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Reactivity of the terminal oxo species $((^t\mathrm{Bu_2PCH_2SiMe_2})_2\mathrm{N})\mathrm{RhO}$†‡

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Reactivity of the 4-coordinate molecule (PNP)RhO (PNP is $(^t\mathrm{Bu_2PCH_2SiMe_2})_2\mathrm{N}$) towards CO proceeds stepwise, first forming an η^2-CO_2 complex, by a mechanism which involves a preliminary adduct of CO on Rh, then a second CO displaces CO_2. Reaction of the oxo complex with CO_2 occurs in time of mixing even at low temperature to form (PNP)Rh(η^2-CO_3), with no intermediate detectable. DFT calculations indicate an initial bond formation between the oxo center and the CO_2 carbon. Reaction of (PNP)RhO with H_2 occurs only at a 1 : 2 molar stoichiometry, to ultimately form (PNP)Rh(H)$_2$ and free H_2O. No intermediate reaches detectable population even at −60 °C, but DFT mapping of various possible mechanisms on the singlet energy surface shows that the nearly equi-energetic (PNP)Rh(H_2O) and (PNP)RhH(OH) are formed, but only the latter readily adds the second molecule of H_2 to proceed to the observed products; these reactions thus *both* involve heterolytic splitting of H_2.

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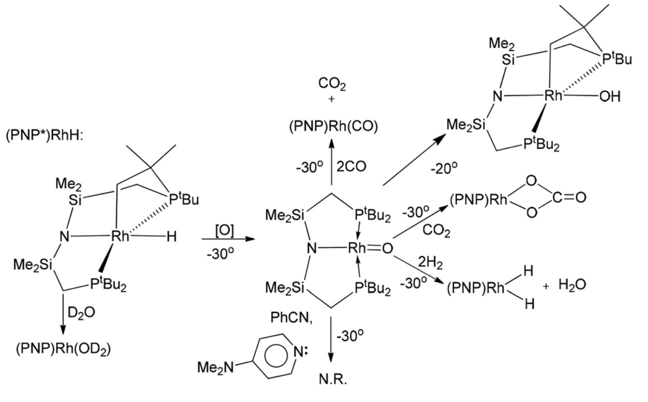
Introduction

Terminal oxo complexes with higher (>6) d electron count are a continuing challenge.[1,2] We reported recently[3] the synthesis and characterization of a remarkable molecule, (PNP)RhO, where PNP is $(^t\mathrm{Bu_2PCH_2SiMe_2})_2\mathrm{N}^{-1}$: superficially trivalent rhodium but only 4 coordinate and nearly planar, and also a ground state triplet, for a d^6 configuration.[4] The synthesis of this molecule starts from a "(PNP)Rh equivalent," since this 3-coordinate monovalent Rh structure is not the ground state, but instead exists (Scheme 1) as the fully characterized form[5] where one ^{t}Bu C–H bond has oxidatively added to the metal, abbreviated (PNP*)RhH. This molecule is in equilibrium, at a rate of ~10^3 s^{-1}, with the authentic (PNP)Rh structure, which leads to unusual fluxionally-averaged NMR at 25 °C. The oxidants Me_3NO, pyridine *N*-oxide, and even N_2O all oxidize this rhodium source to give the same product, (PNP)RhO. We report here a still more convenient reagent for this synthesis. This triplet molecule has a considerable amount (50%) of spin density on the oxo center. Since spin density on oxo leaves that ligand oxidized (*i.e.*, less than an octet), this oxyl character helps to define how low a value of q in an MO^{q+} moiety will still support such oxidation of an "oxo" ligand above its typical charge of 2−. Recent work with the PNP^{-1} ligand on *other* metals has suggested the reactivity of (PNP)RhO might not be localized at the unusual oxo ligand,[6,7] but may involve the Rh/O bond and may also include both spin delocalization and even new bond formation to the PNP nitrogen. We report here on the reaction of (PNP)RhO with seemingly the simplest of reagents, H_2, as well as with simple Lewis bases and with CO or CO_2. A relevant precedent[8,9] will be compared to (PNP)RhO in detail below.



Scheme 1

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† Dedicated to David Cole-Hamilton, for his career-long visionary approaches to challenging problems.

‡ Electronic supplementary information (ESI) available: Computational and spectroscopic results are available. See DOI: 10.1039/c3dt31972e

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Results

Reactivity of (PNP)RhO with non-redox N-donors

Because of its thermolability (isomerizing[3] at and above −20 °C to add one ^{t}Bu methyl CH bond across the Rh/O bond, to form $[N(SiMe_2CH_2P^tBu_2)(SiMe_2CH_2P^tBu(CMe_2CH_2)]Rh(OH)$, Scheme 1), all reactions of (PNP)RhO have employed freshly prepared solutions of the molecule, generally synthesized from *N*-methyl morpholine *N*-oxide in THF. This synthetic oxo transfer reaction is complete in less than 5 h at −30 °C where the rate of attack on ^{t}Bu by the RhO functionality is insignificant. This represents an improved synthesis compared to the N_2O reagent reported earlier.[3]

Samples of (PNP)RhO were combined 1 : 1 in THF with PhCN or with 4-dimethylaminopyridine at −30 °C. No diamagnetic peaks were observed by ^{31}P NMR, indicating no adduct formation or reaction. By its synthetic method, it obviously does not bind neat THF or either donor atom of equimolar *N*-methyl morpholine; its chemical shifts in THF are identical to those in benzene or toluene.

Reactivity of (PNP)RhO with PMe_3

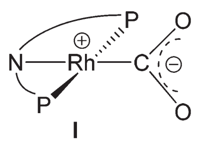
Phosphines are generally an "easy" target for oxo transfer, and we find a facile reaction with (PNP)RhO. Reaction of (PNP)RhO with substoichiometric PMe_3 in THF occurs at −30 °C in less than 5 min to give complete consumption of phosphine with formation of free $OPMe_3$. At this point, unreacted (PNP)RhO remains present, and under these conditions $(PNP)Rh(PMe_3)O$, *if* it is an intermediate at all, is not detected. No $(PNP)Rh(PMe_3)$, also synthesized independently for comparison, was formed.

Reactivity of (PNP)RhO with CO

Reaction of (PNP)RhO with 1 atm CO in THF beginning at −30 °C proceeds over 1 h (Scheme 1) with visible color change. NMR assay after 1–12 h shows the production of (PNP)Rh(CO). To prove that the observed reactivity was not due to the available *N*-methyl morpholine present from the synthesis of (PNP)RhO, we prepared the oxo species from N_2O, then reacted this as above with CO. The product was unchanged: (PNP)Rh(CO). We established that there is no reaction between authentic (PNP)Rh(CO) and 1 atm CO_2 over 24 h at 25 °C in benzene. In contrast, $(PNP)Rh(CO_2)$ (see below) is completely consumed by 1 atm CO within 180 min at 25 °C in benzene to produce only (PNP)Rh(CO). The monocarbonyl (PNP)Rh(CO) does not add more CO over 24 h under 1 atm CO.

Independent synthesis of a potential intermediate: $(PNP)Rh(CO_2)$

(PNP*)RhH reacts in time of mixing in benzene with CO_2 (1 atm) to give complete conversion to a single product, whose ^1H and ^{31}P NMR spectra indicate C_s symmetry. This rules out structures where CO_2 is C-bound (**I**) or O-bound (**II**) to Rh, and is consistent with the more common mode of binding (**III**), provided that the η^2-CO_2 does not undergo rapid rotation about its bond to Rh. This is the structure proposed for a $(PCP)Rh(CO_2)$ pincer complex,[10] which also shows NMR spectra indicating C_s symmetry. The IR spectrum of $(PNP)Rh(CO_2)$ in pentane shows two strong absorptions at 1805 and 1847 cm^{-1}; the values for the $(PCP)Rh(CO_2)$ pincer complex are 1798 and 1592 cm^{-1} hence remarkably lower.



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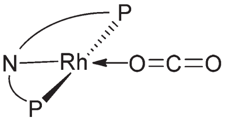

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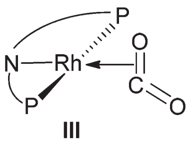

III

Low temperature NMR study

Is a simple adduct (PNP)Rh(CO)O or $(PNP)Rh(CO_2)$ detectable as an intermediate in the reaction of (PNP)RhO with CO? When (PNP)RhO (synthesized from N_2O) is combined with substoichiometric CO (1 : 0.8 mole ratio) at −196 °C and warmed minimally to mix CO with the fluid solution in d_8-THF, and monitored with progressive warming of the NMR probe, one sees 10% (PNP)Rh(CO) already at −80 °C. At −50 °C, (PNP)RhO is still observed by ^1H NMR but brief shaking and warming of the glass surface to dissolve CO from the headspace shows detectable $(PNP)Rh(CO_2)$. Even at 0 °C, some (PNP)RhO remains, and $(PNP)Rh(CO_2)$ is still present, indicating a deficiency of dissolved CO. Finally, after shaking at 25 °C, the CO_2 complex is gone and the amount of (PNP)Rh(CO) has increased. Thus, any (PNP)Rh(CO)O, if it is indeed an intermediate, disappears rapidly and never reaches detectable population, but $(PNP)Rh(CO_2)$ is an intermediate. It also appears that there is no detectable species (PNP)Rh("C_2O_3") which contains both CO and CO_2, and that this reaction is well described as one where CO displaces CO_2 from **III**.

DFT analysis of the CO reaction

We envision that all reactions reported here might occur *via* the available thermal population of a singlet isomer of the ground state triplet (PNP)RhO. Certainly 5-coordinate Rh^{III} species here (*i.e.*, an initial adduct of (PNP)RhO with any substrate L) always have their singlet state far below their triplet, due to the larger coordination number (*vs.* 4 in (PNP)RhO) splitting the d orbitals more. All calculated energies reported here use singlet (PNP)RhO as the reference state; from the triplet, all reaction energies will be less exothermic by the triplet → singlet promotion energy.[11]

DFT(B3LYP) calculation of the minimum energy geometry of the full set of atoms in $(PNP)Rh(CO_2)$ optimized (**B**, Fig. 1) to an η^2-structure (consistent with the NMR conclusion of C_s symmetry) with the Rh-bound C/O bond longer than the unbound one by 0.05 Å. The angle N–Rh–O, 175.4°, is considerably larger than N–Rh–C, 141.1°, and the Rh/O distance, 2.211 Å, is longer than the Rh/C distance, 2.006 Å. The OCO angle is 141.5°. This same minimum was also reached starting from a C_{2v} geometry **I** where only carbon was bound to Rh and all the angles at this carbon were about 120°. The reaction energy to form $(PNP)Rh(CO_2)$ is −66.4 kcal mol^{-1} (Fig. 1).

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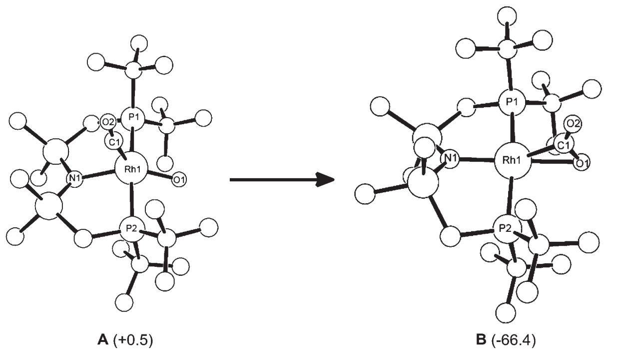
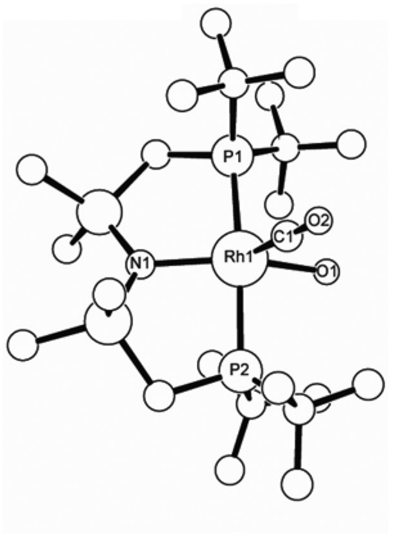


A (+0.5) B (-66.4)

Fig. 1 Structures and electronic energies (kcal mol^{-1} *vs.* (PNP)RhO + CO) for attack on (PNP)RhO by one CO. See ESI‡ for detailed structural parameters.

Regarding the mechanism of this reaction, we identified (Fig. 1) stationary state adduct **A**, a carbonyl complex of trivalent Rh: (PNP)Rh(CO)(O). The electronic energy of this species, +0.5 kcal mol^{-1}, means that its formation is unfavorable when the entropy penalty for adduct formation is considered.[12] This may be one factor which causes the reaction to be slower than that of (PNP)RhO with CO_2 (see below): low population of the primary product adduct. The species **B**, (PNP)Rh(η^2-CO_2), is formed from adduct **A** in a highly exothermic step. The reaction energy for (PNP)Rh(η^2-CO_2) reacting with additional CO to form (PNP)Rh(CO) and free CO_2 is −39 kcal mol^{-1},[11] which explains why it is difficult to detect (PNP)Rh(η^2-CO_2). We sought a TS for the conversion of **A** to **B** by an intramolecular C1/O1 bond formation step. This revealed (Scheme 2) structure $\mathbf{TS_{A\text{-}B}}$, at an energy of +7.3 kcal mol^{-1}, hence only 6.8 kcal mol^{-1} above the adduct (PNP)Rh(CO)O, **A**; this low $\mathbf{TS_{A\text{-}B}}$ energy is consistent with the Hammond postulate that a very exothermic reaction should have a low barrier…and an early $\mathbf{TS_{A\text{-}B}}$, which explains why (PNP)Rh(CO)O is not detected experimentally. Structurally,[11] this $\mathbf{TS_{A\text{-}B}}$ has its biggest change from (PNP)Rh(CO)O, **A**, in angle C/Rh/O, the atoms which must form a bond, but the C/O distance at the TS is still a very long 2.44 Å, hence qualifying as early. (PNP)Rh(CO)(O), **A**, has a CO stretching frequency of 1944 cm^{-1}, which indicates considerable back donation to CO (*cf.* 1932 cm^{-1} in (PNP)Rh(CO)[13]). The Rh–N bond in species **A** is long (2.23 Å), but the Rh/O distance has lengthened only 0.02 Å from that in (PNP)RhO. The N–Rh–O angle has decreased 23° in the process of binding CO.



$\mathbf{TS_{A\text{-}B}}$

Scheme 2

We also sought a TS for direct conversion of (PNP)RhO + free CO to the CO_2 complex without any preliminary Rh/C interaction. This revealed that attack of the CO vector on oxo perpendicular to the Rh═O bond merely collapsed towards the (PNP)Rh(CO)O adduct **A**.

Reactivity of (PNP)RhO with CO_2

There are synthetic reports of reactive capture of CO_2 by both oxo and hydroxo species, but no detailed mechanistic studies.[14–16]

The reaction of dark orange (PNP)RhO with CO_2 (1 atm) was carried out in THF. The reaction occurs in time of mixing at −30 °C, with color bleaching to pale orange, and shows the diamagnetic product to have C_{2v} symmetry, with one ^{t}Bu (virtual triplet), one SiMe (singlet) and one (virtual triplet) CH_2 ^{1}H NMR chemical shift, and one ^{31}P chemical shift (111 Hz coupling to rhodium). The infrared spectrum of the isolated product shows a C═O stretching vibration at 1701 cm^{-1}, consistent with pendant C═O of[17] a bidentate carbonate in (PNP)Rh(CO_3). The CI-mass spectrum shows nothing heavier than the cation of protonated (PNP)RhO, indicating loss of CO_2 under the ionization conditions.

Low temperature NMR study

When (PNP)RhO (synthesized from N_2O) is combined with substoichiometric CO_2 at −196 °C and warmed minimally while mixing CO_2 with the fluid solution in d_8-THF, and monitored with progressive warming of the NMR probe, one sees already at −80 °C full conversion of (PNP)RhO to (PNP)Rh(CO_3); this more complete conversion (*vs.* the CO study reported above) is presumably due in part to the greater molarity of CO_2 (less volatile) than CO. At −50 °C, ^{1}H NMR confirms that all (PNP)RhO has been consumed, and there is no change in the solution composition up to 0 °C, then also at 25 °C. This reaction thus has a very low barrier and no intermediate reaches detectable concentration.

DFT analysis of the CO_2 reaction

A DFT(B3LYP) geometry optimization of (PNP)Rh(κ^2-CO_3) (Fig. 2) gave only one geometry, **D**, C_{2v} symmetric, and with a reaction energy of formation of −34.3 kcal mol^{-1}. This structure has the two C/O distances involving the two Rh-bound carbonate oxygens longer (by 0.1 Å) than that to the terminal oxygen. The two angles NRhO average 149°, and differ by only 5°. The Rh/O distances are similar to those from Rh to OH ligands. The quite favorable reaction energy indicates that the terminal oxo group is nucleophilic. Geometry optimization

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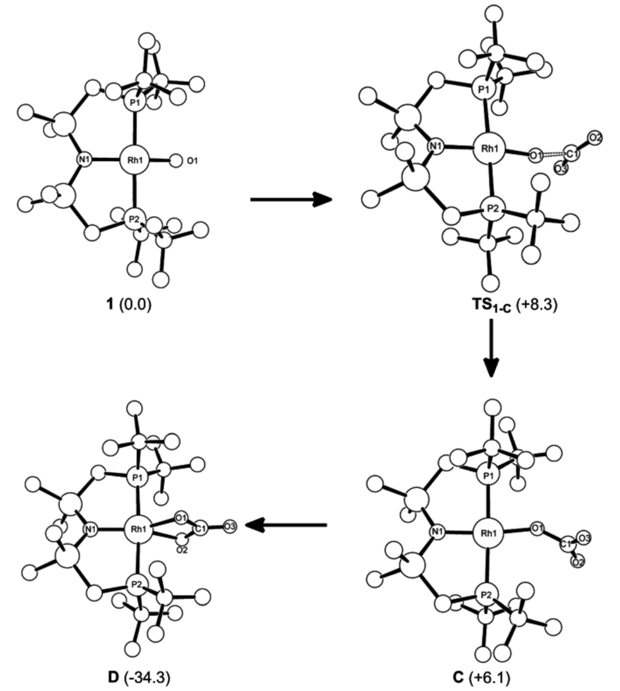
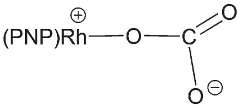


Fig. 2 Structures and electronic energies (kcal mol^{-1}) for attack on (PNP)RhO by CO_2. See ESI‡ for detailed structural parameters.

beginning from a square pyramidal structure of (PNP)Rh(κ^2-CO_3) yielded the same C_{2v} geometry discussed above.

Geometry optimization beginning from a monodentate carbonate structure yielded a stationary state **C**, with κ^1-carbonate, but this is much (40.4 kcal mol^{-1}) less stable than the κ^2-carbonate structure. Thus, 4-coordinated and 14 valence electron Rh^{III} is not favored; another negative factor about this structure is the charge separation (**E**) involved. A $\mathbf{TS_{1\text{-}C}}$, between singlet (PNP)RhO, **1**, and singlet κ^1-carbonate **C** was located for the direct addition of CO_2 *via* only its carbon to the terminal oxo ligand. This attack trajectory is remarkably facile; lying only 8.3 kcal mol^{-1} in electronic energy above the separated particles. The $T\Delta S$ penalty of about 10–12 kcal mol^{-1} at 273 K will still leave a barrier which is consistent with this (observed to be rapid) reaction at −78 °C. The structure of this TS shows (see ESI‡) it to be very early, with little stretching of the Rh/O bond, very little lengthening of the bonds from those in free CO_2 (1.18 Å), and a still-planar geometry around Rh. Only the angle OCO in the approaching CO_2 shows considerable progress towards product, being 149.7°.



$(PNP)Rh^{\oplus}-O-C(=O)-O^{\ominus}$

E

A search for a $\mathbf{TS_{1\text{-}D}}$ connecting species **1** and free CO_2 to form the bidentate carbonate **D** *directly* by a [2 + 2] addition of one C═O bond across the Rh/O bond shows an extreme rise of energy (up to +56 kcal mol^{-1}) in a constrained geometry scan starting from the κ^2-CO_3 structure; subsequent TS search then gave the κ^1-CO_3 structure, indicating that the retention of the C/O bond is energetically dominant. This allows the conclusion that this [2 + 2] mechanism is not energetically viable on the singlet surface.

Reactivity of (PNP)RhO towards H_2

The observed reactivity of M/O bonds is dramatically different for early, oxophilic metals and later transition metals, due to the reduction of M/O bond strength as one moves to the right in the transition series due to population of the π^*_{MO} orbital. TiO_2 does not react with H_2, but CuO does. Alcohols evolve hydrogen with Ti hydrides, but $Ir^{III}OR$,[18] $Ru^{II}OR$[19,20] and $Cu^{I}OR$[21] species react with H_2 to form the metal hydride and liberate ROH. Examples of M/O *multiple* bonds in $M(O)_n$ reacting with H_2 are rare[22] (exceptions, with very high barriers and slow rates, are OsO_4 and MnO_4^-); molybdenum terminal oxo species do not react with H_2 apparently due to thermodynamic preferences. We now report an example of a terminal oxo rhodium complex reacting easily with H_2 to form water.

Reaction of (PNP)RhO with 1 atm H_2 goes to completion already at −30 °C ($\tau_{\frac{1}{2}} \sim 10$ h) in THF to form a molecule of C_{2v} symmetry which we identify as $(PNP)Rh(H)_2$ by comparison to the known NMR spectral data.[3] The liberated water is seen as a broad peak at 2.5 ppm. If (PNP)RhO is combined with 1 atm H_2 at −100 °C in THF, low temperature NMR observations beginning at −90 °C show no new species until the conversion of the oxo complex to $(PNP)Rh(H)_2$ begins (−30 °C). In particular, there is no adduct $(PNP)Rh(H_2)(O)$ formed to a detectable extent. This is in agreement with adduct formation being endothermic, hence also endergonic, from the DFT calculations (see below) and the lack of adducts of (PNP)RhO with amines and nitriles (see above).

The reaction of (PNP)RhO with H_2 is somewhat slower than its reaction with CO or CO_2. The evaluation of the reaction of (PNP)RhO with H_2 is therefore potentially complicated by the fact that (PNP)RhO transforms slowly even at −20 °C to give (Scheme 1) isomeric (PNP*)Rh(OH), which was shown independently[3] to react with H_2 to give $(PNP)Rh(H)_2$ and water at 25 °C. Relative rates thus become important, and so a d_8 THF solution of (PNP)RhO was prepared at −30 °C, then divided into two parts, only one of which was combined with 1 atm H_2, and both were held at −40 °C for 12 h. NMR analysis (done quickly at −20 °C, to prevent conversion of (PNP)RhO to (PNP*)Rh(OH)) after that time showed full conversion under H_2 to $(PNP)Rh(H)_2$, while the control showed primarily unchanged (PNP)RhO together with only traces (<5%) of (PNP*)Rh(OH). This confirms that the oxo species reacts faster with dissolved H_2 than it does by intramolecular isomerization in forming (PNP*)Rh(OH).

Synthesis and characterization of the potential intermediate $(PNP)Rh(H_2O)$

An independent synthesis of the potential intermediate (PNP)-$Rh(H_2O)$ was carried out (see Scheme 1 for D_2O analog) by

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addition of stoichiometric water in THF to (PNP*)RhH. The product molecule has C_{2v} proton and phosphorus NMR spectral features (ESI Fig. p S4‡). Addition of equimolar D_2O to (PNP)Rh(H_2O) shows, within 5 minutes, disappearance of a resonance at 1.8 ppm and growth of a signal at 2.5 ppm attributed to free HDO, consistent with rapid H/D exchange; this confirms the assignment of the 1.8 ppm signal to the protons of coordinated water. In fact, this product of reaction of equimolar (PNP)Rh(H_2O) with D_2O shows a $^{31}P\{^1H\}$ NMR spectrum with multiplets due to Rh(OD_2), Rh(OHD) and Rh(OH_2) isotopomers, resolvable due to an H/D isotope effect (0.04 ppm per deuteron) on the phosphorus chemical shift. The three $^{31}P\{^1H\}$ NMR doublets (from coupling to Rh with J_{PRh} = 148 Hz) show an intensity ratio of 1 : 2 : 1 due to equal populations of H and D in the solution. Finally there is a second set of weak P/Rh doublets (with J_{PRh} = 194 Hz) with P chemical shift displaced by only 0.03 ppm which we assign to a species (PNP)Rh(water) hydrogen bonded to a *second* water molecule.[23]

The possibility that this product is not (PNP)Rh(H_2O) but is instead C_s symmetric (PNP)Rh(H)(OH), was raised by their similar thermodynamic stability (see below). If true, (PNP)Rh(H)(OH) would have to show rapid fluxional exchange between Rh–H and O–H at 25 °C; this was tested by recording its ^1H NMR spectrum at −90 °C. There, and also at −60 and −30 °C, no new species was observed (*e.g.*, there is no second isomer, (PNP)Rh(H)(OH)) and there was no decoalescence of a hydride from a hydroxyl signal; those would both be negative chemical shifts, so their coalesced peak would not be at the observed +1.8 ppm, further arguing against the structural assignment as (PNP)Rh(H)(OH), and thus consistent with the observed structure having the aquo ligand on monovalent Rh. Establishing experimentally the preferred structure of this species is important since the DFT calculations (see below) agree with experiment in having the aquo isomer more stable than (PNP)Rh(H)(OH).

Reaction of (PNP*)RhH with D_2O was carried out in THF to establish where the hydride ligand of the reagent complex is located in the product. ^2H NMR of the resulting product (Scheme 1), taken within 5 min of formation shows only the signal at ~1.8 ppm due to the deuterons already assigned to the coordinated water ligand. This means that the hydride of (PNP*)RhH returns to its carbon faster than any possible scrambling with the acidic water deuterons. This shows that approaching D_2O does not behave as an acid towards the Rh–C bond (forming ~$CH_2DRh(H)(OD)$) or towards the Rh–H bond (forming Rh(HD)(OD)). Indeed since (PNP*)RhH equilibrates[5] with authentic (PNP)Rh at a rate of 10^3 s^{-1} at 25 °C, it is probable that the lack of H/D mixing originates from D_2O attacking T-shaped (PNP)Rh.

Reactivity of (PNP)Rh(H_2O) with H_2

Is (PNP)Rh(H_2O) an intermediate in the hydrogenolysis reaction? Reaction of (PNP)Rh(H_2O) with 1 atm H_2 goes to completion in d_8 THF at 25 °C to form (PNP)Rh$(H)_2$. The released water is detected at 2.5 ppm. This reaction was monitored quantitatively (both product growth and reagent decay) at −30 °C under 1 atm H_2 to yield a half life for conversion of 5 h. This means that (PNP)Rh(H_2O), or (PNP)RhH(OH), which is in rapid equilibrium with it (see below), is a competent intermediate for the reaction of (PNP)RhO with H_2; if the RDS for the overall reaction involves the first molecule of H_2 (as established by DFT results below), this is consistent with the lack of accumulation of detectable population of (PNP)Rh(H_2O).

Addition of 5-fold excess water to N_2O-derived (PNP)RhO under 1 atm H_2 in THF shows no reaction at −30 °C, showing that water is not a catalyst for this hydrogenation reaction. This also shows (see below) that (PNP)RhO shows no net reaction (*e.g.*, proton transfer, forming (PNP)Rh$(OH)_2$) with water under these conditions.

We have tested whether the oxo complex has the ability to oxidize ethanol, which might lead to (PNP)Rh(H_2O) and MeCHO. Under our standard conditions (−30 °C in THF), there is no reaction over 48 h. Not only is there no oxidation of alcohol, but this shows that there is no addition of the O–H bond across the Rh/O bond, which might have formed (PNP)-Rh(OEt)(OH). In this experiment, only unchanged reactants are recovered.

Computational study of possible intermediates, energetics and hydrogenolysis mechanism

Mechanism of (PNP)RhO interacting with the first H_2 molecule

We have considered options where the two H of the arriving H_2 migrate to Rh and O, to Rh and N and to N and O (Fig. 3). Among these, only the electronic energy of the first H_2 adduct lies higher than the separated particles, and overall the complete reaction is highly exothermic. DFT(B3LYP) calculations

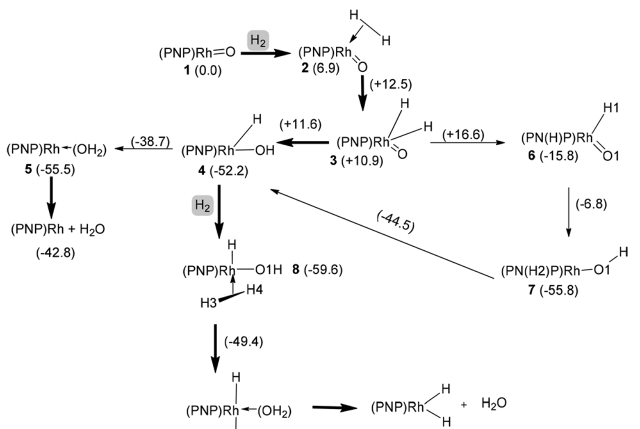

Fig. 3 Structures and electronic energies (kcal mol^{-1}) for sequential reaction of (PNP)RhO with 2 H_2. See ESI‡ for detailed structural parameters. Bold arrows show the lowest energy path and TS energies are beside arrows.

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on candidate intermediates for the reaction of singlet (PNP)RhO with H_2 showed (Fig. 3) a minimum for a possible primary product which is an η^2-H_2 complex, **2**, with a negligibly lengthened H/H distance, but this is endothermic compared to the reagents (ΔE is +6.9 kcal mol^{-1} *vs.* singlet (PNP)RhO, **1**); the Rh/O distance in this structure is negligibly lengthened from that in (PNP)RhO. Remarkably, a Rh^V species, **3**, is a branch point for H migration to N (forming **6**) or O (forming **4**) downstream of the H_2 complex **2**. Forming species **3** is found to be the RDS of the overall reaction. Starting geometry optimization from a structure where the H–H vector lies parallel to the Rh/O vector of **1** yields a trivalent metal species (PNP)Rh(H)(OH), **4**, with no residual H/H bond and new Rh–H and O–H bonds in a square pyramidal geometry. This species **4** is much more stable (by 52.2 kcal mol^{-1}) than the reagents. However, *slightly* more stable (at −55.5 kcal mol^{-1}) than this Rh(III) species is the monovalent, square planar aquo complex (PNP)Rh(H_2O), **5**, containing a pyramidal oxygen; the Rh–OH_2 distance is very long (2.27 Å).

Formal [2 + 2] addition of the H–H bond across the Rh–N bond of (PNP)RhO gives (PN(H)P)RhH(O), **6**, in Fig. 3 but this lies at considerably higher energy than the previously described products. This molecule has only a very long N/Rh distance (2.48 Å), but its angle HRhO is 114.3°, nonlinear due to some N/Rh bonding interaction. More competitive however is the isomeric monovalent, planar species (PN(H)P)Rh(OH), **7**, which lies 55.8 kcal mol^{-1} below the reagents. The similar stability of both trivalent Rh (**4**) and monovalent Rh (**7**) suggests that forming an O–H bond is the dominant thermodynamic stabilizing factor; oxidation of metal (Rh^I *vs.* Rh^{III}) is not the controlling factor.

Note that each pair among **4**, **5**, **6**, and **7** are simply connected by 1,2 hydrogen migrations. TS energies show that **4** and **7** are in facile equilibrium and nearly thermoneutral. However, the activation energy for conversion of **3** to **4** is smaller than for **3** to **6**, making **6** and **7** mechanistically irrelevant. $\mathbf{TS_{6-7}}$ involves two main motions: large decrease (*vs.* **6**) of the angle H1–Rh–O1 and a 0.1 Å lengthening of the Rh–O1 distance. The O1–H1 distance at $\mathbf{TS_{6-7}}$, 1.77 Å, is still long, the Rh–H1 distance is as short as it was in **6** and thus this is not at all a structure where H1 bridges Rh and O1. $\mathbf{TS_{4-7}}$ has a fully developed terminal hydride Rh–H2 distance and a significantly (by 0.1 Å) shortened Rh–N distance, characteristic of a fully developed migrated H2 but with angle H2–Rh–O1 still much larger than in **4**.

The reaction of H_2 with OsO_4 is accelerated by stoichiometric nucleophile,[22] which suggests that an empty metal orbital is not required; in fact, the impact of the nucleophile there is to change from a thermodynamically uphill reaction to a favorable one, which also has the expected impact of lowering the activation energy. With this in mind, can (PNP)Rh(H_2O) also form from (PNP)RhO without the intermediacy of any Rh/H interaction? We have sought a $\mathbf{TS_{1-5}}$ for attack of H_2 on the oxo of (PNP)RhO from a direction *trans* to the RhO vector (Fig. 3). This search for direct attack of H_2 on O, without any Rh/H interaction collapses to species **4**, where one H binds to rhodium; thus, one H interacts with Rh on the lowest energy path for bimolecular encounter of (PNP)RhO with H_2 having maximum opportunity to begin bond formation to oxygen.

Mechanism of reaction with the second H_2 molecule

The reaction (Fig. 3) of a second molecule of H_2 was considered with each of species **4** and **5**, to release H_2O and form (PNP)Rh$(H)_2$, **10**. The reaction energy for a *second* molecule of H_2 to convert the aquo complex **5** to (PNP)Rh$(H)_2$ and free water is −29.3 kcal mol^{-1} (Fig. 3). Experimentally, the *reverse* reaction of operationally unsaturated (PNP)Rh$(H)_2$ with H_2O was tested independently, and no reaction (equimolar in THF) was detected over 24 h at 25 °C. This is consistent with the DFT calculation for the thermodynamics of forming (PNP)Rh$(H)_2$ and water, and serves to show that the absence of weak acid (water)/weak base (hydride on (PNP)Rh$(H)_2$) reactivity has a thermodynamic, not merely a kinetic origin.

Concerning direct attack of H_2 on (PNP)Rh(H_2O), **5**, we were unable to find a minimum energy structure with H_2 *cis* to H_2O in a species (PNP)Rh(H_2)(H_2O). The lack of a minimum for addition of H_2 to planar (PNP)Rh(H_2O) can be attributed to the energetic gain from Rh/H_2 binding being less than the energy to distort the N–Rh–O angle of **5**; such distortion is needed to rehybridize the filled z^2 orbital to form a sterically accessible acceptor orbital to receive the H–H sigma bond electron density, and thus diminish the filled z^2/H_2 repulsion associated with approach of H_2 to a *planar* (PNP)Rh(H_2O). For a similar reason, intact H_2 does not find an energetic minimum bonded to planar, d^8 (PNHP)Rh(OH), **7**. Direct conversion of **5** to **10** is thus not mechanistically viable.

It therefore appears that the minimum energy path for combining with a second H_2 is to rely on the facile equilibrium forming **4** from aquo complex **5**, then add H_2 to form **8** (Fig. 3). There is only a low barrier for one of the H of coordinated H_2 in **8** to migrate to OH, forming the H_2O complex **9** (*i.e.*, α-H migration). Species **9** apparently suffers some destabilization due to the *trans* hydrides, which is what makes loss of H_2O to form **10** highly exergonic. A search for $\mathbf{TS_{9-10}}$ showed structures where the departing water proton hydrogen bonds to one hydride. Regarding possible hydrogen bonding, (PNP)Rh$(H)_2$ with equimolar H_2O in THF showed no change in ^1H NMR chemical shifts at a 1 : 1 stoichiometry.

We sought $\mathbf{TS_{8-9}}$ for H migrating from the anticipated more labile H of the H_2 ligand. $\mathbf{TS_{8-9}}$ has the dihydrogen fully rotated from what it was in **8**, and H3–H4 lengthened by 0.25 Å, and with O1 migrated towards H4. H4–O1 has shortened to 1.27 Å (*vs.* the fully formed OH distance in the hydroxyl of 0.97 Å) and both H3 and H4 are closer to Rh than in **8**. Especially noteworthy is that Rh–O1 has lengthened by 0.15 Å, and in response the Rh–N distance has shortened by 0.05 Å *vs.* **8**.

We have also evaluated a direct path from (PNP)Rh(H_2O) to (PNP)Rh$(H)_2$ by a dissociative mechanism: capture of T-shaped (PNP)Rh, the product of unimolecular H_2O dissociation from

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(PNP)Rh(H_2O), by H_2. The bond dissociation energy of H_2O from (PNP)Rh(H_2O) is +12.7 kcal mol^{-1} (see Fig. 3). The electronic energy rise for dissociating water from (PNP)Rh(H_2O) is probably a good estimate for its transition state free energy, since entropy will not develop significantly until they become translationally independent, so the energy of the Rh/OH_2 bond rupture product must be compared to the $\mathbf{TS_{4-5}}$ energy of −38.7. Within DFT energy errors, those two energies remain competitive, and probably do not allow decisive conclusion as to the fastest route for the second addition of H_2, to form (PNP)Rh$(H)_2$.

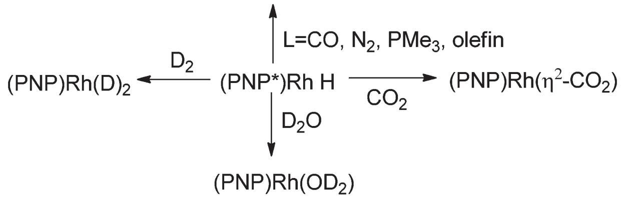
Reactivity of (PNP)RhO towards H_2O

Remarkably, there is no reaction between (PNP)RhO and equimolar water at −30 °C in THF over 48 h. This puts new limits on possible Bronsted basicity of the terminal oxo ligand in this molecule, and also confirms the result, established above, that rhodium in (PNP)RhO is not very Lewis acidic, since it is unable to even coordinate water under these conditions. We feel that the low temperatures employed would not significantly retard the rate of any proton transfer reaction, so our result is a thermodynamic statement.

Discussion and conclusions

From the results reported here and earlier,[5] (PNP*)RhH is established to be a useful synthon (*i.e.*, an equivalent of (PNP) Rh) for reaction with a variety of reagents of very different character (Scheme 3).

In spite of its operational unsaturation, (PNP)RhO (Scheme 1) is not a strong Lewis acid, being inert to conventional Lewis bases as strong as a donor-substituted pyridine. Its reaction with CO_2 is not a redox reaction and is perhaps best viewed as nucleophilic oxo attacking the electrophilic carbon of CO_2. (PNP)RhO forms simple adducts with H_2 or CO only weakly. Examination[3] of the LUMO of singlet (PNP)RhO shows it to be primarily $x^2 - y^2$, hence sterically inaccessible, which helps account for the poor Lewis acidity of this species in the planar structure. The reactions with CO and H_2 are both redox reactions and have enough overall driving force that they may proceed in spite of weak enthalpies of binding to (PNP)-RhO, with heavy involvement of oxo/substrate bond formation at the transition state. On the other hand, the calculated CO stretching frequency of (PNP)RhO(CO), 1944 cm^{-1}, is only 12 cm^{-1} higher than that calculated (identical to that observed experimentally) for (PNP)Rh(CO), 1932 cm^{-1}, suggesting significant π basicity of Rh in the oxo carbonyl. This is perhaps due to 4 electron repulsions from both amide and oxo in (PNP)RhO(CO).



Scheme 3

Because it is multistep (Fig. 3), and because of H–H bond scission absent from CO_x reactions, the H_2 reaction is inherently more complex. We find that the second H_2 molecule encounters a high barrier to directly attack (PNP)Rh(H_2O) **5**. The calculations show that energy rises about 20 kcal mol^{-1} as H_2 approaches (PNP)Rh(H_2O), so it is preferable to isomerize the aquo complex back to (PNP)RhH(OH), **4** which then binds (weakly) H_2, and then collapses to (PNP)Rh$(H)_2$ with loss of water. In short, it is better for H_2 to bind to unsaturated trivalent, *vs.* monovalent, rhodium here, and the $Rh^{III}(H_2)$ complex **8**, once formed, benefits from the high Bronsted acidity of coordinated H_2 to protonate hydroxide intramolecularly. Species **4** is thus a mechanistic branch point for reaction with the second H_2 molecule. Overall the reaction of (PNP)RhO with H_2 on this path occurs as *two* heterolytic cleavages of H_2. However, because of the low bond dissociation energy of the Rh/O bond in (PNP)Rh(OH_2), reaction with the second H_2 molecule by this Rh/O dissociative mechanism may be energetically competitive, and here the second step with H_2 is oxidative addition.

A 5d metal isoelectronic analog of (PNP)RhO, with a phenyl-based P/N pincer, $[^tBu_2PCH_2(C_6H_3)C_2H_4NMe_2]PtO^+$, or $(PCN)PtO^+$, has been reported[8] and shows reactivity analogous to ours here with CO and with H_2. These authors report that it is endergonic for this 4 coordinate species to bind acetone, hence it too is not very Lewis acidic. Its mode of self-annihilation (slower than for our 4d metal analog) is by oxo atom transfer to the phosphorus, in spite of the potentially oxidizable C–H bonds in the ^{t}Bu groups on the phosphine. The key difference with our example is that the platinum case has a singlet ground state.

A potential product *not* observed from (PNP)RhO and H_2O is (PNP)Rh(O_2) + H_2. The calculated reaction energy for this is +57.9 kcal mol^{-1} (calculated with reference to singlet (PNP)RhO), consistent with its non-observation. Regarding further oxidation of metal, (PNP)Rh$(O)_2$ was found to be 18.1 kcal mol^{-1} less stable than (PNP)Rh(O_2), so Rh^V is not a viable option. That (PNP)RhO cannot *oxidize* water (true in certain of these possible products) is perhaps no surprise; what is surprising is that it does not engage in proton transfer, given the basicity to be expected from both the oxo group[22] [compare also its reaction with CO_2], and even from amide N and from Rh. It is also noteworthy that there is no reaction of water at silicon. We also considered the possibility that H_2O might effect nucleophilic attack on the oxo of (PNP)RhO to give (PNP)Rh$(H)_2$ with release of O_2. DFT calculation shows that this reaction has an energy of +44.4 kcal mol^{-1}, and is thus unfavorable. Our no-reaction result is dramatically different than the reactivity[8] of $(PCN)PtO^+$, which reacts with water by simple proton transfer to form (PCN)Pt-$(OH)_2{}^+$.

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Experimental

General considerations

All manipulations were performed using standard Schlenk techniques or in an argon-filled glove box unless otherwise noted. Pentane and THF were purified using an Innovative Technologies solvent purification system Pure Solv 400-6-MD. Benzene-d_6 and d_8-THF were dried under Ph_2CO/Na and each vacuum transferred and stored in the glove box under argon. Water (H_2O and D_2O) was degassed by freeze–pump–thaw technique before use. Hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and dinitrogen monoxide (N_2O) were purchased, as highest purity available, through commercial vendors and used without further purification. All reactions with gases were accomplished with a vacuum line equipped with manometer (0–760 Torr) for accurate dosage. (PNP*)RhH was prepared following the published synthesis.[24] *N*-Methylmorpholine *N*-oxide (NMO) was dried by azeotropic distillation of DMF and water away from a suspension of the monohydrate in DMF, followed by solvent removal from the residue, *in vacuo*. 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 ^1H; 162 MHz ^{31}P). "PNP" is $N(SiMe_2CH_2P{}^tBu_2)_2$. The fact that (PNP*)Rh(OH) (the intramolecular rearrangement product of (PNP)RhO, which forms at trace amounts overnight at −40 °C) was never seen in the CO and CO_2 reactions described below shows that this intramolecular conversion is slower than the reactions with the gaseous reagents.

Generation of (PNP)RhO

Procedure 1, from (PNP*)RhH and NMO (*N*-methylmorpholine *N*-oxide). 25 mg of (PNP*)RhH (0.0453 mmol) and 5.3 mg of NMO (*N*-methylmorpholine *N*-oxide) (0.0453 mmol) were placed into a Schlenk flask and cooled in a Dewar filled with acetone at −40 °C. 3 mL of THF were added dropwise *via* syringe. After one hour of stirring at −20 to −30 °C, formation of (PNP)RhO is complete. ^1H NMR spectra are identical with those reported.[3]

Procedure 2, from (PNP*)RhH and N_2O. 25 mg of (PNP*) RhH (0.0453 mmol) and 0.5 mL of d_8 THF were placed into a J-Young tube and the solution was freeze–pump–thaw degassed and 760 mm Hg of N_2O (~2 equiv.) was added on a vacuum line. The J-Young tube was immediately placed in a Dewar filled with acetone at −40 °C. After all frozen solid melted, the tube was quickly shaken. Formation of (PNP)RhO and $(PNP)RhN_2$ was observed in time of mixing at − 30 °C in a 1 : 1 ratio by ^1H NMR.

Synthesis of $(PNP)Rh(PMe_3)$. To 25 mg of (PNP*)RhH (0.045 mmol) and 0.5 mL of C_6D_6 was added 0.0047 mL of PMe_3 (0.0453 mmol, 3.5 mg). NMR showed complete conversion into the new diamagnetic complex $(PNP)Rh(PMe_3)$. **^1H NMR (25 °C, C_6D_6):** 0.50 (s, SiMe, 12 H), 0.90 (t, J = 4.2, CH_2, 4 H), 1.31 (t, J = 5.6, ^{t}Bu, 36 H), 1.38 (d, J = 6.9, PMe_3, 9 H). **$^{31}P\{^1H\}$ NMR (25 °C, C_6D_6):** −19.2 (dt, J = 45 and 157), 57.0 (dd, J = 45 and 145).

Reaction of (PNP)RhO with PMe_3. Into a sample of (PNP)-RhO in a J-Young tube (generated by procedure 2 in d_8 THF) 1 equivalent of PMe_3 was vacuum transferred. NMR showed complete conversion of (PNP)RhO into the known complex, $(PNP)Rh(PMe_3)$ and $OPMe_3$. Depending upon the temperature used, this reaction, when performed in the presence of excess N_2O or NMO (the former transfers its oxygen faster), recycles rhodium into (PNP)RhO, which then has some tendency to isomerize into (PNP*)Rh(OH), which has no oxidizing ability.

Independent synthesis of Me_3PO. 0.01 mL of PMe_3 (7.4 mg, 0.097 mmol) in 0.5 ml of C_6D_6 was freeze–pump–thaw degassed and 760 mm Hg of O_2 (~1 equiv.) was added on a vacuum line. After all frozen solid melted, the tube was quickly shaken. Slow conversion into Me_3PO was observed (12% after 24 h). **^1H NMR (25 °C, C_6D_6):** 0.88 (d, J = 12.8). **$^{31}P\{^1H\}$ NMR (25 °C, C_6D_6):** 31.5 (s).

Reaction of (PNP)RhO with CO_2. The sample of (PNP)RhO generated by procedure 1 was freeze–pump–thaw degassed and 760 mm Hg of CO_2 was added on a vacuum line. The flask was placed a Dewar filled with acetone at −40 °C and the contents allowed to melt and left stirring for 30 min at −30 °C. The solution color changed from dark orange to orange. All volatiles were removed in vacuum starting at −20 °C and allowing the temperature to increase up to 25 °C. The residual orange solid was dissolved in deuterated benzene. NMR showed complete conversion into the new diamagnetic molecule **$(PNP)RhCO_3$**. **^1H NMR (25 °C, C_6D_6):** 0.09 (s, SiMe, 12 H), 0.87 (t, J = 4.5, CH_2, 4H), 1.32 (t, J = 6.6, ^{t}Bu, 36H). **$^{31}P\{^1H\}$ NMR (25 °C, C_6D_6):** 49.9 (d, J = 111). **IR (pentane solution):** 1701 cm^{-1}. **CI-MS (THF solution, *m*/*z*):** Obs. 551.2156 $[M - CO_3]^+$. $C_{22}H_{52}NP_2RhSi_2$ Theory: 551.2169, and Obs. 568.2222 $[M - CO_2 + H]^+$ $C_{22}H_{53}NOP_2RhSi_2$ Theory: 568.2196. There is no trace of $(PNP)Rh(CO_2)$ product observed here, which proves that all (PNP*)RhH had converted to (PNP)RhO, since this hydride rapidly reacts (see below) with CO_2 to give (PNP)Rh-(CO_2). In the separate low temperature search for intermediates using oxo complex from procedure 2, species $(PNP)Rh(N_2)$ is unreactive with CO_2.

In another experiment at lower temperature, already at −80 °C the amounts of $(PNP)Rh(CO_3)$ and $(PNP)Rh(N_2)$ are equal, and this shows no change up to 0 °C. There is thus a very low barrier to form the η^2-CO_3 species. This means that dissolved $[CO_2]$ exceeded that of [Rh], due in part to the lower volatility of CO_2 during low temperature sample preparation.

Reaction of (PNP*)RhH with CO_2, forming (PNP)Rh-(CO_2). (PNP*)RhH (0.0100 g, 0.018 mmol) was dissolved in C_6D_6 (0.6 ml) in a J-Young NMR tube. This solution was freeze–pump–thawed three times and 1 atm of CO_2 was added. Spectroscopic assay showed complete conversion to a single product. **$^{31}P\{^1H\}$ NMR (C_6D_6):** δ 51.96 (d, $^1J_{RhP}$ 122.6 Hz). **^1H NMR (C_6D_6):** δ 1.40 (vt, $^3J_{HP}$ 13.0 Hz, 18 H, *t*-Bu), 1.37 (vt, $^3J_{HP}$ 12.9 Hz, 18 H, *t*-Bu), 0.88 (vt, $^3J_{HP}$ 9.2 Hz, 2 H, Si–CH_2–P), 0.85 (vt, $^3J_{HP}$ 9.2 Hz, 2 H, Si–CH_2–P), 0.17 (s, 6 H, Si–CH_3), 0.11 (s,

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6 H, Si–CH_3). Solvent was stripped in vacuum, the residue dissolved in pentane and **IR** recorded: ν_{CO} = 1805, 1847 cm^{-1}.

Reaction of (PNP)RhO with CO

Room temperature product analysis. The sample of (PNP)-RhO generated ("standard method") in a flask by procedure 1 in d_8 THF was transferred with Teflon cannula (to minimize heating of the solution) into a J-Young NMR tube capped with a septum and immersed in a Dewar filled with acetone cooled at −40 °C. A plastic syringe (3 mL) was used to push the solution by argon from the flask into the NMR tube. The solution was frozen in liquid nitrogen and the septum was quickly replaced with a Teflon screw cap. The tube was freeze–pump–thaw degassed (−40 °C for melting) and 760 mm Hg of CO (~3.5 equiv.) was added on a vacuum line. The contents were allowed to melt and shaken vigorously and NMR after 5 minutes at 25 °C showed complete consumption of (PNP) RhO and formation of the known (PNP)Rh(CO).[13]

It was necessary to establish how CO reacts with the intramolecular rearrangement product of (PNP)RhO, (PNP*)Rh-(OH). Therefore, (PNP*)Rh(OH) was reacted in a 1 : 2 mole ratio with CO in d_8 toluene was studied beginning at −60 °C. At the lowest observation temperatures, there is already some (PNP)Rh(CO) (probably due to local overheating upon mixing, since the spectrum still shows unconsumed (PNP*)Rh(OH)) but also an AMX pattern in the $^{31}P\{^1H\}$ NMR spectrum which we attribute to a simple monocarbonyl adduct where the phosphine *t*Bu group is still metallated, and the hydroxyl group is still intact. This last point is supported by seeing a signal at −4.8 ppm characteristic of the hydroxyl proton.[25] Already at −40 °C, there is less unreacted (PNP*)Rh(OH), but the AMX intermediate is strong. Spectra then recorded at 25 °C show complete disappearance of the AMX intermediate, with formation of only (PNP)Rh(CO); this is the same product as from (PNP)RhO and *two* moles of CO, so care must be exercised to avoid reaction temperatures where (PNP)RhO converts to (PNP*)Rh(OH).

Reaction of (PNP)RhO with CO with low temperature NMR monitoring. The sample of (PNP)RhO generated by procedure 2 was freeze–pump–thaw degassed and 760 mm Hg of CO was added to the frozen solid on a vacuum line. The flask was placed in a Dewar filled with acetone at −90 °C and allowed to melt. NMR starting from −80 °C showed simultaneous decay of (PNP)RhO and conversion into the known diamagnetic molecule (PNP)Rh(CO). Intermediate (PNP)Rh(CO_2) was detected between −50 °C and 0 °C.

Production, in this experiment, of (PNP)RhO (together with equimolar (PNP)Rh(N_2)) at −80 °C in d_8 THF was confirmed by ^1H NMR prior to adding gaseous carbon monoxide. The successful detection of (PNP)Rh(CO_2) depends on the fact that substoichiometric dissolved CO is available (lack of agitation of head space CO into solution), and this is further confirmed by the observation of unreacted (PNP)RhO at temperatures as warm as 0 °C. Finally after shaking vigorously at 25 °C, not only is (PNP)Rh(CO_2) gone, but the ratio of (PNP)Rh(CO) to (PNP)Rh(N_2) has changed to 8 : 1, indicating that there was indeed available CO in the headspace, but not dissolved, and this finally displaces N_2 from (PNP)Rh(N_2).

Reaction of (PNP)Rh(CO_2) with CO. Independent evaluation of rate of CO addition to (PNP)Rh(CO_2). A sample of 0.045 mmol (PNP)Rh(CO_2) in 0.5 mL C_6D_6 was freeze–pump–thaw degassed and 760 mm Hg of CO (0.090 mmol) was added on a vacuum line. After all frozen solid melted, the tube was quickly shaken. Full conversion into known (PNP)Rh(CO) was observed in less than 3 h of end-over-end agitation at 25 °C. In another experiment, there was 11% conversion after 10 minutes of agitation.

Low temperature monitoring of reaction of (PNP)Rh(CO_2) with CO. A sample of (PNP)Rh(CO_2) synthesized from 25 mg (PNP*)RhH (0.045 mmol) and 1 equivalent of CO_2 in toluene d_8 was freeze–pump–thaw degassed and 760 mm Hg of CO (0.090 mmol) was added to the frozen solid on a vacuum line. Multinuclear NMR at −30 °C did not show any new adduct (PNP)Rh("C_2O_3"), but only slow conversion into known (PNP) Rh(CO).

Synthesis of (PNP)Rh(H_2O). 25 mg of (PNP*)RhH (0.0453 mmol) and 0.5 mL of d_8 THF was placed into a J-Young tube and 0.8 mg (0.045 mmol) of H_2O was added *via* syringe. NMR showed complete conversion into the new diamagnetic aquo complex. **^1H NMR (25 °C, d_8 THF)**: −0.05 (s, SiMe, 12 H), 0.56 (t, *J* = 4.2, CH_2, 4 H), 1.29 (t, *J* = 5.5, ^{t}Bu, 36 H), 1.8 (2H, H_2O). **$^{31}P\{^1H\}$ NMR** (25 °C, THF d_8): 52.8 (d, *J* = 148). When the analogous reaction was run with D_2O, deuterium NMR assay shows only a weak (~10%) signal due to deuterium at the ^{t}Bu chemical shift.

Reaction of (PNP)Rh(H_2O) with H_2. A sample of (PNP)Rh-(H_2O) synthesized from (PNP*)RhH and 1 equivalent of H_2O in d_8 THF was freeze–pump–thaw degassed and 760 mm Hg of H_2 (~2 equiv.) was added on a vacuum line. After all frozen solid melted, the tube was quickly shaken. Full conversion into known (PNP)Rh$(H)_2$ was observed after 3 h of end-on-end agitation at 25 °C; liberated water is partly responsible for conversion of some (PNP)Rh fragment to degradation products, if left dissolved together too long here. The reaction of (PNP)Rh (OH_2) with 1 atm H_2 was also monitored at −30 °C by ^{31}P NMR in THF to follow the decrease of reagent complex and growth of (PNP)Rh$(H)_2$. Aliquots were taken periodically up to 400 minutes, then at 24 hours; assay was by taking a liquid aliquot and rapidly (within 10 min,) recording the $^{31}P\{^1H\}$ NMR of each aliquot in a probe held at +25 °C; this assay is fast compared to the rate of previous observations of this reaction, all executed at +25 °C. The half-life for the reaction at −30 °C was found to be ~330 minutes.

Reaction of (PNP)RhO with H_2 with low temperature NMR monitoring. A sample of (PNP)RhO was generated by the previous "standard procedure." The tube was then held at −40 °C and 760 mm Hg of H_2 (~2 equiv.) was added on a vacuum line. NMR spectra starting from −80 °C showed simultaneous decay of (PNP)RhO and conversion into the known diamagnetic molecule (PNP)Rh$(H)_2$. No intermediate was seen.

Addition of water to (PNP)RhO. 0.0005 mL of H_2O (0.5 equivalents to the Rh) was vacuum transferred to the solution

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of (PNP)RhO generated from 29 mg of (PNP*)RhH and N_2O in 0.5 mL of d_8 THF at −30 °C during 1 h. The solution containing water was monitored by ^1H and ^{31}P NMR and showed no reaction even after 24 h at −30 °C. An additional 0.001 mL of H_2O was then added by vacuum transfer and no reaction was seen after 24 h at −30 °C. The H_2O ^1H NMR peak is seen at 2.7 ppm (it became taller after the second addition of H_2O, showing that it had not been frozen to ice) together with paramagnetic (PNP)RhO. Overall observation time for no reaction was over 48 hours at −30 °C. Higher temperature observations are precluded by the background reaction (Scheme 1) of addition of one methyl C–H bond across the Rh/O bond. Attempts to establish possible small ^1H NMR chemical shift changes due to equilibrium formation of a hydrogen bonded pair {(PNP)RhO; H_2O} were frustrated by the strong T^{-1} chemical shift dependence due to the paramagnetism of (PNP)RhO.

Computational details

All calculations were carried out on the full set of atoms present, using Density Functional Theory with the B3LYP[26–28] functional and the 6-31G** basis set with no symmetry restrictions, which has been shown to work well for many transition metal-containing systems.[29] All transition metals were represented using the Los Alamos basis set (LACVP).[30,31] 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,[32] cc-pVTZ (-f). Since we calculate all intermediates as singlets here, we chose to use the B3LYP functional in spite of its overstabilization of higher spin states (*i.e.*, the singlet was previously[3] calculated to lie 15.3 kcal mol^{-1} above the triplet using a single determinant method). The B3LYP choice was also benchmarked by its calculation of $\Delta G^\circ > 0$ for the addition of H_2 to (PNP)RhO. In any event, our calculations fully establish mechanism *on* the singlet surface. A similar situation was recently reported[33] for $S = 3/2$ $Mo[N(^tBu)Ar]_3$ reacting with nitriles to finally give doublet products; on the quartet surface, binding the nitrile was repulsive, and the mechanism was mapped out on the doublet surface.

Efforts to find a TS for direct addition of H_2 to the terminal oxo of (PNP)RhO: step-scans, beginning from (PNP)Rh(H_2O) but with the H/H distance fixed between 1.54 to 0.9 Å never reached a maximum, and the energy rises fast since the O/H distances remain within bonding range, hence exhibit repulsion. A step-scan search with two fixed OH distances in the range 0.74 to 1.37 Å showed no mutual approach of the two H, but instead showed one H bridging O and Rh, with the other H terminal on O. A search for a $\mathbf{TS_{1-4}}$ for [2 + 2] addition of the H–H bond directly across the Rh/O bond collapsed towards 3, hence showed no new approach trajectory distinct from passing through (PNP)Rh(H_2)O. The calculations show that (PNP*)Rh(OH) is more stable than both singlet and triplet (PNP)RhO, as observed experimentally, and providing another benchmark to the utility of the B3LYP functional. Finally (see ESI‡), the energy of the H_2 adduct of (PNP*)Rh(OH) lies so high (+20.3 kcal mol^{-1} relative to (PNP)RhO + free H_2) that this is the reason why it is possible to find a temperature where this path to (PNP)Rh(H)$_2$ is slower than the reaction *via* H_2 addition to (PNP)RhH(OH).

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