

# Dinitrogen Splitting and Functionalization in the Coordination Sphere of Rhenium

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## Supporting Information

**ABSTRACT:** [ReCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(NCMe)] reacts with pincer ligand HN(CH<sub>2</sub>CH<sub>2</sub>PtBu<sub>2</sub>)<sub>2</sub> (HPNP) to five coordinate rhenium(III) complex [ReCl<sub>2</sub>(PNP)]. This compound cleaves N<sub>2</sub> upon reduction to give rhenium(V) nitride [Re(N)Cl(PNP)], as the first example in the coordination sphere of Re. Functionalization of the nitride ligand derived from N<sub>2</sub> is demonstrated by selective C–N bond formation with MeOTf.

The functionalization of N<sub>2</sub> at ambient conditions still defines a major challenge.<sup>1</sup> Only few homogeneous nitrogen fixation catalysts were reported, all exhibiting low turnover numbers.<sup>2</sup> Schrock's catalyst follows a mechanism of alternating reduction/N-protonation, with gradual N–N bond order reduction,<sup>3</sup> as similarly assumed for [Fe,Mo]-nitrogenase.<sup>4</sup> Initial full N<sub>2</sub> splitting and subsequent N–H bond formation represent an alternative mechanistic scenario, inspired by the Haber–Bosch process.<sup>5</sup> The first report of well-defined N<sub>2</sub> cleavage to molecular nitrides<sup>6</sup> sparked significant efforts to establish further examples.<sup>7</sup> An ML<sub>n</sub> fragment is required, which is capable of multielectron redox reactions and which forms strong M–N bonds, to overcome the large N<sub>2</sub> bond dissociation energy (BDE = 941 kJ/mol). BDEs for diatomic [M≡N]<sup>+</sup> were found to decrease along the transition-metal (TM) series (M = Ti–Cu).<sup>8</sup> Accordingly, terminal nitride formation from N<sub>2</sub> is only known for a few complexes of Mo and Nb.<sup>6,7c,i,p</sup> Even for the formation of bridging nitrides only one example is reported beyond group 6.<sup>7o</sup>

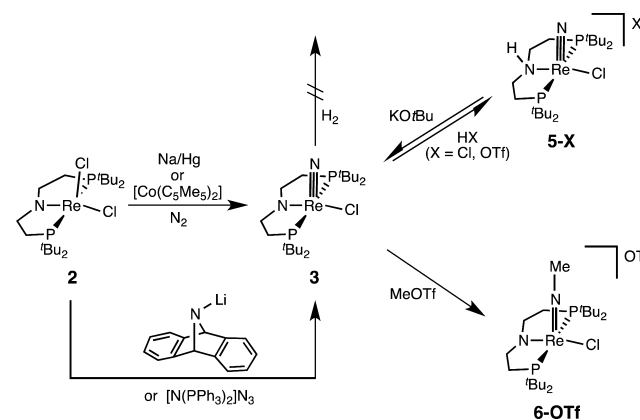
Schrock and co-workers recently reported N<sub>2</sub> splitting upon reduction of a Mo<sup>III</sup> pincer complex to a terminal Mo<sup>IV</sup> nitride.<sup>7p</sup> Isoelectronic Re<sup>V</sup> nitride complexes are well established,<sup>9</sup> and dissociative N<sub>2</sub> chemisorption on Re surfaces was demonstrated more than 30 years ago.<sup>10</sup> However, Re complexes are generally considered to bind N<sub>2</sub> without substantial bond weakening,<sup>11</sup> and previous efforts toward N<sub>2</sub> splitting with Re were unsuccessful.<sup>12</sup>

We recently reported the reactivity of electron-rich nitrido pincer complexes.<sup>13</sup> In this contribution we describe the first example of N<sub>2</sub> splitting in the coordination sphere of Re and functionalization of the resulting nitride with an organic electrophile upon C–N bond formation.

Rhenium(III) complex [ReCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(NCMe)] (1) reacts with HN(CH<sub>2</sub>CH<sub>2</sub>PtBu<sub>2</sub>)<sub>2</sub> (HPNP) in the presence of a base

to amido complex [ReCl<sub>2</sub>(PNP)] (2) in high yield (Scheme 1). The molecular structure of 2 (Figure 1) displays strong

## Scheme 1. Synthesis and Reactivity of Nitrido Complex 3

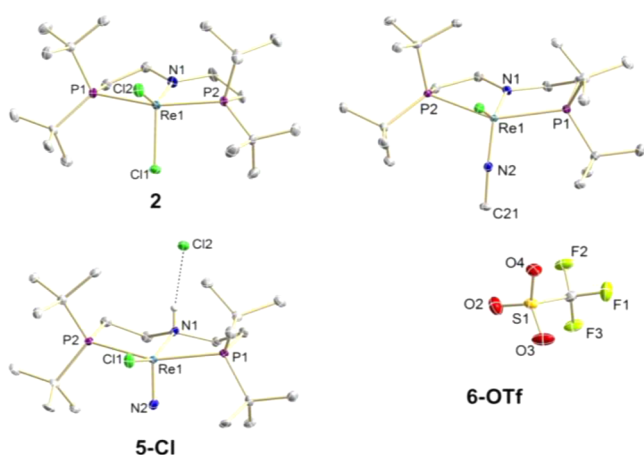


deviation both from trigonal-bipyramidal and square-pyramidal coordination in the solid state ( $\tau = 0.37$ ). The diamagnetic ground state is attributed to N  $\rightarrow$  Re  $\pi$ -donation as indicated by the sum of bond angles around the nitrogen atom ( $360^\circ$ ) and the short Re–N distance (1.923(7) Å).

Complex 2 is rapidly reduced by 1 equiv Na/Hg in THF. Under N<sub>2</sub> atmosphere, rhenium(V) nitride [Re(N)Cl(PNP)] (3) is obtained in 90% spectroscopic yield (Scheme 1) upon comparison (<sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C NMR) with an original sample. The use of <sup>15</sup>N<sub>2</sub> afforded the <sup>15</sup>N-nitride isotopolog of 3 ( $\delta(^{15}\text{N}) = 371$  ppm), confirming N<sub>2</sub> as source for nitride formation. Accordingly, reduction of 2 with Na/Hg under argon only gives an intractable mixture of compounds by NMR, which were not further characterized, and no indication for the formation of 3. Importantly, reduction of 2 with [Co(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] under N<sub>2</sub> also gives 3 with slightly lower yields up to 75%. A hydride complex is found as main side product ( $\delta_{\text{P}} = 31.2$  ppm;  $\delta_{\text{H}} = -9.28$  ppm), which did not incorporate deuterium upon use of d<sub>8</sub>-THF, possibly pointing toward traces of water as origin for the reduced yield. However, to our knowledge, this is the first report of well-defined N<sub>2</sub> splitting into nitrides, which allows the use of organometallic reducing agents as also utilized in protocols for catalytic ammonia generation.<sup>2</sup>

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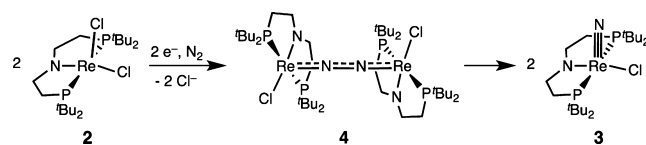
**Figure 1.** Molecular structures of **2**, **5-Cl**, and **6-OTf** in the crystal. ORTEP plot with anisotropic displacement parameters drawn at the 50% probability level. The C–H hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: Re1–Cl1 2.331(2), Re1–Cl2 2.364(2), Re1–N1 1.923(7), Re1–P1 2.402(2), Re1–P2 2.407(3); N1–Re1–Cl1 109.7(3), N1–Re1–Cl2 140.8(3), Cl1–Re1–Cl2 109.49(9), P1–Re1–P2 163.04(9). **5-Cl**: Re1–Cl1 2.4001(12), Re1–N1 2.132(4), Re1–N2 1.642(4), Re1–P1 2.4578(13), Re1–P2 2.4420(12); N1–Re1–Cl1 153.93(12), N1–Re1–N2 99.59(19), Cl1–Re1–N2 106.48(15), P1–Re1–P2 157.35(5). **6-OTf**: Re1–Cl1 2.4030(5), Re1–N1 1.9486(18), Re1–N2 1.700(2), Re1–P1 2.4776(6), Re1–P2 2.4450(6); N1–Re1–Cl1 141.23(6), N1–Re1–N2 115.58(9), Cl1–Re1–N2 103.14(7), P1–Re1–P2 150.99(2), Re1–N2–C21 168.31(17).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** indicate  $C_s$  symmetry as expected for a square-pyramidal nitride complex. All efforts to grow single-crystals suitable for X-ray diffraction were unsuccessful. Computational modeling of **3** confirmed square-pyramidal geometry with the nitride in apical position and a typical  $\text{Re}\equiv\text{N}$  bond length (1.65 Å).<sup>9</sup> The lack of a low-lying, vacant d-orbital results in the absence of  $\text{Re}-\text{N}_{\text{PNP}} \pi$ -bonding with the pincer ligand, as expressed in a long bond distance (2.03 Å), pyramidal nitrogen coordination and high amide basicity (see below).

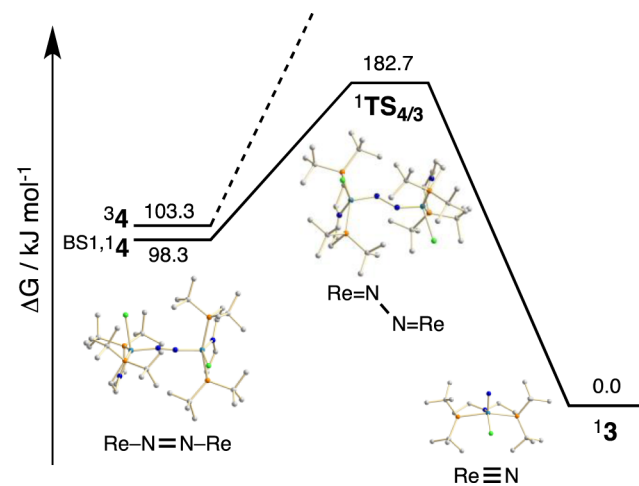
Nitride complex **3** was characterized by cyclic voltammetry (CV) in  $\text{CH}_2\text{Cl}_2$ . A reversible redox wave was found at  $-0.13$  V vs  $\text{FcCp}_2/\text{FcCp}_2^+$  (see SI) assignable to the  $\text{Re}^{\text{V}}/\text{Re}^{\text{VI}}$  redox couple. At more positive potential, an irreversible second oxidation is observed. Comparison with the CV of protonated  $[\text{Re}(\text{N})\text{Cl}(\text{HPNP})]^+$  ( $\text{S}^+$ , see below) suggests  $\text{S}^+$  as decomposition product. Importantly, no reduction of **3** was observed within the electrochemical window of the solvent.

$\text{N}_2$  splitting with Cummins' Mo triamido system proceeds from a linear  $\text{N}_2$ -bridged dimer via a zigzag  $\{\text{Mo}=\text{N}-\text{N}=\text{Mo}\}$  transition state to the final nitrides.<sup>14,15</sup> An analogous mechanism was proposed for reverse N–N coupling with  $[\text{IrN}(\text{PNP}')]_2$  ( $\text{PNP}' = \text{N}(\text{CHCHPtBu}_2)_2$ ).<sup>13b</sup> Given the steric bulk of the  $\text{Re}(\text{PNP})$  platform, a dimeric intermediate like  $[(\text{PNP})\text{ClRe}(\text{N}_2)\text{ReCl}(\text{PNP})]$  (**4**), which is formed upon reduction of **3**, represents a reasonable intermediate (Scheme 2). While at the current stage no experimental mechanistic data are available, this pathway was evaluated computationally (Scheme 3). For dimer **4**, both the triplet ( $^3\mathbf{4}$ ) and an open-shell singlet ( $^{\text{BS1,14}}$ ) states were found to be very close in energy. Both exhibit approximate square-pyramidal metal coordination and an almost linear  $\{\text{Re}-\text{N}=\text{N}-\text{Re}\}$  moiety ( $D_{\text{NN}}$ : 1.20 Å). A transition state toward  $\text{N}_2$  cleavage ( $\text{TS}_{4/3}$ )

## Scheme 2. Proposed Mechanism for $\text{N}_2$ Splitting



## Scheme 3. Computed Free Energies for $\text{N}_2$ Splitting Starting from Dimer **4** (D3-PBE/def2-TZVP//def2-SV(P))



could only be located on the singlet surface with a zigzag  $\{\text{Re}=\text{N}-\text{N}=\text{Re}\}$  conformation ( $D_{\text{NN}}$ : 1.64 Å) at a moderate barrier,  $\Delta G^\ddagger = 84.4$   $\text{kJ mol}^{-1}$  (D3-PBE/def2-TZVP//def2-SV(P)).<sup>16</sup>  $\text{N}_2$  cleavage was computed to be exergonic by  $98.3$   $\text{kJ mol}^{-1}$ , suggesting for this route to be a feasible mechanism for  $\text{N}_2$  cleavage.

We recently reported hydrogenolysis of terminal nitride  $[\text{Ru}^{\text{IV}}(\text{N})(\text{PNP})]$  with  $\text{H}_2$  to ammonia at mild conditions.<sup>13a</sup> In contrast, **3** does not react with  $\text{H}_2$  even under more forcing conditions (3 bar  $\text{H}_2$ , 80 °C, 18 h) or in the presence of base ( $\text{KOtBu}$ ). Presumably, the strong nitride *trans* influence prevents  $\text{H}_2$  heterolysis at the vacant site. Protonation of **3** with several acids ( $\text{HCl}$ ,  $\text{HOTf}$ ) results in exclusive protonation of the amido group giving  $[\text{Re}(\text{N})\text{Cl}(\text{HPNP})]\text{X}$  (**5-X**;  $\text{X} = \text{Cl}$ ,  $\text{OTf}$ ; Scheme 1), even with up to 12 equiv  $\text{HCl}$ . DFT computations confirmed that amide over nitride protonation is thermodynamically favored by  $\Delta G^0 = 31.9$   $\text{kJ mol}^{-1}$ . The identical NMR data of **5-Cl** and **5-OTf** (except N–H) and the molecular structures from single-crystal X-ray diffraction (Figure 1 and SI) indicate that the anions are not coordinated to the metal in solution and in the solid state. This observation reflects the strong nitrido *trans* influence and stabilizing  $\text{N}-\text{H}\cdots\text{X}$  hydrogen bonding. The Re ion in **5-Cl** is square-pyramidally coordinated with only minor distortion ( $\tau = 0.04$ ) and a typical  $\text{Re}\equiv\text{N}$  triple bonding distance (1.642(4) Å).<sup>9</sup>

In analogy to parent **3**, the CV of **5-OTf** features a reversible oxidation wave, yet at more positive potential (+0.64 V, see SI) owing to the positive charge. Importantly, as for **3**, no reduction was observed. Hence, the electrochemical results and reactivity with acid indicate that the formation of ammonia seems not accessible on this route. However, **3** could be functionalized at the nitride ligand with an organic electrophile. Imido complex  $[\text{Re}(\text{N}=\text{Me})\text{Cl}(\text{PNP})]\text{OTf}$  (**6-OTf**) is selectively formed with  $\text{MeOTf}$  (Scheme 1). Methylation of the nitrido, rather than the amido group, is indicated by the absence of  $^1\text{H}$  NOESY cross peaks with the pincer backbone protons and confirmed by

single crystal X-ray diffraction (Figure 1). The square-pyramidally coordinated Re ion ( $\tau = 0.16$ ) in **6-OTf** exhibits a typical bond length (1.700(2) Å)<sup>9</sup> to the slightly bent (168.31(17)°) methylimido ligand. The amido nitrogen features planar coordination, indicating  $N_{\text{PNP}} \rightarrow \text{Re } \pi$ -donation, unlike in parent **3**. Importantly, DFT computations confirm that nitride over amide methylation is, in fact, favored by  $\Delta G^\circ = 33.2 \text{ kJ mol}^{-1}$ , contrasting with the thermodynamic preference of protonation. Caulton and co-workers reported the same selectivity for electrophilic amide vs nitride attack in case of  $[\text{RuN}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{P}t\text{Bu}_2)_2\}]$ , which was attributed to steric effects.<sup>17</sup>

In summary, we presented well-defined  $N_2$  splitting in the coordination sphere of rhenium. Besides strong alkali metal reagents,  $[\text{Co}(\text{C}_5\text{Me}_5)_2]$  proved sufficient as reductant for nitride formation. DFT computations indicate that dimer **4** could represent the intermediate which undergoes N–N bond scission. The cleavage of the  $N_2$  bond is compensated by the formation of strong  $\text{Re}\equiv\text{N}$  triple bonds. Their high stability did not allow for ammonia formation by hydrolysis or hydrogenolysis. However, nitride functionalization was demonstrated by electrophilic attack of MeOTf and C–N bond formation. Hence, the use of more electron rich platforms for  $N_2$  splitting might open the way for new synthetic routes to nitrogen containing organic molecules using  $N_2$  directly as nitrogen source.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental and computational details. This material is free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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