz(Os-H) and ^{31}P NMR: 47.8ppm(s).

The production of nitrito ligand from putative nitrous acid(from HNO decomposition) was tested using an ammonium nitrite source of HONO. The reaction of $PNPOsH_3$ with $[H_2N(Cy)_2][ONO]$ gives $(PN(H)P)OsH_3(ONO)$ which also detected in the reaction mixture of $(PNP)OsH_3$ and NO. Two triplets from ^{t}Bu and two singlets from SiMe as well as one singlet (46.8ppm) in ^{31}P NMR correspond to C_s symmetry. In addition, two hydride signals (-11.6 and -13.3 ppm as broad singlets) with 2:1 ratio and one broad singlet at 6.2 (for PN(H)P) indicates formation of $(PN(H)P)OsH_3(ONO)$.

The complete conversion of $(PNP)OsH(NO)_2$ to (PNP)OsNO in C_6D_6 solution under argon atmosphere was observed over 24 h by ^1H and ^{31}P NMR spectra at room temperature.

$(PNP)Os(H)_2(NO)$, 9

$(PNP)Os(H)_3$ (10 μmol) solution in 0.5 mL of C_6D_6 was prepared in J-Young tube. 1.5 mg of Diazald was added into reaction tube. After 24 hours at room temperature, the color was changed to pale yellow and complete conversion to $(PNP)Os(H)_2(NO)$ was

observed by NMR spectra. In addition, formation of (PNP)Os(NO) through losing H_2 was also observed, and continues to completion over a longer time at room temperature. By NMR spectra, H_2 was seen at 4.46ppm. ^{1}H NMR (C_6D_6, 25 ^{o}C): -9.81 ppm (dt, J_{HH} = 7.2 Hz, J_{HP} = 13.6 Hz, H, Os*H*), -3.37 ppm (dt, J_{HH} = 7.2 Hz, J_{HP} = 21.6 Hz, H, Os*H*), 0.34 (s, 6H, Si*Me*), 0.40 (s, 6H, Si*Me*), 1.20 (vt, J = 6.5 Hz, 18H, P^t*Bu*), 1.24 (vt, J = 6.5 Hz, 18H, P^t*Bu*). ^{31}P{^{1}H} NMR (C_6D_6, 25 ^{o}C): 53.0 ppm (s). IR (solid film): ν(NO) 1653 cm^{-1}. If the reaction is repeated with a 5:1 ratio of Diazald to Os, there is no conversion of (PNP)Os(H)$_2$(NO) to (PNP)OsH(NO)$_2$ even after 24h.

Demonstrating Equilibrium between (PNP)Os(NO) + H_2 and (PNP)Os(H)$_2$(NO)

Given the similar free energies(Scheme 1) of (PNP)Os(H)$_2$(NO) and (PNP)Os(NO) + free H_2, we attempted to test this experimentally, by monitoring the SiMe resonances of both complexes. A sample of (PNP)Os(NO) in benzene initially containing 4% (PNP)Os(H)$_2$(NO) shows, over 3 days at 22 C under 1 atm H_2, increasing conversion to a final steady state concentration of 9% (PNP)Os(H)$_2$(NO).

Variable Temperature NMR of Reaction of (PNP)Os(H)$_3$ with a Deficiency of NO

(PNP)Os(H)$_3$ (10 μmol) was dissolved in 0.5 mL of C_7D_8 in a J-Young NMR tube and was degassed through 3 freeze-pump-thaw cycles using liquid N_2. 0.13 atm of NO(11 MICROmol) was added into the evacuated head space in the tube which was precooled to -78 ^{o}C. After 5 minutes, the NMR tube was placed into NMR probe precooled to – 60 ^{o}C. NMR spectra were collected every 10 ^{o}C increment with 5 minutes interval for thermal stabilization. (PNP)Os(H)$_3$ remained at all reaction temperatures and after 12 hours at room temperature. -60 ^{o}C: the major product is (PNP)Os(H)(NO)$_2$, and minor products are (PNP)Os(H)$_2$(NO) and (PNP)Os(NO). Over all temperatures, the intensity of (PNP)Os(H)$_2$(NO) was not changed significantly. (PNP)OsH(NO)$_2$ increased significantly from -60 ^{o}C to -30 ^{o}C, but from-20 ^{o}C to +20 ^{o}C, its concentration decreased. In the case of (PNP)Os(NO), there was no significant change of its concentration between -60 ^{o}C and -30 ^{o}C, but its concentration increased from -20 ^{o}C to room temperature. After reaching room temperature and being stirred 12

hours, NMR spectra showed a trace of $(PNP)OsH(NO)_2$ and a concentration of $(PNP)Os(H)_2(NO)$ unchanged from the beginning, with (PNP)Os(NO) as the major product.

Attempted EPR Detection of Radical Intermediates.

As with the above NMR experiment, a freeze-pump-thaw degassed toluene solution of $(PNP)Os(H)_3$ was brought to -78 C, then NO was added to the EPR tube headspace, and the cold solution shaken momentarily to mix gas and solution; this causes immediate color change to yellow, which is consistent with conversion to $(PNP)OsH(NO)_2$. No EPR signal was detectable at 77 K in experiments where the Os:NO mole ratio was 1:0.85 or 1:1.6 or 1:2.0. This result indicates a low barrier for all steps up to and including the radical-quenching reactions(which require participation by a total of two NO) in the operative mechanism.

Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 6.0 suite[1] of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP[2-5] functional and the 6-31G** basis set with no symmetry restrictions. Osmium was represented using the Los Alamos LACVP basis[6, 7]. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ξ basis set[8] cc-pVTZ(-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 quality basis. Vibrational frequency calculations based on analytical second derivatives at the B3LYP/6-31G** (LACVP) level of theory were carried out on smaller models to analyze some vibrational modes.

The models used in this study consist of ~90 atoms, which represent the non-truncated substrates that were also used in the experimental work. Although a smaller model may also able to reproduce the most important features of the studied reaction qualitatively, we chose to employ the large scale model faithfully construct a realistic model chemistry. These calculations challenge the current state of computational capabilities. Whereas the numerical efficiency of the Jaguar program allows us to accomplish this task in a bearable time frame, vibrational frequency calculations, which are about an order of magnitude more expensive than geometry optimizations, are currently impossible to carry out on the large-scale model. We have carefully made truncations to the substrate, where the t-butyl of the ligands were replaced with methyl group.

References

1. Jaguar, version 6.0, *Schrödinger, L.L.C, New York, NY, 2005*.
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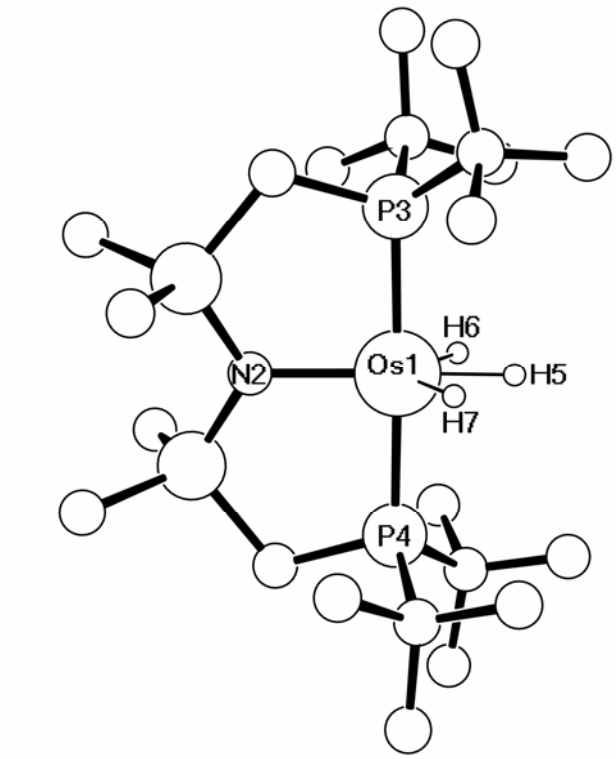
8. Dunning, T. H., *J. Chem. Phys.* **1989,** *90*, 1007.

S1. Optimized structure of (PNP)Os(H)$_3$ (**1**).



Select bond length (in Å) and bond angle (in ˚):

Os1-P3	2.38	H5-Os1-H6	59.2
Os1-P4	2.38	H5-Os1-H7	58.6
Os1-N2	2.09	H5-Os1-P3	91.2
Os1-H5	1.66	H5-Os1-N2	177.4
Os1-H6	1.60	H6-Os1-P3	90.5
Os1-H7	1.60	H6-Os1-N2	118.2
		H7-Os1-N2	124.0
		H7-Os1-P3	89.3
		P3-Os1-N2	89.1
		H6-Os1-H7	117.8
		P3-Os1-P4	178.3

Coordinates:

Os	1.230382254	1.976109180	H	0.201114904	3.787945748
3.158135217			5.508242121		
P	-0.297128897	3.731385753	C	5.737857375	3.660901677
2.651710005			3.912476677		
P	2.800596719	0.271941394	H	5.764783176	4.755750899
3.690481758			3.941371032		
Si	2.491587239	5.052809087	H	5.937167744	3.354065538
3.005835376			2.879875785		
Si	4.092128927	2.957487236	H	6.569292064	3.301641334
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N	2.683392199	3.413501011	C	3.907501301	3.517843710
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C	2.899252482	6.408443280	H	3.831014694	4.606617642
4.277549257			6.451357174		
H	3.951580738	6.386489945	H	4.764388232	3.196167676
4.581829809			6.969000721		
H	2.293229009	6.318280859	H	3.003158853	3.088989887
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H	2.709076835	7.399901902	C	4.240207636	1.053822350
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C	3.588346612	5.357962233	H	5.200752599	0.723168264
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H	4.654473535	5.268652630	H	4.224773568	0.727404495
1.716669341			5.628683570		
H	3.421635936	6.361562322	C	2.214011325	-1.089926771
1.074275924			4.930435515		
H	3.362184266	4.632384998	C	3.334621462	-2.026362627
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C	0.690362714	5.294968900	H	2.944362878	-2.658309166
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H	0.216205402	6.162360124	H	4.191331210	-1.478786169
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H	0.728019003	5.511981598	H	3.698555198	-2.692928639
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C	-1.300614088	3.606731867	C	1.080462977	-1.929001393
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0.558560190			5.081637230		
H	-2.418030756	4.785558367 -	H	1.445305418	-2.595828108
0.426904112			3.520884787		
H	-1.231817583	5.741226589	H	0.298383564	-1.293177485
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H	-2.742674349	5.264827544	C	1.640171643	-0.349302757
1.235512769			6.160992092		
C	-0.300764033	3.191713071 -	H	1.275273722	-1.090162441
0.101662400			6.884161655		
H	-0.825535218	3.161936896 -	H	0.808008808	0.300727193
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H -3.217054385 2.820993813 1.737645948
H -1.967290489 1.581286279 1.511336619
C -1.467851538 4.173245269 4.128213998
C -2.435105025 5.342703744 3.861857455
H -2.887247279 5.658809892 4.811078453
H -3.254765654 5.052935269 3.199069788
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C -2.289012841 2.945855648 4.572651895
H -2.863848230 3.209035833 5.469539561
H -1.645097674 2.099291658 4.819207429
H -3.001636593 2.617800801 3.813557486
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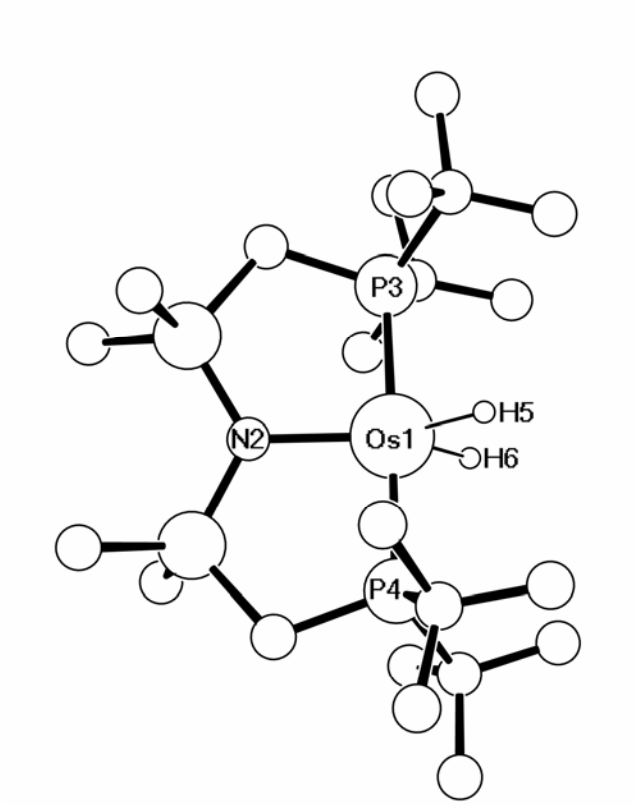
S2. Optimized structure of (PNP)Os$(H)_2$ (**2**).



Select bond length (in Å) and bond angle (in ˚):

Os1-P2	2.38	H5-Os1-H6	81.3
Os1-P3	2.37	H5-Os1-P2	91.6
Os1-N2	2.09	H6-Os1-P2	89.3
Os1-H5	1.63	H5-Os1-N2	137.1
Os1-H6	1.63	H6-Os1-N2	141.6
		P2-Os1-N2	89.6
		P2-Os1-P3	178.7

Coordinates:

Os	1.242501262	1.999414970	3.195552682
P	-0.294476237	3.737011023	2.677651339
P	2.814091899	0.286973699	3.678310574
Si	2.479418834	5.081449612	3.037147286
Si	4.136540602	2.964159808	4.506210568
N	2.708979013	3.435976217	3.600548963
C	2.995588295	6.403272181	4.305338459
H	4.063986637	6.372587019	4.543818324
H	2.444009199	6.287006813	5.245387327
H	2.780056520	7.406522419	3.917530948
C	3.435519743	5.420937189	1.431759349
H	4.517677435	5.342178020	1.581790917
H	3.227857373	6.428958708	1.051341491
H	3.161539311	4.703784518	0.650103348
C	0.620584907	5.363481325	2.700349927
H	0.216678464	6.004951048	3.489804442
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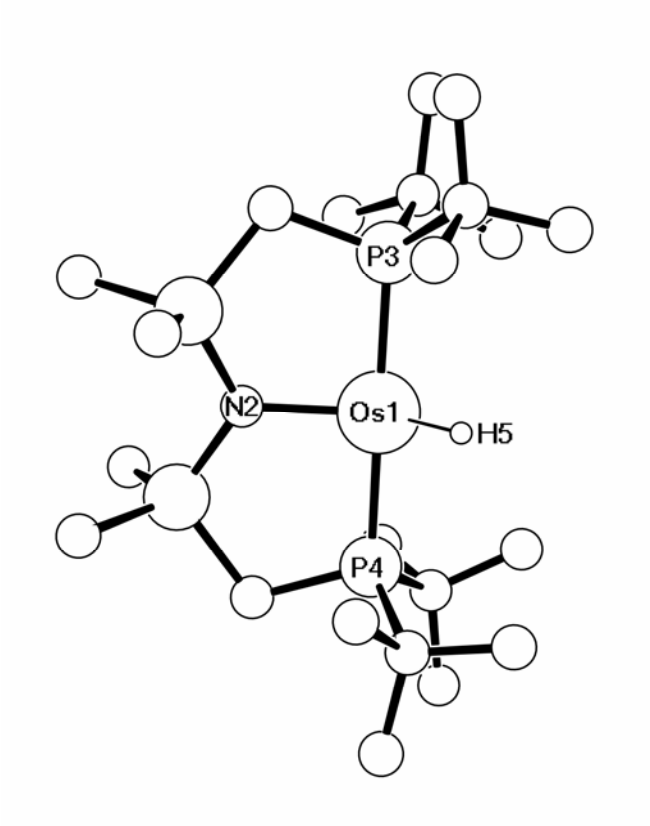
H	5.748633766	4.853141577	3.972710125
H	5.932487108	3.518093460	2.829012424
H	6.601586448	3.389160685	4.461020307
C	3.970188160	3.388831517	6.348344999
H	3.898130351	4.470922853	6.502660855
H	4.833920991	3.030706309	6.922421545
H	3.069713168	2.936539711	6.777293920
C	4.375330926	1.078680398	4.326701660
H	5.195415228	0.905974351	3.623448906
H	4.685565832	0.627228727	5.274454522
C	2.296253571	-0.941037520	5.068369858
C	3.345859484	-2.021794018	5.389880729
H	3.058275146	-2.543659997	6.311952511
H	4.346534462	-1.607410962	5.548334534
H	3.409976347	-2.776940149	4.602430011
C	0.957421765	-1.620872752	4.715450679
H	0.603616239	-2.189136477	5.585305941
H	1.052267149	-2.323596852	3.884752657
H	0.194368730	-0.884143982	4.453365122
C	2.067075199	-0.077743185	6.328981201
H	1.675194176	-0.713325605	7.133032778
H	1.337334571	0.715238994

0.168774321
H 0.757647051 4.555837151 -0.023754729
C -1.839440039 2.361200106 0.695300877
H -2.087514268 2.256476866 -0.368755061
H -2.781406178 2.358943503 1.248648375
H -1.260074629 1.485812909 0.998628644
C -1.666068951 3.998909745 4.011351488
C -2.474068470 5.303788871 3.870320739
H -3.102881085 5.433131344 4.760787057
H -3.140010351 5.291555600 3.005467294
H -1.837707854 6.190724299 3.793847121
C -2.638105390 2.802706555 4.037777579
H -3.253217848 2.855792601 4.945206940
H -2.104909980 1.848507287 4.045571078
H -3.322030933 2.810188766 3.184966233
C -0.913341598 4.036672527 5.361578466
H -1.640333100 4.147375081 6.176299865
H 2.988624172 0.382280627 6.697442858
C 3.436410099 -0.654403479 2.108641228
C 2.331111234 -1.564648759 1.538295232
H 2.615681974 -1.892055041 0.530107578
H 1.373182054 -1.042792138 1.465881537
H 2.191753522 -2.466574363 2.141041777
C 4.717007779 -1.489244080 2.309591756
H 5.044754892 -1.876624246 1.336243451
H 4.560237703 -2.349004436 2.963216596
H 5.546522693 -0.904062944 2.716827668
C 3.736153332 0.451119669 1.069659183
H 4.092013141 -0.011979894 0.140235769
H 4.511209262 1.146507909 1.408337114
H 2.839829181 1.033650554 0.837631662
H 0.066350228 1.231471496 4.018916830
H 0.665085275 1.063543725 1.984998272

S3. Optimized structure of (PNP)OsH (**3**).



Select bond length (in Å) and bond angle (in ˚):

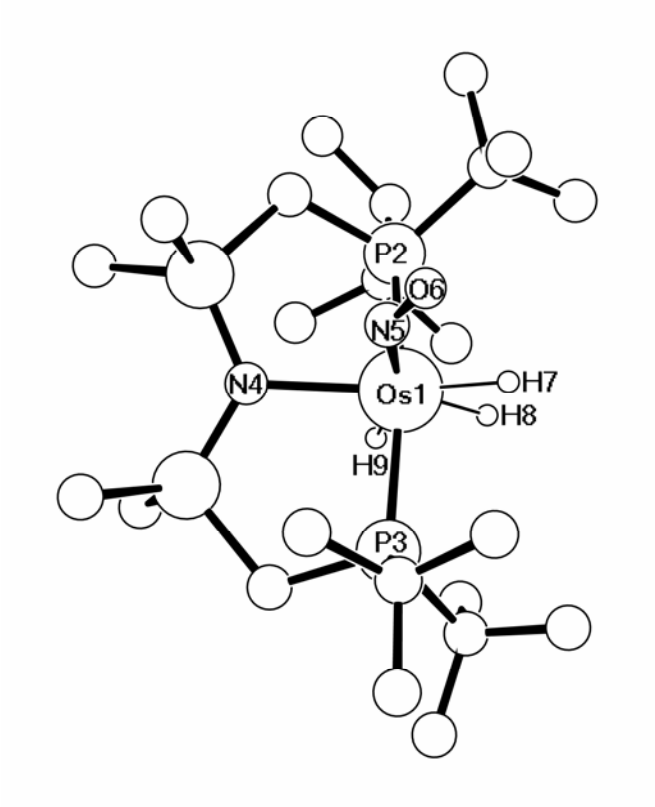
Os1-H5	1.64	P3-Os1-P4	178.7
Os1-N2	2.02	N2-Os1-P3	90.2
Os1-P3	2.38	N2-Os1-H5	133.2
Os1-P4	2.35	H5-Os1-P3	91.8

Coordinates:

Os 1.277710396 2.024581571 3.201704104
P -0.296635748 3.738282554 2.728838687
P 2.806307148 0.315513231 3.714640243
Si 2.453666653 5.052848807 3.018864339
Si 4.152276431 2.961607932 4.498174183
N 2.666257163 3.415986715 3.649132359
C 3.092389422 6.388540604 4.211441435
H 4.169922994 6.325696936 4.394601235
H 2.584226225 6.337664361 5.180418730
H 2.895286891 7.380562347 3.786321707
C 3.341474947 5.285075340 1.359581398
H 4.428189078 5.217135588 1.476306364
H 3.117175759 6.264920036 0.920011024
H 3.038899811 4.514961394 0.642872920
C 0.592550578 5.376244479 2.763366672
H 0.205919837 6.014434266 3.563553472
H 0.433052093 5.918157158 1.826844329
C -1.110014098 3.722423277 0.976369435
C -1.929557401 4.978018394 0.616382000
H -2.208522573 4.928864306 -0.444136989
H -1.363434143 5.904076644 0.755021697
H -2.853591578 5.060456155 1.189749215
C 0.058932670 3.612248794 -0.029367826
H -0.348871448 3.506976229 -1.043257980
H 0.690101143 2.746527267 5.393701757
H -0.513302359 5.285764026 5.593437616
H -0.051449441 3.584379709 3.694027170
C 5.733294541 3.649895323 4.744318593
H 5.769003783 3.687037005 3.310023271
H 5.832173721 2.656871533 3.301688310
H 6.617423722 4.242266649 3.548866740
C 4.102435741 6.300658023 4.637686748
H 4.028543580 6.383849661 3.235941989
H 5.006749096 6.837463439 3.238062049
H 3.118372210 6.818342175 1.063333433
C 4.319584847 4.504000665 0.775175270
H 5.224745902 3.962511315 0.697913718
H 4.440683995 5.527938647 2.089364298
C -0.908099272 5.018287220 2.941138458
C -2.157498401 5.298718412 2.523101946
H -2.702299508 6.155811373 3.976997484
H -1.903236746 5.547670410 2.951712534
H -2.849462363 4.452388335 0.680504700
C -1.323503256 4.543965993 0.195553348
H -1.935745600 5.315322571 0.698168410
H -1.905886621 3.620214784 0.051555956
H -0.440114189 4.377706998 1.918514420
C -0.119144640 6.336075193 1.358443106
H -0.734361452 7.051868462 1.362090874
H 0.809134749

0.184732895
H 0.690789524 4.506057444 -0.025200067
C -1.999751249 2.474139033 0.819405176
H -2.295800225 2.366834064 -0.232000368
H -2.920072418 2.545850688 1.406641336
H -1.467838218 1.563253037 1.110953158
C -1.640643917 3.883171177 4.108732751
C -2.747086925 4.921935210 3.857436568
H -3.334635512 5.060377504 4.774835950
H -3.443096804 4.602699712 3.077384750
H -2.343115006 5.900635900 3.577636762
C -2.269380886 2.490979744 4.328625754
H -2.954099198 2.527497789 5.186097384
H -1.494006680 1.748715781 4.551227254
H -2.842162825 2.142779520 3.465725221
C -0.892569394 4.259362325 5.408143058
H -1.587107227 4.183147778 6.254468438
H 0.690789524 4.506057444 -0.025200067
C -1.999751249 2.474139033 0.819405176
H -2.295800225 2.366834064 -0.232000368
H -2.920072418 2.545850688 1.406641336
H -1.467838218 1.563253037 1.110953158
C -1.640643917 3.883171177 4.108732751
C -2.747086925 4.921935210 3.857436568
H -3.334635512 5.060377504 4.774835950
H -3.443096804 4.602699712 3.077384750
H -2.343115006 5.900635900 3.577636762
C -2.269380886 2.490979744 4.328625754
H -2.954099198 2.527497789 5.186097384
H -1.494006680 1.748715781 4.551227254
H -2.842162825 2.142779520 3.465725221
C -0.892569394 4.259362325 5.408143058
H -1.587107227 4.183147778 6.172378077
H 2.875566467 0.128545841 6.805213400
C 3.547764063 -0.649114397 2.212790150
C 2.465002785 -1.513812483 1.538965960
H 2.845492650 -1.890511965 0.580834156
H 1.558333844 -0.936889674 1.336803575
H 2.198222462 -2.386442097 2.143354318
C 4.769502328 -1.535038247 2.530473935
H 5.174682156 -1.930503707 1.589988231
H 4.521555919 -2.390260131 3.160947983
H 5.578480123 -0.982242664 3.016949030
C 3.988007070 0.443870361 1.211920425
H 4.367422510 -0.031983302 0.297972656
H 4.793521967 1.068498196 1.613024006
H 3.153366603 1.098578404 0.948957794
H 0.895969132 1.224124402 1.826155963

S4. Optimized structure of (PNP)Os(NO)$(H)_3$ (**4**).



Select bond length (in Å) and bond angle (in ˚):

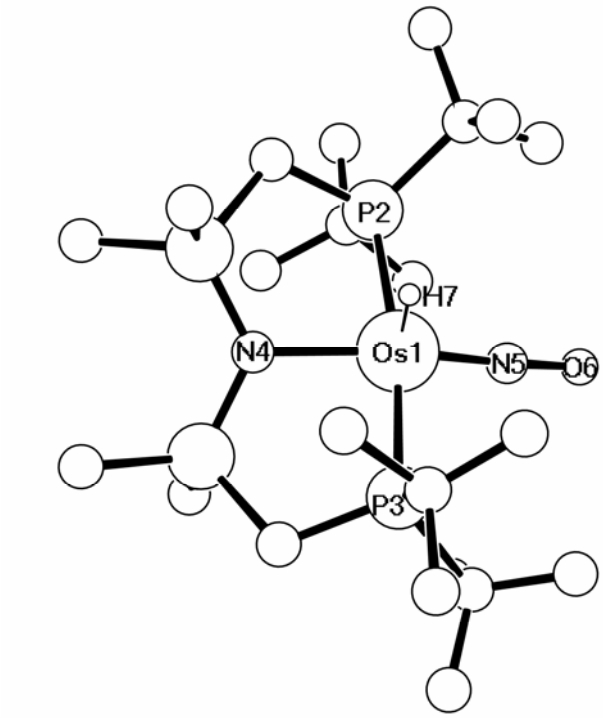
Os1-P2	2.44	P2-Os1-P3	162.8
Os1-P3	2.41	N5-Os1-N4	82.5
Os1-N4	2.24	H9-Os1-N5	161.4
Os1-N5	1.99	H9-Os1-H8	66.1
N5-O6	1.19	H8-Os1-H7	56.0
Os1-H7	1.63	H7-Os1-N5	76.9
Os1-H8	1.61	O6-N5-Os1	148.2
Os1-H9	1.64		
H7-H8	1.52		
H8-H9	1.77		

Coordinates:

Os	1.091002131	1.942662783	3.433063810
P	-0.304665932	3.725921288	2.590748512
P	2.825618518	0.262062840	3.650622674
Si	2.608591469	4.933800803	2.815078508
Si	4.052122394	2.968756108	4.681100295
N	2.735814114	3.448464961	3.676542430
C	2.938819567	6.482350444	3.872872779
H	3.979922424	6.506602940	4.216501930
H	2.303094150	6.516961773	4.763321273
H	2.769282090	7.402403628	3.299434006
C	3.771429410	5.087727495	1.312419690
H	4.825216134	5.062856208	1.610703717
H	3.604085579	6.032588396	0.779129114
H	3.614049122	4.272161761	0.596931852
C	0.841085064	5.075574706	2.051410658
H	0.397046676	6.064830547	2.206929028
H	0.972689134	4.965478911	0.969281304
C	-1.331705878	3.318359459	1.003059689
C	-1.820174147	4.579850193	0.256733786
H	-2.321294676	4.267625678	-0.667943459
H	-0.993133304	5.235235861	-0.030431785
H	-2.535590193	5.169156420	0.828537379
C	-0.426253760	2.537232311	0.024267219
H	-0.975833033	2.385447234	-0.913127884
H	-0.148293512	1.559489769	3.433063810
C	5.757251638	3.617870271	4.129633542
H	5.803764074	4.711885346	4.184717618
H	6.009568215	3.332199890	3.103505377
H	6.545832159	3.232244533	4.787974626
C	3.886761852	3.495579880	6.500778127
H	3.853919280	4.588544126	6.582508727
H	4.737421664	3.147026664	7.100803179
H	2.970278993	3.107142714	6.956194392
C	4.138727473	1.034461419	4.702094545
H	5.136323048	0.660781759	4.445185619
H	3.943830476	0.715616108	5.732548358
C	2.355202288	-1.366481909	4.575938782
C	3.576309101	-2.140282847	5.116798254
H	3.218471891	-2.983759617	5.720624857
H	4.200853948	-1.520013913	5.766296137
H	4.209281669	-2.550915749	4.330458040
C	1.515637295	-2.284244316	3.666290772
H	1.103126207	-3.106148712	4.265052513
H	2.108492356	-2.735722955	2.866183947
H	0.674737465	-1.746636616	3.217173404
C	1.482944025	-0.965109593	5.783710522
H	1.233118764	-1.868558902	6.353971809
H	0.552023777	-0.491130515	5.471114636
H	1.998840132	-0.283148391	6.466648583
C	3.715688582	-0.159370257	

0.418049239
H 0.494846563 3.076654485 -0.218800808
C -2.537717546 2.425583494 1.354664493
H -2.995503308 2.052796606 0.429789552
H -3.312731844 2.971479714 1.899393463
H -2.239301414 1.559149363 1.952584900
C -1.435510380 4.553901746 3.918110675
C -2.393416241 5.626758007 3.362741575
H -2.846791969 6.162968722 4.206240860
H -3.212133462 5.193878361 2.782647633
H -1.882601641 6.371125700 2.744223541
C -2.267799168 3.483954641 4.655770252
H -2.841542785 3.971751978 5.453838262
H -1.643203151 2.717679138 5.113945844
H -2.983708241 2.987030699 3.997466312
C -0.497951193 5.247501564 4.931786504
H -1.088033840 5.561254071 5.801458725
H -0.039029501 6.144409038 4.507695483
H 0.301731033 4.594851480 5.286917554
1.993672196
C 2.701523905 -0.553096828 0.899083662
H 3.249663527 -0.772281490 -0.025856320
H 2.004040740 0.259233419 0.691813046
H 2.122997710 -1.443571770 1.155010358
C 4.759350069 -1.286139324 2.127657684
H 5.349504672 -1.330016893 1.203598564
H 4.300079297 -2.268775801 2.259706620
H 5.458732487 -1.115768267 2.952036405
C 4.454903852 1.116156825 1.532669563
H 4.824733286 0.959950377 0.511529511
H 5.320989536 1.333750857 2.163371793
H 3.804336229 1.992309224 1.533943426
N 0.884728196 2.231695930 5.393515067
O 0.307785250 1.956174568 6.395471324
H -0.198381579 1.015480570 3.812522768
H 0.393637976 0.913486842 2.410679577
H 1.637983204 2.056231756 1.890284494

S5. Optimized structure of (PNP)Os(NO)(H) (**5**).



Select bond length (in Å) and bond angle (in ˚):

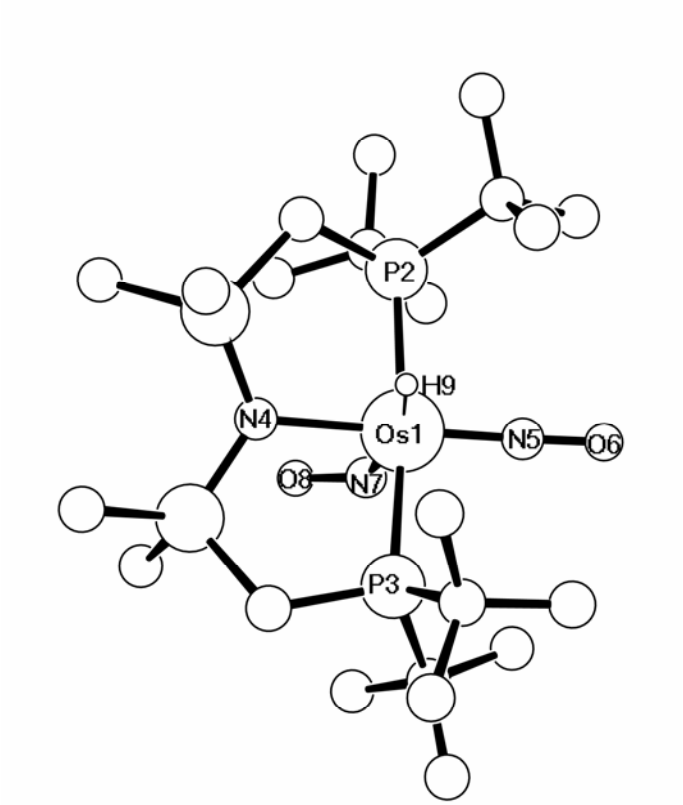
Os1-P2	2.43	H7-Os1-N5	106.5
Os1-P3	2.45	O6-N5-Os1	176.8
Os1-N4	2.15	H7-Os1-N4	88.0
Os1-N5	1.78	P2-Os1-P3	170.5
N5-O6	1.20	N5-Os1-N4	165.5
N5-H9	1.03		
Os1-H7	1.63		

Coordinates:

Os	1.095709764	2.037215098	H	0.593021166	4.468836222
		3.601431274			5.761490716
P	-0.358186577	3.911939194	C	5.369411174	4.095892323
		3.085286741			5.202178643
P	2.860692487	0.420047938	H	5.264129615	5.142575683
		4.106100740			5.503792284
Si	2.558161456	4.976974925	H	5.818090845	4.077099129
		3.051815564			4.202516079
Si	3.721399576	3.149587065	H	6.086269300	3.633084292
		5.269645614			5.892054317
N	2.593507128	3.531991745	C	3.023775478	3.395015869
		4.011198106			7.019256569
C	3.153479952	6.547075876	H	2.802872811	4.450867714
		3.945001530			7.213811997
H	4.239600337	6.559650447	H	3.737252630	3.062984453
		4.077878144			7.784065980
H	2.694600432	6.664025589	H	2.093583366	2.833901807
		4.932841862			7.161820458
H	2.892250550	7.432595007	C	4.155057557	1.290331671
		3.352397026			5.106291054
C	3.559727552	4.850685221	H	5.144927704	1.153926980
		1.444075613			4.660151540
H	4.621223636	4.668370445	H	4.198360305	0.842929756
		1.647293357			6.103073289
H	3.490107125	5.775239542	C	2.333392449	-1.060433494
		0.856836889			5.232492808
H	3.197017968	4.027970380	C	3.520436503	-1.803498633
		0.818202677			5.883859367
C	0.737315839	5.284992458	H	3.120611132	-2.589261021
		2.516829805			6.537050734
H	0.360003701	6.260876646	H	4.136272703	-1.151625775
		2.840193100			6.509321595
H	0.713541497	5.286179712	H	4.172536146	-2.287326160
		1.422231228			5.156447509
C	-1.594476031	3.645862642	C	1.486276660	-2.082562016
		1.626314630			4.447057768
C	-2.100486030	4.973085421	H	1.057902615	-2.805867862
		1.020773192			5.152622716
H	-2.744709217	4.743925206	H	2.088992033	-2.650998519
		0.162533889			3.733309671
H	-1.284561730	5.600969878	H	0.655728709	-1.618466267
		0.652494239			3.911703252
H	-2.691571213	5.563863751	C	1.470286489	-0.468897284
		1.721750925			6.370453016
C	-0.837664892	2.875322399	H	1.186450357	-1.277415908
		0.521862724			7.056084196
H	-1.500135880	2.760914528	-	H	0.556345892	-0.006137625
		0.345625647			5.993996020
H	-0.530865419	1.884210542	H	2.014357629	0.280362912

0.859948130
H 0.059668444 3.404213165
0.184587350
C -2.805088153 2.794828775
2.061727741
H -3.404306163 2.552897931
1.174569869
H -3.461750616 3.328701280
2.754127435
H -2.505893390 1.850472945
2.522518846
C -1.283244561 4.600956539
4.626409935
C -2.311614622 5.704233913
4.314965668
H -2.670883535 6.133933046
5.259087816
H -3.186594739 5.322445564
3.782801713
H -1.881243248 6.523575457
3.729819224
C -1.977492362 3.440413898
5.369803778
H -2.447948541 3.829532573
6.281536652
H -1.255525545 2.672601448
5.661657705
H -2.757758888 2.959300771
4.776231489
C -0.206900539 5.186260943
5.566373247
H -0.675993036 5.446597382
6.523406323
H 0.241978315 6.098935050
5.163416264
6.955304685
C 3.778651261 -0.209887117
2.533595501
C 2.753728036 -0.740436949
1.509302965
H 3.278191508 -1.000173466
0.581067208
H 2.000887775 0.016542658
1.277559807
H 2.237826218 -1.638575628
1.855968323
C 4.836519481 -1.293944523
2.813387942
H 5.425688343 -1.462391609
1.902729141
H 4.386096680 -2.252239227
3.084839397
H 5.536381303 -1.003430807
3.603860121
C 4.483306480 1.016420063
1.911947913
H 4.884834969 0.732773160
0.931184601
H 5.324748361 1.366057334
2.517977990
H 3.791722655 1.849208117
1.771121958
N -0.241735558 0.863608151
3.696964372
O -1.166820099 0.097524575
3.703455322
H 1.561009643 2.081119530
2.039434089

S6. Optimized structure of (PNP)Os$(NO)_2$(H) (**6**).



Select bond length (in Å) and bond angle (in ˚):

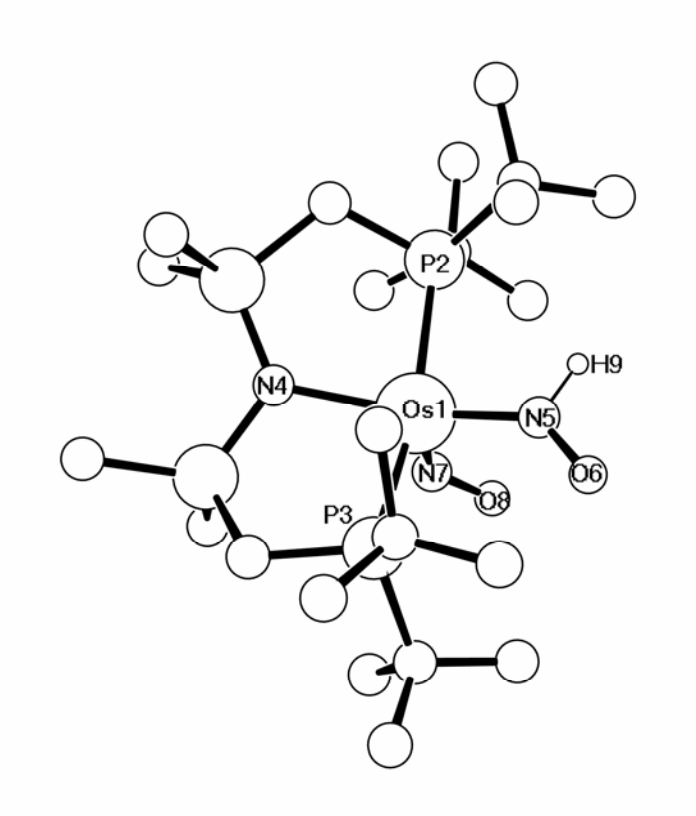
Os1-P2	2.47	O6-N5-Os1	172.0
Os1-P3	2.48	O8-N7-Os1	128.7
Os1-N4	2.17	P2-Os1-P3	167.8
Os1-N5	1.78	N5-Os1-N4	174.6
N5-O6	1.19	H9-Os1-N7	166.3
Os1-N7	2.07		
N7-O8	1.21		
Os1-H9	1.65		

Coordinates:

Os	1.095709764	2.037215098	3.601431274
P	-0.358186577	3.911939194	3.085286741
P	2.860692487	0.420047938	4.106100740
Si	2.558161456	4.976974925	3.051815564
Si	3.721399576	3.149587065	5.269645614
N	2.593507128	3.531991745	4.011198106
C	3.153479952	6.547075876	3.945001530
H	4.239600337	6.559650447	4.077878144
H	2.694600432	6.664025589	4.932841862
H	2.892250550	7.432595007	3.352397026
C	3.559727552	4.850685221	1.444075613
H	4.621223636	4.668370445	1.647293357
H	3.490107125	5.775239542	0.856836889
H	3.197017968	4.027970380	0.818202677
C	0.737315839	5.284992458	2.516829805
H	0.360003701	6.260876646	2.840193100
H	0.713541497	5.286179712	1.422231228
C	-1.594476031	3.645862642	1.626314630
C	-2.100486030	4.973085421	1.020773192
H	-2.744709217	4.743925206	0.162533889
H	-1.284561730	5.600969878	0.652494239
H	-2.691571213	5.563863751	1.721750925
C	-0.837664892	2.875322399	0.521862724
H	-1.500135880	2.760914528	-0.345625647
H	-0.530865419	1.884210542	0.593021166	4.468836222	5.761490716
C	5.369411174	4.095892323	5.202178643
H	5.264129615	5.142575683	5.503792284
H	5.818090845	4.077099129	4.202516079
H	6.086269300	3.633084292	5.892054317
C	3.023775478	3.395015869	7.019256569
H	2.802872811	4.450867714	7.213811997
H	3.737252630	3.062984453	7.784065980
H	2.093583366	2.833901807	7.161820458
C	4.155057557	1.290331671	5.106291054
H	5.144927704	1.153926980	4.660151540
H	4.198360305	0.842929756	6.103073289
C	2.333392449	-1.060433494	5.232492808
C	3.520436503	-1.803498633	5.883859367
H	3.120611132	-2.589261021	6.537050734
H	4.136272703	-1.151625775	6.509321595
H	4.172536146	-2.287326160	5.156447509
C	1.486276660	-2.082562016	4.447057768
H	1.057902615	-2.805867862	5.152622716
H	2.088992033	-2.650998519	3.733309671
H	0.655728709	-1.618466267	3.911703252
C	1.470286489	-0.468897284	6.370453016
H	1.186450357	-1.277415908	7.056084196
H	0.556345892	-0.006137625	5.993996020
H	2.014357629	0.280362912

0.859948130
H 0.059668444 3.404213165
0.184587350
C -2.805088153 2.794828775
2.061727741
H -3.404306163 2.552897931
1.174569869
H -3.461750616 3.328701280
2.754127435
H -2.505893390 1.850472945
2.522518846
C -1.283244561 4.600956539
4.626409935
C -2.311614622 5.704233913
4.314965668
H -2.670883535 6.133933046
5.259087816
H -3.186594739 5.322445564
3.782801713
H -1.881243248 6.523575457
3.729819224
C -1.977492362 3.440413898
5.369803778
H -2.447948541 3.829532573
6.281536652
H -1.255525545 2.672601448
5.661657705
H -2.757758888 2.959300771
4.776231489
C -0.206900539 5.186260943
5.566373247
H -0.675993036 5.446597382
6.523406323
H 0.241978315 6.098935050
5.163416264
6.955304685
C 3.778651261 -0.209887117
2.533595501
C 2.753728036 -0.740436949
1.509302965
H 3.278191508 -1.000173466
0.581067208
H 2.000887775 0.016542658
1.277559807
H 2.237826218 -1.638575628
1.855968323
C 4.836519481 -1.293944523
2.813387942
H 5.425688343 -1.462391609
1.902729141
H 4.386096680 -2.252239227
3.084839397
H 5.536381303 -1.003430807
3.603860121
C 4.483306480 1.016420063
1.911947913
H 4.884834969 0.732773160
0.931184601
H 5.324748361 1.366057334
2.517977990
H 3.791722655 1.849208117
1.771121958
N -0.241735558 0.863608151
3.696964372
O -1.166820099 0.097524575
3.703455322
H 1.561009643 2.081119530
2.039434089

S7. Optimized structure of (PNP)Os(NO)(HNO) (**7**).



Select bond length (in Å) and bond angle (in ˚):

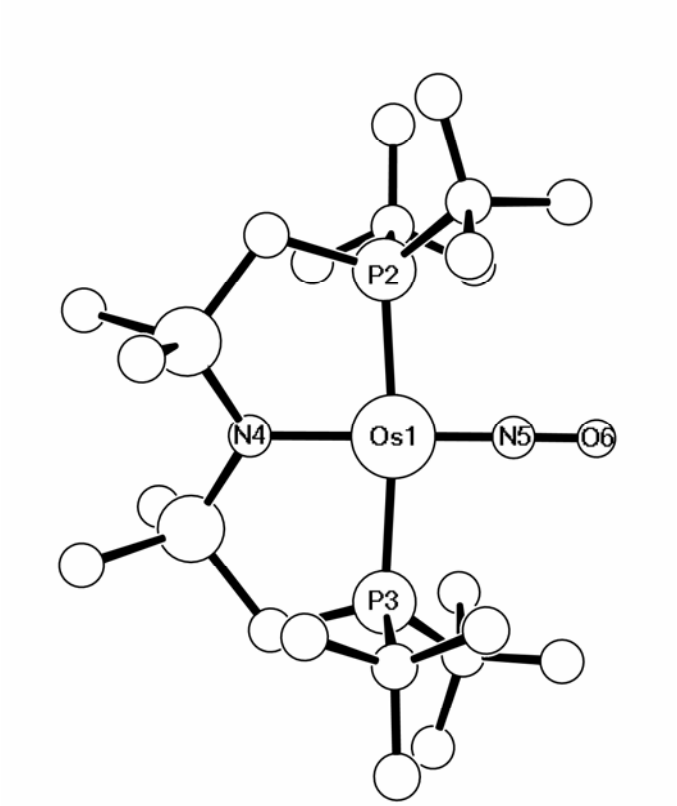
Os1-P2	2.49	O6-N5-Os1	133.7
Os1-P3	2.49	O8-N7-Os1	135.2
Os1-N4	2.19	P2-Os1-P3	160.6
Os1-N5	1.93	N5-Os1-N4	161.5
N5-O6	1.26	N7-Os1-N4	103.1
N5-H9	1.03	N7-Os1-N5	95.4
Os1-N7	1.85		
N7-O8	1.21		
Os1-H9	2.57		

Coordinates:

Os	0.722169213	1.418984843	C	5.284606465	3.043692930
2.511101193			3.247940287		
P	-0.879241741	3.324971922	H	5.437841591	4.126827974
2.386107513			3.194751613		
P	2.346100194	-0.226533801	H	5.400022347	2.648605455
3.433627025			2.233683727		
Si	2.006403219	4.469876239	H	6.098165057	2.636686594
2.216483582			3.861860042		
Si	3.590621551	2.613754521	C	3.528308417	3.483787186
4.004314860			5.695705646		
N	2.221287887	2.934726204	H	3.610441839	4.571658446
3.001720939			5.602394867		
C	2.901365987	5.950176914	H	4.347676734	3.149737865
3.016017158			6.345076857		
H	3.992346002	5.866878635	H	2.585120681	3.268095609
2.975228663			6.212031345		
H	2.615102761	6.096610914	C	3.563850490	0.747150222
4.063094397			4.425066409		
H	2.633211374	6.865746311	H	4.558137220	0.290398526
2.473375965			4.384207437		
C	2.554670068	4.448052812	H	3.241887630	0.685864300
0.403877483			5.469237632		
H	3.650263367	4.426248488	C	1.705747930	-1.513411820
0.356252722			4.748822879		
H	2.221771165	5.338637379	-	C	2.839646282	-2.021817500
0.142922204			5.669956094		
H	2.184536328	3.562398258	-	H	2.412505824	-2.742650213
0.118976760			6.378298070		
C	0.155029418	4.862038233	H	3.291163427	-1.221747282
2.435002402			6.260565368		
H	0.094917880	5.274512281	H	3.636050126	-2.531088103
3.446410949			5.126199536		
H	-0.237670002	5.631897638	C	1.038725533	-2.751424198
1.764548989			4.110998497		
C	-1.906391298	3.528615392	H	0.545962449	-3.334866391
0.769151976			4.898220870		
C	-2.921681903	4.686039897	H	1.769452621	-3.406799475
0.863160116			3.630941011		
H	-3.378544194	4.831319204	-	H	0.273233226	-2.511629453
0.123838489			3.367205866		
H	-2.455584324	5.635630245	C	0.676402477	-0.787003472
1.145377080			5.646522224		
H	-3.732000098	4.475648897	H	0.401566423	-1.448487014
1.564843265			6.477602186		
C	-0.921684191	3.852516168	-	H	-0.238884719	-0.522208852
0.376659050			5.114994316		
H	-1.492565814	3.919787896	-	H	1.083595945	0.131293711
1.310874617			6.082884945		
H	-0.168282748	3.075297874	-	C	3.402376235	-1.130708496

0.508199737
H -0.411252298 4.809144718 -0.239259202
C -2.646243775 2.225120911 0.407955755
H -3.162229421 2.377451224 -0.548963140
H -3.390660151 1.942789405 1.152886241
H -1.959630816 1.384898504 0.297765340
C -2.003769972 3.502578254 3.960246932
C -2.421139997 4.962460433 4.245634220
H -3.057235529 4.966492160 5.139623951
H -2.999406743 5.406401499 3.433921393
H -1.573255342 5.618791055 4.456162309
C -3.278921239 2.639508830 3.880153783
H -3.785525175 2.674938803 4.853568004
H -3.050705721 1.601292628 3.638806519
H -3.986215123 3.019302656 3.137154701
C -1.144201436 3.007473146 5.143635222
H -1.701895480 3.144697811 6.078951043
H -0.201064844 3.557427855 5.233320110
H -0.905270081 1.945021065 5.043216251
2.103401120
C 2.486969304 -1.894543512 1.122568683
H 3.105017061 -2.302574633 0.313052052
H 1.732776664 -1.252530476 0.667060767
H 1.981166619 -2.739445979 1.594954418
C 4.436850340 -2.112061993 2.689510181
H 5.094557105 -2.452533669 1.880026645
H 3.970294042 -3.002820080 3.118209424
H 5.075390500 -1.654123338 3.451476465
C 4.163372866 -0.034032545 1.326615978
H 4.675654364 -0.498116492 0.475052982
H 4.926568408 0.444802873 1.945704715
H 3.497827652 0.740116376 0.938081469
N -0.693368701 0.119958727 2.690109964
N 0.929919101 1.199772138 0.687608897
O -1.950698376 0.174348650 2.565965289
O 0.457911724 0.463528569 -0.147283930
H -0.416378172 -0.845683958 2.938890821

S8. Optimized structure of (PNP)Os(NO) (**8**).



Select bond length (in Å) and bond angle (in ˚):

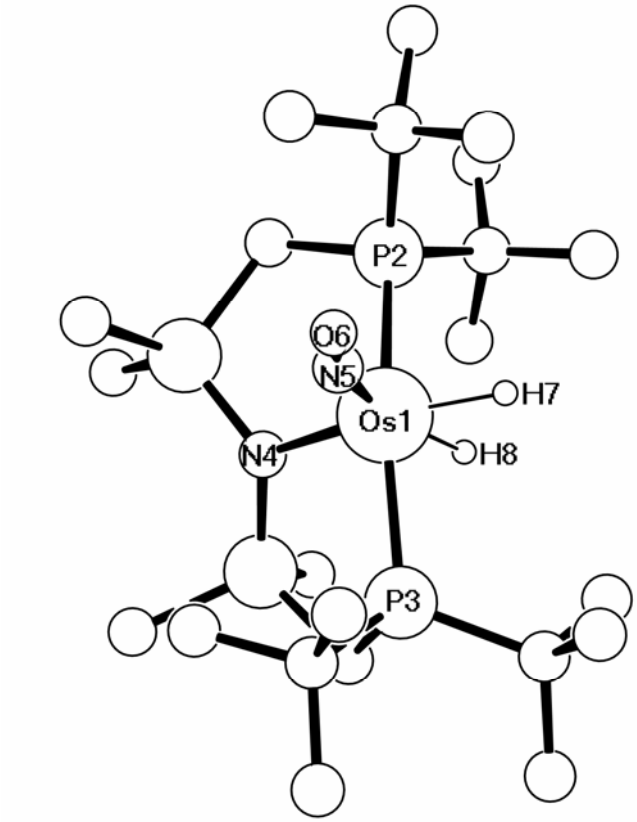
Os1-P2	2.43	O6-N5-Os1	179.0
Os1-P3	2.43	N5-Os1-P2	92.7
Os1-N4	2.09	N5-Os1-N4	179.1
Os1-N5	1.75	P2-Os1-P3	173.8
N5-O6	1.20	N4-Os1-P2	87.2

Coordinates:

Os	1.194246123	1.973381381	H	0.095294960	5.822664508
3.266558774			5.036226161		
P	-0.286788678	3.822566952	H	0.441486122	4.148261251
2.744210372			5.514177277		
P	2.874182722	0.298112868	C	5.698672813	3.723155616
3.790730194			4.084893792		
Si	2.571691463	4.995426711	H	5.726876706	4.816909897
2.891679723			4.056539726		
Si	4.025980857	3.023035503	H	5.961139977	3.360615230
4.661354776			3.085074497		
N	2.684910448	3.394933799	H	6.490139879	3.399068677
3.596254697			4.772066874		
C	3.054629215	6.411974302	C	3.732323620	3.616976996
4.066857129			6.438737304		
H	4.109114398	6.380935647	H	3.636313912	4.706312248
4.359100208			6.496111219		
H	2.457882243	6.406775943	H	4.559116191	3.323112143
4.984686439			7.097721625		
H	2.888639743	7.375412581	H	2.810274580	3.183107599
3.568913812			6.841769087		
C	3.634408115	5.169612775	C	4.227328123	1.126675670
1.329776683			4.740428347		
H	4.700109937	5.036608519	H	5.215194844	0.804872147
1.542948970			4.395452340		
H	3.509987889	6.158387468	H	4.146708585	0.822435404
0.870343557			5.787732960		
H	3.351033045	4.415810873	C	2.312665109	-1.138361234
0.586228781			4.948965992		
C	0.765129683	5.289656361	C	3.485548121	-1.883632879
2.347612251			5.621251033		
H	0.345010958	6.214957955	H	3.075440779	-2.636198563
2.755164836			6.306543817		
H	0.773542479	5.402788235	H	4.121495870	-1.222317820
1.259100791			6.215755679		
C	-1.383874148	3.615461536	H	4.120283674	-2.407706803
1.170989569			4.904892672		
C	-1.917066602	4.954832697	C	1.441376677	-2.165788258
0.619244017			4.198160445		
H	-2.464707843	4.757910538	-	H	1.026481722	-2.875558469
0.311092895				4.925390281		
H	-1.115949414	5.658653519	H	2.022954202	-2.749528775
0.377510847			3.478873547		
H	-2.607072113	5.450642450	H	0.601214103	-1.704132495
1.303926193			3.675774292		
C	-0.473704184	2.977071875	C	1.458748499	-0.479697012
0.097888095			6.056017925		
H	-1.050911717	2.837749308	-	H	1.122487926	-1.253714331
0.825163874				6.757784381		
H	-0.088181242	2.008188921	H	0.582908718	0.025214095

0.422751934
H 0.385272839 3.611862268 -0.145245270
C -2.577288029 2.673180501 1.428000349
H -3.085026637 2.478296919 0.474609011
H -3.317472173 3.119483968 2.098061989
H -2.270991219 1.709287983 1.839168857
C -1.346316162 4.346071956 4.259027672
C -2.384901795 5.443763780 3.965058373
H -2.832422163 5.777892435 4.910042678
H -3.200814761 5.085774121 3.331680519
H -1.940054153 6.324069710 3.488796408
C -2.045991841 3.101043877 4.844021252
H -2.578307929 3.386666034 5.760215309
H -1.313571206 2.329018150 5.095638152
H -2.777868149 2.664600174 4.160715894
C -0.357996982 4.869506214 5.323533920
H -0.901868307 5.035921223 6.261719041
5.642605826
H 2.028037084 0.259185274 6.630402907
C 3.723216425 -0.380570034 2.205152077
C 2.643887362 -0.859589383 1.212048235
H 3.127541126 -1.159755523 0.273747284
H 1.935152323 -0.056070555 0.993888981
H 2.080025338 -1.719261383 1.580957604
C 4.736486886 -1.510321381 2.462101061
H 5.282982243 -1.722472795 1.534028098
H 4.250607469 -2.440526788 2.768764228
H 5.479091480 -1.243100774 3.221468242
C 4.457645759 0.814471975 1.558016312
H 4.833507535 0.508482072 0.573709313
H 5.319137269 1.143641507 2.146961209
H 3.787297950 1.667264752 1.420247985
N -0.063205444 0.787093334 3.015326105
O -0.936036603 -0.019877425 2.859219371

S9. Optimized structure of (PNP)Os(NO)$(H)_2$ (**9**).



Select bond length (in Å) and bond angle (in ˚):

Os1-P2	2.45	H7-Os1-N5	87.1
Os1-P3	2.43	H7-Os1-H8	72.7
Os1-N2	2.22	N5-Os1-P2	99.2
Os1-N5	1.80	N5-Os1-N4	114.6
Os1-H7	1.63	H7-Os1-P2	89.7
Os1-H8	1.65	H7-Os1-N4	158.1
N5-O6	1.19	H8-Os1-P2	83.8
		H8-Os1-N4	85.7
		P2-Os1-N4	84.5
		N5-Os1-H8	159.6
		O6-N5-Os1	162.9
		P2-Os1-P3	160.3

Coordinates:

Os	1.111478271	1.929555256	H	0.286853872	4.337432076
3.394077491			5.346180514		
P	-0.266690354	3.746557634	C	5.522198763	3.933774136
2.562801081			4.808557580		
P	2.946030492	0.309929362	H	5.389115510	4.965339264
3.553900951			5.151402774		
Si	2.653703322	4.908942885	H	5.959443154	3.968844661
2.814360213			3.804486278		
Si	3.897716015	2.942712760	H	6.260985558	3.467486485
4.849620274			5.472430798		
N	2.702407133	3.439547775	C	3.296147007	2.974876278
3.711562420			6.648854998		
C	2.987964322	6.490936096	H	3.121759901	4.009160177
3.822814393			6.968704541		
H	4.048804567	6.571707920	H	4.034598013	2.539861113
4.084339960			7.334087947		
H	2.417580207	6.529015719	H	2.355506731	2.430767549
4.756454430			6.776904177		
H	2.734624311	7.384713498	C	4.377796921	1.136414398
3.238558366			4.392843353		
C	3.875401517	4.974364436	H	5.227043532	1.177255828
1.355907824			3.704033010		
H	4.914106458	4.919529240	H	4.706658369	0.556879863
1.701596263			5.260362683		
H	3.770898468	5.906338927	C	2.519518086	-1.219122732
0.785380460			4.656342948		
H	3.715482293	4.140043509	C	3.582959057	-2.335628332
0.663867854			4.632138529		
C	0.914409752	5.052818417	H	3.366936496	-3.042179514
1.999106681			5.443449047		
H	0.484281212	6.054634329	H	4.597704924	-1.957895070
2.100230097			4.790603706		
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