Reactivity of $^{\bullet}$NO with an osmium polyhydride: Reductive elimination and reductive nitrosylation on the path from odd- to even-electron molecules†

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The reaction of $^{\bullet}$NO with $(PNP)Os(H)_3$, where PNP is $N(SiMe_2CH_2P^tBu_2)_2$, involves H_2 loss from a 1 : 1 adduct to form the intermediate $(PNP)OsH(NO)_2$, which then forms coordinated HNO; loss of this triatomic molecule forms the final metal complex product in high yield: (PNP)Os(NO). Under a different concentration of gaseous reagents, a second path leads to the same products. These results are supported by spectroscopic observations at various temperatures, as well as by DFT calculations of the energies of alternative transition states and intermediates.

How will the persistent radical $^{\bullet}$NO react with a transition metal polyhydride? There is little precedent on which to answer. The versatile reactivity[1–8] of NO (forming NO^+, $NO^{\bullet}$ or NO^-) makes predictions of its reactivity difficult. In reactions with metal complexes, electron transfer to or from the metal further complicate this situation. Given the even-electron counts inherent in the 18-electron rule, predictions of reactivity of an even-electron metal complex with one $^{\bullet}$NO molecule become especially challenging; what is the fate of the resulting radical complex? When an even-electron complex reacts, one possibility is that two (linear) $^{\bullet}$NO ligands take the place of three Lewis bases (3 × 2 = 2 × 3 in eqn. (1)).[9]

$$Fe(CO)_5 + 2^{\bullet}NO \rightarrow Fe(CO)_2(NO)_2 + 3CO \qquad (1)$$

Alternative reactivity exists if the reagent complex carries a reactive one-electron donor, and also when the reagent complex itself has only 16 valence electrons (eqn. (2)).[10]

$$2RuHCl(CO)L_2 + 2^{\bullet}NO \rightarrow RuCl(NO)(CO)L_2 + RuHCl(HNO)(CO)L_2 \qquad (2)$$

In this example, $^{\bullet}$NO appears to behave as a hydrogen atom abstractor, but a full mechanistic study[10] shows a more complex reality; the products are clearly unpredictable. We describe here the reactivity of a more complex reagent,[11] the even-electron operationally unsaturated[12–14] polyhydride complex $(PNP)Os(H)_3$ (PNP = $N(SiMe_2CH_2P^tBu_2)_2$) with the radical $^{\bullet}$NO. The final osmium product, obtained in high yield, is (PNP)OsNO (eqn. (3)).

$$(PNP)Os(H)_3 + 2^{\bullet}NO \rightarrow (PNP)Os(NO) + HNO + H_2 \qquad (3)$$

Thus, three one-electron donor ligands are replaced by one three-electron donor. However, the mechanism is certainly not simple and the fate of the three hydrogens is of interest. The influence of the hydrides is evident, since non-hydride (PNP)RuCl reacts[15] with $^{\bullet}$NO to give $(PNP)Ru(NO)_2{}^+$.

If radical products are thermodynamically unfavorable (*cf.* the 18-electron rule), a $^{\bullet}$NO : Os ratio of at least 2 : 1 is required to create even-electron products. The overall product of the reaction of $(PNP)Os(H)_3$ with ∼3 equivalents of $^{\bullet}$NO in benzene (after 12 h at 22 °C)† is (PNP)Os(NO), a diamagnetic molecule of C_{2v} symmetry with $\nu_{NO} = 1682\ cm^{-1}$.[16] These observations are consistent with a planar molecule with a linear OsNO unit,† but with much back donation due to Os^0 augmented by π-donation from the amide nitrogen.

Details of the multistep mechanism are furnished by changing the reaction solvent to pentane.† There, yellow crystals of an intermediate formed within 10 min. NMR spectra of these crystals recorded rapidly in d_6-benzene showed it to be a monohydride (hydride-coupled ^{31}P NMR doublet) of C_s not C_{2v} symmetry, and was also detected during reaction in benzene. An infrared band observed at 1775 cm^{-1} was attributed to a linear OsNO unit, but an X-ray crystal structure determination‡ (Fig. 1) showed that diamagnetic $(PNP)OsH(NO)_2$, which co-crystallized with (PNP)OsH(ONO)(NO),‡ resulted from the addition of two $^{\bullet}$NO molecules. The molecule has a linear nitrosyl *trans* to the amide nitrogen and a hydride *trans* to a bent nitrosyl, whose NO stretch was observed at 1586 cm^{-1}. This yielded an oxidation state of Os^{II} and an 18-electron configuration at Os without the need for amide π-donation. However, compared to the 2.226(2) Å Os–N distance[11] in $(PNP)Os(H)_2(\equiv CAryl)$, the $Os–N_{amide}$ distance in $(PNP)OsH(NO)_2$, 2.080(4) Å, suggests some N → Os π-donation *via* a push/pull (by NO^+) interaction. A pure sample of $(PNP)OsH(NO)_2$ in benzene at 22 °C, in the absence of free $^{\bullet}$NO (or H_2), transforms spontaneously into (PNP)OsNO at a rate consistent with this dinitrosyl being a competent intermediate.

Loss of H_2 early in the mechanism is indicated by these observations. This is quite consistent with the results of a DFT study† of the mechanism (Scheme 1). Unimolecular pre-equilibrium loss of H_2 from **1** (eqn. **a**) is very thermodynamically

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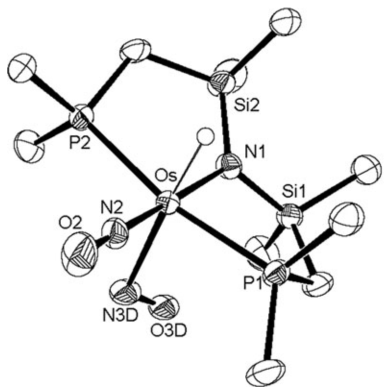
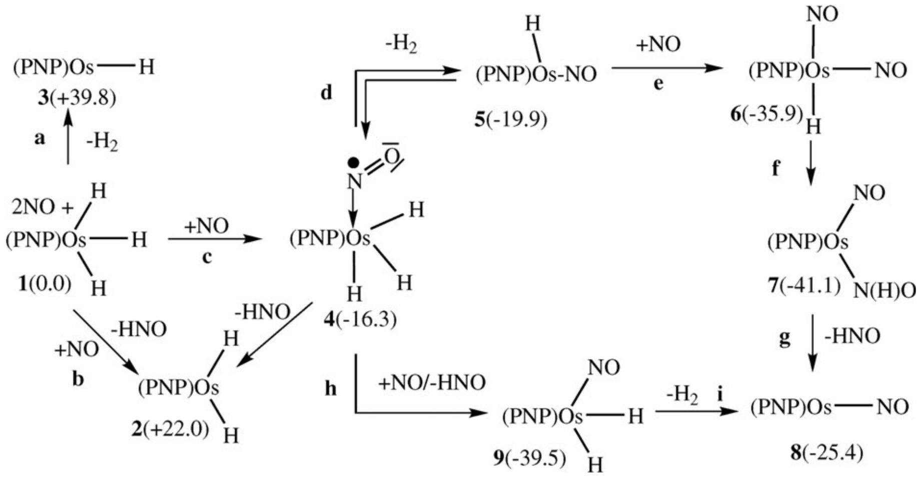


Fig. 1 ORTEP view (50% probability) of (PNP)OsH(NO)$_2$ with selected atom labelling; the unlabelled atoms are carbon, and the hydride is placed in an idealized location. The ^{t}Bu methyl carbons have been omitted for clarity. Selected bond lengths (Å) and angles (°): Os–N1 2.080(4) Å, Os–N2 1.739(4), Os–N3D 2.275(12) (this distance is unreliable due to disorder with an ONO ligand at this site†), Os–P1 2.4372(14), O2–N2 1.179(6), N3D–O3D 1.252(16); N2–Os–N1 176.2(2), N2–Os–N3D 89.5(4), O2–N2–Os 175.5(5), Os–N3D–O3D 114.3(8).

unfavorable (*i.e.* the enthalpy of binding H$_2$ to (PNP)OsH is large) and hydrogen atom abstraction by $^\bullet$NO from (PNP)Os(H)$_3$ (eqn. **b**) is thermodynamically much less favorable than simple addition of $^\bullet$NO (eqn. **c**). The operationally unsaturated character of (PNP)Os(H)$_3$, allowing adduct formation, influences this preference. Loss of H$_2$ from **4** (eqn. **d**) is favorable, and the resulting unsaturation in **5** makes its binding of a second $^\bullet$NO exothermic (eqn. **e**). We have evaluated other isomers of **6** (location of hydride and also linear/bent NO alternatives), and the isolated form (Fig. 1) is the most stable. The modestly favorable conversion ("insertion," eqn. **f**) of hydride and $^\bullet$NO ligands to η^1-HNO is found to occur by H-coupling with the initially linear nitrosyl N. Loss of HNO from the coordination sphere (eqn. **g**) is energetically uphill, but benefits from a favorable $T\Delta S$ change,[17] as well as from the follow-up conversion[5,18–20] of free HNO to N$_2$O and H$_2$O (both observed†). In other words, HNO is not bound weakly to the (PNP)OsNO moiety (compare the energies of reactions **e** and the reverse of **g**). The radical quenching step in this mechanism is eqn. **e**. While hydrogen atom abstraction by $^\bullet$NO from **4** (eqn. **h**) also quenches the radical character (contrast this energy change to that in eqn. **b**) and is energetically attractive (followed by H$_2$ loss in eqn. **i**), it fails to account for the experimental observation of **6**. The origin of the selectivity at the mechanistic branch point **4** is probably that unimolecular loss of H$_2$ can be faster than its bimolecular attack by $^\bullet$NO under our intentionally $^\bullet$NO-poor conditions. The reality of eqn. **i** was demonstrated† by the independent synthesis of **9** from (PNP)Os(H)$_3$ and tolylSO$_2$NMe(NO); **9** showing inequivalent hydrides and a NO stretching frequency of 1653 cm^{-1} (DFT angle Os–N–O = 162.9°). In solution overnight, **9** converted to **8** by loss of H$_2$, showing no tendency to lose HNO. Conversely, (PNP)Os(NO) under 1 atm H$_2$ slowly formed a small amount of (PNP)Os(H)$_2$NO.† Finally, as H$_2$ accumulated late in the reaction *via* **6**, we did observe some **9**, which decayed to **8**, indicating that pathway **h** becomes competitive with **d**. The path to product **8** can thus vary with the conditions, and there is a temperature-dependent equilibrium between species **4** and **5**. This last point is demonstrated by the observation that the reaction executed at −60 °C showed a higher initial yield of (PNP)Os(H)$_2$(NO) than at room temperature, consistent with reduced loss of H$_2$ from **4**. This dependence of the conditions on the path to the product could also be manipulated† by employing excess $^\bullet$NO, which preferentially traps **4** in step **h** and leads to an increased concentration of the intermediate **9**.

The calculated radical **4** (Fig. 2) is a trihydride (H/H > 1.52 Å) with a bent OsNO group, but the angle (148.2°) is too large for authentic NO$^-$ (*cf.* 128.7° calculated for **6**), and quite consistent with RuHCl(NO)(CO)(P^{i}Pr$_3$)$_2$, where a sp^2 nitrogen binds *via* its nitrogen lone pair (143.9°) and where the major spin density remains on N.[10] The nitrosyl spin densities in **4** are 0.61 on N and 0.37 on O. Thus, the (PNP)Os^{IV}(H)$_3$



Scheme 1 Candidate reaction pathways with energies given in kcal mol^{-1}.

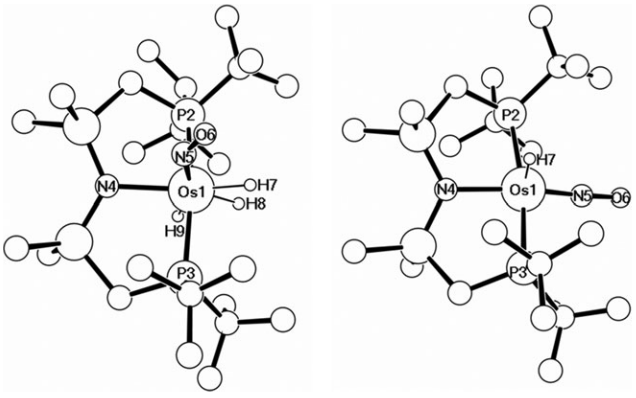


Fig. 2 DFT-optimized structures of the radicals (PNP)Os(H)$_3$($^{\bullet}$NO) (**4**) and (PNP)Os$^{\bullet}$H(NO) (**5**).

moiety is unable to reduce $^{\bullet}$NO to "fully bent" NO$^-$. However, (PNP)OsH(NO) (**5** in Fig. 2) has a square pyramidal geometry with a linear NO *trans* to amide, meaning that the (PNP)Os^{II}H moiety is reduced by $^{\bullet}$NO in **5**. The spin densities in **4** contrast to those in **5**, where the spin density on Os is 0.62, with only 0.14 on the nitrosyl N and 0.08 on the nitrosyl O.

Because of the use of a hydride-rich reagent, this work reveals several different reactivity types for $^{\bullet}$NO. Coordination of the initial $^{\bullet}$NO ligand triggers H$_2$ loss, precisely because ≥ 2H are present and because the strong π-acid $^{\bullet}$NO makes the metal less electron rich; two hydrides are thus intramolecularly oxidized to H$_2$ and the back donation required to bind molecular H$_2$ to the Os is opposed by the nitrosyl ligand. This is the same reason why there are no isolable polyhydride carbonyl complexes MH$_m$(CO)$_n$ ($m \geq 3$). Binding of a second $^{\bullet}$NO to quench the radical character of **5** leaves HNO formation as the only option for reaction chemistry between $^{\bullet}$NO and a single hydride. The lack of detection of coordinated HNO here is due to its rate of formation (eqn. **f**) being slower than its rate of release. Release can be fast because bent (one-electron donor) nitrosyl (in **7**)† becomes linear (three-electron donor) in a sort of internal displacement reaction. This is an intramolecular redox reaction as **7** (Os^{II}) → **8** (Os^0). A "least motion" hydrogen atom transfer path from **5** + $^{\bullet}$NO directly to **8** + HNO would have a transition state whose energy lacked the good bond formation that characterizes the longer path of eqns. **e** + **f**. The approach trajectory that brings $^{\bullet}$NO to the open coordination site of square pyramidal **5** may also be less hindered than the direct attack of $^{\bullet}$NO on the hydride.

The broader implications of this work are as follows. Even with sub-stoichiometric $^{\bullet}$NO, the reaction runs at a 2 : 1 $^{\bullet}$NO : Os ratio, although the final product complex has a 1 : 1 ratio. Double $^{\bullet}$NO addition is possible because (a) (PNP)Os(H)$_3$ is operationally unsaturated and (b) H$_2$ loss opens up additional coordination sites. The redox change Os^{IV} → Os^0 of the overall reaction is made possible by a collection of three different redox reactions (eqn. (4), eqn. (5) and eqn. (6)), only one electron of which comes from $^{\bullet}$NO.

$$2H^- \rightarrow H_2 + 2e^- \tag{4}$$

$$^{\bullet}NO \rightarrow NO^+ + e^- \tag{5}$$

$$H + {}^{\bullet}NO \rightarrow HNO + e^- \tag{6}$$

In summary, a combination of π-acid-induced reductive elimination of H$_2$ and N–H bond formation (insertion, which is a redox process—eqn. (6)) are the factors that dominate the reaction of $^{\bullet}$NO with polyhydride (PNP)Os(H)$_3$, leading from radical reagents to even-electron products. Eqn. (6) is the reductive nitrosylation process that originates,[21] and has seen recent applications[22,23] with RO$^-$ and OH$^-$ nucleophiles, but which is now shown here to also apply to hydride ligands.

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‡ CCDC reference number 644903. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702078c

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