Metal-Ligand Cooperative Synthesis of Benzonitrile via Electrochemical Reduction and Photolytic Splitting of Dinitrogen

Florian Schendzielorz,[a] Markus Finger,[a] Josh Abbenseth,[a] Christian Würtele,[a] Vera Krewald,[b] and Sven Schneider*[a]

Dedicated to Prof. Dr. F. Tuczek on the occasion of his 60th birthday

Abstract: Thermal nitrogen fixation relies on strong reductants to overcome the extraordinarily large N–N bond energy. Photochemical strategies that drive N2 fixation are scarcely developed. Here, the synthesis of a dinuclear N2-bound complex is presented upon reduction of a rhenium(III) pincer platform. Photocatalytic splitting into terminal nitride complexes is triggered by visible light. Clean N2 transfer with benzoyl chloride to free benzamide and benzonitrile is enabled by cooperative 2H+/2e- transfer of the rhenium ligand. A three-step cycle is demonstrated for N2 to nitrile fixation that relies on electrochemical reduction, photochemical N2-splitting and thermal N2-transfer.

The Haber-Bosch process consumes large amounts of energy, for the generation of H2. Electrocatalytic N2 reduction has therefore been targeted as an attractive alternative.1,2 Nitrogen fixation at ambient conditions with molecular catalysts has seen remarkable progress,3 in some cases also for electrochemical ammonia generation.4 The direct synthesis of other compounds than NH3 from N2 remains a formidable challenge. Catalytic protocols are only known for trisilylamine,5 Nitrides,6-7 isocyanates,9 silylamines,10,11 and borylamines,12 have been synthesized with stoichiometric, cyclic reaction sequences that allow for evaluating strategies to offset the extremely strong N–N bond (225 kcal/mol), enable E–N (E = C, Si, B) bond formation and deliver six reduction equivalents. All reported “synthetic cycles” proceed through initial N2 cleavage into nitride complexes. Subsequent N-transfer typically requires strong electrophiles like alkyl triflates. The thermochemistry of N2 splitting must therefore be tuned to avoid nitride overstabilization and enable functionalization with reagents that are more compatible with reductive conditions.

We have examined N2 activation and splitting, i.e. triggered by chemical or electrochemical reduction of pincer halide complexes.13,14 The rhenium(III) precursor [ReCl3(PNP(µ-Bu))2] (1; PNP(µ-Bu) = N(CH2CH2P(Bu)2)) exhibits a complex mechanism via rapid ReIII/ReI-reduction, N2-binding, halide loss, ReI/ReII-reduction and ReI/ReII-comproportionation.15 Splitting of the resulting dinuclear complex [(µ-N2)(ReCl(PNP(µ-Bu))2)] (2) is rate-determining and gives the nitride complex [ReNCl(PNP(µ-Bu))] (3). A simple electronic structure model for the Re–N–N–Re core of key intermediate 2 (π-Re2-core configuration; Scheme 1) provides a starting point to tune the thermochemistry.16 We now report a modified platform that splits N2 photolytically into more reactive nitrides that can be transferred with benzoyl chloride. The pincer ligand serves as 2e+/2H+ reservoir, enabling electrochemical N2 reduction, photocatalytic splitting and thermal transfer within a three-step cycle.

![Scheme 1. Schematic frontier orbital correlation diagram for the splitting of N2-bridged complex 2 into two nitrides 3 (n.b. = non bonding).](https://example.com/scheme1)

The ReII complex [ReCl3(HPnPPh)] (4) was obtained in 70 % isolated yield.18 In contrast to 1, the amide complex [ReCl3(PNPPh)] could not be isolated in analytical purity. 4 displays strongly shifted NMR resonances, as exemplified by the 31P(1H)-NMR signal (δp = -1525.9 ppm). However, the sharp signals exhibit well-resolved J-coupling. This observation can be rationalized with a magnetic, energetically isolated ground state that results from excited state admixture via spin-orbit coupling. Contributions from temperature independent paramagnetism (TIP) are well documented for 3D row complexes with d⁵ (octahedral Re⁵, Os⁵) and d⁶ configuration (square-planar, Os⁶).19 Single-crystal X-ray diffraction confirmed meridional coordination of the neutral diphosphinoamine ligand (Figure 1a).

---

[a] M. Sc. F. Schendzielorz, Dr. Markus Finger, M. Sc. J. Abbenseth, Dr. C. Würtele, Prof. Dr. S. Schneider
Georgia-August-Universität
Institut für Anorganische Chemie
Tammannstrasse 4, 37077 Göttingen (Germany)
E-mail: sven.schneider@chemie.uni-goettingen.de
[b] Dr. Vera Krewald
Department of Chemistry
University of Bath
Claverton Down, Bath BA2 7AY, United Kingdom

Supporting information for this article is given via a link at the end of the document.
Complex 4 was investigated by cyclic voltammetry (CV) under argon. Quasireversible, scan rate dependent reduction is observed at -1.84 V suggesting chloride loss on the CV timescale.\textsuperscript{16, 18} Chemical reduction with 1 equiv. CoCl\(_2\) in tetrahydrofuran (THF) under an N\(_2\) atmosphere (Scheme 2) gives an intensely blue product (5) in around 60\% isolated yield. Complex 5 exhibits sharp and strongly shifted NMR signals suggesting an even-electron compound with a TIP contribution. Symmetric N\(_2\) binding was confirmed by a single signal in the \(\text{\textsuperscript{15}}\text{N}\{\text{H}\}\text{-NMR} \) spectrum and a band at 1733 cm\(^{-1}\) (\(\text{\textsuperscript{15}}\text{N}_2\): 1675 cm\(^{-1}\)) in the resonance Raman spectrum.\textsuperscript{16} Two doublets in the \(\text{\textsuperscript{31}}\text{P}\{\text{H}\}\text{-NMR} \) spectrum (\(\delta = -370.6/-380.4 \text{ ppm}\)) with mutual trans-coupling (\(\tau_{\text{PP}} = 237 \text{ Hz}\)), eight \(^1\text{H}\) NMR signals assignable to C\(_\text{H}\)-groups and one amine NH-signal are in agreement with an N\(_2\) bridged, dinuclear compound with C\(_2\) symmetry, in analogy to 2.\textsuperscript{16b} Structural assignment as \([\text{µ-\text{N}}_2]\text{[ReCl}_2\text{(HPNP)}\text{]}\text{]}_2\) further substantiated by LIFDI mass spectrometry.

The molecular structure was confirmed by single crystal X-ray diffraction (Figure 1b).\textsuperscript{16} The asymmetric unit features two octahedrally coordinated, linearly N\(_2\)-bridged Re-ions. The N–N bond length (1.169(5) Å) is slightly shorter compared with 2 (1.202(10) Å),\textsuperscript{16b} indicating moderate N\(_2\) activation in agreement with the Raman data. In contrast to 2, the pincer nitrogen atoms are located trans to the N\(_2\) bridge. The two \([\text{ReCl}_2\text{(HPNP)}\text{]}\) fragments are twisted with respect to each other by 75.5° giving rise to idealized C\(_2\) symmetry.

Unlike 2, complex 5 shows remarkable thermal stability. No decomposition was observed over several days, even upon heating to 60 °C in THF. Thermal splitting was therefore examined computationally. Density functional theory (DFT) nicely reproduced the geometry of 5.\textsuperscript{16} In analogy to 2,\textsuperscript{16b} an electronic triplet configuration was obtained as the ground state. While any spin-orbit coupling effects likely present in this dimer are insufficiently described by DFT, the high kinetic barrier (\(\Delta G^\ddagger_{\text{298}} = 41.8 \text{ kcal mol}^{-1}\)) computed for thermal cleavage of 5 into the trans-dichloro nitride \([\text{ReN}\text{(trans-Cl)}\text{(HPNP)}\text{]}\) (6\textsuperscript{trans}) is in accord with experiment and contrasts with cleavage of 2 (\(\Delta G^\ddagger_{\text{298}} = 26.9 \text{ kcal mol}^{-1}\)). Interestingly, splitting of 5 into 6\textsuperscript{trans} is almost thermoneutral (\(\Delta G^\ddagger_{\text{298}} = 2.2 \text{ kcal mol}^{-1}\)), as compared with strongly exergonic splitting of 2 into square-pyramidal 3 (\(\Delta G^\ddagger_{\text{298}} = -40.3 \text{ kcal mol}^{-1}\)).\textsuperscript{16b}

The less favorable thermochemistry for six-coordinate 6\textsuperscript{trans} is attributed to the nitride trans-influence as expressed by a long Re-N\(_{\text{PNP}}\) bond (2.53 Å) and distorted pincer binding. Accordingly, relaxation to isomeric \([\text{ReN} \text{(cis-Cl)}\text{(HPNP)}\text{]}\) (6) is strongly favorable (\(\Delta G^\ddagger_{\text{298}} = -11.0 \text{ kcal mol}^{-1}\) per molecule).

The striking thermal stability of 5 vs. 2 can be rationalized by qualitative molecular orbital (MO) considerations. Thermal cleavage of a linearly N\(_2\) bridged Mn:N\(_2\) core proceeds via electron transfer into an MO with M–N–N–M \(\pi^*\) character (Scheme 1) within a zig-zag shaped transition state (TS).\textsuperscript{15, 13b, 15} Ligands \textit{trans} to the N\(_2\)-bridge raise this MO in energy, thereby disfavoring N\(_2\)-splitting. A classic case for such geometry controlled reactivity might be the trisanilides \([\text{[RArN]_2}\text{Mo}_2\text{(N}_2\text{)}]\),\textsuperscript{20} which split into nitrides in contrast to analogous triamidoamine complexes.\textsuperscript{3a}

To overcome kinetically hindered N\(_2\)-splitting we sought to populate N–N antibonding MOs by electronic excitation.\textsuperscript{5, 21, 22} Photolysis of 5 in THF with a Xe arc lamp (\(\lambda > 305 \text{ nm}\)) led to gradual color change to yellow over 2 h.\textsuperscript{15} P and \(^1\text{H}\) NMR spectra revealed the formation ofcis-dichloro nitride complex 6 (Scheme 2) in 95 \% spectroscopic yield upon comparison with an original sample.\textsuperscript{16} Use of \(^{15}\text{N}\)-labelled 5 confirmed photolytic splitting of the N\(_2\) ligand by \(^{15}\text{N}\{\text{H}\}\) NMR spectroscopy. A quantum yield below 1 \% was estimated by actinometry.\textsuperscript{16} The configuration of 6 requires isomerization before or after N\(_2\)-splitting. Photolysis was therefore carried out in the presence of NHexCl (0-500 equiv.).\textsuperscript{16} The independence of the reaction rate excludes isomerization by chloride (photo)dissociation prior to or as the rate determining step.
In the solid state (Figure 1c),\textsuperscript{16} 6 retains octahedral coordination with one significantly elongated Re--Cl bond (2.4309(7) Å vs. 2.6712(7) Å), reflecting the nitride trans-influence. In turn, the Re≡N bond (1.669(2) Å) is longer compared to five-coordinate [Re(N)(HPNP\textsuperscript{P=N})Cl] (1.642(4) Å).\textsuperscript{12a} Addition of NaBAr\textsubscript{4}d (BAr\textsubscript{4}d = tetrakis-[3,5-(trifluoromethyl)phenyl]borate) to 6 in THF results in two new \textsuperscript{13}P NMR signals that are assigned to two isomers of [Re(N)(HPNP\textsuperscript{P=N})Cl].\textsuperscript{15} In turn, 6 is fully restored upon addition of NH\textsubscript{3}Cl. Hence, six-coordinate [Re(N)(Cl)(HPNP\textsuperscript{P=N})] is the dominant species in solution. Reduced steric shielding facilitates chloride coordination and thereby weakening of metal nitride bonding.

Heating of 6 with PhC(O)Cl (2 equiv.) at 80 °C in 1,4-dioxane over 15 h gives a new rhenium species (7) in 71% yield (Scheme 2). Paramagnetically shifted and sharp NMR signals support reduction to Re\textsuperscript{II}. Two chemically inequivalent P-atoms (\(\delta_p = -1592.6, -1615.5 \text{ ppm;} \ 2\delta_p = 248 \text{ Hz}) and the \(^1\text{H}\) and \(^{13}\text{C}\) NMR signatures are in agreement with pincer oxidation to an imine ligand.\textsuperscript{15} Formation of [ReCl\textsubscript{3}(P=NP\textsuperscript{P=N})] (P=NP\textsuperscript{P=N} = (CH\textsubscript{2}CH\textsubscript{2}Pr\textsubscript{2})(CH\textsubscript{2}CH\textsubscript{2}Pr\textsubscript{2})) was confirmed by LIFDI-MS and comparison with an authentic sample.\textsuperscript{16} Crystallographic characterization (Figure 1d) evidences nitride transfer and pincer dehydrogenation.\textsuperscript{16} Two products account for 94 % of the nitride ligand, i.e. benzamide (30 %), and benzonitrile (64 % with equimolar benzoic acid), respectively. PhCN and PhCO\textsubscript{2}H are products from the reaction of benzamide with benzyol chloride,\textsuperscript{23} supporting that PhC(O)NH\textsubscript{2} is the immediate product of nitride benzoylation and 2e/2H\textsuperscript{+} transfer from the pincer ligand. Related reactivity was observed for [Ru(N)(HPNP\textsuperscript{P=N})\textsuperscript{P=N}], which gives [Ru(NH\textsubscript{3})(O)(CPh)(P=NP\textsuperscript{P=N}P=N)] upon reaction with para-methoxy benzoic acid.\textsuperscript{24} However, in that case azide was used as nitrogen source rather than N\textsubscript{2}.

Next, re-reduction of the imine pincer ligand was examined to evaluate the amine/imine redox couple as cooperating ligand reservoir for 2e/2H\textsuperscript{+} proton coupled electron transfer (PCET). 7 does not react with H\textsubscript{2} under thermal or photolytic conditions. However, chemical reduction is possible with stepwise addition of Li[HBEt\textsubscript{3}] and diphenylammonium chloride (Scheme 2). On this route, 4 is obtained in 62 % spectroscopic yield due to the formation of rhenium hydrides as byproducts, which reform 7 upon hydrolytic quenching.

We therefore turned to electrochemical regeneration of 4. The CV of 7 exhibits quasi-reversible reduction at -1.70 V. Titrating in benzoic acid (0-15 eq.; Figure 3a) results in a pronounced increase of the cathodic current and buildup of a second, quasi-reversible reduction feature at -1.84 V, which is assigned to parent 4. The strong increase of the first wave is indicative of multielectron reduction in the presence of acid. In fact, the viable intermediate [ReCl\textsubscript{3}(P=NP\textsuperscript{P=N})] (8) exhibits a quasi-reversible reduction at -1.16 V,\textsuperscript{16} confirming a potential inversion after the first e/2H\textsuperscript{+}-transfer to 7. The electrochemical data in the presence of acid is therefore rationalized with two subsequent PCET steps at around ~1.7 V that regenerate 4.

Controlled potential electrolysis (CPE) of 7 at the half peak potential of the first reduction feature (\(E = -1.65 \text{ V}) did not give appreciable amounts of 4 in the presence of benzoic acid (10 eq). 2,6-Dichlorophenol (DCP) was therefore employed, which exhibits about same p\textsubscript{Ka} as benzoic acid (p\textsubscript{Ka}(\textsubscript{THF}) = 25.1)\textsuperscript{25} yet a conjugate base that is less prone to metal coordination. In fact,
bulk electrolysis of 7 at $E = -1.65$ V in the presence of DCP (10 eq.) for 7 h results in full consumption of 7 and formation of 4 as the only electroactive species. $^1$H NMR spectroscopy confirmed a yield of 99 % and coulometry the transfer of 1.96 e$^-$ per 7.

The quantitative regeneration of 4 motivated the examination of in situ electrochemical N$_2$ activation. In a CPE experiment, 7 was electrolyzed with DCP (10 eq.) under N$_2$ for 8 h at $E = -1.65$ V, followed by 5 h at $E = -1.85$ V, i.e. the half potential of the reduction of 4 (Figure 3b). Overall, 3.32 e$^-$ per Re atom were transferred. Formation of complex 5 during the second electrolysis step was indicated by the deep blue color and confirmed by $^1$H and $^{31}$P($^1$H) NMR spectroscopy. UV/Vis spectroscopic quantification gave a yield around 70 % (Scheme 3). In situ photolysis (390 nm LED) of this mixture revealed N$_2$ splitting to nitride 6 as the only detectable product by $^{31}$P($^1$H) and $^1$H NMR spectroscopy. However, the yield in 6 dropped to 14 % with respect to parent 7, i.e. considerably lower compared to photolysis of isolated 5.

In summary, a three-step cycle for the generation of benzamide/benzonitrile from N$_2$ in overall 61 % yield (with respect to N) was established that relies on electrochemical N$_2$ activation, photochemical splitting into nitrides and thermal nitrogen transfer (Scheme 3). This model reveals some basic principles in comparison to our previously reported system. Use of a sterically less encumbered pincer ligand stabilizes higher coordination numbers. In consequence, thermal N$_2$ splitting becomes less favorable which can be overcome by photolysis with visible light. Based on the experimental and theoretical data, the photochemical reactivity is associated with the population of a dissociative state with Re–N$_2$ MLCT character. The higher coordination number weakens nitride bonding, thus enabling the use of a weaker electrophile than alkyl triflates. Importantly, the cooperating pincer ligand serves as a reservoir for nitrogen hydrogenolysis upon 2e$^-$/2H$^+$-PCET and electrochemical rehydrogenation. Our results demonstrate how metal-ligand cooperativity and photo- and electrochemical approaches can facilitate the design of platforms for N$_2$ fixation.

Figure 3. Left: CV of 7 in presence of 0–15 eq. benzoic acid. Right: CV of 7 with 10 eq 2,6-dichlorophenol under N$_2$ before CPE (orange), after 8 h CPE at -1.65 V (pink) and after subsequent 5 h CPE at -1.85 V (blue).

Scheme 3. Optimized, three-step synthetic cycle.

Acknowledgements

This work was supported by the European Research Council (ERC Consolidator Grant Agreement 646747, grant holder S.Sch.). V.K. acknowledges a 50th Anniversary Prize Fellowship from the University of Bath and its Balena High Performance Computing (HPC) Service. The authors thank Dr. C. Volkmann for solving the crystal structure of complex 8.

Keywords: Nitrogen Fixation • Rhenium • Pincer Ligand • Photochemistry • Electrochemistry

[1] S. L. Foster, S. I. Perez Bakovic, R. D. Duda, S. Maheshwari, R. D. Milton, S. D. Minteer, M. J. Janik, J. N. Renner, L. F. Greenlee, Nat. Catal. 2018, 1, 490.
[2] B. M. Lindley, A. M. Appel, K. Krogh-Jespersen, J. M. Mayer, A. J. M. Miller, ACS Energy Lett. 2016, 1, 698.
[3] (a) R. Schrock, Angew. Chem., Int. Ed. 2008, 47, 5512. (b) H. Tanaka, Y. Nishibayashi, K. Yoshihara, Acc. Chem. Res. 2016, 49, 987. (c) R. J. Burford, M. D. Fryzuk, Nat. Rev. Chem. 2017, 1, 00261.
[4] (a) C. J. Pickett, J. Talarmin, Nature 1985, 317, 652. (b) J. Y. Becker, B. Posin, J. Electroanal. Chem. Interfacial Electrochem. 1988, 250, 385. (c) J. Y. Becker, S. Avraham, B. Posin, J. Electroanal. Chem. Interfacial Electrochem. 1987, 230, 143. (d) N. P. Luneva, S. A. Miranova, A. E. Shilov, M. Y. Antipin, Y. T. Struchkov, Angew. Chem., Int. Ed. Engl. 1993, 32, 1178. (e) T. Munisamy, R. R. Schrock, Dalton Trans. 2012, 41, 130. (f) T. J. Del Castillo, N. B. Thompson, J. C. Peters, J. Am. Chem. Soc. 2016, 138, 5341. (g) M. J. Chatley, T. J. Del Castillo, B. D. Matson, J. C. Peters, J. Am. Chem. Soc. 2018, 140, 6122.
[5] Y. Tanabe, Y. Nishibayashi, Coord. Chem Rev. 2013, 257, 2551.
This is the peer reviewed version of the following article: F. Schendzielorz et al., Angew. Chem. Int. Ed., 2019, 58, 830-834, which has been published in final form at DOI: 10.1002/anie.201812125. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

[6] (a) J. S. Figueras, N. A. Piro, C. R. Clough, C. C. Cummins, J. Am. Chem. Soc. 2006, 128, 940. (b) J. J. Curley, E. L. Sceats, C. C. Cummins, J. Am. Chem. Soc. 2006, 128, 14036.

[7] (a) I. Klopsch, M. Kinauer, M. Finger, C. Würtele, S. Schneider, Angew. Chem. Int. Ed. 2016, 55, 4786. (b) I. Klopsch, F. Schendzielorz, C. Volkmann, C. Würtele, S. Schneider, Z. Anorg. Allg. Chem. 2018, 644, 916.

[8] M. M. Guru, T. Shima, Z. Hou, Angew. Chem. Int. Ed. 2016, 128, 12504.

[9] A. J. Keane, W. S. Farrell, B. L. Yonke, P. Y. Zavalij, L. R. Sita, Angew. Chem. Int. Ed. 2015, 54, 10220.

[10] Q. Liao, A. Cavaillé, N. Saffon-Merceron, N. Mézailles, Angew. Chem. Int. Ed. 2016, 128, 11378.

[11] L. M. Duman, L. R. Sita, J. Am. Chem. Soc. 2017, 139, 17241.

[12] M. F. Espada, S. Bennaamane, Q. Liao, N. Saffon-Merceron, S. Massou, E. Clot, N. Nebra, M. Fustier-Boutignon, N. Mézailles, Angew. Chem. Int. Ed. 2018, 130, 13047.

[13] (a) I. Klopsch, M. Finger, C. Würtele, B. Milde, D. B. Werz, S. Schneider, J. Am. Chem. Soc. 2014, 136, 6881. (b) B. M. Lindley, R. S. van Alten, M. Finger, F. Schendzielorz, C. Würtele, A. J. M. Müller, I. Siewert, S. Schneider, J. Am. Chem. Soc. 2018, 140, 7922.

[14] G. Silantiyev, M. Förster, B. Schluschaß, J. Abbenseth, C. Würtele, C. Volkmann, M. C. Holthausen, S. Schneider, Angew. Chem. Int. Ed. 2017, 56, 5872.

[15] I. Klopsch, E. Y. Yuzik-Klimova, S. Schneider, Top. Organomet. Chem. 2017, 60, 71.

[16] For synthetic, spectroscopic, computational and crystallographic details see Electronic Supporting Information (ESI).

[17] (a) J. Chatt, G. J. Leigh, D. M. P. Mingos, J. Chem. Soc. (A) 1969, 1674. (b) J. Abbenseth, M. Diefenbach, S. C. Betel, C. Würtele, C. Volkmann, S. Demeshko, M. C. Holthausen, S. Schneider, Chem. Commun. 2017, 53, 5511.

[18] All electrochemical data is reported vs. FeCp²⁻/FeCp²⁺.

[19] C. E. Laplaza, M. J. A. Johnson, J. C. Peters, A. L. Odom, E. Kim, C. C. Cummins, G. N. George, I. J. Pickering, J. Am. Chem. Soc. 1996, 118, 8623.

[20] C. E. Laplaza, C. C. Cummins, Science 1995, 268, 861.

[21] V. Krewald, Dalton Trans. 2018, 47, 10320.

[22] (a) J. J. Curley, T. R. Cook, S. Y. Flores, P. Müller, C. C. Cummins, J. Am. Chem. Soc. 2008, 130, 9394. (b) H. Kunkely, A. Vogler, Angew. Chem. Int. Ed. 2010, 49, 1591. (c) A. S. Hüüs, J. J. Curley, C. C. Cummins, D. A. Blank, J. Phys. Chem. B 2013, 117, 1429. (d) T. Miyazaki, H. Tanaka, Y. Tanabe, M. Yuki, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, Angew. Chem. Int. Ed. 2014, 53, 11488. (e) L. M. Duman, W. S. Farrell, P. Y. Zavalij, L. R. Sita, J. Am. Chem. Soc. 2016, 138, 14856.

[23] D. Davidson, H. Skovronek, J. Am. Chem. Soc. 1958, 80, 376.

[24] (a) B. Askevold, J. Torres Nieto, S. Tussupbayev, M. Diefenbach, E. Herdewick, M. C. Holthausen, S. Schneider, Nature. Chem. 2011, 3, 532. (b) B. M. Lindley, Q. J. Bruch, P. S. White, F. Hasanayn, A. J. M. Miller, J. Am. Chem. Soc. 2017, 139, 5305.

[25] a) D. Barrón, J. Barbosa, Anal. Chim. Acta 2000, 403, 339. b) D. Barrón, J. Barbosa, Anal. Chim. Acta 1992, 269, 157.
COMMUNICATION

Cooperative Fixation: N₂ fixation to benzonitrile and benzamide is reported within a three-step cycle that utilizes electrochemical reduction, photochemical N₂ splitting and thermal N-transfer with benzoyl chloride. Product formation is enabled by cooperativity of the functional pincer ligand, which serves as a 2H⁺/2e⁻ reservoir.

F. Schendzielorz, M. Finger, J. Abbenseth, C. Würtele, V. Krewald, * S. Schneider*

Page No. – Page No.
Metal-Ligand Cooperative Synthesis of Benzonitrile via Electrochemical Reduction and Photolytic Splitting of Dinitrogen