(Electro-)chemical Splitting of Dinitrogen with a Rhenium Pincer Complex

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Abstract: The splitting of N₂ into well-defined terminal nitride complexes is a key reaction for nitrogen fixation at ambient conditions. In continuation of our previous work on rhenium pincer mediated N₂ splitting, nitrogen activation and cleavage upon (electro)chemical reduction of [ReCl₂(L²)] {L²=N(CHCH₂P₄Bu₂)₂} is reported. The electrochemical characterization of [ReCl₂(L²)] and comparison with our previously reported platform [ReCl₂(L₁)] {L₁=N(CH₂CH₂P₄Bu₂)₂} provides mechanistic insight to rationalize the dependence of nitride yield on the reductant. Furthermore, the reactivity of N₂ derived nitride complex [Re(NCl)(L²)] with electrophiles is presented.

Introduction

Industrial ammonia synthesis by the Haber–Bosch process is carried out at a scale of 150 Mt/a, using hydrogen produced via steam reforming of fossil fuels that accounts for massive energy consumption and CO₂ emission.[1] The replacement of H₂ as reductant is therefore highly desirable to enhance the sustainability of nitrogen fixation. The electrochemically driven nitrogen reduction reaction (NRR) is an appealing alternative to feed renewable energy from photovoltaic harvesting.[2] Electrocatalytic NRR has seen tremendous progress in recent years. Faraudic yields up to 73.3 % have been reported, yet with current densities far below the US Department of Energy targets.[3,4] Furthermore, the mechanistic basis of heterogeneous electrocatalysts remains comparatively ill-defined. Homogeneous (model) NRR catalysts could give detailed insight on key reaction steps and thermochemical and kinetic parameters.[5] However, molecular NRR electrocatalysts are highly limited.[6]

Two general mechanisms have been proposed for the NRR with molecular catalysts. The “bio-inspired” route is comprised of successive proton coupled electron transfer (PCET) steps at terminally coordinated N₂, in analogy to the mechanism proposed for the [Fe,Mo]-nitrogenase enzyme.[7,8] Initial full cleavage of the N≡N triple bond via N₂-bridged, multinuclear complexes and subsequent PCET of the resulting nitrides, as in the Fe-catalyzed Haber–Bosch process, has been alternatively considered.[9] The splitting of dinitrogen into well-defined nitride complexes was pioneered by Laplaza and Cummins 25 years ago and several examples are known by now.[10,11] Recently, group 6 and 7 pincer platforms attracted particular attention (Scheme 1).[9,12] Our group reported N₂ splitting upon chemical

Scheme 1. Selected examples for N₂-splitting into terminal nitride complexes with transition metal pincer platforms.
N₂ binding via (electro)chemical ReIII/ReII reduction (Scheme 2).[14,15e,15k] Starting from [ReCl₂(N₂)₂] (3⁴) via the N₂-bound dimeric intermediate [[ReCl(L)]₂(μ-N₂)] (3⁴) formed via an EC(EC)ECdim type mechanism.

Reduction [Na/Hg, Co(Cp*)₂] of the rhenium(III) PNP pincer complex [ReCl₂(L)₁] [(L₁ = NC(CH₂CH₂P(Pr)₂)₂)] to the nitrido complex [Re(NCl(L)₁)] (2⁴; Scheme 2).[126] Miller, Siewert, Schneider and co-workers jointly examined electrochemically driven N₂ cleavage for this platform, which allowed for detailed mechanistic study by cyclic voltammetry (CV).[129] The reaction goes through rate determining splitting of the N₂-bridged dirhenium complex [[ReCl(L)₁]₂(μ-N₂)] (3⁴; \( t_{1/2} = 35 \) s). Intermediate 3⁴ is formed within a complex EC(EC)ECdim pathway via (electro)chemical Re⁹/Re⁰ reduction \( (E_r) \) of 1¹, followed by N₂ binding (C(N₂)), chloride loss (C⁺), Re⁹/Re⁰ reduction \( (E_r) \) and subsequent comproportionation with parent 1¹ (C(dim)). Besides mechanistic insight, this study provided the first example of N₂ splitting into nitrido complexes by controlled potential electrolysis (CPE at \(-1.90 \) V vs. Fc⁰/⁰) with yields around 60 %. Recently, Masuda and co-workers demonstrated electrochemically driven N₂ splitting upon anodic oxidation of trans-[Mo(N₂)₂(depe)₂] (depe = Et₂PCH₂CH₂PEt₂).[13] However, further systematic studies are required to identify the key parameters that control the N₂ splitting reaction.

Here, (electro-)chemical N₂ splitting with a modified Re pincer platform is reported. The divinylamide ligand NC(CH₂CH₂P(Pr)₂)₂ (L₂⁻) was previously utilized for the stabilization of a wide variety of transition metal complexes.[14,15] The enhanced rigidity resembles that of "archetypical" amide pincer ligands, like Milstein’s pyridine-based dearomatized ligand NC₆H₄(CH₂P(Pr)₂)₂, with increased steric protection, as compared to phenylene-bridged diphosphinoamide NC₆(CH₂P(Pr)₂)₂.[16] In comparison to parent L₁, backbone unsaturation leads to significant reduction of N-N stretching frequencies of Ru and Ir complexes.[14,15e,15k] Starting from [ReCl₂(L₂)] (1²), the effects of backbone unsaturation on the reduction potential, N₂ splitting yields and functionalization of the nitride product are discussed.

### Results and Discussion

#### Synthesis and Characterization of 1²

Complex 1² was synthesized starting from 1¹ by templated ligand modification via hydrogen atom abstraction with excess 2,4,6-tert-butylyphenoxyl radical (TBP) at 50 °C (Scheme 3), as similarly reported for other L₂ complexes.[15] Small amounts of a paramagnetic side-product found by \(^1\)H NMR spectroscopy could be identified as overoxidized rhenium(IV) complex [ReCl₃(L₂)] (4²) upon comparison with an original sample that was independently synthesized. Facile conversion of the side product 4² to 1² is accomplished by situ reduction with Co(Cp)₂, providing the analytically pure product in 63 % isolated yield. The \(^1\)H NMR spectrum of 1² indicates \( C_2v \) symmetry in solution. In the \(^{31}\)P(¹H) NMR spectrum, a sharp singlet resonance was found at \( \delta_{31P} = -275 \) ppm (Figure S3). In analogy to other rhenium(III) phosphate complexes and 1¹,[12h,17] the high-field shift is attributed to mixing of the ground-state with low-lying excited states leading to temperature independent paramagnetism (TIP),[19] as substantiated for 1¹ and 1² by SQUID magnetometry \( \chi_{mol} 10^{-6} \times cm^³/mol⁻¹ = 280 \) (1¹), 300 (1²); Figure S26. Despite several attempts, single crystals of 1² suitable for X-ray analysis could not be obtained.

#### N₂ Splitting by (Electro-)Chemical Reduction

Reduction of 1² with an equimolar amount of Co(Cp)*₂ in THF under 1 atm N₂ results in rapid conversion to a mixture of sev-

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Scheme 2. (Electro)chemical N₂-activation from [ReCl₂(L₁)] (1⁴) into [Re(NCl(L)₁)] (2⁴) via the N₂-bound dimeric intermediate [[ReCl(L)]₂(μ-N₂)] (3⁴) formed via an EC(EC)ECdim type mechanism.

Scheme 3. Synthesis of complex 1² by ligand oxidation starting from 1¹ using the 2,4,6-tert-butylphenoxyl radical and different routes for the synthesis of complex 2² by either (electro)chemical N₂-splitting, or via reaction with TMS(N).
eral diamagnetic products, according to $^1$H and $^{31}$P($^1$H) NMR spectroscopy. The rhenium(V) nitride [Re(N(Cl(L2))] (2$L^2$) was identified as the major species (60 % yield by NMR spectroscopy, see Figure S7) by comparison to an authentic sample prepared by reaction of $^1$L2 with trimethylsilyl azide (Scheme 3). All attempts to identify intermediates by NMR monitoring at low temperatures were unsuccessful. The yield in 2$L^2$ is slightly lower compared with parent 2$L^1$ [75 % with Co(Cp*)2] and notably depends on the reductant. Considerably lower spectroscopic nitride yields are obtained with alkali metal reductants, such as Na/Hg (approx. 30 %) or KC₈ (approx. 20 %), under otherwise identical conditions. In comparison, 80 % yield in 2$L^1$ was obtained upon reducing 1$L^1$ with Na/Hg under N₂. Notably, with Na/Hg or KC₈ as reductant, yet not with Co(Cp*)₂, the liberation of isobutene was detected spectroscopically for 1$L^2$ (Figure S14), as previously observed for the thermal decomposition of [OsCl(L2)].[15] suggesting fragmentation of the L2 ligand platform upon overreduction. Strong dependence of N₂ splitting yields on the nature of the reductant has been previously reported.[21] However, in most cases these effects are poorly understood.

Multinuclear NMR spectroscopic characterization of 2$L^2$ indicates C₃ symmetry with a peak at $\delta_{31}$P = 71.8 ppm in the $^{31}$P($^1$H) NMR spectrum. Single crystal X-ray characterization (Figure 1) reveals a slightly distorted square pyramidal geometry ($\tau_5 = 0.15$) with the nitride [Re–N₂ 1.647(18) Å] in apical position. These bond metrics are close to those of 2$L^1$ [Re≡N = 1.643(6) Å, $\tau_5 = 0.14$], which was recently characterized crystallographically.[23] The planar ligand backbone with shortened C=C bonds [2$L^2$: 1.35(2) Å; 2$L^1$: 1.545(10)/1.526(10) Å] confirms the presence of vinylene linkers in the pincer ligand backbone. Electrochemical characterization of the nitrido species was carried out by cyclic voltammetry (CV) in THF (Figure S21). A reversible oxidation at $+0.21$ V (vs. Fc⁺/0)[24] was assigned to the ReV/ReVI couple and is significantly anodically shifted with respect to 2$L^1$ ($E_{1/2} = –0.086$ V).[12g] This potential shift is consistent with reduced electron density at the rhenium ion of 2$L^2$ due to weaker donation by pincer ligand L2. 2$L^2$ features an additional, irre-
versible reduction feature at low potential \( (E_{1/2} = -3.3 \text{ V vs. } \text{Fc}^{+/0}) \).

CPE of \( 1^{12} \) under 1 atm \( N_2 \) was carried out in THF at \( E = -1.67 \text{ V} \), i.e. the cathodic peak potential of the first reductive feature (Figure 2, top left; vide infra for discussion). Thus, the use of ligand \( L_2 \) enables electrolysis at approx. 230 mV less negative potential with respect to \( 1^{11} \), presumably due to the poorer \( \pi \)-donor properties of the unsaturated pincer. Transfer of approximately 1.2 electrons per Re over the course of 2 h was accompanied by a gradual color change from brown to light brown/green. Spectroscopic yields of nitride \( 2^{12} \) of approx. 15 \% were obtained (Figure S8), which are significantly lower than the electrolysis yields of nitride \( 2^{11} \) (60 \%). The low electrolysis yield in \( 2^{12} \) is in stark contrast with Co(Cp*)\(_2\), and closer to other heterogeneous reductants (Na/K, KC\(_8\)).

In order to rationalize the lower \( N_2 \) splitting yields, the stability of \( 1^{12} \) in THF in the presence of \( N_2 \) and chloride ions was assessed. NMR spectroscopic monitoring under 1 atm \( N_2 \) reveals partial conversion to several unidentified new species in the spectral range \( \delta_{31P} = 20-60 \text{ ppm} \) (Figure S15). CV characterization at higher \( N_2 \)-pressure initially shows a slight rise in the current of the reduction feature by around 5 \% upon increasing pressure from 1 to up to 11 bars (Figure S20). However, over the course of 45 min at 11 bars of \( N_2 \) (see Experimental Section), the current drops by about 20 \% suggesting chemical instability of \( 1^{12} \) under these conditions. \(^{3}\)P\(^{(1)H}\) NMR spectroscopic analysis after this experiment shows complete conversion of \( 1^{12} \) to an intractable reaction mixture (Figure S16). More rapid decay was even found upon addition of a chloride source, suggesting that accumulation of chloride ions released during electrolysis may accelerate decomposition. A mixture of \( 1^{12} \) and (nBu\(_4\)N)Cl under 1 atm \( N_2 \) gradually changes color from light brown to green over the course of a couple of hours, with concomitant formation of a mixture of diamagnetic and paramagnetic species (Figure S17). Comparison with \(^{1}H\) NMR spectra of mixtures of authentic \( 1^{12} \), (nBu\(_4\)N)Cl, and \( 4^{12} \) (Figure S18) supports the assignment of a broad signal at +12 ppm to rhenium(IV) complex \( 4^{12} \). This observation suggests that the chloride-induced decay of \( 1^{12} \) proceeds via disproportionation of \( [\text{Re}^{\text{III}}\text{Cl}_2(\text{L}_2)^-] \) to \( 4^{12} \) and further, unstable rhenium(II) species as outlined in Scheme 4.

\[
[\text{Re}^{\text{III}}\text{Cl}_2(\text{L}_2)^-] + \text{Cl}^- \xrightarrow{K_{\text{Cl}}} [\text{Re}^{\text{III}}\text{Cl}_2(\text{L}_2)] + \xrightarrow{K_{\text{Cl}^2}} [\text{Re}^{\text{IV}}\text{Cl}_2(\text{L}_2)] + \text{Cl}^- \xrightarrow{K_{\text{Cl}^2}} \xrightarrow{\text{decomp.}} 4^{12} \xrightarrow{\text{decomp.}} 1^{12}
\]

Scheme 4. Proposed chloride-induced disproportionation of \( 1^{12} \).

The relevance of the decay pathway shown in Scheme 4 for the electrochemical transformations was evaluated from available thermochemical data (see also Electronic Supporting Information, Section 5). The invariance of \( \delta_{31P}(1^{12}) \) and inability to detect a new signal for \( [\text{Re}^{\text{III}}\text{Cl}_2(\text{L}_2)^-] \) in the presence of added chloride (5 equiv.) allows for estimating an upper limit of the chloride association constant \((K_{\text{Cl}} \leq 0.015 \text{ M}^{-1})\); \( \Delta G^{\text{f}}_{\text{Cl}^-} \geq 2.5 \text{ kcal mol}^{-1} \). Subsequent disproportionation of \( [\text{Re}^{\text{IV}}\text{Cl}_2(\text{L}_2)]^- \) with \( 1^{12} \) to \( [\text{Re}^{\text{III}}\text{Cl}_2(\text{L}_2)^-] \) and \( 4^{12} \) is defined by the reduction potentials of \( 4^{12} \) \((E_{1/2} \approx -0.9 \text{ V vs. } \text{Fc}^{+/0}; \text{Figure S22}) \) and \( 1^{12} \) \((E_{1/2} = -1.75 \text{ V vs. } \text{Fc}^{+/0}; \text{vide infra}) \), giving \( K_{\text{Cl}^2} \approx 4 \times 10^{-15} \). The chloride-induced decomposition pathway outlined in Scheme 4 would therefore have to be driven by the decay of \( [\text{Re}^{\text{III}}\text{Cl}_2(\text{L}_2)]^- \). However, the overall effective kinetic barrier needs to be larger than \( \Delta G^{\text{f}} \geq 22.5 \text{ kcal mol}^{-1} \). In consequence, chloride induced decomposition is irrelevant on the CV timescale but might reduce electrolysis yields, which goes over hours.

In comparison, parent \( 1^{11} \) proved stable under these conditions over an extended period of time. Structural comparison of \( 2^{11} \) and \( 2^{12} \) shows only minor differences, like the steric shielding as expressed by the pincer bite angle \( \text{[P–Re–P: 156.16(7)° (2^{11}) \text{,} 155.11(13)° (2^{12})]}. \) We therefore tentatively associate the reduced stability to electronic reasons. Backbone unsaturation changes the donor properties (poorer \( \pi \)-donation) and increases the metal Lewis acidity. Furthermore, ligand \( L_2 \) is potentially non-innocent and can undergo versatile proton/ electron transfer at the vinyl groups.\(^{[15]}\) The reduced stability of \( 1^{12} \) in the presence of \( N_2 \) and chloride will contribute to lowering the electrolysis yields. Electrochemical reduction occurs on a longer time scale (2 h) than chemical \( N_2 \)-splitting, e.g. with Co(Cp*)\(_2\), as reductant (5 min). Thus, \( 1^{12} \) will be exposed to \( N_2 \) and released free chloride during electrolysis for a longer time. However, the estimated decay rates suggest that further processes contribute to the low nitride electrolysis yields. Therefore, the reduction of \( 1^{12} \) was examined in depth by CV, which is presented in the next section.

CV Examinations

The CV of \( 1^{12} \) under \( Ar \) (Figure 2) reveals two irreversible, reductive features at \( E_{\text{PC,1}} = -1.75 \text{ V} \) and \( E_{\text{PC,2}} = -1.95 \text{ V} \) (vs. \( \text{Fc}^{+/0}; \nu = 0.1 \text{ V s}^{-1} \)), respectively. The peak currents \( i_{\text{PC,1}} \) and \( i_{\text{PC,2}} \) scale linearly with \( \nu^{1/2} \), indicating diffusion-controlled electron transfer. Both reductions exhibit distinct cathodic potential shifts with rising current ratio \( i_{\text{PC,1}}/i_{\text{PC,2}} \) at increasing scan rates (Figure 2, top right). The current characteristics suggest the presence of competing chemical reaction pathways after initial reduction of \( 1^{12} \) including decay to a redox-inactive species.

Changing from \( Ar \) to \( N_2 \) (1 bar), the irreversible first reduction of \( 1^{12} \) shifts anodically by about 85 mV to \( E_{\text{PC,1}} = -1.67 \text{ V} \) (Figure 2, top left) accompanied by a small peak current increase (approx. 5 \%). The second reduction feature present under \( Ar \) vanishes under \( N_2 \) without appearance of new reductive events. The anodic potential shift and the disappearance of the \( \text{Re}^{\text{IV}}/\text{Re}^{\text{II}} \) reduction are in agreement with \( N_2 \)-activation at the rhenium(II) stage, as proposed for \( 1^{11} \).\(^{[12]}\) The anodic shift with respect to \( 1^{11} \) (approx. 230 mV) compares well with the shift found for the corresponding nitrides \( 2^{11} \) and \( 2^{12} \) (vide infra) and is therefore associated with weaker \( \pi \)-donation by pincer ligand \( L_2 \). Besides the first reduction (\( \text{Re}^{\text{IV}}/\text{Re}^{\text{II}} \)), the second reduction feature (\( \text{Re}^{\text{IV}}/\text{Re}^{\text{II}} \)) that is obtained in the absence of \( N_2 \) is even more anodically shifted, leading to decreased peak separation for \( 1^{12} \) (\( \Delta E = 0.17 \text{ V} \)) as compared to \( 1^{11} \) (\( \Delta E = 0.29 \text{ V} \)). In consequence, strong reductants, like Na/Hg (\( E' < -2.3 \text{ V} \)),\(^{[23]}\) have potentials that are well beyond the \( \text{Re}^{\text{IV}}/\text{Re}^{\text{II}} \) couple of \( 1^{12} \). Unproductive overreduction in case of incomplete trapping of the rhenium(II)
intermediate by dinitrogen might therefore be a contributing factor to the lower nitride yields obtained with Na/Hg or KC8, respectively, vs. Co(Cp*)2 ($E^\circ = -1.84$ V).

Further insight was obtained by electrochemical evaluation at varying conditions. Due to the limited chemical stability of $1^{12}$ in the presence of N2 and low electrolytic Faradaic yields, we focused on the decay kinetics under argon to identify pathways that could lead to the reduced nitride yields with respect to $1^{11}$. The effect of added ($n$Bu4N)Cl on the CV response was examined to probe for coupled chloride loss. Modest increase in reversibility and a slight cathodic shift are obtained for the first reduction event $E_1$ with rising chloride concentrations (Figure 2, bottom left), in line with coupled, fast and reversible chloride dissociation after reduction of $1^{12}$. The peak current decrease is attributed to slow decomposition of $1^{12}$ in presence of excess chloride (vide supra). Scanning both reduction events $E_1$ and $E_2$ (Figure 2, bottom right), the second feature drops in current and shifts cathodically with increasing chloride ion concentration. The concentration dependence in $1^{12}$ (0.5–4.0 mM) shows increasing $i_{pc,1}/i_{pc,2}$ current ratio at higher $c_{Re}$ (Figure S20), indicating a bimolecular decay route between the two reduction events.

Our previous electrochemical study for the reduction of parent $1^{11}$ allowed for rationalization of the CV data under Ar by an $EClE$ minimum model with ReIII/ReII and ReII/ReI redox couples that are connected by chloride dissociation between electron transfers. Quantitative kinetic modelling by digital simulation of the CV data further required the introduction of a unimolecular decay step at the rhenium(II) stage after chloride loss. For $1^{12}$, the data indicates at least two coupled chemical reactions after the first reduction event: chloride dissociation that forms [ReCl(L2)] (as proposed for $1^{11}$) and competing bimolecular decay of [ReCl2(L2)]–, respectively. A best fit over all CV data of $1^{12}$ under Ar was found for the kinetic model and simulation parameters presented in Scheme 5.

![Scheme 5. Minimum kinetic model for the digital simulation of the electrochemical reduction of $1^{12}$ under Ar and thermodynamic and kinetic parameters (formal potentials, rate constants, and electron transfer parameters) obtained from CV data simulation;[a] for bimolecular decay of [ReCl2(L2)]–. Typical simulation data are shown in Figure 3 and Figures S24/S25. Within the model, reduction of $1^{12}$ ($E_1$) is succeeded by reversible chloride dissociation ($K_1$) and irreversible ReII/ReI reduction ($E_2$). Importantly, a satisfactory minimum model required two decay routes to account for the concentration dependence of $i_{pc,1}/i_{pc,2}$: unimolecular decay of [ReCl2(L2)]– after chloride loss as proposed for $1^{11}$, but also bimolecular decay before chloride dissociation ($k_3$). Assuming formation of electrochemically silent species, bimolecular decay of [ReCl2(L2)]– was modeled since an alternative reaction of [ReCl2(L2)]– with parent [ReCl2(L2)] would exhibit decreasing normalized $i_{pc,1}$ at increasing concentration, which is not observed. It is tempting to assume disproportionation of ReII to ReIII and ReI as bimolecular pathway. However, simple disproportionation is not consistent with the experimentally observed decrease in chloride ion concentration. A more plausible route is the formation of an electrochemically silent complex [ReCl2(L2)]– that is not further reduced under Ar.

Figure 3. Experimental (black lines) and simulated (red dashed lines) CV data [0.2 M ($n$Bu4N)PF6 in THF] of $1^{12}$ under Ar; mechanism and simulation parameters according to Scheme 5. Left: Concentration dependent data, $v = 0.1$ V s–1. Right: Chloride dependent data, $v = 0.5$ V s–1.
bimolecular rate constant and parent \(1^{12}\) after chloride loss from \([\text{ReCl}_2(\text{L}2)]^{-}\) should lead to increasing overall currents at higher chloride concentrations, which is not in agreement with the data. In consequence, disproportionation requires the introduction of additional decay routes, e.g. at the Re(I) stage, which was renounced to avoid overparameterization of the model. However, disproportionation cannot be fully excluded. The quality of the simulations is quite sensitive with respect to doubling or halving the decay rate constants \(k_2\) or \(k_3\), respectively. However, the two parameters are correlated: a higher bimolecular rate constant \(k_3\) could be partially compensated by lower \(k_2\) (and vice versa), yet with poorer resemblance of reversibility. For the rate and equilibrium constants of chloride loss \((k_1, K_1)\), the fit proved highly sensitive with respect to variations.

Rapid \(N_2\)-activation \((k > 5 \times 10^7 \text{ M}^{-1}\text{s}^{-1})\) by anionic \([\text{ReOCI}_2(\text{L}1)]^{-}\) was demonstrated as key step for \(N_2\) splitting with \(1^{11}\). \(1^{11}\)) Thus, the lifetime of the rhenium(II) intermediate pre-determines the \(N_2\) splitting yield. In case of \(1^{12}\), the chloride dissociation preequilibrium \((K_3)\) is followed by unimolecular decay \((k_3)\) that is about an order of magnitude faster as compared with \(1^{11}\). In addition, a bimolecular decay pathway \((k_2)\) prior to chloride loss may further reduce the lifetime of rhenium(II) species. Besides lowering the electrosynthetic yield, the bimolecular decay may also be detrimental for heterogeneous reductants (Na/Hg, KC₈). Hence, high local surface concentrations of reduced species are expected as opposed to homogeneous reduction, e.g. with \(\text{Co(CP}^\ast)^2\), which gave the highest \(N_2\) splitting yields for \(1^{12}\).

### Conclusions

The unsaturated PNP complex \(2^{12}\) provides the second example of reductive, electrochemically driven \(N_2\) splitting. In analogy to parent \(2^{11}\), Brønsted acid protonates the pincer backbone of \(N_2\)-derived nitride \(2^{12}\), yet at a distinctly different site. However, this product may serve as starting platform for nitrogen incorporation into organic molecules as demonstrated by nitride methylation with \(\text{MeOTf}\). A strong dependence of the nitrogen splitting yield on the nature of chemical reductants \((\text{CoCp}^\ast)^2\): 60 %, Na/Hg: 30 %, KC₈: 20 %) or electrolysis (15 %) was found, which markedly differs from parent \(1^{11}\) \((\text{CoCp}^\ast)^2\): 75 %, Na/Hg: 80 %, electrolysis: 60 %). The unproductive decomposition pathways that diminish the yield in \(2^{12}\) were not examined in detail. However, detailed comparison of electrochemical data for \(1^{12}\) vs. parent \(1^{11}\) allowed for identifying three key differences that provide a qualitative basis to rationalize the trends in rhenium mediated \(N_2\) splitting yields with different pincer ligands and reductants:

- **a)** Unlike \(1^{11}\), the starting complex \(1^{12}\) exhibits slow decomposition in the presence of \(N_2\) and chloride ions. The decreased stability against chloride is partly attributed to decay via chloride-induced disproportionation. The reduced chemical stability should affect electrosynthetic vs. chemical reduction yields which proceed on much slower timescales with concomitant free chloride buildup.
- **b)** Weaker \(N → M\) π-donation by pincer ligand \(L2\) results in an anodic shift of the \(\text{Re}^{11+/0}\) and \(\text{Re}^{11/0}\) redox couples and a smaller separation of their potentials. This allows for electrochemically driven \(N_2\) splitting at more desired, less negative potentials. However, unproductive \(\text{Re}^{11/0}\) reduction prior to \(N_2\) activation and additional \(L2\) ligand fragmentation pathways via isobutene liberation might be more accessible with strong chemical reductants, such as Na/Hg or KC₈, leading to decay due to over-reduction.
- **c)** In addition to the kinetic model proposed for \(1^{12}\), a rapid bimolecular decay pathway was found for the key rhenium(II) species \([\text{ReCl}_2(\text{L}2)]^{-}\) that can compete with productive \(N_2\) activation. This pathway will be particularly detrimental for heterogeneous chemical (Na/Hg, KC₈) and electrochemical reduction where high local \(\text{Re}^\ast\) concentrations are expected.

This study exemplifies the subtle interplay of the underlying thermodynamics and kinetics of electron transfer processes and coupled chemical steps, respectively, as determining parameters for the yields in reductive \(N_2\) splitting. Future work will have to focus on the nature of the decay pathways to design improved platforms for (electro-)chemical \(N_2\) fixation.
Experimental Section

Materials and Synthetic Methods

All experiments were carried out under inert conditions using standard Schlenk and glove-box techniques under Ar or N₂. HPLC grade solvents (Sigma Aldrich/Merck) were dried using an MBRAUN Solvent Purification System. THF was additionally dried with Na/K (D₈THF) or 4 Å molecular sieves (C₆D₆). ¹H NMR, Si(CH₃)₃N₃, Co(Cp)₂, Co(Cp*)₂, hexamethylbenzene, P(OSi(CH₃)₃)₂, PPh₂ were used as purchased. HOFF and MeOtt were distilled prior to use. Na/Hg (1M) was prepared from sieves (C₆D₆). ¹⁵N₂, Si(CH₃)₃N₃, Co(Cp)₂, Co(Cp*)₂, hexamethylbenzene, 2,4,6-tri-tert-butylphenol were sublimed off overnight at 75 °C. ¹¹B is obtained as a brown powder in 63 % yield. Anal. Calcd for C₂₀H₄₀Cl₂NP₂Re: C, 37.01; H, 6.57; N, 2.28; found C, 38.81, H, 6.63; N, 2.14. NMR (CD₂Cl₂, ppm): δ = 1.18 (A9XX A), N = [J₃C₊₉P₄] = 7.2 Hz, 3H, 18H, P(CH₃)), 1.49 (A₉XX A', N = [J₃C₊₉P₄] = 7.0 Hz, 18H, P(CH₃)), 2.29 (A₉XX B', A'', N = [J₃C₊₉P₄] = 2.2 Hz, 7H, 18H, P(CH₃)), 7.00 (A₉XX B', A'', N = [J₃C₊₉P₄] = 17.1 Hz, 3H, 6H, 2H, NHCH). ¹³C (125.76 MHz): δ = 28.5 (br, 6C, P(CH₃)), 29.4 (br, 6C, P(CH₃)), 34.9 (AXXX', N = [J₃C₊₉P₄] = 10.3 Hz, 2C, P(CH₃)), 36.7 (AXXX', N = [J₃C₊₉P₄] = 11.8 Hz, 2C, P(CH₃)), 91.8 (AXXX', N = [J₃C₊₉P₄] = 20.9 Hz, 2C, P(CH₃)), 170.3 (AXXX', N = [J₃C₊₉P₄] = 6.8 Hz, 2C, NCH). ³¹P(H) (161.25 MHz): δ = 71.8 (s). LIDFI-MS (toluene, [m/z]): 613.1 (100 %, [M]+).

Re(NiCl₂) (2¹¹B): N₂ route. Degasged THF (0.45 mL) is vacuum-transferred to a mixture of 1¹¹B (5.0 mg, 8.1 μmol, 1.0 equiv) and reductant (Co(Cp)₂: 3.0 mg, 9.0 μmol, 1.1 eq; NaHg (1M): 121.3 mg, 9.0 μmol, 1.1 eq or KC₈: 1.1 mg, 8.1 μmol, 1.0 equiv in a J-Young NMR tube and placed under an N₂-atmosphere. After thawing of the mixture, the mixture is shaken vigorously with gradual colour change from dark brown to light brown. After 30 min at r.t., the solvent is removed, hexamethylbenzene (1 eq via a 0.08M stock solution in THF) is added and the solvent is removed again. Spectroscopic yields of the title compound are obtained by integration of the ¹₂J ligand backbone ¹¹B NMR signals vs. the internal standard C₆Me₆ (60 % for Co(Cp)₂: 30 % for Na/Hg; 20 % for KC₈). 2¹¹B is not isolated via this route.

Azaide route. 1¹¹B (25.0 mg, 40.7 μmol, 1.0 equiv) is dissolved in THF (1 mL) and added dropwise over a period of 5 min to a stirring solution of Me₃SiN₃ (26.78 μL, 23.5 mg, 203 μmol, 5.0 equiv) in THF (0.5 mL). The solution is stirred at rt. for 1.5 h after which the solvent is removed in vacuo. After extraction with pentane (4 x 5 mL) and removal of the solvent, 2¹¹B is obtained as a light brown solid in 72 % yield. Anal. Calcd for C₂₂H₄₀Cl₆NP₄Re (%) : C, 37.75; H, 6.17; N, 2.26; found C, 37.73; H, 6.15; N, 2.25. NMR (CD₂Cl₂, ppm): δ = 1.18 (A9XX A'), N = [J₃C₊₉P₄] = 7.2 Hz, 3H, 18H, P(CH₃)), 1.49 (A₉XX A'', N = [J₃C₊₉P₄] = 7.0 Hz, 18H, P(CH₃)), 2.29 (A₉XX B', A', N = [J₃C₊₉P₄] = 2.2 Hz, 7H, 18H, P(CH₃)), 7.00 (A₉XX B', A', N = [J₃C₊₉P₄] = 17.1 Hz, 3H, 6H, 2H, NHCH). ¹³C (125.76 MHz): δ = 28.5 (br, 6C, P(CH₃)), 29.4 (br, 6C, P(CH₃)), 34.9 (AXXX', N = [J₃C₊₉P₄] = 10.3 Hz, 2C, P(CH₃)), 36.7 (AXXX', N = [J₃C₊₉P₄] = 11.8 Hz, 2C, P(CH₃)), 91.8 (AXXX', N = [J₃C₊₉P₄] = 20.9 Hz, 2C, P(CH₃)), 170.3 (AXXX', N = [J₃C₊₉P₄] = 6.8 Hz, 2C, NCH). ³¹P(H) (161.25 MHz): δ = 71.8 (s). LIDFI-MS (toluene, [m/z]): 592.1 (100 %, [M]+).

ReCl₃(L₂) (2¹¹B): ReCl₃(L1) (15.3 mg, 0.024 mmol) and 2,4,6-tri-tert-buty1phenyl 15N₂ (33.9 mg, 0.12 mmol, 5.4 equiv) are combined in C₆H₆ (dried with Na/K). After heating at 60 °C for 1.5 h, the solvents are evaporated in vacuo. After extensive washing with pentane, and lyophilization (C₆H₆), 4¹¹B is obtained in 70 % yield (10.6 mg; 0.016μmol). Anal. Calcd. for C₆Cl₆Li₃NP₄Re (%) : C, 37.01; H, 6.21; N, 2.16; found C, 36.66; H, 6.29; N, 1.96. ¹¹B NMR (300 MHz,
CδDδ: 15.2 ppm (s, Jα/β = 7.5 Hz), -51.7 (s, Jα/β = 14.8 Hz), -194.6 (s, Jα/β = 30.3 Hz). LiFDI-MS (Toluene, [m/z]): 648.1 (100 %, [M]+), calculated 648.1. 

([ReCl(H2)2OTf] (5H2L2-OTf): 2L2 (5.0 mg, 8.4 μmol, 1.0 equiv.) is dissolved in EtO (1 mL) and H2OTF (0.74 μL, 8.4 μmol, 1 equiv.) is added via an Eppendorf pipette. Upon stirring for 1 h, a red-brownish precipitate forms which is collected by filtration, washed with 28.7 (d, 2JCP = 14.8 Hz, 9H, CH3), 1.32 (d, 3JCP = 15.9 Hz, 9H, CH3), 1.60 (d, 3JCP = 15.6 Hz, 9H, CH3), 3.79 (dd, 2JCP = 21.2 Hz, 2JCP = 7.7 Hz, 1H, P-CH2-CH), 4.40 (dd, 2JCP = 21.2 Hz, 2JCP = 7.4 Hz, 1H, P-CH2-CH), 6.66 (d, 2JCP = 6.7 Hz, 1H, P-CH), 8.02 (dd, 2JCP = 27.8 Hz, 6.6 Hz, 1H, N-CH=CH), 9.35 (d, 3JCP = 20.9 Hz, 1H, N=CH-CH3). 13C{1H} NMR spectroscopically in C6D6) (see Figure S8). 

N2-pressure dependent CV: 1L2 (25.0 mg, 44.2 μmol, 1.0 equiv.) and MeOTf (5.26 μL, 46.4 μmol, 1.1 equiv.) are dissolved in chloroform (1 mL) and MeOTf (5.26 μL, 46.4 μmol, 1.1 equiv.) is added as an electrochemical reference. The solution was transferred to the Parr reactor and subsequently pressurized with N2 to obtain CVs at 1, 3, 5, 7, 9, 11 bars. At 11 bars, the system was allowed to stay for 45 minutes while regular CVs were measured (see Figures S20). After depolarizing, the reactor was transferred back in the glovebox and the reaction mixture was analysed by 31P{1H} NMR spectroscopy (see Figure S16). 

Acknowledgments

This work was supported by the European Research Council (ERC Consolidator Grant Agreement 646747, grant holder S.Sch.). Dr. J. Abbenseth and J. C. Becker are acknowledged for supporting synthetic work and Dr. E. Yuzik-Klimova for providing high-pressure CV data. A.J.M.M. acknowledges support from the National Science Foundation Chemical Catalysis program under Grant No. CHE-1665135.

Keywords: Nitrogen fixation · Rhenium · Pincer complexes · Electrochemistry · Cyclic voltammetry

[1] B. S. Patil, V. Hessel, L. C. Seefeldt, D. R. Dean, B. M. Hoffman, B. J. Cook, L. J. Murray, Nitrogen Fixation. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley: 2017.
[2] a) S. L. Foster, S. I. Perey Bakovic, R. D. Suda, S. Maheshwari, R. D. Milton, S. D. Minteer, M. J. Janik, J. N. Renner, L. F. Greenlee, Nat. Catal. 2018, 1, 490–500; b) Z. Yan, M. Ji, J. Xia, H. Yhu, Adv. Energy Mater. 2019, 1902020.
[3] L. Tan, N. Yang, X. Huang, L. Peng, C. Tong, M. Deng, X. Tang, L. Li, Q. Li, Z. Wei, Chem. Commun. 2019, Advance Article. DOI: https://doi.org/10.1039/C9CC06132X.
[4] L. J. McPherson, T. Sudmeier, J. Fellowes, C. S. E. Tsang, Dalton Trans. 2019, 48, 1562–1568.
[5] N. Ostermann, I. Siewert, Curr. Opin. Electrochem. 2019, 15, 97–101.
[6] a) M. J. Chalkey, T. J. Del Castillo, B. D. Matson, J. C. Peters, J. Am. Chem. Soc. 2018, 140, 6122–6129; b) T. J. Sherbow, E. J. Thompson, A. Arnold, R. I. Sayler, R. D. Britt, L. A. Berben, Chem. Eur. J. 2019, 25K, 454–458.
[7] R. R. Schrock, Angew. Chem. Int. Ed. 2008, 47, 5512–5522; Angew. Chem. 2008, 120, 5594.
[8] B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean, L. C. Seefeldt, Chem. Rev. 2014, 114, 4041–4062.
[9] a) K. Arashiba, A. Eizawa, H. Tanaka, K. Nakajima, K. Yoshizawa, Y. Nishi-bayashi, Bull. Chem. Soc. Jpn. 2017, 90, 1111–1118; b) Y. Ashida, K. Arashiba, K. Nakajima, Y. Nishibayashi, Nature 2019, 568, 536–540.
[10] C. E. Laplaca, C. C. Cummins, Science 1995, 268, 861–863.
[11] I. Klopsch, E. Yuzik-Klimova, S. Schneider, Top. Organomet. Chem. 2017, 60, 71–112.
[12] a) T. J. Hebben, R. R. Schrock, M. K. Takase, P. Müller, Chem. Commun. 2012, 48, 1851–1853; b) I. Klopsch, M. Finger, C. Württele, B. Milde, D. B.
[22] All potentials in this article are internally referenced to the ferrocenium/ferrocene reduction potential, $Fe^{2+}/^0$. 

[23] N. G. Connelly, W. E. Geiger, Chem. Rev. 1996, 96, 877–910. 

[24] V. Ritleng, D. V. Yandulov, W. W. Weare, R. R. Schrock, A. S. Hock, W. M. Davis, J. Am. Chem. Soc. 2004, 126, 6150–6163. 

[25] V. W. Manner, T. F. Markle, J. H. Freudenthal, J. M. Mayer, F. Hasanayn, A. J. M. Miller, J. Am. Chem. Soc. 2019, 141, 11185–11191. 

[26] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. J. Verschoor, J. Chem. Soc., Dalton Trans. 1984, 1349–1356. 

[27] J. Abbenseth, M. Diefenbach, S. C. Bette, C. Würtele, B. de Bruin, S. Schneider, Inorg. Chem. 2016, 55, 9290–9302; g) J. Abbenseth, M. Finger, C. Würtele, M. Kasanmascheff, S. Schneider, Inorg. Chem. Front. 2016, 3, 469–477; h) P. O. Lagaditis, B. Schluschaß, S. Demeshko, C. Würtele, S. Schneider, Inorg. Chem. 2016, 55, 4529–4536; i) F. Schnecke, M. Finger, M. Tromp, S. Schneider, Chem. Eur. J. 2017, 23, 33–37; j) J. Abbenseth, M. Diefenbach, S. C. Bete, C. Würtele, C. Volkman, S. Demeshko, M. C. Holtzhausen, S. Schneider, Chem. Commun. 2017, 53, 5511–5514; k) Q. Bruch, B. M. Lindley, B. Askevold, S. Schneider, A. J. M. Miller, Inorg. Chem. 2018, 57, 1964–1975. 

[28] A. Katayama, T. Ohta, Y. Wasada-Tsutsui, T. Inomata, T. Ozawa, T. Ogura, H. Masuda, Angew. Chem. Int. Ed. 2019, 131, 11401–11406. 

[29] B. Askevold, J. Meiners, S. Schneider, Eur. J. Inorg. Chem. 2012, 412–429. 

[30] A. J. M. Miller, P. O. Lagaditis, B. Schluschaß, S. Schneider, Angew. Chem. Int. Ed. 2008, 47, 8184–8187; Angew. Chem. 2011, 123, 8334; b) M. Scheibel, B. Askevold, F. Heinemann, E. I. Reijerse, B. de Bruin, S. Schneider, Nat. Chem. 2012, 4, 552–558; c) M. G. Scheibel, Y. Wu, A. C. Stucki, L. Krause, E. C. Karl, D. Stalke, B. de Bruin, S. Schneider, J. Am. Chem. Soc. 2013, 135, 17719–17722; d) M. Kinauer, M. Scheibel, J. Abbenseth, F. W. Heinemann, P. Stollberg, C. Würtele, S. Schneider, Dalton Trans. 2014, 43, 4506–4513; e) B. Askevold, M. M. Khusniyarov, W. Kroener, K. Giep, P. Müller, E. Herdtweck, F. W. Heinemann, M. Diefenbach, M. C. Holtzhausen, V. Vieru, L. F. Chibotaru, S. Schneider, Chem. Eur. J. 2015, 21, 579–589; f) M. G. Scheibel, J. Abbenseth, M. Kinauer, F. W. Heinemann, C. Würtele, B. de Bruin, S. Schneider, Inorg. Chem. 2015, 54, 9290–9302; g) J. Abbenseth, M. Finger, C. Würtele, M. Kasanmascheff, S. Schneider, Inorg. Chem. Front. 2016, 3, 469–477; h) P. O. Lagaditis, B. Schluschaß, S. Demeshko, C. Würtele, S. Schneider, Inorg. Chem. 2016, 55, 4529–4536; i) F. Schnecke, M. Finger, M. Tromp, S. Schneider, Chem. Eur. J. 2017, 23, 33–37; j) J. Abbenseth, M. Diefenbach, S. C. Bete, C. Würtele, C. Volkman, S. Demeshko, M. C. Holtzhausen, S. Schneider, Chem. Commun. 2017, 53, 5511–5514; k) Q. Bruch, B. M. Lindley, B. Askevold, S. Schneider, A. J. M. Miller, Inorg. Chem. 2018, 57, 1964–1975. 

[31] N. G. Connelly, W. E. Geiger, Chem. Rev. 1996, 96, 877–910. 

[32] V. Ritleng, D. V. Yandulov, W. W. Weare, R. R. Schrock, A. S. Hock, W. M. Davis, J. Am. Chem. Soc. 2004, 126, 6150–6163. 

[33] W. M. Manner, T. F. Markle, J. H. Freudenthal, J. M. Mayer, F. Hasanayn, A. J. M. Miller, J. Am. Chem. Soc. 2019, DOI: https://doi.org/10.1021/jacs.9b10031. 

[34] J. M. Figg, P. L. Holland, T. R. Cundari, Inorg. Chem. 2012, 51, 7546–7550; b) K. V. MacLeod, F. S. Menges, S. F. McWilliams, S. M. Craig, B. O. Mercado, M. A. Johnson, P. L. Holland, J. Am. Chem. Soc. 2016, 138, 11185–11191. 

[35] J. Abbenseth, M. Diefenbach, S. C. Bette, C. Würtele, B. de Bruin, S. Schneider, Inorg. Chem. 2015, 54, 12236–12273; Angew. Chem. 2015, 127, 12406. 

[36] B. Schluschaß, J. Abbenseth, S. Demeshko, C. Würtele, B. de Bruin, S. Schneider, Inorg. Chem. 2016, 55, 4529–4536; i) F. Schnecke, M. Finger, M. Tromp, S. Schneider, Chem. Eur. J. 2017, 23, 33–37; j) J. Abbenseth, M. Diefenbach, S. C. Bete, C. Würtele, C. Volkman, S. Demeshko, M. C. Holtzhausen, S. Schneider, Chem. Commun. 2017, 53, 5511–5514; k) Q. Bruch, B. M. Lindley, B. Askevold, S. Schneider, A. J. M. Miller, Inorg. Chem. 2018, 57, 1964–1975.