Synthesis of Benzonitrile from Dinitrogen

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Dedicated Prof. Dr. A. C. Filippou on the occasion of his 60th birthday.

Abstract: The rhenum mediated synthesis of benzonitrile is reported with direct use of N₂ as a nitrogen source. The reaction affords benzonitrile in about 30% overall yield upon N₂ splitting and benzylation of resulting terminal nitrile. Subsequent oxidation of an intermediate phenylketimido compound restores the parent rhenum complex within a full four-step synthetic cycle. The reaction shows that previously observed nitrile tautomerization is not a prerequisite for nitrile synthesis from N₂ with this system.

The Haber-Bosch process (HBP) currently provides synthetic ammonia at a massive scale (approx. 150 Mt/a). The high energy demand has fueled many efforts to develop bioinspired catalysts for nitrogen fixation at ambient conditions. Remarkable recent progress followed Schrock’s seminal work, with turn-over numbers up to 230 for the currently most active catalysts.

![Scheme 1. Oxidative release of acetonitrile from ketimido complex 1 as part of a synthetic cycle for direct N-transfer from N₂ to acetonitrile.][1]

About 20% of the industrially produced ammonia serves as feedstock for nitrogen containing chemicals, such as amines, nitriles or N-heterocyclic compounds. Direct N₂ conversion to organic products therefore is an attractive goal from the point of atom, energy and redox economy. Stoichiometric C–N functionalization of N₂, e.g. with C-electrophiles, heterocumulenes, or carbon monoxide, is well established and several quasi-catalytic synthetic cycles were reported as a proof-of-principle. Inspired by Cummins’ work, we recently reported a synthetic cycle for the transformation of N₂ to acetonitrile, which is an attractive target as judged by the similar bond energies of C=N and N≡N triple bonds. The reaction proceeds via rhenum mediated splitting of N₂ and subsequent functionalization of the resulting nitriles, by alkylation, deprotonation and ligand oxidation with N-chlorosuccinimide.

Examination of this final oxidation step by stepwise 1-electron oxidation of ketimido intermediate 1[Br] (Scheme 1) gave an unprecedented rhenum(V) vinyl imido complex (2), i.e. a tautomer of the unobserved rhenum(III) nitrile species. Acetonitrile release is finally triggered by addition of a chloride source and catalytic amounts of base (e.g. DBU) presumably to enable vinylimido tautomerization. This observation raises the question whether nitriles that cannot tautomerize, such as arylnitriles ArCN, are also accessible through such a reaction sequence. Here we present a full synthetic cycle for the direct synthesis of benzonitrile from dinitrogen via N₂ splitting into nitrates.

Chemical or electrochemical reduction of the rhenum pincer complexes [ReCl₃(PNP)] or [ReCl₃(PNP)] (3; PNP = (CH₂)₆P(Bu₃)₂) under N₂ (1 bar) affords the rhenum(V) nitrile complex [Re(NCl)(PNP)] (4).[7,8,11] Starting from the rhenum(IV) chloride, isolated yields between 60-70% are obtained with Na/Hg as reductant in THF at room temperature (Scheme 2). The terminal nitrile complex can be selectively alkylated at the nitrile moiety with alkyltriflates ROTf (R = Me, Et) giving the imido complexes [Re(NR)(PNP)]OTf (R = Me (5), Et (5')),[7,8,11] In contrast to these triflate reagents, benzylation is not stable at room temperature. PhCH₂OTf was therefore prepared in situ according to published procedures for other alkyltriflates from excess benzylbromide and AgOTf. Unlike with methyl- and ethyltriflate, only the previously reported protonation product of 4,[7,8] i.e. the amine complex [Re(NCl(HN(CH₂)₆P(Bu₃)₂))OTf], was obtained almost quantitatively as indicated by comparison of the NMR spectra. The origin of the proton remains unclear at this point. However, nitrile benzylaion is observed upon addition of a non-nucleophilic base. The benzylnitrido complex [Re(NCH₂Ph)(PNP)]OTf (5P) is obtained in up to 90% yield with in situ generated benzynitride in the presence of ca. 2 eq of 2,6-di-tert-butyl-4-methylpyridine (Scheme 2).

The green benzylnitrido complex 5P exhibits C₆ symmetry on the NMR timescale. The chemical shift of the ¹H NMR signal (δ(C=N) = 90.3 ppm) resembles the respective methyl- and ethylnitrido complexes 5M (δ(C=N) = 90.7 ppm) and 5E (δ(C=N) = 90.1 ppm), respectively.[7,8] Similarly, the ¹H NMR signatures of their pincer ligands reveal closely related characteristics. The methylene protons of the benzylnitrido moieties (CH₆(Ph)) of 5P are found as a singlet resonance at 4.60 ppm in the ¹H NMR spectrum. Furthermore, this signal and the aromatic ¹H NMR signals exhibit cross peaks in the NOESY spectrum with the same set of 4Bu groups, yet not with pincer backbone protons. This observation confirms selective nitrile rather than pincer amide benzylaion.

Benzylidene complex 5P is quantitatively deprotonated by strong bases, such as KOtBu or K(SiMe₃)₂. For example, with K(SiMe₃)₂, the azavinylidene complex [Re(NCH₂Ph)(PNP)]OTf (1P, Scheme 2) is obtained in about 80% isolated yield. ¹P, ¹H and ¹³C NMR spectroscopic characterization indicates two full sets of

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Supporting information for this article is given via a link at the end of the document.

[1] DOI: 10.1002/zaac.201800181

This is the peer reviewed version of the following article: “I. Klopsch et al., Z. Anorg. Allg. Chem., 2018, 916,” which has been published in final form at DOI: 10.1002/zaac.201800181. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.
signals with a ratio of approx. 2:3 for ketimide $^1_{\text{Ph}}$. As for the methylketimido complex $^1_{\text{Ph}}$, the two sets are assigned to the two stereoisomers that are interconverted by the hindered rotation around the C=N-Re azavinylidene core. The vinylidene (PhCHN) protons of the two isomers are observed as signals at $\delta = 3.75$ ppm and 5.47 ppm, respectively, both exhibiting coupling with the two pincer $^{31}$P nuclei ($J_{\text{P-N}} = 2.0$ and 2.2 Hz).$^{1,2}$H-$^1$H-COSY and -NOESY spectra at room temperature (Figure S7 and S8) allow for an unequivocal assignment of the partially superimposed aromatic proton signals for both isomers. Particularly the ortho protons are considerably broadened at room temperature. Therefore, the isomer mixture was investigated by variable temperature NMR spectroscopy (-70 to +60°C, Figure S9). At 60°C each isomer shows three sharp signals in the aromatic region for ortho, meta and para protons, respectively. Upon cooling, the ortho- and the meta-protons of both isomers split into two sharp sets, respectively, at -70°C, i.e. confirmed by 1H-1H COSY spectroscopy (Figure S11). The dynamics are in agreement with frozen rotation of the phenyl ring around the Ph–C bond, while interconversion of the two isomers (rotation around C=N-Re) is not observed within this temperature interval.

![Molecular structure of complex $^1_{\text{Ph}}$ derived by single-crystal X-ray diffraction (one of two independent molecules in the asymmetric unit). ORTEP plots with anisotropic displacement parameters set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re1-N1 1.938(2), Re1-N2 1.798(2), Re1-C11 2.3964(6), N2-C21 1.289(3), N1-Re1-N2 114.54(10), N1-Re1-C11 137.19(6), P1-Re1-P2 161.80(2), Re1-N2-C21 170.2(2).](image)

**Figure 1.** Molecular structure of complex $^1_{\text{Ph}}$ derived by single-crystal X-ray diffraction (one of two independent molecules in the asymmetric unit). ORTEP plots with anisotropic displacement parameters set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re1-N1 1.938(2), Re1-N2 1.798(2), Re1-C11 2.3964(6), N2-C21 1.289(3), N1-Re1-N2 114.54(10), N1-Re1-C11 137.19(6), P1-Re1-P2 161.80(2), Re1-N2-C21 170.2(2).

In summary, we demonstrated the synthesis of benzonitrile upon direct use of molecular N$_2$ as nitrogen source via splitting into terminal nitrides, benzylization, deprotonation and oxidation of phenylketimido intermediate $^4_{\text{Ph}}$. The putative nitrile complex that is formed form oxidation of $^1_{\text{Ph}}$ with NCS prior to product release is inherently not capable of nitrile (M=N=CHR) / enimido (M=N–CH=CR) tautomerization. Therefore, this rearrangement that was observed in acetonitrile formation is not a prerequisite for nitrile formation with this platform. Our rhenium platform might therefore be suitable for a broad range of organonitrile target molecules.

**Experimental Section**

The synthetic cycle for the synthesis of benzonitrile directly from N$_2$ (DTBMP = 2,6-di-tert-butyl-4-methylpyridine).

Single crystals suitable for X-ray diffraction were obtained by crystallization from pentane (Figure 1). The unit cell contains two crystallographically independent molecules with bond metrics within 0.01 Å and 3.5°, respectively. The coordination environment around the Re center can be described as strongly distorted square pyramidal (ts = 0.4)$^{13}$ with the benzylidene moiety in apical position. The short C-N bond (C21-N2: 1.289(3) Å) and the almost linear coordination (C21-N2-Re1: 170.2(2)°)$^{14}$ of the benzylidene moiety are in agreement with the ketimide formulation. In the solid state, the phenyl ring is coplanar with the ketimide moiety (C27-C22-C21-N2: 3.5(3)°) and the shortend C$_{\text{Ph}}$-CN bond (C22-C21: 1.458(4) Å) indicates partial double bond character, which is in line with the NMR spectroscopic observations (vide supra).

In analogy to previously published acetonitrile release,$^{7e}$ $^4_{\text{Ph}}$ was tested towards generation of benzonitrile upon reaction with N-chlorosuccinimide (NCS). Addition of 2 eq. NCS to $^1_{\text{Ph}}$ leads to the detection of free benzonitrile by $^1$H NMR spectroscopy in approx. 57% yield relative to hexamethylbenzene as internal standard (Scheme 2). The reaction is accompanied by the formation of rhenium(IV) chloride 3. From there, the full synthetic cycle can be closed by reduction under an N$_2$ atmosphere in over 70% yield (Scheme 2).$^{7e}$ Hence, a total yield in benzonitrile has been achieved around 28% over all four steps, slightly lower compared with rhenium mediated acetonitrile synthesis (approx. 50%).$^{7e}$ In comparison, Cummins and co-workers obtained benzonitrile with a molybdenum trianilide platform in five steps and an overall yield around 40%. The other synthetic cycle for arylnitrile synthesis from N$_2$ reported by Hou and co-workers gave 38% in $p$-benzylbenzonitrile over five reaction steps starting from a cyclopentadienyl titanium(IV) chloride.$^{7i,14}$

**Scheme 2.** Synthetic cycle for the synthesis of benzonitrile directly from N$_2$ (DTBMP = 2,6-di-tert-butyl-4-methylpyridine).
Materials and methods. All experiments were carried out using standard Schlenk and glove-box techniques (Ar or N₂ atmospheres). Non-deuterated solvents were dried and deoxygenated using an MBraun solvent system. Deuterated solvents were obtained from Euiros-Top GmbH, dried over Na/K (Cs₂D and d₂-TfH), distilled by trap-to-trap transfer in vacuo, and degassed by three freeze-pump-thaw cycles, respectively.

N-Chlorosuccinimide (Acrös Organics) was sublimed and benzylbromide (Sigma Aldrich) was stirred with Cs₂D or d₂-TfH and stirred for 15 min.

K[N(SiMe₃)₂] (Sigma Aldrich) was used as purchased. Complex 4 was synthesized as previously published. Elemental analyses were obtained with an Elementar Vario EL 3 analyzer. NMR spectra were recorded on Bruker Avance III 300 or Bruker Avance III 400 MHz and calibrated to the solvent residual proton resonance (CD₂Cl₂, δ = 7.16 ppm, δc = 128.3; d₂-TfH, δ = 3.58 ppm). 

31P and 19F chemical shifts are reported relative to external phosphoric acid and CFCl₃ (δ = 0 ppm). Signal multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). LIFDI mass spectrometry was carried out on a JEOL AccuTOF JMS-T101GGC spectrometer.

Syntheses. ([P(NP)Re(NCH₂Ph)Cl]OTf) (59). AgOTf (6.6 mg, 33.6 µmol, 1 eq) was dissolved in EtO and cooled to -40°C before benzylbromide (ex.) is added. Immediate formation of a yellow precipitate (AgBr) indicates conversion to benzyl triflate. 2,6-Di-tert-buty1-4-methylpyridine (13.8 mg, 67.2 µmol, 2 eq) is added and the mixture stirred for additional 10 min. The reaction solution is filtered off and added to a solution of nitrile 4 (20.0 mg, 33.6 µmol, 1 eq) in PhMe (1 mL). Storage at -40°C for 48–72 h affords a green precipitate, which is filtered off, washed with Et₂O, extracted with benzene and lyophilized. Yield: 24.4 mg (28.2% mol). Anal. calc.(found) for C₄₀H₃₂N₄O₄P₄ReS(C₁₈H₂₆):  C, 41.01 (41.04); H, 6.17 (6.23); N, 3.30 (3.32). 1H NMR (300 MHz, CD₂Cl₂): δ = 7.06 ppm (8H, d, J = 8.9 Hz, 1H, CH₃), 7.27 ppm (10H, d, J = 8.7 Hz, 1H, CH₃), 7.35 ppm (8H, d, J = 8.2 Hz, 1H, CH₃, CH₃, CH₃), 7.42 ppm (8H, d, J = 7.5 Hz, 1H, CH₃), 7.51 ppm (8H, d, J = 7.2 Hz, 1H, CH₃).

Release of benzonitrile. 1H NMR (19.4 mg, 7.14 µmol, 1 eq) and hexamethyldizene (1.2 mg, 7.14 µmol, 1 eq) as internal standard are dissolved in CD₂Cl₂ in a J-Yong NMR tube. The solution is frozen and N-chlorosuccinimide (1.9 mg, 14.28 µmol, 2 eq) is added. The mixture is shaken until warmed to room temperature with concomitant darkening of the solution. Formation of 3 (1H: 10.53 ppm) and benzonitrile (38% vs. C₆D₆) is confirmed by 1HNMR spectroscopy.

Crystallographic results. Suitable single crystals for X-ray structure determination of 19 were selected from the mother liquor under argon, transferred into protective perfluoro polymer oil, and after selection to the cold gas stream on the diffractometer. Diffraction data were obtained at 100 K on a Bruker D8 three-circle diffractometer, equipped with a PHOTON 100 CMOS detector and an INCOATEC microfocus source with Quazar mirror optics (Mo-Kα radiation, λ = 0.71073 Å). The data were integrated with SINT and a semi-empirical absorption correction was applied using SADABS. The structure was solved and refined using the Bruker SHELX 2014 software package.11 All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically on calculated positions with their Uiso values constrained to 1.5 times those of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. Detailed crystal data, structure refinements parameters, bond lengths and angles are summarized in the Supporting Information (Tables S1–S3). Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre (CCDC-1839248). This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the European Research Council (ERC Grant Agreement 646747).

Keywords: Rhenium • Pincer Ligand • Dinitrogen • Nitrile • N₂ Splitting


The synthesis of benzonitrile directly from \( \text{N}_2 \) as nitrogen source in about 30% yield over four steps is presented. The reaction sequence proceeds via \( \text{N}_2 \) splitting, nitride benzylation, imide deprotonation and final ligand oxidation within a quasi-catalytic synthetic cycle. This result demonstrates that nitrile/vinylimido-tautomerization is not a mechanistic prerequisite for this system.
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