Photoelectrochemical Conversion of Dinitrogen to Benzonitrile: Selectivity Control by Electrophile- versus Proton-Coupled Electron Transfer

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Abstract: Nitride complexes are key species in homogeneous nitrogen fixation to NH\textsubscript{3} via stepwise proton-coupled electron transfer (PCET). In contrast, direct generation of nitrogenous organic products from N\textsubscript{2}-derived nitrides requires new strategies to enable efficient reductive nitride transfer in the presence of organic electrophiles. We here present a 2-step protocol for the conversion of dinitrogen to benzonitrile. Photoelectrochemical, reductive N\textsubscript{2} splitting produces a rhenium(V) nitride with unfavorable PCET thermochemistry towards ammonia generation. However, N-benzoylation stabilizes subsequent reduction as a basis for selective nitrogen transfer in the presence of the organic electrophile and Brønsted acid at mild reduction potentials. This work offers a new strategy for photoelectrosynthetic nitrogen fixation beyond ammonia—to yield nitrogenous organic products.

Introduction

Proton-coupled electron transfer (PCET) is a key concept for the design of efficient redox catalysts.\textsuperscript{[3]} As a prominent example, Nishibayashi reported that Mo pincer catalysts generate over 4000 eq. of NH\textsubscript{3} in the nitrogen reduction reaction (NRR) at ambient conditions with the model PCET reductant SmI\textsubscript{2}/H\textsubscript{2}O.\textsuperscript{[2]} In fact, most homogeneous NRR catalysts are anticipated to operate via initial PCET to metal-coordinated N\textsubscript{2} as a thermochemically challenging step.\textsuperscript{[3]} An alternative, Haber–Bosch-like pathway that has been considered commences with full N\textsubscript{2} splitting prior to N–H bond formation.\textsuperscript{[4, 5]} However, terminal nitride complexes that result from reductive N\textsubscript{2} splitting generally exhibit low to moderate hydrogen atom affinities. This is expressed by N–H bond dissociation free energies (BDFE\textsubscript{N–H}) of the corresponding parent imides that are typically below \(\approx 45\) kcal mol\textsuperscript{-1} (Scheme 1a).\textsuperscript{[6]} In consequence, the first PCET step after N\textsubscript{2} splitting defines a thermochemical bottleneck for ammonia-selective nitrogen reduction vs. competing H\textsubscript{2} evolution.\textsuperscript{[7]} PCET-based strategies will be key to establish efficient, photo- and electro-
chemically driven NRR catalysis that does not rely on sacrificial chemical reductants. [6]

N₂ splitting also provides a potential entry towards nitrogenous products beyond ammonia. This was demonstrated by several stoichiometric (cyclic) reaction sequences,[5,8] as well as the catalytic formation of triisylamines and recently triboryllamines,[10] directly from N₂. However, several challenges remain to be addressed to obtain more complex targets, like primary amines or amides. However, several challenges remain to be addressed to obtain more complex targets, like primary amines or amides. For example, electrolysis of a Mo(V) alkylimide complex in acidic solution (AcOH) required potentials that are incompatible with most organic electrophiles (−2.3 V vs. FeCl₃). One-pot or even catalytic product formation via reductive N₂ splitting in the presence of both electrophiles and Brønsted acid necessitates strategies to reduce the overall overpotential and control the N–C vs. N–H bond formation selectivity.

Our groups previously examined N₂ splitting and nitride transfer enabled by (electro-)chemical reduction of rhenium complexes with bulky PNP-pincer ligands.[13] Light-driven N₂ splitting of the modified platform 1a (Scheme 1b) gave the more reactive nitride 2a, which converts benzylic chloride to benzamide upon PCET from the pincer backbone, but only at elevated temperatures.[14] We here present a PCET-based synthetic strategy for direct, cathodic product release in the presence of electrophile and acid. This enabled the development of a one-pot protocol for photoelectrochemical N₂ splitting and benzonitrile formation at mild potentials and ambient temperature (Scheme 1c).

Results and Discussion

We first aimed at replacing BzCl by benzoylation reagents of the higher halides as being better nucleofuge. For that purpose, N₂ splitting with [ReX₃(PNP)] (1b: X = Br, 1c: X = I; Scheme 2) was examined to avoid complications from halide scrambling during subsequent benzoylation. The bromide and iodide complexes were synthesized from [ReBr₃(PPh₃)₂(MeCN)] and by halide metathesis for 1c, respectively. Spectroscopic and crystallographic characterisation of 1b/c support rhenium(III) in meridional octahedral coordination.[15] As a typical trend for the halide precursors,[13b,16] cyclic voltammetry (CV) showed that the first reduction of 1b (E₁/₂ = −1.70 V vs. FeCp₂) [17] and 1c (E₁/₂ = −1.52 V) are at significantly less negative potentials with respect to 1a (E₁/₂ = −1.84 V).[18] At lower scan rate, the ReIII couple becomes irreversible for all three halides, which is attributed to X⁻ loss from [ReX₃(PNP)]⁻ as a prerequisite to N₂ activation. Scan rate dependent data allowed for estimating first order halide dissociation rate constants. The increase by almost two orders of magnitude along the halide series (k_diss = 0.05 s⁻¹ (1a), 0.33 s⁻¹ (1b), 1.97 s⁻¹ (1c); Figures S67–S69) correlates with increasing halide ionic radii and polarizability, viz leaving group properties.[19,20] Accordingly, the higher halides allowed for photoelectrochemical N₂ splitting by controlled potential electrolysis (CPE) at less negative potentials (Scheme 2).[13c]

Furthermore, the productive photolysis window favourably extends further into the visible range. CPE of the halide series (E_app = −1.73 V (1b), −1.53 V (1c)) under N₂ with irradiation by a blue LED (λ_e = 456 ± 10 nm) gave increased yields of the nitride complexes 2b (37 %; Faradaic Efficiency (FE) = 22 %) and 2c (53 %; FE = 53 %) with respect to the parent chloride (1b). Complexes 2b and 2c were fully characterized, including crystallography (Figures S98 and S99),[15] which confirmed cis-configurations in the solid state as was found for 2a.[14]

In contrast to 2a phenylation, benzoylimide formation is directly observed upon addition of excess PhC(O)Br to 2b in THF. Crystalization gave [Re(NBz)(HPNP)]Br (3b) in high yield (Scheme 3). While isolated 3b is stable in CH₂Cl₂ over several days, re-dissolving in THF leads to rapid dissociation of benzoyl bromide and a small equilibrium constant was obtained in a titration experiment monitored by ³¹P NMR spectroscopy (K_eq = 1.1 × 10⁻⁹ M⁻¹; Figure S31). However, benzoylimide formation can be driven by halide exchange with NaBAR₃ ([BAR₃] = [3.5-(CF₃)₂C₆H₄]⁻), giving 3BAR in 90% yield (Scheme 3). In the solid state, the rhenium(V) benzoyl imido complexes 3b and 3BAR (Figure 1 and Figure S101) exhibit a structural reorganization with respect to the parent nitride 2b (see above). The trans-dibromide configuration of the cation of 3b and 3BAR reflects the decreased trans-influence of the multiply bonded nitrogen ligand, as expressed by the significantly longer Re–N multiple bond length (3b 1.724(3) Å (exp), 1.734 Å (DFT); 2b: 1.663(5) Å (exp), 1.677 Å (DFT); Table S3/S5). ¹H NOESY characterization (Figure S30/S37) confirmed the trans configuration also in

| Complex | X | E_app. | Wavelength | Yield (FE) |
|---------|---|--------|------------|------------|
| 1a | Cl | −1.90 V (1.13 e⁻/Re) | 390 nm | 20% (18%) |
| 1b | Br | −1.73 V (1.70 e⁻/Re) | 456 nm | 37% (22%) |
| 1c | I | −1.53 V (1.0 e⁻/Re) | 456 nm | 53% (53%) |

Scheme 2. Photoelectroreductive N₂ splitting with precursors 1a–c (FE = Faradaic Efficiency).

Scheme 3. Benzoylation equilibriu of 2b and benzoyl bromide.
solution and computations favoured trans-3⁺ over the cis isomer by $\Delta G_{\text{DFT}}^{\text{cis}\rightarrow\text{trans}} = 3.8 \text{ kcal mol}^{-1}$.

Starting from 3⁺, reduction was examined first in the absence of acid. The CV of 3[4]BF₄ in THF shows a reversible reduction at $E_{1/2} = -0.71 \text{ V (v = 1.0 V s}^{-1}$; Scheme 4) and a reduction at $E_{1/2} = -1.63 \text{ V (v = 0.1 V s}^{-1}$, which was irreversible at all scan rates (Figure S61). Notably, at lower scan rates, the first reduction also becomes increasingly irreversible and a new feature at $E_{1/2} = -0.42 \text{ V}$ grows in the reverse oxidative scan, while the ratio of the cathodic and the sum of the anodic peak currents stays close to unity (Figure S62). These observations are in line with an ECE mechanism, namely a chemical step that follows reduction within the CV timescale, which can be attributed to trans to cis isomerization (see below). Chemical reduction of 3[4]BF₄ with cobaltocene enabled the isolation of the rhenium(IV) benzoylimido complex [Re(NBz)Br₂(HPNP)] (4) in 85 % yield (Scheme 4). Notably, only five-coordinate ReIV oxo and imido complexes were previously reported,[21] and ReIV oxo species have been proposed as reactive intermediates in C–H activation.[22]

The X-band EPR signal of 4 in toluene at room temperature exhibits large $^{185} \text{Re}$ hyperfine interaction ($g = 1.92$, $a_{\text{iso}} = 700 \text{ MHz}$; Figure S40), supporting a low-spin ReIV complex.[23] Structural characterization in the solid state (Figure 1) indicates isomerization to the cis-dibromide configuration. Comparison of the molecular structures of 3⁺ and 4 shows a significant elongation of the Re–N bond by 0.09 Å upon reduction despite reduced trans-influence in the cis-configuration. Isolated 4 exhibits a reversible oxidation at $E_{1/2} = -0.48 \text{ V}$ (Figure S64). We therefore attribute the ECE signature of the reduction of 3⁺ to slow isomerization of trans-4 to cis-4 with an estimated rate constant of $k_{\text{iso}} \approx 0.04 \text{ s}^{-1}$ (Figure S70). The potential shift ($\Delta E_{1/2} = 0.23 \text{ V}$; $\Delta G^{\text{cis} \rightarrow \text{trans}} = 5.3 \text{ kcal mol}^{-1}$) arises from the difference between the cis/trans-isomerization equilibria in the oxidized (cis/trans-3⁺) and reduced (cis/trans-4) states, respectively, which is well reproduced by DFT ($\Delta G_{\text{DFT}}^{\text{cis} \rightarrow \text{trans}} = 6.7 \text{ kcal mol}^{-1}$; Figure S94). Isomerization of trans-4 to the more stable cis-

![Figure 1. Molecular structures of 3, 4, 5 and 6 in the solid state drawn at the 50% probability level. Hydrogen atoms except N–H are omitted for clarity.](image)

![Figure 2. Structural characterization in the solid state drawn at the 50 % probability level.](image)

![Figure 3. Isomerization of 3 to 4.](image)

![Figure 4. Cyclic voltammetry of the ReIV couple of 3[6]BF₄ (1 mM in THF, 0.1 M N'BuPF₆) at varied scan rate (currents are normalized to v¹/²).](image)

![Figure 5. Isomerization of 3[6]BF₄ in presence of 10 eq. [LutH]OTf/ Lutidine (1 mM in THF, 0.1 M N'BuPF₆) at varied scan rate. *Isolated yield.](image)
configuration was computed exergonic by $\Delta G^\circ_{\text{DFT}} = 2.9$ kcal mol$^{-1}$.

The irreversible Re$^{VIII}$ redox couple was examined by chemical reduction of 3$^{\text{BAF}}$ with CoCp$_2$ (2 eq.). Two-electron reduction is associated with a substantial structural reorganization. Bromide loss, ortho-metallation, tautomerization and kN-to-$\pi$O isomerization gives diamagnetic [Re$^{\text{III}}$(C$_6$H$_4$C(O)NH$_2$Br(PNP))] (5; Scheme 4) in 68% isolated yield. Bromide ion dissociation after the second reduction is probably a prerequisite to cyclometalation. Conceivable yield. Bromide ion dissociation after the second reduction is probably a prerequisite to cyclometalation. Conceivable electron reduction is associated with a substantial structural elongation of the Re$^{\text{IV}}$ imide to benzamide, yet at high overpotential.

For simplicity, the trans-configurations were used for all states. Note that the cis-configuration is slightly more stable for 4 ($\Delta G = 2.9$ kcal mol$^{-1}$). See Supporting Information for the cis-isomers. (IV) imide trans-7 (BDFE$_{\text{N-H}}$ = 33.2 kcal mol$^{-1}$) which is very close to that of the related complex [Re(NH)$_2$(N-(CH$_3$)$_2$CNNBu$_2$)]) (Scheme 1), rendering 7 thermodynamically unstable with respect to hydrogen evolution (BDFE$_{\text{H,0}}$ = 52 kcal mol$^{-1}$ in THF).$^{[29]}$ Furthermore, as judged from a thermochemical cycle, the protonation of 2b requires strong acids ($pK_a^{\text{THF}}$(trans-8) $\approx$ 5).

The thermochemical bias in favour of benzoyl- vs. proton-coupled reduction can be rationalized by $\pi$-bonding within the [ReN=N-Cu] complex (R = Bz, H). While the Re$^{\text{V}}$ imides 3$^3$ and 8$^+$ as well as the Re$^{\text{V}}$ imide 4 are nearly linear, 7 was computed to be distinctly bent (\text{Re-N-H:} 120°). This conformational reorganization can be attributed to population of a molecular orbitals (MO) with $\pi^*_{\text{Re-N}}$ character. Bending of the Re-N-H moiety reduces the 3-electron interaction of the d$_{ab}$ and p$_s$ atomic orbitals. In contrast to hydrogen, the benzoyl substituent is a moderate $\pi$-acceptor. In fact, Nielson et al. previously described the acylimidic ligand (NC(O)H)$_2$ as a single faced $\pi$-donor.$^{[30]}$ The population of a molecular orbital with [Re=N=H] $\pi^*_{\text{Re-N}}$ character in 4 (Scheme 5) is in line with the significant elongation of the Re=$\text{N}$ bond with respect to 3$^+$ (see above). In turn, $\tau_{\pi_{\text{C}}}$ and $\tau_{\pi^*_{\text{C}}}$ character of the SOMO of 4 leads to contraction of the N=C ($\Delta d = 0.08$ Å) and elongation of the C-O ($\Delta d = 0.07$ Å) bonds. Hence, charge delocalization into the benzoyl substituent contributes to the remarkable anodic shift of the reduction potential with respect to the nitride and parent imide complexes.

This thermochemical framework emphasizes that ammonium formation will be hampered by the unfavourable first PCET to 2b. We therefore aimed at utilizing the preference in favour of Bz$^-$/e$^-$ transfer to control the selectivity of nitride transfer. Full release of organic products requires further reduction and addition of electrophiles. For this purpose, PCET of the benzoylimido complex was examined. Addition of 2,6-dichlorophenol (11 eq.; $pK_a^{\text{THF}}$ = 25.1) to 3$^{\text{BAF}}$ leads to a significant anodic shift of the irreversible, second reduction by around +400 mV, suggesting PCET (Figure S63). In the presence of the stronger acid lutidinium triflate ([LutH]OTf; 10 eq.; $pK_a^{\text{THF}}$ = 7.2),$^{[31]}$ the first wave retains the reversible reduction, yet with anodically shifted potential ($E_{1/2} = -0.66$ V; $\Delta E_{\text{r}} = 50$ mV) and significantly higher peak current, supporting a multi-electron process (Scheme 4). Accordingly, chemical reduction of 3$^{\text{BAF}}$ with CoCp$_2$ and lutidinium bromide (2 eq. each) gives rhenium(III) carboxamide complex 6 in 87% spectroscopic yield (Scheme 4) and traces of 1b (3%). Crystallographic characterization of 6 confirms single bond character of the Re=N=N bond ($d_{\text{Re-N}}$ = 2.113(4) Å) after 2e$^-$/H$^+$ reduction (Figure 1). The full, chemically driven nitrogen transfer can be obtained upon addition of the strong acid [Ph$_3$NH$_2$]Br ($pK_a^{\text{THF}}$ = 0.6)$^{[32]}$ giving free benzamide and 1b in yields of 56% and 80%, respectively (Scheme 4).

Motivated by these results, we developed protocols for direct, one-pot (electro-)chemically driven nitride transfer from 2b. Addition of benzoyl bromide (3 eq.), [LutH]Br, FeCp$_2$ (3 eq.), and the mild chemical reductant FeCp$_2$ (3 eq.; $E_{1/2} = -0.43$ V)$^{[31]}$ to 2b in THF-$d_8$ (Scheme 6, Entry 1 and Figure S74) gives parent 1b as the only detectable product.
by $^{31}$P NMR spectroscopy in 55% yield, together with an equimolar amount of benzonitrile (56%). The use of the $^{15}$N labelled nitride complex from photoelectrochemical splitting of $^{15}$N$_2$ confirmed nitride transfer to the organic product (Figure S76). Ammonium as a potential product is not detected. Besides PhCN, benzoyl anhydride (43%) and benzoic acid (23%) are observed. This is in line with initial formation of benzamide, which subsequently reacts with additional BzBr to benzonitrile and the anhydride/acid.\[34\]

The formation of some 4-bromobutyl benzoate (26%) is attributed to electrophilic ring opening of THF with benzoyl bromide, which is catalysed by Lewis acids.\[35\]

In summary, we have demonstrated a two-step photoelectrosynthetic cycle for the fixation of dinitrogen with benzoyl bromide to yield benzonitrile. Moving to the higher halide precursors significantly shifts both reductive N$_2$ activation to less negative potentials and photolytic N–N splitting deeper into the visible range. The unfavourable first PCET step renders the resulting nitride (X = Br) unsuitable for efficient ammonia generation. PCET cannot compete with benzoylation/reduction, which can at least in part be attributed to π-stabilization of the unusual rhenium(IV) imido state by the benzoyl substituent. This thermochemical bias provides a PCET-based, conceptual basis to enable selective, electrochemical formation of nitrogenous organic products over ammonia production. We have demonstrated this by the development of an electrochemical one-pot protocol for nitride transfer upon reduction at mild potential ($E_{\text{appl}} = -0.74$ V), which is compatible with the organic electrophile (BzBr) and acid (Et$_3$NH$^+$), to restore parent 1b. The release of benzonitrile in 66% yield is attributed to two PCET steps that follow benzoylation of the nitride with increased driving force and subsequent trapping of benzamide. Our results provide a new, PCET-based N$_2$ fixation protocol for one-pot electrochemical nitride transfer from N$_2$ derived nitride 2b to give 1b and benzonitrile. All yields refer to rhenium nitride complex 2b; FE = Faradaic Efficiency.\[a\] The yield in BzOH defines an upper limit; it was indirectly estimated by $^1$H-NMR spectroscopy from integration of the signals of BzO-(CH$_2$)$_2$Br, which are superimposed with those of BzOH (see Supporting Information pp. S54–S58).

| Entry | PCET reagents | Yields (FE) |
|-------|---------------|-------------|
|       | red or $E_{\text{appl}}$ [H$^+$] | Re | PhCN | BzO | BzOH | BzO(C(=O)CH$_3$)Br |
| 1     | Fe$^{2+}$ / [LutH]BAr$^{24}$ | 55% (1b) | 56% | 43% | 23% | 26% |
| 2     | Fe$^{2+}$ / [Et$_3$NH]BAr$^{24}$ | 82% (1b) | 77% | 78% | 17% | 84% |
| 3     | Fe$^{2+}$ (without acid) | 9% (1b) | 10% | <1% | 58% | 60% |
| 4     | -0.68 V / [LutH]BAr$^{24}$ (1.62 e$^-$/Re) | 66% (1b) | 51% | 63% | 18% | 57% | 117% |
| 5     | -0.74 V / [Et$_3$NH]BAr$^{24}$ (1.86 e$^-$/Re) | 69% (1b) | 66% | 70% | 47% | - | 133% |

by $^{31}$P NMR spectroscopy in 55% yield, together with an equimolar amount of benzonitrile (56%). The use of the $^{15}$N labelled nitride complex from photoelectrochemical splitting of $^{15}$N$_2$, confirmed nitride transfer to the organic product (Figure S76). Ammonium as a potential product is not detected. Besides PhCN, benzoyl anhydride (43%) and benzoic acid (23%) are observed. This is in line with initial formation of benzamide, which subsequently reacts with additional BzBr to benzonitrile and the anhydride/acid.\[34\]

The formation of some 4-bromobutyl benzoate (26%) is attributed to electrophilic ring opening of THF with benzoyl bromide, which is catalysed by Lewis acids.\[35\]

Entry 2). Without additional acid, benzonitrile yields are strongly reduced (10%; Scheme 6, Entry 3). Furthermore, instead of 1b the rhenium(III) imine complex [ReBr$_3$(N- (CHCH$_2$PPr$_2$)(CH$_2$CH$_2$PPr$_2$))] (9) is spectroscopically observed in 9% yield as the only identified rhenium product upon comparison with an original sample. Complex 9 is most conveniently obtained from reaction of 1 with 2,4,6-triisobutylphenoxyl radical and was fully characterized including X-ray crystallography.\[36\]

The dehydrogenation of the PNP ligand during reductive nitride transfer underlines the necessity of acid for full nitrogen release, presumably via PCET after N-benzoylation.

One-pot electrochemical nitride transfer is accomplished upon CPE of 2b at the potential of the first reduction ($E_{\text{red}} = -0.68$ V) in the presence of BzBr (5 eq.) and [LutH]BAr$^{24}$ (3 eq.) for 22 h (Scheme 6, Entry 4). Similar yields in benzamide (51%; FE = 63%) and 1b (66%; FE = 81%) could be obtained compared to chemical reduction (Scheme 6, Entry 1). The spectroscopic yield in 1b is in line with the transfer of 1.62e$^-$ per Re during electrolysis. With [Et$_3$NH]BAr$^{24}$ (Scheme 6, Entry 5), slightly increased yields in benzonitrile (66%; FE = 70%) and 1b (69%; FE = 73%) are obtained, whereas 1.88e$^-$ per Re are transferred. For the electrochemical protocols, slightly higher amounts of BzBr (5 eq.) are required to compensate for an increased formation of the side product from THF ring opening, 4-bromobutyl benzoate (117% and 133%), as compared with the use of chemical reductants. A control electrolysis experiment without 2b confirmed the absence of PhCN, BzO, and BzOH, yet indicated formation of the THF ring-opening product. The electrochemical protocol closes a 2-step electrosynthetic cycle for benzonitrile generation from N$_2$ after photoelectrochemical N$_2$ splitting (Scheme 7).

**Conclusion**

In summary, we have demonstrated a two-step photoelectrochemical cycle for the fixation of dinitrogen with benzoyl bromide to yield benzonitrile. Moving to the higher halide precursors significantly shifts both reductive N$_2$ activation to less negative potentials and photolytic N–N splitting deeper into the visible range. The unfavourable first PCET step renders the resulting nitride (X = Br) unsuitable for efficient ammonia generation. PCET cannot compete with benzoylation/reduction, which can at least in part be attributed to π-stabilization of the unusual rhenium(IV) imido state by the benzoyl substituent. This thermochemical bias provides a PCET-based, conceptual basis to enable selective, electrochemical formation of nitrogenous organic products over ammonia production. We have demonstrated this by the development of an electrochemical one-pot protocol for nitride transfer upon reduction at mild potential ($E_{\text{appl}} = -0.74$ V), which is compatible with the organic electrophile (BzBr) and acid (Et$_3$NH$^+$), to restore parent 1b. The release of benzonitrile in 66% yield is attributed to two PCET steps that follow benzoylation of the nitride with increased driving force and subsequent trapping of benzamide. Our results provide a new, PCET-based N$_2$ fixation route.
strategy for the selective formation of organic, nitrogenous products.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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