A Metastable Ru^{III} Azido Complex with Metallo-Staudinger Reactivity

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A Metastable Ru^{III} Azido Complex with Metallo-Staudinger Reactivity

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The metastable purple [(Py$_5$Me$_2$)Ru^{III}(N$_3$)]$^{2+}$ species undergoes a reaction with PPh$_3$ at room temperature to form the Ru^{II} phosphinimine complex [(Py$_5$Me$_2$)Ru^{II}(N(H)PPh$_3$)]$^{2+}$ and free [H$_2$NPPh$_3$]$^+$ observed in a combined 23% conversion. Mechanistic studies suggest that this is the first metallo-Staudinger reaction of a late transition metal that bypasses the nitrido mechanism and instead follows a phosphazide mechanism via a Ru–N=N=N–PPh$_3$ intermediate.

Phosphoraniminato ligands, R$_3$PN$^-$, and their congeners are currently of interest, giving metal complexes with a broad range of important properties.[1–3] Traditionally preferred routes to phosphoraniminato complexes typically involve the use of reagents such as R$_3$PNSiMe$_3$,[4] which already contain the P–N bond. But it is also possible to construct the P–N bond at a metal center, most commonly, by reaction of PR$_3$ with an early, mid, or late transition metal nitrido group[4–6] or, less commonly, by reaction of PR$_3$ with an early transition metal azido complex.[4a,5] The latter route may be termed a "metallo-Staudinger" reaction, in reference to the 100 year old method for producing iminophosphoranes via reaction of an organic azide with a tertiary phosphine.[7] Often, a M–N(H)PR$_3$ product is obtained rather than a M–NPR$_3$ product, either due to protonation or H-atom abstraction.[8] Mechanistically, Staudinger reactions have been shown to proceed via reversible phosphazide formation followed by elimination of N$_2$ rather than the alternative nitrene mechanism (Scheme 1).[9]

Metallo-Staudinger reactions may also proceed via a phosphazide mechanism, but this has only been well-established for high oxidation state early transition metal azide complexes with a d^0 electron count.[4a,5] For mid-to-late transition metals, phosphoraniminato formation has only been

shown to occur via electrophilic nitrido intermediates, as supported either by isolation of the nitrido complex,[2a,10] spectroscopic characterization,[11] isolation of an intramolecular C–H bond insertion product[12] or kinetic studies.[13] For example, the reaction of [(14-TMC)Ru^{III}(N$_3$)$_2$]$^+$ (**1**) (14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) with PPh$_3$ was reported in 2012 by Che and coworkers to yield the corresponding phosphoraniminato complex in a reaction that is first order in [Ru] and zeroth order in [PPh$_3$]; on the basis of these kinetic results, a putative Ru^V-nitrido intermediate was proposed.[13]
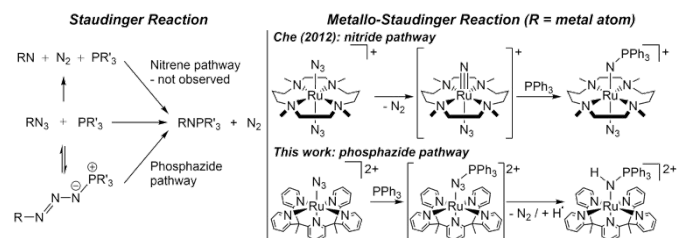
Scheme 1 The organic Staudinger reaction, which follows the phosphazide pathway (left). Mechanistic differentiation of the metallo-Staudinger reaction discussed in this work (right).

Based on our previous work with bimetallic and monometallic Ru complexes,[11a,14,15] we sought to detect an elusive Ru^V-nitrido species by using the pentadentate supporting ligand Py$_5$Me$_2$ (2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine). Although we were disappointed to find that the nitrido complex [(Py$_5$Me$_2$)Ru^V≡N]$^{2+}$ is neither accessible nor detectable, we were quite surprised to find that the Ru^{III}-azide complex [(Py$_5$Me$_2$)Ru^{III}(N$_3$)]XY (**3**, X = Y = PF$_6$; **3'**, X = PF$_6$, Y = SbCl$_6$) is nevertheless extremely reactive and undergoes a P–N bond-forming reaction with PPh$_3$. Thus, we report what is, to our knowledge, the first example of a metallo-Staudinger reaction of a late transition metal that follows a phosphazide mechanism rather than a nitrido mechanism.

Reaction of [(Py$_5$Me$_2$)Ru^{II}(N$_3$)]PF$_6$ (**2**) with one equivalent of [(4-BrC$_6$H$_4$)$_3$N](PF$_6$) results in an immediate color change from

yellow to purple (λ_{max} = 551 nm). When the product was isolated as a dark purple solid, its IR spectrum showed that the azide stretching frequency decreases from 2046 to 2005 cm^{-1} (Fig. S1), suggesting the identity of the product as a monometallic Ru^{III} terminal azide complex. Monometallic terminal azide complexes of Ru^{III} are rare, with only three examples in the Cambridge Structural Database.[13,16] To gain structural evidence, crystals were grown at low temperature and we have determined the structure of the complex [(Py$_5$Me$_2$)Ru^{III}(N$_3$)](PF$_6$)$_2$ (3) by X-ray crystallography (Fig. 1a). The Ru–N(azide) bond distance shrinks expectedly from 2.097(4) Å in 2 to 1.934(7) Å in 3 upon oxidation. Compound 3 is sensitive to temperature and to visible light. After storage at -25 °C for >1 week, 3 is found to be reduced in acetone solution to yield a Ru^{II} solvent adduct, [(Py$_5$Me$_2$)Ru^{II}(acetone)](PF$_6$)$_2$ (4) (Fig. 1b). Light-driven decomposition of 3 at -78 °C follows first order kinetics, as monitored by UV/vis spectroscopy (see SI). The decay is very fast even at -78 °C with k_1 = 5.4(1) × 10^{-3} s^{-1} and a half-life of 130 seconds. However, in the absence of light, the azide complex is robust at -78 °C, as evidenced by the persistence of the dark purple color for two months.
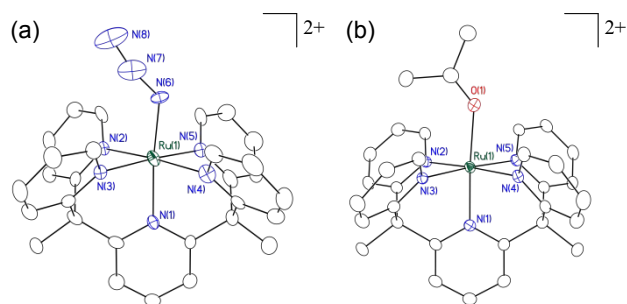
Fig. 1 (a) Crystal structure of 3. (b) Crystal structure of 4 obtained upon prolonged storage of the Ru^{III} azide at -25 °C. All hydrogen atoms, counteranions and solvent molecules are omitted. Ellipsoids are drawn at 50% probability.

Photolysis of a Ru^{III}-azide complex could follow one of two reaction pathways.[14,17] Photooxidation involves loss of N$_2$ and the formation of a Ru^V-nitrido species. Alternatively, photoreduction could occur, producing a Ru^{II} complex and azide radical. To probe for the operative photolysis pathway, photolysis of complex [(Py$_5$Me$_2$)Ru^{III}(N$_3$)](PF$_6$)(SbCl$_6$) (3') in frozen acetone solution was monitored by quantitative EPR spectroscopy. Compound 3' displays a rhombic EPR signal with g = (2.38, 2.30, 1.83) (Fig. 2a). At a concentration of 0.98 mM for 3', the EPR signal for 3' vanishes, consistent with the formation of a diamagnetic major product. A new S = 1/2 signal appears in a 7.5% conversion after 2 hours, but gradually disappears over prolonged photolysis (Fig. 2b). The g tensor (2.09, 2.09, 1.98) of this new species is centered around g = 2. This result contrasts with the expected g values for a Ru^V-nitrido species, which are (g$_\perp$ ~ 2; g$_\parallel$ ≤ 1) in analogy to reported Fe^V-nitrido compounds.[18] The observed signal is more consistent with a reduced Ru^{II} compound with a coordinated ligand radical.[19] Consistent with this assignment, at an elevated concentration of 6.3 mM for 3', this new S = 1/2 species exhibits a diminished signal intensity,

presumably due to more rapid radical recombination (Fig. S10). Both results suggest that the predominant process from cryogenic photolysis is photoreduction. This was further supported by a MALDI-TOF measurement on a powder sample of 3, which displayed the largest signal at m/z = 545 ([3 − 2 PF$_6$ − N$_3$]$^+$). Thawing of the photolyzed samples at room temperature and subsequent crystallization gave crystals of Ru^{II} complexes [(Py$_5$Me$_2$)Ru^{II}(Cl)](SbCl$_6$) and [(Py$_5$Me$_2$)Ru^{II}(Cl)](PF$_6$) (Fig. S13-S15), where the chloride ion derives from the hexachloroantimonate anion.
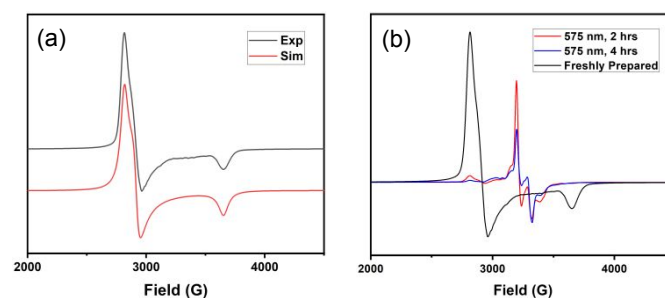
Fig. 2 (a) EPR spectrum of 3' collected at 20 K, alongside the simulated spectrum with g = (2.38, 2.30, 1.83). (b) Visible light photolysis of 3' (0.98 mM) at -196 °C monitored by EPR collected at 20 K.

Although the Ru^V nitride was not achievable photochemically, we were curious whether 3 could still be thermally activated towards a metallo-Staudinger reaction with PPh$_3$. This seemed plausible since the reaction of 1 with PPh$_3$ was also reported to be thermal in nature.[13]

For 1, a nitrido intermediate was proposed (though not observed) on the basis of the rate of reaction with PPh$_3$ being independent of PPh$_3$ concentration.[13] In contrast, the rate of decomposition of 3 in the presence of PPh$_3$ differs from the rate of its decomposition without PPh$_3$. Due to the extreme light sensitivity of 3, PPh$_3$ dependence was monitored using EPR spectroscopy instead of UV/vis spectroscopy. Reactions were performed in the dark at -78 °C in dry acetone with aliquots analyzed by EPR spectroscopy. Clear diminishing of the parent signal is observed over time in the presence of 1 equivalent of PPh$_3$, an effect that is not observed when no PPh$_3$ is present (Fig. S11). Moreover, the deep purple color of 3 disappears completely within 40 minutes in the presence of 25 equivalents of PPh$_3$, but this takes >8 hours with 1 equivalent of PPh$_3$ under identical conditions. These observations suggest a mechanism for the formation of the phosphinimide complex that does not involve pre-formation of the nitride prior to reaction with PPh$_3$.[13] Instead, we propose that 3 reacts directly with PPh$_3$ via a phosphazide mechanism (Scheme 1).

Electronic structure calculations on 3 suggest that the lowest unoccupied molecular orbital (LUMO) features lobes on the distal and proximal nitrogen atoms in the azide ligand (Fig. S18). This MO is occupied in 2 but only singly occupied in the Ru^{III} oxidation state and hence is important for the reactivity observed exclusively in the Ru^{III} oxidation state by functioning as an electron acceptor orbital for PPh$_3$ attack.

Electronically, the two Ru^{III} azide complexes **1** and **3** are similar; however, the Py_5Me_2 ligand seems slightly π-accepting ($\Delta_o \approx 4.66$ eV for **1** and 5.02 eV for **3**, based on the energies of α-spin MOs). With lower energy t_{2g}-type orbitals, the higher Ru^V oxidation state is not as accessible for **3** as in **1** (Fig. S18). TD-DFT calculations provide insights into the origins of their different photo-reactivity. The main visible absorption feature of **3** stems from an electronic transition that leads to promotion of an electron from a Ru–N(azide) bonding MO to a Ru–N antibonding MO and light absorption thereby weakens the Ru–N(azide) bond, whereas for the analogous transition in **1**, the electron originates from a Ru–N nonbonding MO (Fig. S20, S21).

Interestingly, when **3** is allowed to react with 25 equivalents of PPh_3 at -78 °C in the dark without warming, **2** is the only observed Ru product isolated in 79% yield, indicating a one-electron reduction of **3** by PPh_3 that is likely inner sphere in nature, facilitated by a Ru–N=N=N–PPh_3 phosphazido intermediate. However, when the reaction mixture is allowed to warm to room temperature, in addition to the products formed at low temperature, spectral features assignable to $[(Py_5Me_2)Ru^{II}(N(H)PPh_3)]^{2+}$ (**5**) are detected by ^1H and ^{31}P NMR spectroscopy, in addition to ESI-MS. Several other phosphorus products are observed from this reaction, consistent with the intermediacy of free $HNPPh_3$ and $PPh_3^{\bullet+}$ radical species.[20] Thus, we propose that there is a branching point in reactivity from the [Ru^{III}–N=N=N–PPh_3] phosphazide intermediate that favors inner-sphere single electron transfer at low temperature, but that metallo-Staudinger reactivity (expulsion of N_2) becomes viable at room temperature. A summary of the metallo-Staudinger reaction and subsequent H-atom abstraction from solvent molecules is provided in Scheme 2, indicating all the products that we have been able to identify by NMR spectroscopy. We note that the phosphorus products in the bottom of Scheme 2 could be formed from **5**, or from further branching of reactivity from the putative phosphazide intermediate; $OPPh_3$ arises from either hydrolysis or solvolysis of P–N products.
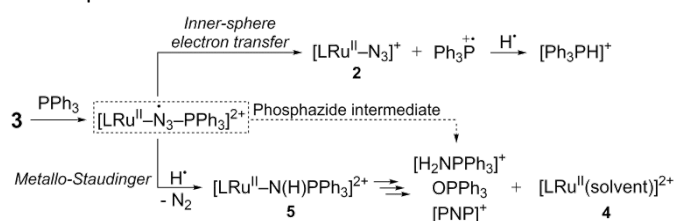

Scheme 2 Products generated in the reaction of **3** with PPh_3, where $[PNP]^+ = [Ph_3PNPPh_3]^+$.

The phosphazide intermediate was not detected by EPR spectroscopy, however, as the activation energy for homolytic cleavage of the N–P bond in [Ru^{III}–N=N=N–PPh_3] is calculated to be only 78.4 kJ/mol, which is comparable to the activation energy of subsequent reactions. Although the reduction of **3** by PPh_3 is not thermodynamically favorable based on standard redox potentials,[15,21] calculations suggest that coordination of PPh_3 to the azide ligand effectively induces a transfer of spin from the Ru^{III} center to the phosphazide ligand, suggesting that the [Ru–N=N=N–PPh_3] intermediate is best described as a Ru^{II}

species with a coordinated neutral N_3PPh_3 radical ligand (Fig. S12).

Our results indicate that the ability of PPh_3 to coordinate to **3** and undergo productive Staudinger-type reactivity under thermal conditions enable the compound to bypass the nitride route that was invoked for the closely related Ru^{III} compound, **1**. Computational studies support this result, showing that the $\Delta G^{\ddagger}$ for PPh_3 coordination to **3** is ~ 60 kJ/mol lower than the $\Delta G^{\ddagger}$ for nitride formation upon extrusion of N_2 from **3** (Fig. 3). Relaxed surface scans were used to probe for a mechanism reminiscent of the organic Staudinger reaction, where PPh_3 attacks the distal nitrogen atom in the azide ligand and then undergoes a four-membered transition state to expel N_2 and form the [Ru^{III}–NPPh_3] intermediate.[22] We attempted to find this transition state, which appears to be ~ 140 kJ/mol higher in energy compared to the [Ru–N=N=N–PPh_3] intermediate based on relaxed surface scans, but have not been successful so far. We have, however, found two alternative pathways that involve lower energy transition states – (1) initial coordination of PPh_3 to the proximal nitrogen; (2) initial coordination of PPh_3 to the distal nitrogen, followed by a stepwise isomerization to the [Ru–N(PPh_3)=N=N] intermediate (Fig. 3). From this proximal phosphazide intermediate, loss of N_2 requires an activation energy of only ~ 10 kJ/mol.
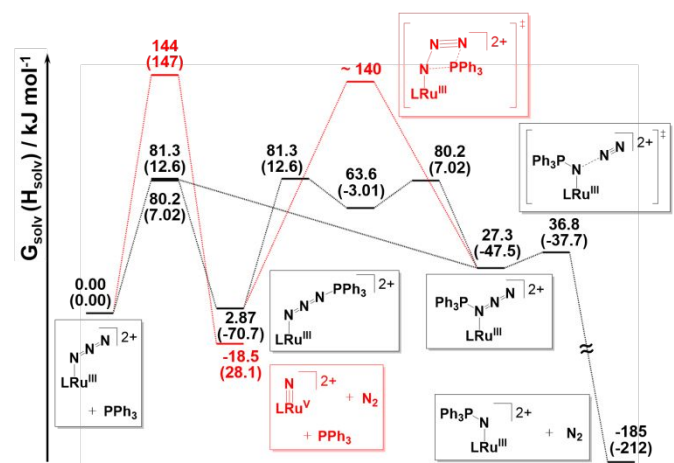
Fig. 3 Reaction coordinate diagram computed for the reaction of **3** with PPh_3. Shown in red are pathways that involve high energy transition states and are therefore less favored.

In this study, we report a rare example of a crystallographically characterized Ru^{III} azide complex that can undergo a direct reaction with PPh_3 to afford a phosphinimide complex. This is, to our knowledge, the first example in which a late transition metal azide complex undergoes a metallo-Staudinger reaction via direct reaction of the azide species with PPh_3, bypassing the nitride route. In contrast to metallo-Staudinger reactions utilizing closed-shell azide complexes of early transition metals, in our work, reactivity was switched on upon one-electron oxidation of the otherwise inactive closed-shell Ru^{II} species. The critical gate for this type of reactivity appears to be the occupancy of a metal-t_{2g}/azide-π_{nb} orbital combination. When this orbital is filled, as in **2** and other late transition metal complexes, metallo-Staudinger reactivity is not

observed.[23] When this orbital is empty, as in early transition metal complexes, metallo-Staudinger reactivity can occur. We now show that this type of reactivity is available when this critical orbital is singly occupied (TOC figure and Fig. S19).

Conflicts of interest

There are no conflicts to declare.

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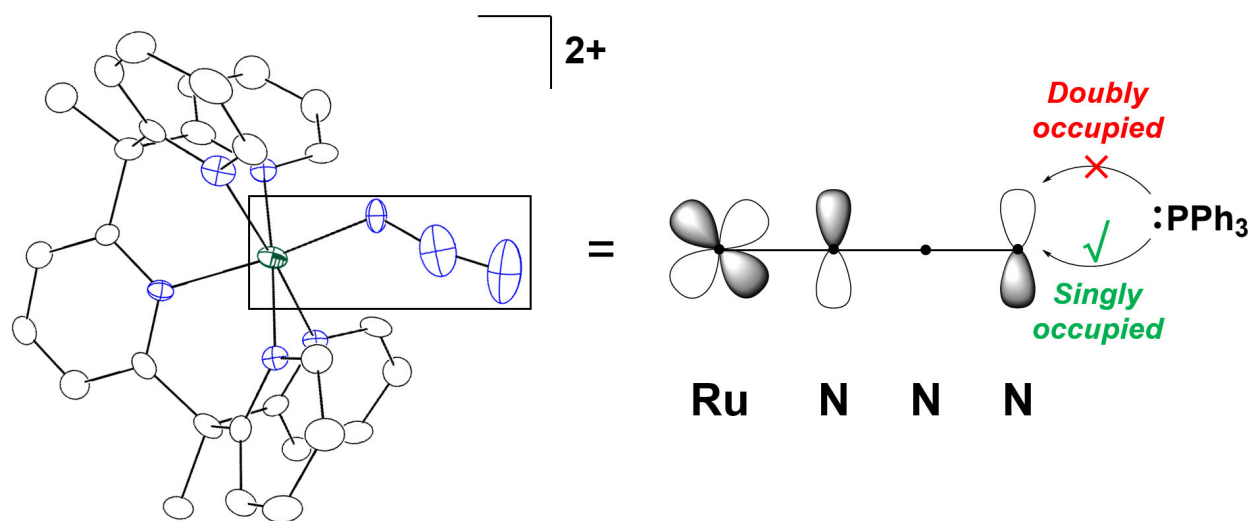
One-electron oxidation of $[(Py_5Me_2)Ru^{II}(N_3)]^+$ to $[(Py_5Me_2)Ru^{III}(N_3)]^{2+}$ switches on metallo-Staudinger reactivity towards PPh_3, forming $[(Py_5Me_2)Ru^{II}(N(H)PPh_3)]^{2+}$ through a putative $[Ru-N=N=N-PPh_3]$ intermediate.