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PAPER

An evaluation of monovalent osmium supported by the PNP ligand environment†

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Nitrogen is essential to reaction of (PNP)OsI (PNP is $N(SiMe_2CH_2P^tBu_2)_2$) and Mg powder in THF, to give equimolar (PNP)OsH(N_2) and hydrido carbene $[(^tBu_2PCH_2SiMe_2)N(SiMe_2CH_2P^tBu(CMe_2CH)]OsH$. This reaction is attributed to H_2 evolution from solid magnesium, rather than high energy H atom transfer between molecules, but relies also on the strong π-basicity of Os in favoring α-H migration from the metallated ^{t}Bu group on Os to form the second product, the hydrido carbene species. The path to two different products begins because the simple N_2 adduct of (PNP)OsI undergoes spontaneous heterolytic H–C splitting of the ^{t}Bu methyl group, to produce a secondary amine intermediate $[(^tBu_2PCH_2SiMe_2)N(H)(SiMe_2CH_2P^tBu(CMe_2CH_2)]OsI(N_2)$ which can then be dehydrohalogenated by Mg. The analogous reaction for (PNP)RuCl shows production of only (PNP)RuH(N_2), with none of the hydride carbene dehydrogenation product. Comparative (Ru *vs.* Os) DFT calculations reveal the reaction steps where the Os analog is much more exothermic, accounting for certain reaction selectivities.

Introduction

Radical chemistry of "organometallic" species lacks the systematic character that has been built up based on the 18-electron rule for even-electron species.[1–12] Often monomeric odd-electron species dimerize, *via* metal–metal bonding, indicating that odd-electron species have some of the same preferences as main group radicals. The PNP ligand (PNP is $N(SiMe_2CH_2P^tBu_2)_2$) has sufficient steric bulk that it discourages[11,12] bringing two such sterically shielded complexes together into one molecule, so (PNP)M radical species might be a fertile place to establish reactivity patterns intrinsic to such monomeric radicals. Given the increasing development of "non-innocent" ligands,[13–18] where spin delocalization can "leak" between metal and ligand, blurring the meaning of formal metal oxidation states, there is also the possibility that the amide nitrogen in a PNP ligand can mitigate radical character at a metal center. In addition, we already know that the amide nitrogen is an active functionality, by virtue of it accepting a proton, or forming a bond to an electrophilic ligand on its metal. The PNP ligand as a whole is showing increasing reactivity.[11,19–25] We report here our attempts to access monomeric monovalent osmium, a metal which has been shown to have generally the highest reducing power of the Fe, Ru, Os series. For comparison, the analogous ruthenium chemistry[26] will also be briefly evaluated. The results confirm the high reducing power of these low valent, odd-electron oxidation states, but also the high reactivity of pendant ^{t}Bu C–H bonds.

Results

Magnesium reduction of osmium(II)

Reaction of (PNP)OsI[27] with powdered Mg in THF under 1 atm N_2 proceeds slowly, and only following the magnesium-independent ~1 h induction period while N_2 coordinates to osmium and C–H heterolysis occurs, forming **A** (Scheme 1) [27] The same reaction without N_2 gives little or no conversion of (PNP)OsI under the same conditions. The reaction is slow at 25 °C, but proceeds over several days of shaking with color change to red, with complete consumption of (PNP)OsI to give equimolar amounts (by both ^{1}H and ^{31}P NMR integrations) of two compounds, the known[28] (PNP)OsH(N_2), **C**, and (PNP=)OsH, **D**, where PNP= is a modified ligand where one ^{t}Bu methyl carbon has been doubly dehydrogenated to form a carbene. The magnesium has done its job in fully removing the halide ligand from both products. The ^{1}H NMR spectrum of the unseparated product solution shows that there are no paramagnetic products. **D** has no symmetry, hence shows three intact ^{t}Bu proton NMR signals, and four SiMe signals. The $^{31}P\{^1H\}$ NMR spectrum is an AB pattern with $J_{PP'}$ = 324 Hz. The carbene proton appears at the characteristic far downfield chemical shift of +15.3 pm as a doublet of doublets, and the hydride is also a doublet of doublets; both these confirm the inequivalence of the two phosphines caused by the conversion of a ^{t}Bu methyl to a carbene functionality. The far upfield hydride chemical shift of **C**, −34.8 ppm, indicates the hydride is *trans* to an

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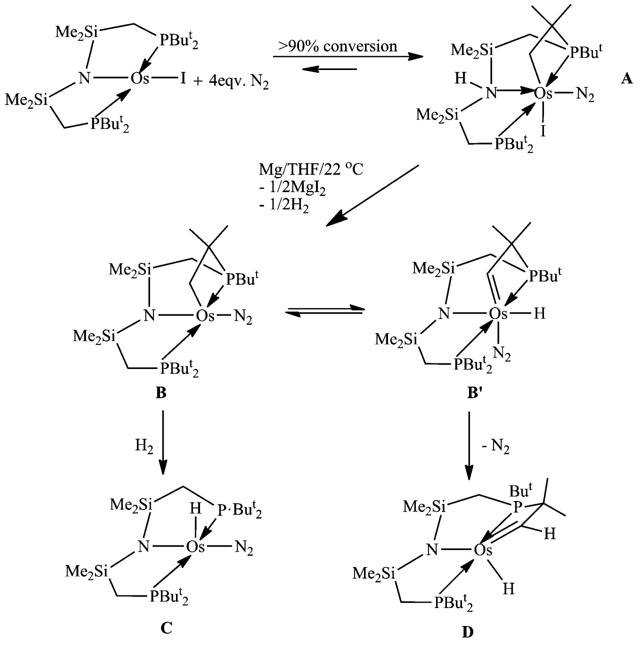


Scheme 1

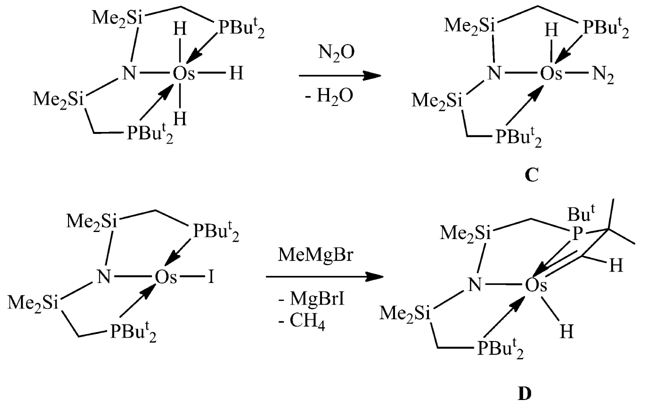
empty site in a square pyramidal species. The source of the new hydride ligand is confirmed to be within the PNP ligand, and not from radical abstraction from solvent, since, if the above reaction is repeated in THF-d$_8$, the stoichiometric amount of hydride is detected by ^{1}H NMR. In terms of conversion of (PNP)OsI, species **C** is "(PNP)Os + H" (ignoring added N$_2$) and **D** is "(PNP)Os − H", hence equimolar amounts of **C** and **D** give full material balance.

To summarize, this reaction (eqn (1)) occurs with complete removal of iodide from Os, and removal of two hydrogens from one methyl group, with transfer of one of these hydrogens to a second osmium. Single H atom transfer is apparent radical chemistry, and is apparently symptomatic of the fact that reduction of (PNP)Os^{II} to monovalent Os is followed by events which return to even-electron species. The other relevant point is that reduced osmium is anticipated to be a powerful reducing agent, which generally is manifest[29] by transforming alkyl groups into strong π acids (*e.g.* carbene).

$$2(\mathrm{PNP})\mathrm{OsI} + \mathrm{Mg} + \mathrm{N_2} \rightarrow \mathbf{C} + \mathbf{D} + \mathrm{MgI_2} \qquad (1)$$

Mechanistic speculation (Scheme 1) hinges on knowing the detailed connectivity of the species formed from N$_2$ and (PNP)OsI, **A**, prior to reaction with Mg. This already has suffered *heterolytic* splitting of one H–C bond, and is an amine complex of divalent osmium. We suggest that it is the acidity of the secondary amine proton that mediates this reactivity towards Mg. If **A** contacts the Mg surface and leaves H on the surface, this can avoid higher energy mechanisms, and accumulate H on the Mg to then liberate H$_2$. Magnesium thus becomes a reservoir for H atoms and for forming H$_2$, and liberates the hypothesized dehalogenated Os^{II} species **B** which has favorable structure and composition to be persistent. If the strained ring of the metallated ^{t}Bu group in **B** encounters H$_2$, hydrogenolysis of the Os–C bond generates (PNP)OsH(N$_2$).[28] Alternatively, species **B** can undergo an intramolecular α-H migration to make **B′**, which then loses N$_2$ (the carbene dominates N$_2$ for back donation so N$_2$ is lost) to form the second observed product **D**. Ultimately the 1 : 1 stoichiometry at the branch point **B**/**B′** is controlled by the amount of available H$_2$, *i.e.* 50 mol% of that of the osmium. In short, the acidity of the amine proton and the reducing power of the magnesium conspire to avoid high energy paths associated with a hydrogen atom intermediate. Indeed, because we propose that the iodo ligand in **A** also transfers to the bulk Mg at the time of H transfer (*i.e.* dehydrohalogenation), Os stays at oxidation state +2, and never reaches Os^{I}. By collecting H "atoms" at the bulk metal reductant, H$_2$ is the effective hydrogen carrier, and radical reactions are avoided from a very early point in the mechanism.[30]

Independent synthesis of **D** was achieved (Scheme 2) by reaction of equimolar (PNP)OsI with MeMgBr at −20 °C, followed by warming to 25 °C in THF/benzene. These react in less than 5 min to give an observable primary product, diamagnetic and of C_{2v} symmetry, which we identify as *trans*-(PNP)Os(THF)$_2$(CH$_3$). This evolves over time at 25 °C, or within 10 min at 90 °C, to form a single product with ^{1}H and ^{31}P NMR spectra identical to those observed above, the hydrido carbene complex **D**. These methane elimination reactions resemble those reported earlier[23] for (PNP)Ru(CH$_3$) but there the chemistry all happened below −50 °C.



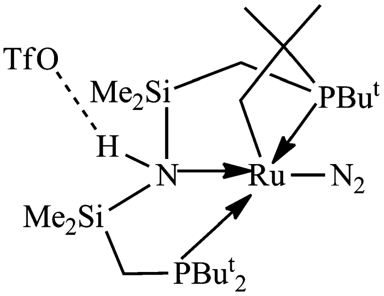
Scheme 2 Independent synthesis of **C** and **D**.

To test the proposed intermediacy of **A**, we attempted to trap it with a more traditional base, LiN^{i}Pr$_2$ (*i.e.* to effect dehydrohalogenation) and thus eliminate available H$_2$. If successful (*i.e.* in the absence of magnesium), this would reduce the amount of product **C**, (PNP)OsH(N$_2$), and divert it to the carbene hydride, (PNP=)OsH, **D**. A sample of (PNP)OsI was first reacted with N$_2$ in benzene to convert it to **A**. The lithium amide (Li : Os = 1 : 1) was then added as a benzene solution at 25 °C, the N$_2$ was replenished, and the time evolution of this solution was then monitored over 15 h. This showed increasing conversion of **A** to primarily **D**, with smaller amounts of **C** still detected. Throughout, the red color of **D** intensifies, and the signals of HN^{i}Pr$_2$ grow. After 15 h, the ratio of **D** to **C** is at least 2 : 1, confirming the trapping of **A** with base, even if this is not completely efficient at this amide : Os mole ratio. By 15 h, the reaction had reached a steady state (verified by observation at 24 h) with about 50% unreacted **A**. We suspected that the amide had suffered reduced reactivity by complexation of LiN^{i}Pr$_2$ by liberated HN^{i}Pr$_2$. Therefore, an additional 2 equiv of LiN^{i}Pr$_2$ was added. Within 12 additional hours, the reaction had gone to completion with a ratio of **D** to **C** of 7 : 1.

Comparison to ruthenium

Reaction of (PNP)RuCl with powdered magnesium under N_2 in THF at 25 °C occurs over 4 h to give a single diamagnetic benzene-soluble product whose ^1H and ^{31}P NMR spectra (in C_6D_6) indicate C_s symmetry, and which shows a hydride signal (^{31}P NMR doublet under conditions of selective hydride coupling), all consistent with (PNP)RuH(N_2), and similar to its osmium analog and independently synthesized by reaction of (PNP)RuH_3 with N_2O (analogous to Scheme 2). Its ν_{NN} stretching frequency is 2042 cm^{-1}. No second ruthenium product (*e.g.* no carbene hydride) is produced. Thus, the reducing power of the heavier analog Os is well developed, showing a better ability of osmium to convert alkyl substituents into π-acid ligands. The (PNP)MH(N_2) species for M = Os shows the lower NN stretching frequency (2004 cm^{-1}), consistent with the 5d metal being the stronger π-base. In general, this action of an apparent "reducing agent" (*e.g.* Mg) to dehydrohalogenate a Brønsted acidic metal complex bears consideration more widely as a synthetic tool. The ruthenium carbene hydride has been reported by an independent synthesis, from (PNP)$RuCH_3$, and characterized[23] at −40 °C because it decomposes to intractable products at 22 °C.

With ruthenium,[31] independent observation shows that the formation constant for (PNP)RuCl(N_2) is low so that this adduct can only be observed by NMR at low temperature and does not *detectably* attack the ^{t}Bu group. In contrast, for the four-coordinate, paramagnetic (PNP)Ru(OTf) analog, N_2 causes a rapid reaction with displacement of triflate from the coordination sphere and heterolytic (Scheme 3) splitting of the H–C bond of one ^{t}Bu methyl group. Thus again, N_2 produces a secondary amine with enough Brønsted acidity to potentially react with Mg, although this is less favorable (*vs.* triflate) than the chloride case.

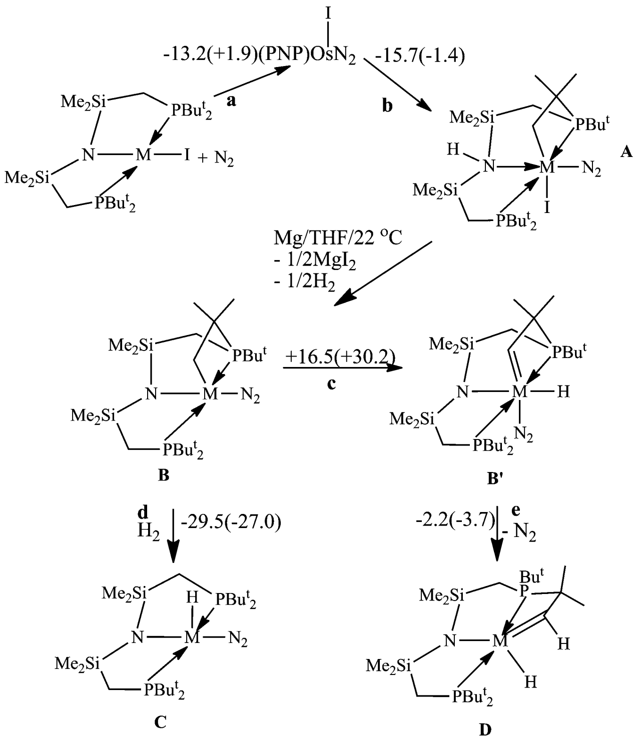


Scheme 3

We have repeated the reaction of (PNP)RuCl with N_2 and Mg in d_8-THF, in order to establish the origin of the hydride ligand on Ru in (PNP)RuH(N_2). This shows dramatic differences from the reaction in protio THF: the reaction is slower by a factor of at least 7, and it proceeds with deposition of a large amount of black powder, apparently ruthenium metal. The same N_2 complex is still produced, but as a mixture of RuH and RuD isotopomers (evident by both the broadening of the $^{31}P\{^1H\}$ NMR signal and by the reduced intensity of the ^1H NMR hydride signal). This we interpret as an isotope effect on the rate of scavenging deuterium atoms from solvent, as well as decay of some transient reduction product by inefficient hydrogen scavenging and scavenging of some H from PNP ligand. In general, any monovalent ruthenium monomer produced here is much more effectively scavenged by solvent C–H than by C–D bonds.[32]

DFT computational study of structures and reaction energies

DFT(B3LYP) geometry optimization was carried out for the species in Scheme 1, together with their Ru analogs. Energies are given in Scheme 4 for Os followed in parentheses by those for Ru.



Scheme 4 Reaction energies in kcal mol^{-1} for M = Os(Ru).

a. **Os**. For (PNP)OsI, the triplet is more stable than the singlet by only 1.7 kcal mol^{-1}. The spin density is 1.93 e on Os, so there is little delocalization of spin density onto other atoms. The electronic energy of binding N_2 (essentially the BDE of the Os–N_2 bond) is 13.2 kcal mol^{-1} (reaction **a**), so the $\Delta G°$ value, solvent-corrected for THF, is + 3.9 kcal mol^{-1}; this near-zero value is consistent with observation in that little adduct is found at 22 °C, but more is found at −60 °C. Addition of one ^{t}Bu C–H bond across the Os–NSi_2 bond (Scheme 4, reaction **b**) in this adduct is favorable, which shows the strong Brønsted basicity of the amide N in (PNP)OsI(N_2). The most stable isomer of **A** is that with an intramolecular hydrogen bond between NH and iodide, and is more stable by 2.0 kcal mol^{-1} than the next best isomer (see ESI†). Three isomeric products of loss of HI were located, and the most stable one, **B**, has the alkyl carbon apical in a square pyramid. Since 5-coordinate species are invariably stereochemically non-rigid, the product of HI removal will rapidly relax to its most stable isomeric structure. In every structure with a metallated ^{t}Bu carbon, the main geometric distortion is to make the Os–P–C angle unusually strained, at about 88°. Because the most stable structure of the carbene hydride species **B′** (PNP═)OsH(N_2) lies 16.5 kcal mol^{-1} above **B**, this is an energetic high point among available intermediates, consistent with the fact that it is never detected. The high energy of **B′** is also the reason why loss of N_2

from this species in energetically favored by 2.2 kcal mol^{-1} (reaction **e**), *i.e.* the BDE of N_2 *trans* to carbene in this species is less than zero. Hydrogenation of **B** (reaction **d**) to give (PNP)OsH(N_2) is very favorable, by 29.5 kcal mol^{-1}. In the overall conversion from **B** (through **B′**) to **D**, the favorable entropy change will give ΔG° of nearly zero, and this reaction is easily accomplished, but entropy-driven. The carbene hydride **D** has a Y-shaped geometry with a short Os=C bond (1.89 Å).

b. **Ru**. Calculations have been done for the iodide, for best comparison to osmium. The corresponding reaction energies are shown in Scheme 4 (Ru in parentheses, following the value for Os). Consistent with experiment, these show that (reaction **a**) adduct formation (PNP)MI(N_2) is less favorable for M = Ru, as is (reaction **b**) addition of a ^{t}Bu C–H bond across the M–amide bond. α-H migration (reaction **c**) of (PNP*)M(N_2)[33] is also less favorable for M = Ru, while loss of N_2 from (PNP=)MH(N_2) (reaction **e**) is comparably favorable for both metals. The major notable observation from all these reaction energies is that addition of H_2 across the C–M bond of (PNP*)M(N_2) (reaction **d**) is about equally favorable for both metals. This remarkable metal independence allows the generalization that metal identity, *via* back donation (stronger for Os), does not significantly influence bond hydrogenolysis, apparently since the reaction involves no change in metal oxidation state or electron count, and involves no strong π acid ligand. The α-H migration for M = Ru is so highly endothermic (reaction **c**) that this alone can explain the production of only (PNP)RuH(N_2), without forming any carbene partner; this of course then requires an alternative source of the hydride ligand in the observed formation of (PNP)RuH(N_2).

Other d^8 analogs

Comparison to the d^8 case is also informative. Treatment of (PNP)PtCl with Mg powder in THF under argon with vigorous agitation over 4 h shows no reaction. After 12 h, then 5 days additional reaction time, (PNP)PtCl is consumed but the appearance of first 5, then 13 ^{31}P{^{1}H} NMR singlets shows the reaction to be unselective. None of these ^{31}P NMR signals comprise an AX pattern, indicating that metallation of a ^{t}Bu H–C bond is not involved, which also distinguishes these reactions from those of osmium. Since we observe that (PNP)PtCl shows no reaction with N_2, this serves as another control experiment in that, in the absence of conversion of the reagent complex to some species with at least weak Brønsted acidity, there is no clean dehalogenation to a monovalent (PNP)Pt moiety. Reduction to monovalent state, by "simple" dehalogenation, only happens, and easily there,[34] for the 3d species (PNP)MCl for M = Fe, Co and Ni.

Conclusions

The reaction conditions employed here can be described as "hydrogen poor" and under those conditions an unsaturated metal tries to "recruit" ligands from unlikely places. Dinitrogen serves that role, but clearly quite poorly, since it is not a very strongly binding ligand in general, and since it is present in only one of two osmium products. Moreover, both products are superficially unsaturated. Curiously, the primary function of N_2 here is to create a Brønsted acid, which then has enhanced reactivity towards Mg. The magnesium effects net dehydrohalogenation (*i.e.* − HI) so formally it is not a reducing agent for osmium. (PNP*)Os^{II}(N_2), **B**, is the mechanistic branch point, where the magnesium-derived H_2 (0.5 mole per Os) consumes half of that intermediate, while the other half of the osmium undergoes α-H migration from the metallated alkyl to yield a carbene hydride **B′**, followed by N_2 loss.

The osmium chemistry here is slower than that for the Ru analog, but this is generally true for 5d *vs.* 4d reactions. Of special interest is that there are two products, produced in stoichiometric amounts, for osmium while the analogous ruthenium chemistry forms a single product. The origin of this difference may be in the relative thermodynamics of, or the persistence of, a carbene for Os *vs.* for Ru. The reducing power (π-basicity) of osmium is demonstrated to be stronger for Os than for Ru (*e.g.* ν_{NN} of (PNP)M(H)(N_2)), as is evident for example in the ground state of the Grubbs catalyst class, $RuCl_2(CHR)L_2$, *vs.* the redox isomer $OsCl_2H(CR)L_2$.[29] In general, osmium has the greater propensity to convert hydrocarbon fragments into the strongest π acid ligand.[29] Thus it may be that the unobserved [N(SiMe$_2$CH$_2$P^{t}Bu$_2$)(SiMe$_2$CH$_2$P^{t}Bu(CMe$_2$CH)]RuH hydrido carbene is simply too high in energy (+26.5 kcal mol^{-1} for **B** → **D** when M = Ru) to be accessible from the reagents used here. Ruthenium thus scavenges hydrogens to the point where it can have oxidation state +2, and with the weak π acid ligand N_2 complemented by the amide π-donor.

Experimental

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. Deuterated THF and benzene were also dried under Ph_2CO/Na, vacuum transferred and stored in the glovebox under argon. N_2 was used as received from commercial vendors. NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. 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). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. "PNP" is N(SiMe$_2$CH$_2$P ^{t}Bu$_2$)$_2$.

Activation of Mg. Diluted HCl (1 mL of concentrated HCl was dissolved in 10 mL of H_2O) was slowly added into 3.3 gm Mg in 40 mL of THF with vigorous stirring. After 5 min, the Mg was filtered, washed three times with 20 mL of dry THF and dried in vacuum.

Reaction of (PNP)OsI with Mg in the presence of N_2. 30 mg of activated Mg (32 equivalents, 1.25 mmol) and 30 mg of (PNP)OsI (0.039 mol) were placed into a Schlenk flask in 5 mL of THF. Following degassing by 3 freeze–pump–thaw cycles using liquid N_2, 760 mm of N_2 was added to the evacuated head space of the frozen solution. The flask was stirred for 5 d at 22 °C, during which time the color of the solution turned red. All volatiles were removed in vacuum, 1.0 mL of C_6D_6 was added and filtered through the glass filter into a J-Young NMR tube. ^{1}H and ^{31}P NMR reveals formation of equimolar **C** and **D** (spectra below).

Scavenging with base: reaction of A with LiN^{i}Pr$_2$ (LDA). 17.7 mg of (PNP)OsI (0.023 mmol) in a J-Young NMR tube was dissolved in 0.5 mL of C_6D_6. The solution was degassed through 3 freeze–pump–thaw cycles using liquid N_2. 760 mm of N_2 (4 equiv.) was added to the evacuated head space of the frozen solution and the reactants were stirred for 1 h at 22 °C. During the reaction the color of the solution turned yellow indicating 90% conversion (by the ^{31}P NMR) to **A**. 9 mg of LDA (3 equivalents, 0.073 mmol) was added to the solution. One freeze–pump–thaw cycle was done using liquid N_2. 760 mm of N_2 was added to the evacuated head space of the frozen suspension, and the reaction mixture was shaken for 12 h. NMR showed complete consumption of the Os starting materials with formation of **D** (spectra shown below) and **C** in 9 : 1 ratio. Spectra of (PNP)OsH(N_2) have been reported.[28]

Alternative synthesis of (PNP=)OsH. 20 mg of (PNP)OsI (0.026 mmol) in a Schlenk flask was dissolved in 5 mL of THF. The solution was cooled to −20 °C, and MeMgBr (solution in THF, 1 equivalent) was added *via* syringe. The reaction mixture was slowly warmed to 22 °C and ^{31}P NMR of the THF solution after 1 h reveals formation of a diamagnetic product, (PNP)Os(CH_3)(THF)$_2$. All volatiles were removed under vacuum, 20 mL of pentane was added and the suspension was filtered. Pentane was again removed under vacuum. NMR of the residue after only 10 min showed the same diamagnetic methyl complex with a singlet by ^{31}P NMR, together with a small amount of a new AB pattern, **D**. Consumption of the primary product (PNP)Os(CH_3)(THF)$_2$ and formation of **D** was observed at 22 °C. Heating the solution at 90 °C for 10 min showed complete conversion to this second product, **D**. **^{1}H NMR** (PNP)Os(CH_3)(THF)$_2$ (C_6D_6, 25 °C): 0.34 (s, 12 H, SiMe), 1.00–1.06 (m, 4 H, CH_2), 1.29 (t, 36 H, J = 4.8, Bu^t). Os–Me was not located due to overlap with other signals. **^{31}P{^{1}H} NMR** (C_6D_6, 25 °C): 42.2 (s). **^{1}H NMR** of **D** (C_6D_6, 25 °C): −3.0 (dd, 1 H, J = 12.2 and 15.3, Os–H), 0.14, 0.18, 0.53, 0.54 (all s, 3 H each, SiMe), 1.86 (d, 3 H, J = 13.1, CH_3), 1.10 (d, 9 H, J = 12.7 Hz, Bu^t), 1.19 (d, 3 H, J = 12.3 Hz, CH_3), 1.30 (t, 9 H, J = 13.5 Hz, Bu^t), 1.38 (t, 9 H, J = 12.7 Hz, Bu^t), 15.30 (dd, 1 H, J = 10.7 and 36.5, = CH). **^{31}P{^{1}H} NMR** (C_6D_6, 25 °C): 27.1 and 54.0 (both d, J = 324 Hz).

Reaction of (PNP)RuCl with Mg in the presence of N_2. 40 mg of activated Mg (32 equivalents, 1.64 mmol) and 30 mg of (PNP)RuCl [26] (0.051 mol) was placed into the Schlenk flask in 5 mL of THF. The solution and Mg was degassed through 3 freeze–pump–thaw cycles using liquid N_2. 760 mm of N_2 was then added to the evacuated head space of the frozen solution. The reagents were stirred for 1 d at 22 °C and the color of the solution turned red. All volatiles was removed under vacuum, 1.0 mL of C_6D_6 was added to dissolve all red solid and filtered through the glass filter into a J-Young NMR tube. NMR reveals formation of (PNP)RuH(N_2). **^{1}H NMR** (C_6D_6, 25 °C): −27.3 (t,1 H, J = 18.2, Ru–H), 0.31 and 0.33 (both s, 6 H each, SiMe), 0.76–0.80 (m, 4 H, CH_2), 1.25 (t, 36 H, J = 6 Hz, all Bu^t, accidentally degenerate). **^{31}P{^{1}H} NMR** (C_6D_6, 25 °C): 71.4 (s). **IR** (C_6D_6 solution): $\nu(N_2)$ 2042 cm^{-1}.

Alternate synthesis of (PNP)RuH(N_2). **a**. 10 mg of (PNP)RuCl (0.017 mol) in a J-Young NMR tube was dissolved in 0.5 mL of C_6D_6. The solution was degassed through 3 freeze–pump–thaw cycles using liquid N_2. 760 mm of H_2 (5 equiv.) was added to the evacuated head space of the frozen solution. The tube was shaken for 30 min at 22 °C and the solution color turned to green followed by yellow. NMR (^{1}H and ^{31}P) showed complete conversion to (PN(H)P)RuH_3Cl. **^{1}H NMR** (C_6D_6, 25 °C): −12.97 (t, 3 H, J = 14.7, RuH_3), 0.23, 0.41 (both s, 6 H each, SiMe), 0.69, 0.74 (both t, 1 H each, J = 5.5, CH_2), 1.15, 1.43 (both t, 18 H each, J = 6.1, Bu^t), 3.17 (br s, 1 H, NH). **^{31}P{^{1}H} NMR** (C_6D_6, 25 °C): 76.4 (s).

b. This reaction tube was degassed through one freeze–pump–thaw cycle and 4.2 mg (0.034 mol) of LiN^{i}Pr$_2$ was added to the solution. The color of the suspension turned orange. NMR (^{31}P) after 15 min showed complete conversion into a new compound, **(PNP)RuH$_3$**. **^{1}H NMR** (C_6D_6, 25 °C): −15.09 (t, 3 H, J = 13.1, RuH_3), 0.45 (s, 12 H, SiMe), 0.81 (t, 4 H, J = 4.5, CH_2), 1.13 (t, 36 H, J = 6.3, Bu^t). **^{31}P{^{1}H} NMR** (C_6D_6, 25 °C): 84.5 (s).

c. All volatiles from the above solution of (PNP)RuH_3 were removed under vacuum, 20 mL of pentane was added and the suspension was filtered. Pentane was again removed under vacuum and the residue was dissolved in C_6D_6. The resulting orange solution was degassed through 3 freeze–pump–thaw cycles and 200 mm of N_2O (2 equiv.) was added to the evacuated head space of the frozen solution. NMR (^{31}P) after 10 min at 25 °C showed ~30% conversion into the new compound, **(PNP)Ru(H)(N_2)**, and the color of the solution had turned red. **^{31}P{^{1}H} NMR** (C_6D_6, 25 °C): 71.4 (s). The color of the solution turned black in another 10 min and ^{31}P NMR showed decay of the unreacted (PNP)RuH_3 signal together with an unchanged amount of (PNP)Ru(H)(N_2). The NMR spectra of the product of this reaction is identical to that of the (PNP)RuH(N_2) produced above. In this reaction mixture, the water produced by hydrogenolysis of N_2O decomposes the residual (PNP)RuH_3 within about 20 min.

(PNP)PtCl. To 0.12 g (0.32 mmol) of Pt(COD)Cl$_2$[35,36] in 10 mL THF was added (PNP)MgCl(dioxane), 0.19 g (0.32 mmol). After stirring vigorously for 24 h at 25 °C, the volatiles were removed under vacuum, the solid residue was extracted with toluene, and these toluene extracts were concentrated, then mixed with an equal volume of pentane, and the resulting solution cooled for 2 days to yield 0.14 g of solid (63% yield). **^{1}H NMR (C_6D_6)**: 0.31 (12H, SiMe), 0.67 (t, 4 H, J = 6, CH_2), 1.40 (t, 36 H, J = 8, ^{t}Bu). **^{31}P{^{1}H} NMR (C_6D_6)**: 41.6 (singlet with ^{195}Pt satellites, J_{PtP} = 2592). **ESI + MS** (in MeCN): M$^+$, 680; (MH − Cl)$^+$, 644, both with correct isotopic pattern.

Computational details. All calculations were carried out using Density Functional Theory as implemented in the Jaguar 6.0 suite[37] of *ab initio* quantum chemistry programs. Geometry optimizations were performed with the B3LYP[38–41] functional and the 6-31G** basis set with no symmetry restrictions. Transition metal was represented using the Los Alamos LACVP basis.[42,43] The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using Dunning's correlation-consistent triple-ζ basis set[44] 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-ζ quality basis.

The models used in this study consist of ~90 atoms, which represent the non-truncated substrates that were also used in the experimental work.

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