DOI: 10.1002/ejic.201000503

Redox and Lewis Acid Reactivity of Unsaturated Os^{II}

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Keywords: Osmium / Pincer / Oxygen reduction / Hydrogen / C-H bond cleavage

A synthesis of [(PNP)OsI] {PNP = $(tBu_2PCH_2SiMe_2)_2N$} permits evaluation of its reactivity, both Lewis acidity and reducing power (i.e., ability to be oxidized). It binds two molecules of PhCN, into *trans* sites, but only one of ethylene, and, upon binding of one N_2, there is heterolytic splitting of one *t*Bu C–H bond to put the proton on amide N and the carbon on Os, leaving divalent metal in [{PN(H)P*}Os(N_2)(*I*)]. Two moles of H_2 add, forming [{PN(H)P}OsH(H_2)I], via H–H bond heterolysis. Thermolysis of [(PNP)OsI] gives the product of adding a *t*Bu methyl C–H bond across the Os/N bond, and also net dehydrogenation of this intermediate, forming a carbene complex; the released H_2 forms [(PNP)OsH_2I], and the chemistry of [(PNP)Os] hydridohalides is described. Reaction with O_2 occurs with no detectable intermediate, to completely split the O=O bond, and form *trans*-[(PNP)Os$(O)_2$I], a product of four electron redox change. Attempted two electron oxidation by oxygen atom transfer with pyridine *N*-oxide or Me_3NO or N_2O surprisingly effect transposition of N from its silyl substituents onto the metal, and replace N by O, forming a nitride complex of a bis(silyl ether, phosphane) chelate whose oxygen fails to bind to Os. The product is thus four-coordinate, tetrahedral [(POP)Os(N)I], with an Os/N triple bond.

Introduction

Four-coordinate d^6 species are rare,[1] due to the special stability of more saturated square pyramidal five-coordinate, or octahedral alternatives. Synthetic approaches must be carried out in the absence of potential donors, including N_2, but also with massive steric shielding to avoid halide bridging which pervades divalent Ru and Os chemistry. This led us to the d^6 Ru^{II} compounds (PNP)RuX {PNP = $(tBu_2PCH_2SiMe_2)_2N$; X = Cl, F, O_3SCF_3}[2,3] The unusual triplet ground state for these molecules requires that two d orbitals have an energy separation comparable to spin pairing energy, and this separation is influenced by the degree of amide→Ru π-donation. We were interested in how things change on going to the osmium analogs of (PNP)RuX, where d orbital splitting is generally larger than for 4d metals, but where amide/d_π overlap should be larger. Direct comparison of any osmium analog of the unusual four-coordinate, 14 valence electron, planar, spin triplet d^6 molecule (PNP)RuX requires avoiding a synthetic precursor, $[areneOsX_2]_2$, bearing benzylic hydrogens, since $[(CH_3C_6H_4iPr)OsCl_2]_2$ has been shown[4] to react with Li(PNP) with triple intramolecular dehydrogenation of the methyl group to form the carbyne complex [(PNP)Os(≡CC_6H_4iPr)$(H)_2$]. The unique opportunities which d^6 (PNP)MCl species offer are to probe the extent to which a spin change influences reaction rate and character, as well as the functionality of the amide center. In addition, if osmium here is truly a potent reductant, then there is the possibility that it can function to create a π acid ligand, even by H–C(sp^3) bond cleavage to yield a carbene.

In this report, we furnish a synthesis of [(PNP)OsI] which permits evaluation of its reactivity, both Lewis acidity and reducing power (ability to change to higher formal oxidation state). Being so very unsaturated, it binds many donors within time of mixing, but it also rapidly consumes two molecules of H_2, heterolytically splitting[5–9] one and coordinating the other intact. In the absence of any suitable reaction partner, a higher activation barrier process for [(PNP)OsI] gives the product of net dehydrogenation of a methyl group, a carbene complex; the released H_2 forms [(PNP)OsH_2I], and the chemistry of unusual "daughter" *radical* (PNP)Os^{III} hydridohalides is described. In contrast to some of these nonredox heterolyses, reaction with O_2 occurs with no detectable intermediate, to completely split the O=O bond, and form *trans*-[(PNP)Os$(O)_2$I], a product of four electron redox change; the mechanism of this transformation is deduced, from experimental and DFT studies. Attempted two electron oxidation, by oxygen atom transfer with pyridine *N*-oxide or Me_3NO or N_2O, surprisingly effect transposition of N from its silyl substituents onto the metal, and replace N by O, forming tetrahedral [(POP)Os(N)I] with a bis(silyl ether, phosphane) chelate and an Os/N triple bond.

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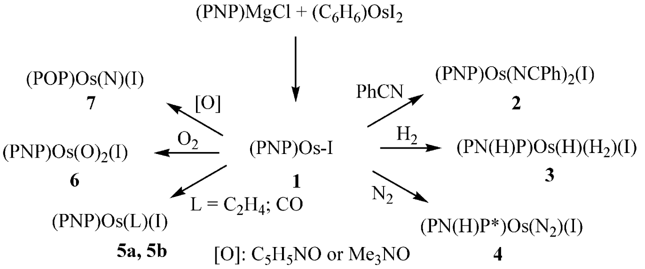
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201000503.

Results and Discussion

Synthesis of (PNP)OsI (1)

Reaction of $[(C_6H_6)OsI_2]_2$ with (PNP)MgCl in THF for 48 h at 22 °C forms pentane soluble green [(PNP)OsI] in 40% yield. Judging by the absence of a ^{31}P NMR signal (due to extremely rapid relaxation) and three ^1H NMR chemical shifts in the range +4 to –5.5 ppm, the molecule is paramagnetic and of C_{2v} symmetry. The ^1H NMR signals are so sharp that the *t*Bu resonance can be resolved into a virtual triplet (6 Hz P/H spin coupling). A DFT(B3LYP) geometry optimization of this species[10] shows that the triplet is the ground state, but the singlet is only 1.7 kcal/mol higher, whereas the singlet for the Ru analog lies 12.8 kcal/mol higher. The spin density is 1.93 e on Os, indicating little delocalization onto the ligands. We describe now (Scheme 1) how the molecule shows its unsaturation by binding of PhCN, H_2, or C_2H_4, each in time of mixing[11] at 25 °C.



Scheme 1.

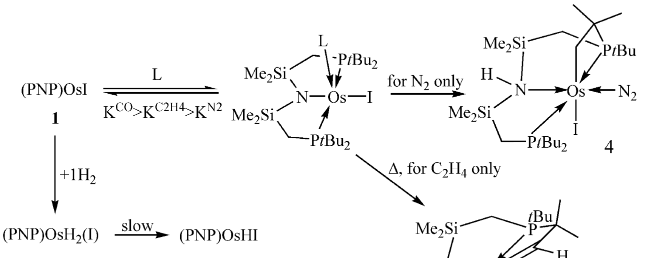
Lewis Base Adducts

a. Benzonitrile

Addition of PhCN (2 equiv.) to [(PNP)OsI] in benzene forms (Scheme 1) diamagnetic *trans*-$[(PNP)OsI(PhCN)_2]$, **2**, identifiable by ^1H and ^{31}P NMR spectra consistent with C_{2v} symmetry. Binding two benzonitriles in *trans* positions is also characteristic of (PNP)RuCl.

b. Ethylene

Green [(PNP)OsI] reacts in time of mixing[11] with ethylene (3 equiv.; 1 atm) to give (Scheme 1 and Scheme 2) a dark red diamagnetic 1:1 adduct **5a**, $[(PNP)Os(C_2H_4)I]$, characterized by its ^1H NMR intensities, including that of coordinated ethylene, and also the presence of two chemical shifts each for *t*Bu, for SiMe, and for $SiCH_2$ protons. This unexpected 1:1 stoichiometry may be associated with the fact that one ethylene binds in a way that folds iodide downwards, crowding the sixth coordination site.



Scheme 2.

c. Dihydrogen

This reagent gives both an η^2-H_2 adduct and H_2 addition across the Os–N bond, thus no redox change at osmium.[12] This reaction also shows the unsaturation of [(PNP)OsI], but with the additional feature of heterolytic splitting at the amide nitrogen. Reaction of [(PNP)OsI] with 2 equiv. (or 1 atm) H_2 in benzene at 25 °C forms (Scheme 1) only C_s-symmetric diamagnetic $[\{PN(H)P\}OsH(H_2)I]$, **3**, in time of mixing. This shows an NH proton at 2.3 ppm and intensity 2:1 hydride signals at –13.9 and –12.7 ppm. The T_1(minimum) value of this intensity 2 signal, 92 ms at 500 MHz, indicates it to be a molecular dihydrogen ligand, but with a highly elongated H···H distance.[13]

Reaction of [(PNP)OsI] with only equimolar H_2 in benzene forms diamagnetic red $[(PNP)OsH_2I]$ (see below for fuller characterization). Addition of 1 atm of H_2 to a solution of $[(PNP)OsH_2I]$ causes complete conversion in less than 5 min to yellow $[\{PN(H)P\}OsH(H_2)I]$. With regard to possible H_2 transfer reactions, we observed that combining equimolar [(PNP)OsI] and $[\{PN(H)P\}OsH(H_2)I]$ in benzene shows NMR signals of only the individual species, so this is not a viable synthesis of $[(PNP)OsH_2I]$, and there is no ^1H or ^{31}P NMR coalescence of these two species.

Independent Syntheses and Characterization of the Halohydrides [(PNP)OsH$_x$(halide)]

While the above reactivity with H_2 shows a reluctance to reach Os^{IV}, we find a significant preference for *trivalent* osmium in paramagnetic monomeric species.

[(PNP)OsH$_2$Cl]

Reaction of $[(PNP)Os(H)_3]$[4] with *N*-chlorosuccinimide (NCS) in benzene occurs within minutes (in spite of the poor solubility of the NCS), with complete consumption of Os reagent to give mainly diamagnetic $[(PNP)OsH_2Cl]$ in addition to small amounts of [(PNP)OsHCl] (see below). The major conversion here is the H/Cl replacement reaction typical of radical Cl sources. While $[(PNP)OsH_2Cl]$ shows only one hydride NMR signal, a triplet, there are two *t*Bu and two SiMe chemical shifts, indicating C_s symmetry. The hydrides are therefore either a dihydrogen molecule, or fluxional and coalesced, in a *cis*-dihydride of Os^{IV}.

Similarly, the reaction of orange $[(PNP)Os(H)_3]$ with equimolar *N*-iodosuccinimide (NIS) in benzene or THF gives complete conversion within less than 10 min to the metastable (see below) C_s-symmetric $[(PNP)OsH_2I]$.

[(PNP)OsHCl]

The reaction of $[(PNP)OsH(N_2)]$[14] with equimolar (or excess) *N*-chlorosuccinimide (NCS) in benzene or toluene (for low-temperature studies) gives rapid reaction and complete conversion of the reagent complex to form [(PNP)OsHCl], identifiable by its unusual (i.e., paramagnetically shifted) proton chemical shifts from +12 to –19 ppm (hydride not detected). There are two *t*Bu chemical shifts and two SiMe chemical shifts, which prove C_s, not C_{2v} symmetry, showing that this molecule is stereochemically rigid and that it cannot be planar [(PNP)OsCl] (see Exp. Section), whose Ru analog[2] is paramagnetic (a ground-state spin-triplet in spite of the d^6 configuration). The molecule shows no ^{31}P NMR signal, consistent with rapid relaxation broadening the phosphorus NMR signal to invisibility. The line widths of the proton NMR signals are typically 115 Hz. An Evans method magnetic susceptibility determination in benzene at 22 °C gave μ = 1.73 B.M., consistent with S = 1/2 and thus oxidation state Os^{III}. The selectivity of this NCS reaction is remarkable, since it might have been expected to replace hydride by Cl {as it does with [(PNP)Os(H)$_3$], above}, not add Cl. The loss of N_2 ligand here is wholly consistent with the reaction being an oxidation at Os (less back donation in the product), so apparently the radical Cl source NCS simply encounters a reducing agent, (PNP)Os^{II}, not an H atom donor towards the imidyl radical, due to the stability characteristic of trivalent osmium.

Reactivity of [(PNP)OsH$_2$Cl]

Over a period of 5 days at 25 °C in benzene, [(PNP)OsH$_2$Cl] is observed to convert to [(PNP)OsHCl], which is apparently a thermodynamic sink in this class of molecules. This reaction is slow, apparently due to the need to transfer only one H.

Over the course of hours to days at 25 °C, the iodo analog [(PNP)OsH$_2$I] also converts to paramagnetic [(PNP)OsHI], and the released H_2 combines with [(PNP)OsH$_2$I] to form [{PN(H)P}OsH(H$_2$)I]. As a result, the reaction (above) of [(PNP)Os(H)$_3$] with NIS already produces some amounts of [(PNP)OsHI] and [{PN(H)P}OsH(H$_2$)I] even within 2 h of mixing. The overall balanced reaction would convert 3 [(PNP)OsH$_2$I] into a 2:1 ratio of [(PNP)OsHI] and [{PN(H)P}OsH(H$_2$)I]. In this reaction, there are no significant rate differences between these chloride and iodide analogs. In an independent experiment, reaction of the radical [(PNP)OsHI] with 1 atm H_2 also causes conversion to [{PN(H)P}OsH(H$_2$)I], but only first detectable after 2 h. The slow rate of this reaction is suggested to be due to the fact that the first step, delivering one H from H_2, encounters some significant barrier.

The single-crystal X-ray structure of [(PNP)OsHCl] determined on crystals grown from benzene (Figure 1 and Table 1) shows a square pyramidal geometry with basal chloride. This is consistent with a formula [(PNP)OsHCl], where the hydride (not detected in the X-ray determination) is deduced from the bending of the chloride ligand out of the OsP_2N plane. The Os–N(amide) distance, 2.020(3) Å, is significantly shorter than comparable distances for d^6 compounds of five-coordinate (PNP)M^{II} structures (M = Os or Ru). This can be explained by the Singly Occupied Molecular Orbital of the trivalent metals being π*(M/N) in character, so going from a d^5 to a d^6 configuration further populates an M/N *anti*-bonding orbital, thus lengthening the bond. This of course supports the idea that the amide N is a π donor to the metal.

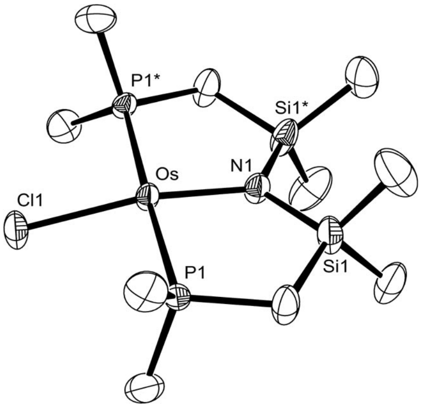


Figure 1. ORTEP drawing (50% probability ellipsoids) of [(PNP)OsHCl], with hydrogen atoms deleted. Unlabelled atoms are carbons, *t*Bu methyls have been deleted, and the hydride was not evident in the X-ray determination. See also Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for (PNP)M(H)Cl*.

	M = Os	M = Ru
M–N1	2.020(3)	2.029(4)
M–P1	2.3679(7)	2.3733(8)
M–C11	2.3951(14)	2.4260(16)
N1–M–P1	89.074(15)	89.22(2)
P1*1–M–P1[a]	178.15(3)	178.43(4)
P1*1–M–C11	90.80(4)	90.18(4)
N1–M–C11	163.29(5)	161.51(6)
P1–M–C11	90.80(4)	91.31(4)

[a] *Cell constants, Ru[Os]: a = 20.682(2) Å [20.714(2)]; b = 9.9430(8) [9.9650(10)]; c = 15.5568(12) [15.6128(16)]; β = 110.993(4)° [110.728(2)].

Independent synthetic work attempting to install an alkyl group on the (PNP)Ru fragment led instead to crystallization of the molecule (PNP)RuHCl, identified only by its crystal structure (Table 1). The synthetic method was reaction of (PNP)RuCl with $LiCH_2SiMe_3$ in THF at –70 °C, and subsequent crystal growth by slow evaporation of solvent; the product showed no ^{31}P NMR signal, consistent with paramagnetism. For this Ru analog, the hydride was visible in the difference Fourier maps, as well as by its inferred influence on bending the angle N–Ru–Cl from 180°. In fact the Ru analog is crystallographically isomorphous with the Os compound, so they pack identically. Table 1 compares the structural parameters of the two analogs, showing both to be square pyramidal.

Thermolysis of Olefin Adducts of [(PNP)OsI]

The general tendency[15] of the 5d metals to transform hydrocarbyl moieties into π-acid ligands is evident in the reaction of [(PNP)OsI]. Heating [(PNP)OsI(C_2H_4)] in benzene for 1 h at 90 °C completely consumes this reagent (Scheme 2), forming primarily carbene **8**, **"**(PNP=)OsI," and a small amount of [(PNP)OsH_2I], due its characteristic conversion (see above) to the also observed paramagnetic [(PNP)OsHI]. Carbene [(PNP=)OsI] is identified by the characteristic $M = CH(R)$ ^1H NMR signal at $\delta = 16$ ppm as a doublet of doublets (carbene H coupling to inequivalent phosphorus), and also three *t*Bu and four SiMe signals. Free ethylene is observed, indicating that it is not a *fully* effective scavenger of the released hydrogen. Since this reaction is faster than thermolysis of [(PNP)OsI] itself (see Experimental), it does not involve that species, in spite of forming some of the same products.

Reaction of [(PNP)OsI] with *tert*-butyl ethylene (1:2 mol ratio) in C_6D_6 completely consumes the Os reagent in 4 h at 90 °C to form [(PNP=)OsI], together with some amount of paramagnetic [(PNP)OsHI] and a 50% yield of a diamagnetic hydride complex assigned as [(PNP)Os(H)(*I*)-(CH=CH*t*Bu)] due to resonances consistent with C_s symmetry. This is the product of vinylic C–H oxidative addition to [(PNP)OsI]. Again this disappearance of [(PNP)OsI] is faster than that of pure [(PNP)OsI] under the same conditions, which shows the active participation of the olefin.

Synthesis and Reactivity of [(PNP)Os(N_2)I]

Adding 1 atm N_2 at –70 °C to [(PNP)OsI] in THF forms (Scheme 2) a diamagnetic 1:1 adduct (characterized by NMR spectra at low temperature to get higher conversion to adduct) consistent with C_s symmetry. Low-temperature infrared spectra in pentane show the adduct has an NN stretching frequency of 2112 cm^{-1} and this stretch loses intensity as the sample warms, consistent with this same evolution evident in the following variable temperature NMR spectra. A sample mixed and conserved at low temperature evolves, beginning already at 0 °C and completely within 0.5 h at 25 °C, to form one product. One contribution to this slow rate is that the N_2 adduct formation is less at higher temperatures. The lack of symmetry, via the resolution of four SiMe and three *t*Bu chemical shifts together with two intensity three methyl signals are all consistent with a product where a C–H bond of one *t*Bu methyl group has been cleaved to give [{PN(H)P*}OsI(N_2)] (**4**). Detection of one NH proton establishes that this is an example of H–C(sp^3) bond heterolysis. The osmium oxidation state is thus unaltered. The NN stretching frequency of [{PN(H)P*}-OsI(N_2)] is 2038 cm^{-1}, indicating only modest back donation to the relatively poor π-acid N_2. This C–H bond heterolysis contrasts starkly with the lack of such reaction at 25 °C with an ethylene ligand, giving instead the simple adduct [(PNP)Os(C_2H_4)I], and suggests that these two ligands elicit very different selectivities: apparently the π-acidity of N_2 leaves Os sufficiently electrophilic that it can bind, then rapidly heterolytically split an alkyl C–H bond. This reaction bears some similarity to that of N_2 with (PNP)Ru(OTf), OTf = O_3SCF_3, which triggers H–C bond heterolysis to give {[PN(H)P*]RuN_2}OTf, where the triflate hydrogen bonds to the NH proton, instead of binding to the metal (cf. iodide on Os here in **8**);[16] the difference in products here is that Ru is five coordinate, while Os is six coordinate.

DFT(B3LYP) calculation shows that N_2 binds, to form a simple adduct with [(PNP)OsI] with a ΔE of –13.2 kcal/mol (for Ru this is changed to + 1.9 kcal/mol), consistent with observation. However, calculated to be still 15.7 kcal/mol more stable is the observed product, **4**, of heterolytic splitting of one of the *t*Bu C–H bonds across the Os/NSi_2 bond; in contrast to this is the corresponding energy for C–H splitting involving ruthenium, which is only –1.4 kcal/mol.

Monocarbonyl Adduct [(PNP)Os(CO)I]

It is thus unusual that it is not the hydrogen acceptor ligand L = C_2H_4 in [(PNP)OsI(L)] that *readily* (25 °C) gives the carbene, but rather L = N_2. To test whether π-acidity is the causal factor, we considered the example where L = CO. It is possible to synthesize the five coordinate analog [(PNP)Os(CO)I] by careful addition of equimolar CO to a frozen solution of [(PNP)OsI] in C_6D_6, with vigorous mixing during melting. Even here, some [(PNP)Os$(CO)_2$I] is also formed, and fails to conproportionate with unreacted [(PNP)OsI] to form [(PNP)Os(CO)I], due apparently to steric bulk of these two molecules. Addition of more CO converts the mixture completely to [(PNP)Os$(CO)_2$I], identified as the *trans* isomer by its NMR indicating C_{2v} symmetry. The monocarbonyl shows C_s symmetry by its ^{31}P and ^1H NMR spectra. The observed CO stretching frequency of *trans*-[(PNP)Os$(CO)_2$I] is 1941 cm^{-1}, while that of the monocarbonyl is lower, 1892 cm^{-1}, as expected. The monocarbonyl shows no sign of metallation of its C–H bond after 24 h at 25 °C. It is thus not simply the π-acidity of L that promotes C–H bond heterolysis in unsaturated [(PNP)Os(L)I].

Reaction of [(PNP)OsI] with O_2

Oxygen provides an opportunity to probe the multielectron reducing potential of Os^{II} in the PNP ligand environment. Reaction (1:1 O_2/Os) of these reagents occurs in time of mixing at 25 °C with a color change from green to yellow to give complete conversion (Scheme 1) to a benzene-soluble diamagnetic product **6** of C_{2v} symmetry (^1H and ^{31}P NMR evidence). The CI (methane) mass spectrum of the isolated product shows $[(PNP)OsO_2]^+$ as the highest mass, supporting a formula (PNP)OsO_2I for **6**, which, together with the C_{2v} symmetry, would require full scission of the O/O bond (i.e., a rare 4-electron redox change)[17–19] or, if iodide were not coordinated, then a salt of the cation $(PNP)OsO_2^+$. Crystals grown by cooling from toluene were determined by X-ray diffraction (Figure 2) to be the molecular species [(PNP)Os$(O)_2$I] with the two oxido ligands mutually *trans* [O/Os/O = 174.90(13)°]. The geometry has no rigorous symmetry, but is in fact very close to C_2-symmetric. The Os/O distances, 1.749(3) and 1.751(3) Å, are identical to those in *trans*-[Os(O)$_2$(P*i*Pr$_3$)$_2$].[20] The Os/I distance, 2.8140(3) Å is unexceptional. The NSi$_2$ group is twisted to a large degree (dihedral angles 31 and 35°), as if to avoid overlap of the amide lone pair (N is planar) with the one filled d_π orbital. When the reaction is observed (low-temperature ^{1}H and ^{31}P NMR) following mixing at –78 °C in toluene, no intermediate is detected; only reactant disappearance and growth of the above product are seen, in spite of C_s-symmetric [(PNP)Os(η^1 or η^2-O$_2$)I] being anticipated. The barriers for two reaction steps (the 4 electron redox change and the isomerization of the two O to being mutually *trans*) are thus both low. Likewise, when these reagents are combined at 25 °C in an Os/O$_2$ mol ratio of 1:0.5, only 50% yield of [(PNP)Os(O)$_2$I] together with 50% unreacted [(PNP)OsI] are observed, so no mono-oxido species or intermediate is seen in this way.

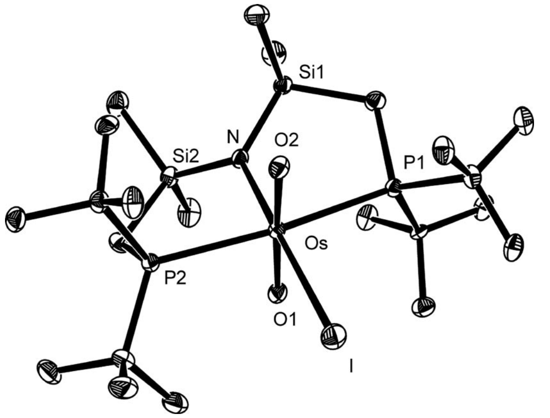
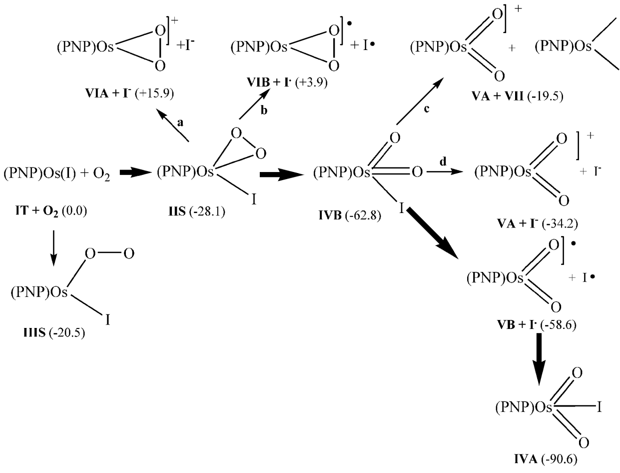


Figure 2. ORTEP drawing (50% probabilities) of the non-hydrogen atoms of [(PNP)Os(O)$_2$I], showing selected atom labeling. Unlabelled atoms are carbon. Selected structural parameters: Os–O1, 1.749(3) Å; Os–O2, 1.751(3); Os–N, 2.082(3); Os–P1, 2.5212(10); Os–P2, 2.5024(10); Os–I, 2.8140(3); N–Os–I, 179.18(9)°; O1–Os–O2, 174.90(13); P2–Os–P1, 172.08(3);O1–Os–N, 92.55(13); O2–Os–N, 92.55(13).

Scheme 3 (see also Supporting Information) shows relative DFT(B3LYP) electronic energies (corrected for solvation using a self-consistent reaction field based on numerical solutions of the Poisson–Boltzmann equation) of a variety of candidate intermediates; bold arrows map the lowest energy intermediates for what is seen to be a highly exothermic process. Ionic mechanisms (**a**, **c**, and **d**) to change the oxido stereochemistry to *trans* involve large energy penalties, but homolysis of the Os–I bond in hexavalent *cis*-[(PNP)Os(O)$_2$I] is remarkably easy (BDE is 4.2 kcal/mol), and is repaid by a much larger BDE (32.0 kcal/mol) of forming *trans*-[(PNP)Os(O)$_2$I]. Since this 4.2 kcal/mol BDE is less than $T\Delta S$ at our operating temperatures, Os–I bond homolysis from **IVB** will be spontaneous, and isomerization will probably occur in a geminate radical pair, thus preventing the *cis* intermediate from achieving detectable concentration, in agreement with experiment. The weak bond in *cis*-[(PNP)Os(O)$_2$I] is reflected in a very long Os–I distance (3.119 Å vs. 2.971 in the *trans* isomer), and a large ∠O–Os–O (121.5°) and yet the *heterolytic* splitting of this bond is not unusually easy (ΔE = 28.6 kcal/mol in eq. **d**). The special stability of the doublet [(PNP)Os(O)$_2$] radical **VB** is perhaps reflected in the fact that 25% of the spin density is located on each oxido ligand; the formal metal oxidation state is thus less than +5 since spin density on the oxido ligand means it is less negative than 2–. Note also that ∠O–Os–O (127.8°) in [(PNP)Os(O)$_2$] is nearly unchanged from that in *cis*-[(PNP)Os(O)$_2$I].



Scheme 3. Relative energies [ΔE(SCF) + ΔG(solv) in kcal/mol] for reactions of O$_2$ with [(PNP)Osl].

If indeed the mechanism involves Os–I bond homolysis, this step should be much more endothermic if the halogen is fluorine. The energy of forming neutral F$^\cdot$ will be very unfavorable, hence halting the reaction at *cis*-[(PNP)Os(O)$_2$F]. Indeed, reaction of [(PNP)OsF] with equimolar O$_2$ at 22 °C in benzene immediately yields a C_s-symmetric product showing a J_{PF} coupling (48 Hz) in both ^{31}P and ^{19}F NMR spectra; the ^{1}H NMR spectrum confirms these conclusions, thus supporting the homolysis mechanism for the conversion of *cis* to *trans* dioxido product. This *cis* species is sufficiently kinetically trapped regarding *cis*→*trans* conversion that this isomerization is never observed. Instead, with a half-life of ca. 10 min, it deposits a black solid (metal oxide).

Single O-Atom Transfer Product, [“(PNP)Os(O)I].”

We also sought a monoxide complex, [(PNP)Os(O)I]. Equimolar [(PNP)OsI] and pyridine *N*-oxide react in time of mixing in THF, with color change from green to dark red, to give a single product **7**. Removal of all volatiles and recrystallization from pentane at –40 °C gives a single product, exhibiting one ^{31}P chemical shift, two *t*Bu (triplets), two SiMe and two CH$_2$ proton chemical shifts, all, consistent with C_s symmetry and diamagnetism. The methane CI mass spectrum shows a molecular ion for mass [“(PNP)OsOI].” Equimolar [(PNP)OsI] and Me$_3$NO also react completely in time of mixing at 25 °C to give this same product. While metallocentric thinking, and the idea that this Os^{II} center is a reducing agent, would assign this product as [(PNP)Os(O)I], in fact the product has undergone a surprising transposition of the atoms N and O compared to this formula. A single-crystal X-ray diffraction structure determination (Figure 3) shows the molecule to have the C_s symmetry deduced from NMR spectra, but the monatomic ligand attached to Os has bond length too short for Os/O but appropriate for an Os/N triple bond.[21] The heteroatom in the pincer ligand does not coordinate to Os, but is 3.14 Å distant from it, consistent with a poorly nucleophilic bis(silyl ether) O atom. The molecule is thus [(POP)Os(N)I], containing four coordinate osmium, with a flattened tetrahedral coordination geometry. The uncharged POP ligand thus spans a wide edge of the tetrahedron, with a P1–Os1–P2 angle of 138.35(3)°, but the other angles around Os range from 96 to 117°. The Os···N distance, 1.638(4) Å, is identical to the Ru···N distance in (PNP)RuN.[22] Does the oxido group ever reside on Os in intermediates in any of these amine oxide reactions, or are these all examples of oxygen attack directly on silicon? One approach to this is the observation that addition of non-nucleophilic N_2O to [(PNP)OsI] at –78 °C, followed by mixing with minimal heating of the solution, shows that the reaction has gone to completion to form the product characterized above; no intermediate is detected. We believe that N_2O lacks the nucleophilicity to directly attack silicon. This suggests that the unobserved primary product [(PNP)Os(O)I], when formed from N_2O, has a low barrier to double $Si \rightarrow O$ migration. The rapid rate of this migration also excludes [(PNP)Os(O)I] as an intermediate in the reaction of [(PNP)OsI] with O_2.

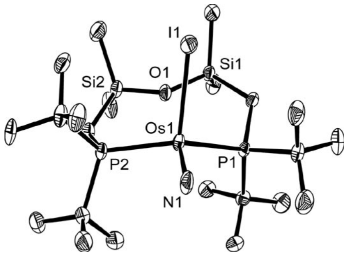


Figure 3. ORTEP drawing of the non-hydrogen atoms of [(POP)Os(N)I] (50% probability) showing selected atom labeling. Unlabelled atoms are carbon. Selected structural parameters: Os1–N1, 1.638(4) Å; Os1–P1, 2.3928(9); Os1–P2, 2.3938(10); Os1–I1, 2.7486(3); Si1–O1, 1.643(3); Si2–O1, 1.639(3); N1–Os1–P1, 101.64(11)°; N1–Os1–P2, 100.48(12); P1–Os1–P2, 138.35(3); N1–Os1–I1, 117.33(14); P1–Os1–I1, 96.24(2); P2–Os1–I1, 104.21(2); Si2–O1–Si1, 140.24(18). Nonbonded Os–O1 = 3.14 Å.

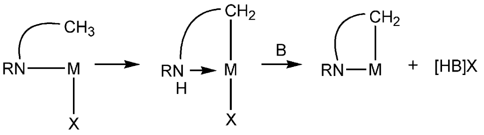
DFT(B3LYP) geometry optimization calculations on the two isomeric structures[10] gave five coordinate [(PNP)Os(O)I] as well as the observed four coordinate POP structure, with the latter in very good agreement with experiment with regard to bond lengths and angles. Consistent with the logic above, the calculated Os···O distance, 1.81 Å, is distinctly longer than the Os···N distance, 1.65 Å. The nitride isomer is more stable than the terminal oxido isomer by 20.9 kcal/mol, something that probably could not be predicted since the two isomers have the same metal oxidation state and valence electron count. In summary, the oxido in undetected [(PNP)Os^{IV}OI] is evidently sufficiently nucleophilic that it is thermodynamically preferred to have two Si migrate there, leaving a nitride ligand instead of oxido.

Conclusions

This work shows the low barrier for [(PNP)OsI] to adduct formation with Lewis bases, as well as the reaction with H_2. When no such reagent (or solvent, e.g. benzene) is available, then, with a higher barrier, attack on its own *t*Bu group can occur twice, forming **8**. Note however that [(PNP)OsI] is protected by a high activation energy from attacking its own ligand.

In the thermolysis and hydrocarbon reactivity work reported here, only [(PNP)OsH_2(halide)] and [(PNP)OsHI(CH=CH*t*Bu)] are Os^{IV}. The remainder of the halide species stays at the divalent oxidation state of the reagent. Even when this involves cleavage of an H–C(sp^3) bond, the favored oxidation state is Os^{II}, and this is possible by formal addition of the C–H bond across the Os–amide bond, a process best described as C–H bond heterolysis. This is not the favored reaction for pincer ligands with sp^2 or sp^3 C atom at the central anionic site,[23–27] but it is the reaction between Ru–NR_2 and the H_2 σ bond, in the Noyori hydrogenation catalyst, forming H–Ru–NHR_2.[5–9] This difference is attributed to the lone pair on the central pincer donor for anionic PNP pincers.

The heterolytic character of the C–H cleavage offers a special advantage when, as is often the case here, a halide ligand is present [Equation (1)]. If a base B can be found to subsequently do dehydrohalogenation, then a metal/alkyl functionality has been formed from an alkyl group without need of alkali metal or Grignard reagents and *without* oxidizing the metal. Success in such dehydrohalogenation depends on finding a base stronger than the amide nitrogen.



(1)

Why does N_2 trigger C–H bond heterolysis? This could be due to the fact that product **4** is an 18 electron species, which is less true of [(PNP)OsI(N_2)] due to $Si_2N \rightarrow Os$ π-donation. But this five-coordinate adduct also apparently has a more electron rich amide nitrogen than does [(PNP)OsI], thus preparing it for C–H bond heterolysis. Finally product **4** annihilates any 4 electron repulsion between the amide lone pair and an occupied d orbital in [(PNP)OsI(N_2)].

Although halogen effects are often not very dramatic, the F/I comparison used here offers special mechanistic potential. In addition, the DFT calculations here reveal that M–I bond *homolysis* should be considered more generally, especially where the metal oxidation state is high. Regarding a synthetic application, one can disfavor some mechanisms by choosing the metal fluoride variant, allowing kinetic to dominate thermodynamic product control.

The exceptions to the above tendency to retain Os^{II} are the more potent reagents amine oxide and O_2, where Os^{IV} and Os^{VI}, respectively, are achieved. In these products, the strength of the multiple bonds to O and N dominate the thermodynamics, and $N \rightarrow Os$ π-donation in $[(PNP)Os(O)_2I]$ diminishes the amide basicity to the extent that C–H heterolysis does not occur there.

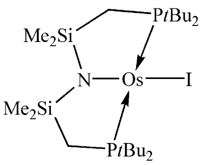
These results show both reductive and Brønsted basic reactivity of the Os-amide bond in [(PNP)OsI], as well as kinetic facility of accessing higher oxidation states, leading to rapid formation of the thermodynamic isomer of the Os^{VI} dioxido species. The ability of the PNP ligand to support metal oxidation states from +2 to +6 may be one of its special strengths.

Experimental Section

General Considerations: All manipulations were performed using standard Schlenk techniques or in an argon-filled glovebox unless otherwise noted. Pentane and THF were purified using an Innovative Technologies solvent purification system, Pure Solv 400-6-MD. $[D_8]$THF and $[D_6]$benzene were dried under Ph_2CO/Na, vacuum transferred and stored in the glovebox under argon. N_2O, H_2, N_2, C_2H_4 and O_2 were used as received from commercial vendors. $OsCl_3 \cdot 3H_2O$ was purchased from Colonial Metals, Inc. 1,3-Cyclohexadiene was distilled. PhCN was distilled from P_2O_5 and degassed. C_5H_5NO was distilled in vacuo (1 mm at 130 °C, 170 °C oil bath) to give a colorless liquid, which crystallized in 15 min into a white solid. $[(PNP)Os(H)_3]$ was synthesized according to the literature.[4] NMR chemical shifts are reported in ppm relative to protio impurities in the deuterio solvents; "ps.-t" stands for pseudo-triplet. Coupling constants are given in Hz. ^{31}P NMR spectra are referenced to external standards of H_3PO_4. NMR spectra were recorded with a Varian Unity INOVA instrument (400 MHz ^{1}H; 162 MHz ^{31}P; 101 MHz ^{13}C). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Mass spectra were acquired on a PE-Sciex API III triple quadrupole spectrometer. "PNP" is $N(SiMe_2CH_2PtBu_2)_2$.

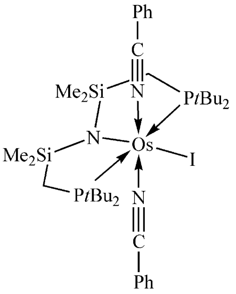
$[(C_6H_6)OsI_2]_2$:[28] 1.00 g of $OsCl_3 \cdot 3H_2O$, 2.0 mL of cyclohexa-1,3-diene and 1.2 g of I_2 was dissolved in the 50 mL of EtOH. The reaction mixture was refluxed with vigorous stirring for 12 h, cooled and a brown powder was filtered, washed with EtOH (10 mL) and Et_2O (10 mL). 1.48 g (99%) of product was obtained after drying in vacuo. This reagent was used without further purification. Its solubility in benzene is too low to produce a proton NMR signal, but it dissolves, with adduct formation, in MeCN. ^{1}H NMR (CD_3CN, 25 °C): δ = 6.07 (s, C_6H_6) ppm.

[(PNP)OsI] (1):



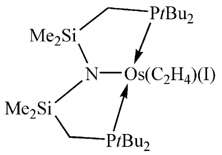
1.83 g of (PNP)MgCl[29] (0.0030 mol) was added to a suspension of 1.60 g of dimer $[C_6H_6OsI_2]_2$ (0.0015 mol) in 40 mL of THF. The reaction was stirred for 48 h at 22 °C. All volatiles were removed in vacuo, 40 mL of pentane was added and stirred for 24 h at 22 °C, then filtered. The pentane solution was concentrated to 5 mL and kept overnight at –40 °C. Green powder was filtered and dried; yield 0.94 g (40%). ^{1}H NMR of species **1** (C_6D_6, 25 °C): δ = –5.42 (t, J = 4.6 Hz, 4 H, CH_2), –0.62 (t, J = 6.1 Hz, 36 H, *t*Bu), 4.62 [s, 12 H, $Si(CH_3)_2$] ppm. CI-MS (*m/z*): 765.1687; calcd. for $C_{22}H_{50}INOsP_2Si_2$: $[M - 2H]^+$ 765.1616.

Reaction of [(PNP)OsI] (1) with PhCN:



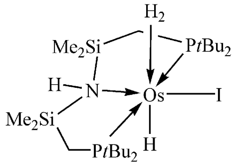
10 mg of [(PNP)OsI] (0.013 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of C_6D_6. 2.7 mg of PhCN (0.026 mmol, $2.6 \cdot 10^{-3}$ mL) was added to the solution via syringe. The green reaction mixture turned to purple in time of mixing with complete conversion to $[(PNP)Os(PhCN)_2I]$ (**2**). ^{1}H NMR (C_6D_6, 25 °C): δ = 0.59 (s, 12 H, SiMe), 1.24 (t, J = 4.6 Hz, 4 H, CH_2), 1.57 (br.s, 36 H, *t*Bu), 6.8–6.9 (m, 6 H, Ar), 7.51 (d, J = 7.6 Hz, 4 H, *o*-Ar) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ = 4.8 (s) ppm. In benzene, excess PhCN slowly displaces the iodide to precipitate a red solid, shown by ^{1}H NMR integration (in CD_2Cl_2) and mass spectrometry to give a cation containing three PhCN; the product is thus the salt $[(PNP)Os(NCPh)_3]I$. ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 0.30 (s, 12 H, SiMe), 1.30 (t, J = 4.4 Hz, 4 H, CH_2), 1.46 (t, J = 6.4 Hz, 36 H, *t*Bu), 7.55–7.70 (m, 15 H, Ar) ppm. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ = 20.9 (s) ppm. ESI-MS (THF): (*m/z*) 949.3994; calcd. for $C_{43}H_{67}N_4OsP_2Si_2$: $[M]^+$ 949.3994.

Reaction of [(PNP)OsI] (1) with C_2H_4:



20 mg of [(PNP)OsI] (0.026 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of C_6D_6 and was degassed through three freeze-pump-thaw cycles using liquid N_2. 760 mm of C_2H_4 (3.5 equiv.) was added to the evacuated head space of the frozen solution in the tube. The green reaction mixture turned to dark red in time of mixing upon thawing, with complete conversion to $[(PNP)Os(C_2H_4)I]$ (**5**). ^{1}H NMR (C_6D_6, 25 °C): δ = 0.45, 0.47 (both s, 6 H each, SiMe), 0.73 (dt, J = 12 and 4.6 Hz, 2 H, CH_2), 1.12 (br.s, 18 H, *t*Bu), 1.23 (dt, J = 12 and 4.6 Hz, 2 H, CH_2), 1.43 (t, J = 6.1 Hz, 18 H, *t*Bu), 4.11 (br.s, 4 H, C_2H_4) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 25 °C): δ = –10.5 ppm.

Reaction of [(PNP)OsI] (1) with H_2:



20 mg of [(PNP)OsI] (0.026 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of C_6D_6 and was degassed through three freeze-pump-thaw cycles using liquid N_2. 760 mm of H_2 (ca. 1.7 equiv.) was added to the evacuated head space of the frozen solution. The green reaction mixture turned to yellow in time of mixing with complete conversion to [{PN(H)P}Os(H)(H_2)I], **3**. ^{1}H NMR (C_6D_6, 25 °C): δ = –13.92 [t, J = 11.9 Hz, 2 H, Os(H_2)], –12.67 (t, J = 15.6 Hz, 1 H, OsH), 0.17, 0.41 [both s, 6 H each, Si(CH_3)$_2$], 1.21 (t, J = 5.8 Hz, 18 H, *t*Bu), 1.49 (t, J = 6.3 Hz, 18 H, *t*Bu), 2.32 (br.s, 1 H, NH) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ = 42.6 (s) ppm. T_1 values of a solution in THF were measured at 500 MHz in the range +25 to –55 °C. The signal for the intensity two hydrogens on Os reaches a broad minimum from about –45 to –55 °C, at a value of 92 ms. At this same temperature, the T_1 value for the intensity one hydride is always larger, and is 174 ms at –55 °C.[10]

Reaction of [(PNP)Os(H)$_3$] with NCS to [(PNP)OsH$_2$Cl]: 6 mg of [(PNP)Os(H)$_3$] (10 µmol) in a J-Young tube was dissolved in 0.5 mL of C_6D_6. 1.5 mg of NCS was added to the tube. In 20 min, complete consumption of [(PNP)Os(H)$_3$] was observed by NMR spectroscopy. Formation of [(PNP)OsH$_2$Cl] was confirmed by NMR spectra with a small amount of [(PNP)OsHCl] also evident. ^{1}H NMR of [(PNP)OsH$_2$Cl] (C_6D_6, 25 °C): δ = 0.26 (s, 6 H, Si*Me*), 0.35 (s, 6 H, Si*Me*), 1.18 (ps.-t, J = 6 Hz, 18 H, P*tBu*), 1.48 (ps.-t, J = 6 Hz, 18 H, P*tBu*) ppm. Os*H$_2$* and SiC*H$_2$* signals were not observed, the latter due to overlapping with other resonances. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ = 42.4 (s) ppm. Over 5 days, the signals from [(PNP)OsH$_2$Cl] decreased while the NMR signals for new diamagnetic product and paramagnetic [(PNP)OsHCl] increased. We assigned the new diamagnetic product to [{PN(H)P}Os(H)$_2$Cl(succinimide)].[30] ^{1}H NMR (C_6D_6, 25 °C): δ = –7.10 (t, J_{HP} = 10.8 Hz, 2 H, Os*H$_2$*), 0.02 (s, 6 H, Si*Me*), 0.29 (s, 6 H, Si*Me*), 1.31 (ps.-t, J = 6 Hz, 18 H, P*tBu*), 1.56 (ps.-t, J = 6 Hz, 18 H, P*tBu*) ppm. SiC*H$_2$* signals were not observed due to overlapping with other resonances. ^{31}P{^{1}H} NMR (C_6D_6, 25 °C): δ = 15.4 (s), This declines in intensity, with growth of [(PNP)OsH$_2$Cl] and [(PNP)OsHCl] as described above, all due to reaction with available H_2. Finally this reaction comes to equilibrium with some [{PN(H)P}Os(H)$_2$Cl(succinimide)] persisting, due to the limited amount of available H_2 ppm.

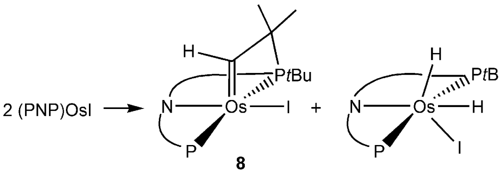
Reaction of [(PNP)Os(H)$_3$] with NIS: 15.8 mg of [(PNP)Os(H)$_3$] (0.0246 mmol) was dissolved in 10 mL of THF. 5.8 mg (0.0258 mmol) of *N*-iodosuccinimide was added at one time, with vigorous stirring. The brown reaction mixture turned dark red in time of mixing. After 2 h of stirring all volatiles were removed in vacuo, the residue was extracted with pentane (2 × 20 mL), filtered through Celite, and the pentane extracts concentrated to dryness in vacuo. Both ^{1}H and ^{31}P NMR (C_6D_6) showed the formation of the mixture of paramagnetic [(PNP)OsHI] and diamagnetic [(PNP)OsH$_2$I] (see spectra below) and [{PN(H)P}Os(H_2)(H)(*I*)] in ratio 1:0.1:0.23. ^{1}H NMR (C_6D_6, 25 °C) of paramagnetic [(PNP)OsHI]: δ = –19.2 and –18.7 (two br. s, 2 H each, CH_2); –5.74 and –4.11 (two br. s, 18 H each, *t*Bu); 11.26 and 11.48 (two br. s, 6 H each, SiMe$_2$) ppm.

[(PNP)OsH$_2$I]: ^{1}H NMR ([D$_8$]toluene, 25 °C): δ = 0.27 and 0.31 (both s, 6 H each, SiMe), 1.16 and 1.55 (both t, 18 h each, P*t*Bu) ppm. ^{31}P{^{1}H} NMR ([D$_8$]toluene, 25 °C): δ = 45.0 (s) ppm. For a sample of [(PNP)OsH$_2$I] generated from [(PNP)OsI] and 1 equiv. of H_2, ^{1}H NMR ([D$_8$]toluene, –50 °C): δ = –12.2 and –25.2 (both broad, equal intensity, Os*H$_2$*) ppm; these signals vanish due to broadening (fluxionality) upon raising the temperature. ^{31}P NMR was unchanged at this temperature.

Reaction of [(PNP)OsHI] with H_2: A sample of [(PNP)OsHI] (solution in C_6D_6) was degassed through three freeze-pump-thaw cycles. 760 mm of H_2 (ca. 3.6 equiv.) was added to the evacuated head space of the frozen solution. The reaction mixture was allowed to melt and was stirred at 22 °C. NMR was recorded periodically, showing slow (completed in 24 h) formation of known [{PN(H)P}Os(H_2)(H)(*I*)].

Reaction of [(PNP)OsH(N_2)] with *N*-Chlorosuccinimide (NCS), Forming [(PNP)OsHCl]: [(PNP)OsH(N_2)] (10 µmol) solution in 0.5 mL of C_6D_6 was prepared in a J-Young tube. 1.3 mg of NCS was added to the reaction tube. After 30 min, the volatiles were removed in vacuo. The mixture was extracted into pentane and undissolved solid was removed by filtration. The filtrate was dried in vacuo to yield 5.8 mg (86%) of [(PNP)OsHCl]. ^{1}H NMR (C_6D_6, 25 °C): δ = –19.72 (br. s, 4 H, SiC*H$_2$*), –5.16 (br. s, 18 H, *tBu*), –3.66 (br. s, 18 H, *tBu*), 10.29 (br. s, 6 H, Si*Me$_2$*), 12.01 (br. s, 6 H, Si*Me$_2$*); Os-*H* signal was not observed due to paramagnetic broadening of the signal ppm.

Thermolysis of [(PNP)OsI] in Inert Solvent: Studies where 20 mg [(PNP)OsI] is heated (1 to 18 h) in [D$_{12}$]cyclohexane in the the range 60–90 °C and periodically monitored by ^{1}H and ^{31}P NMR spectroscopy show formation first of a species with an AX ^{31}P{^{1}H} NMR pattern, and more slowly the formation of the dehydrogenation product (PNP=)OsI, **8** (see below for characteristic NMR signature), together with [(PNP)OsH$_2$I] (see above). We have been unable to fully identify the AX product (designated here as **X**), but believe it to involve reaction of one backbone silicon with the iodide; its ^{1}H NMR spectrum shows two ^{1}H NMR *t*Bu doublets but apparently three silyl methyl chemical shifts. The amounts of (PNP=)OsI and [(PNP)OsH$_2$I] are approximately equal, in agreement with the stoichiometry shown in Equation (2).



(2)

Formation of **8** is accelerated by the presence of equimolar PhN=NPh, which scavenges hydrogen (new aryl and NH signals appear during this conversion). At no time during the thermolysis of [(PNP)OsI] is any hydride signal detected by ^{1}H NMR except for that of [(PNP)OsH$_2$I].

Unidentified Product X: ^{1}H NMR (C_6D_{12}, 25 °C): δ = 0.17, 0.22, 0.37 (all s, 3 H each, SiMe), 1.04 and 1.25 (both d, P*tBu*) ppm. ^{31}P{^{1}H} NMR (C_6D_{12}, 25 °C): δ = –8.1 (d, J = 302 Hz), 51.1 (d, J = 302 Hz) ppm.

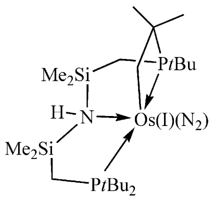
[(PNP=)OsI] (8): ^{1}H NMR (C_6D_6, 25 °C): δ = –0.11, 0.20, 0.46, 0.46 (all s, 3 H each, SiMe), 0.70 and 1.28 (both d, 3 H each, CMe$_2$), 1.40, 1.48, 1.51 (all d, 9 H each, P*t*Bu), 15.98 (d.d, J = 10.6

and 34.7 Hz, Os-CH=) ppm. $^{31}P\{^1H\}$ NMR (C_6D_{12}, 25 °C): δ = 0.71 (d, J = 349 Hz), 24.51 (d, J = 349 Hz) ppm.

Thermolysis of [(PNP)OsI(C_2H_4)]: A solution of [(PNP)OsI(C_2H_4)] was heated in benzene for 1 h at 90 °C. ^{31}P NMR showed complete conversion of [(PNP)OsI(C_2H_4)] to a mixture of [(PNP=)OsI] (54%), **X** (15%), and [(PNP)OsH_2I] (4%). ^1H NMR showed paramagnetic peaks for [(PNP)OsHI].

Thermolysis of [(PNP)OsI] in the Presence of (*t*Bu)HC=CH_2: 20 mg of [(PNP)OsI] (0.026 mmol) and 2.2 mg of *tert*-butyl ethylene (0.026 mmol) were dissolved in 0.5 mL of C_6D_6. Heating at 90 °C for 3.5 h showed (^1H and ^{31}P NMR) complete consumption of [(PNP)OsI] and formation of a mixture of [(PNP=)OsI], together with some amount of paramagnetic [(PNP)OsHI], including 50% [(PNP)Os(H)(*I*)(CH=CH*t*Bu)]: ^1H NMR (C_6D_6): δ = –10.3 (t, J = 18.7 Hz, 1 H, Os-H), 0.09, 0.34 (both s, 6 H each, SiMe), 1.36, 1.62 (both t, J = 6.1 and 6.3 Hz, 18 H each respectively, *t*Bu) ppm; other signals were not seen due to complexity of the mixture. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 22.9 (s) ppm.

Reaction of [(PNP)OsI] (1) with N_2:



10 mg of [(PNP)OsI] (0.013 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of C_6D_6 and was degassed through three freeze-pump-thaw cycles using liquid N_2. 760 mm of N_2 (7 equiv.) was added to the evacuated head space of the frozen solution. The green reaction mixture turned to yellow in two hours with 92% conversion to [{PN(H)P*}Os(N_2)(*I*)], **4**. ^1H NMR (C_6D_6, 25 °C): δ = –0.01, 0.01, 0.72, 0.79 (all s, 3 H each, SiMe), 1.01 (d, J = 11.5 Hz, 9 H, *t*Bu), 1.35 (d, J = 13.2 Hz, 9 H, *t*Bu), 1.56 (d, J = 12.5 Hz, 9 H, *t*Bu), 1.73 (d, J = 13.5 Hz, 3 H, CH_3C), 2.71 (ddd, J = 27.6, J = 10.5, J = 2.4 Hz, 1 H, Os-CH_2) ppm. 0.5–0.2 (SiCH_2); other CH_2 signals and the other CH_3 signal are hidden by the *t*Bu signals. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = –32.9 (d, J = 286 Hz), 20.8 (d, J = 285 Hz) ppm. IR (C_6D_6 solution): $\tilde{\nu}(N_2)$ = 2038 cm^{-1}.

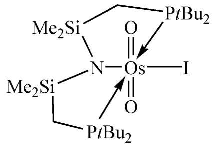
Variable-Temperature NMR Monitoring of Reaction of [(PNP)OsI] with N_2: 20 mg of [(PNP)OsI] (0.026 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of [D_8]THF and was degassed through three freeze-pump-thaw cycles using liquid N_2. 760 mm (3.4 equiv.) of N_2 was added to the evacuated head space of the frozen solution in the tube. This solution was put far into the Dewar (to cool the upper glass walls) with acetone at –80 °C, allowed to melt, then the tube was shaken fast to minimize heating at the walls and NMR spectra were recorded beginning from –60 °C. The green reaction mixture turned to dark green in time of mixing with more than 90% conversion to [(PNP)Os(N_2)I]. The reaction mixture was warmed to 25 °C, with recording ^1H and ^{31}P NMR every 10°. For [(PNP)Os(N_2)I], ^1H NMR (THF, –60 °C): δ = 0.19, 0.35 (both s, 6 H each, SiMe), 1.42, 1.55 (br.s, 18 H each, *t*Bu) ppm; CH_2 were not assigned with confidence. $^{31}P\{^1H\}$ NMR (THF, –60 °C): δ = 23.40 ppm. NMR observations at –50, –40, –30, –20, and –10 show decay of the adduct with formation of starting [(PNP)OsI]. Initial formation of final product **4** was seen at 0 °C (this is the only diamagnetic product at 25 °C in 40 min).

Low-Temperature IR Study of the Reaction of [(PNP)OsI] with N_2: 5 mg of [(PNP)OsI] (0.007 mmol) was dissolved in 0.5 mL of pentane and was degassed through three freeze-pump-thaw cycles using liquid N_2. 760 mm (14 equiv.) of N_2 was added to the evacuated head space of the frozen solution. This solution was put far into the Dewar (to cool the upper glass walls) with acetone at –80 °C, allowed to melt, then the tube was shaken fast to minimize heating at the walls. The cold tube was transferred into the glove box where the solution was transferred into the pre-cooled (–40 °C) IR cell. The IR spectrum was recorded as quickly as possible to prevent sample warming. **IR** (pentane, approximately –40 °C): $\nu(N_2)$ 2112 cm^{-1}. IR spectra observed upon progressive warming shows decay of this adduct, [(PNP)Os(N_2)I], with formation of **4**.

Reaction of [(PNP)OsI] (1) with CO: 20 mg of [(PNP)OsI] (0.026 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of C_6D_6 and was degassed through three freeze-pump-thaw cycles using liquid N_2. 220 mm of CO (1 equiv.) was added to the evacuated head space of the frozen solution in the tube. The green reaction mixture turned to deep green in time of mixing with 90% conversion to [(PNP)Os(CO)I]. Also present in the solution is [(PNP)Os$(CO)_2$I]. For **5b**, ^1H NMR (C_6D_6, 25 °C): δ = 0.31, 0.36 (both s, 6 H each, SiMe), 0.74–0.80 (m, 2 H, CH_2), 1.33, 1.41 (both t, J = 6.4 Hz, 18 H each, *t*Bu) ppm; the other Si-CH_2 was not observed due to overlapping with other stronger resonances. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 41.1 ppm. IR (C_6D_6): $\tilde{\nu}$ = 1892 cm^{-1}. NMR observation after 12 h did not reveal any changes in ^1H and ^{31}P NMR spectroscopy. Another 220 mm of CO was then added to the evacuated head space of the frozen solution. The green reaction mixture turned to yellow in time of mixing with complete conversion to [(PNP)Os$(CO)_2$I]. ^1H NMR (C_6D_6, 25 °C): δ = 0.32 (s, 12 H, SiMe), 1.10–1.12 (m, 4 H, CH_2), 1.38 (br.s., 36 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 24.6 ppm. IR (**C_6D_6**): $\tilde{\nu}$ = 1941 cm^{-1}.

Reaction of [(PNP)OsI] (1) with O_2

Variable-Temperature Monitoring of Reaction of [(PNP)OsI] with O_2:



20 mg of [(PNP)OsI] (0.026 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of [D_8]THF and was degassed through three freeze-pump-thaw cycles using liquid N_2. 220 mm (1 equiv.) of O_2 was added to the evacuated head space of the frozen solution in the tube. This solution was put far into a Dewar (to cool the upper glass walls) with acetone at –80 °C, allowed to melt, then the tube was shaken fast to minimize heating at the walls and NMR spectra were recorded beginning from –60 °C. The green reaction mixture turned to yellow in time of mixing with complete conversion to [(PNP)Os$(O)_2$I] (**6**). Observation of ^1H and ^{31}P NMR at –60 °C revealed the absence of the starting complex and formation of **6**. The reaction mixture was warmed to 25 °C, where ^1H and ^{31}P NMR showed no changes.

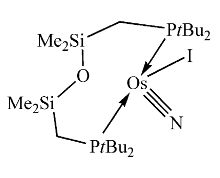
NMR Assay with Different Os/O_2 Ratios: 20 mg of [(PNP)OsI] (0.026 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of deuterated benzene and was degassed through three freeze-pump-thaw cycles using liquid N_2. 110 mm (0.5 equiv.) of O_2 was added to the evacuated head space of the frozen solution in the tube. NMR observation after 10 min at 22 °C revealed the formation of the mixture of the product and starting material in ratio 1:1. Addition of another 0.5 of equivalent of O_2 showed complete conversion to the product. Addition of 1 more equivalent of O_2 showed no changes, even after 24 h at 22 °C. Crystals of [(PNP)OsO_2I] suitable for X-ray determination analysis were grown by cooling of saturated toluene solution at –40 °C. ^1H NMR (C_6D_6, 25 °C): δ = 0.38 [s, 12 H, $Si(CH_3)_2$], 1.03 (t, J = 6.3 Hz, 4 H, CH_2), 1.44 (t, J = 6.4 Hz, 36 H, *t*Bu) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 21.1 (s) ppm. IR (pentane solution): $\tilde{\nu}$(Os=O) 836 cm^{-1}, assigned by comparison to the solution IR of [(PNP)OsI]. CI-MS (*m/z*): 672.2596; calcd. for $C_{22}H_{52}NO_2OsP_2Si_2$: $[M - I]^+$ 672.2621.

[(PNP)OsCl]: 105 mg of [(PNP)OsI] (0.137 mmol) and 94 mg of Bu_4NCl (0.411 mmol, 3 equiv.) in 50 mL of Et_2O were vigorously stirred for 24 h at 22 °C. Following filtration, the filtrate was concentrated and dried to give 86 mg of [(PNP)OsCl] (93%). ^1H NMR (25 °C, benzene): δ = –2.51 (t, J = 4.5 Hz, 4 H, CH_2), 0.79 (t, J = 7.1 Hz, 36 H, *t*Bu), 2.27 [s, 12 H, $Si(CH_3)_2$] ppm. These chemical shifts indicate paramagnetism.

[(PNP)OsF]: 18 mg of [(PNP)OsCl] (0.027 mmol), 2.5 mg of NMe_4F (0.027 mmol) and 12.3 mg (0.081 mmol) of CsF in 0.6 mL of [D_8]THF were stirred for 2 h at 22 °C. All volatiles was removed in vacuo, 10 mL of pentane was added and stirred for 10 min at 22 °C, then filtered. The pentane solution was concentrated and dried in vacuo to give 16 mg (90%) of [(PNP)OsF]. ^1H NMR (25 °C, benzene): δ = 0.28 (t, J = 4.6 Hz, 4 H, CH_2), 0.46 [s, 12 H, $Si(CH_3)_2$], 1.68 (t, J = 6.1 Hz, 36 H, *t*Bu) ppm. No ^{31}P NMR signal could be detected. Direct synthesis of [(PNP)OsF] from [(PNP)OsI] was not successful due to high base sensitivity of the latter to F^-, evident by a product with an AB $^{31}P\{^1H\}$NMR spectrum due to attack on a *t*Bu CH bond.

Reaction of [(PNP)OsF] with O_2: 16 mg of [(PNP)OsI] (0.026 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of deuterated benzene and was degassed through three freeze-pump-thaw cycles using liquid N_2. One equivalent of O_2 was added to the evacuated head space of the frozen solution in the tube. NMR observation after 10 min at 22 °C revealed the formation *cis*-[(PNP)$Os(O)_2$F]. ^1H NMR (C_6D_6, 25 °C): δ = 0.43, 0.52 [both s, 6 H each, $Si(CH_3)_2$], 1.37, 1.42 (both t, J = 7.2 Hz, 18 H each, *t*Bu), CH_2 protons were not seen due to overlap with other signals ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 49.1 (d, J = 48 Hz) ppm. ^{19}F NMR (C_6D_6, 25 °C): δ = –201.5 (t, J = 48) ppm. Signals of this compound in the reaction solution decay within 1 h with formation of unidentified products.

Reaction of [(PNP)OsI] with C_5H_5NO:



20 mg of [(PNP)OsI] (0.026 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of C_6D_6. 2.5 mg of C_5H_5NO (0.026 mmol) was added to the tube at 22 °C and tube was shaken. The color of the reaction mixture turned dark red and NMR observation after 5 min showed complete conversion of [(PNP)OsI] to the new single product **7**. The same product is obtained analogously using Me_3NO or N_2O. Crystals suitable for X-ray diffraction analysis were grown by cooling of saturated solution in pentane at –40 °C. ^1H NMR (C_6D_6, 25 °C): δ = –0.06, 0.30 (both s, 6 H each, SiMe), 1.37 (ps.-t, J = 6.3 Hz, 18 H, *t*Bu), 1.51 (ps.-t, J = 7.5 Hz, 18 H, *t*Bu), 1.80–1.88 (m, 2 H, CH_2) ppm; the other CH_2 group is masked by other signals. $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 82.4 (s) ppm. CI-MS (*m/z*): 783.1725; calcd. for $C_{22}H_{52}INOOsP_2Si_2$: $[M]^+$ 783.1717.

CCDC-778419 [for (PNP)RuHCl], -778420 [for (PNP)OsHCl], -778421 [for (PNP)$Os(O)_2$I], and -778422 [for (PNP)Os(N)I] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): T1 measurement for [{PN(H)P}Os(H)(H_2)I], details of X-ray structure determination, computational details, and NMR spectra.

Acknowledgments

This work was supported by the National Science Foundation (NSF) (NSF-CHE-0544829). We thank Dr. Michael Ingleson for the crystalline sample of (PNP)RuHCl.

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[10] See Supporting Information.

[11] The appropriateness of this phrase is generally indicated by an immediate color change.

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Received: May 4, 2010