Synthesis of Benzonitrile from Dinitrogen

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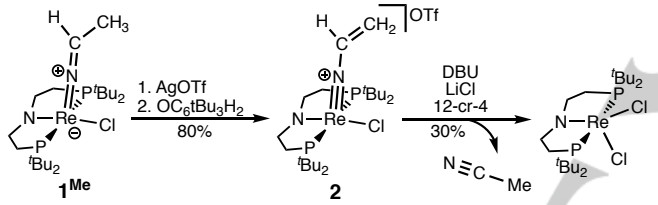
Dedicated Prof. Dr. A. C. Filippou on the occasion of his 60th birthday.

Abstract: The rhenium mediated synthesis of benzonitrile is reported with direct use of N_2 as a nitrogen source. The reaction affords benzonitrile in about 30% overall yield upon N_2 splitting and benzylation of resulting terminal nitride. Subsequent oxidation of an intermediate phenylketimido compound restores the parent rhenium complex within a full four-step synthetic cycle. The reaction shows that previously observed nitrile tautomerization is not a prerequisite for nitrile synthesis from N_2 with this system.

The *Haber-Bosch* process (HBP) currently provides synthetic ammonia at a massive scale (approx. 150 Mt/a).[1] The high energy demand has fueled many efforts to develop bioinspired catalysts for nitrogen fixation at ambient conditions.[2] Remarkable recent progress followed Schrock's seminal work,[3,4,5] with turn-over numbers up to 230 for the currently most active catalysts.[6]



Scheme 1. Oxidative release of acetonitrile from ketimide complex **1** as part of a synthetic cycle for direct N-transfer from N_2 to acetonitrile.[7e]

About 20% of the industrially produced ammonia serves as feedstock for nitrogen containing chemicals, such as amines, nitriles or *N*-heterocyclic compounds. Direct N_2 conversion to organic products therefore is an attractive goal from the point of atom, energy and redox economy. Stoichiometric C–N functionalization of N_2, e.g. with *C*-electrophiles, [7] heterocummulenes,[8] or carbon monoxide,[9] is well established and several quasi-catalytic synthetic cycles were reported as a proof-of-principle.[10] Inspired by Cummins' work,[7a,b] we recently reported a synthetic cycle for the transformation of N_2 to acetonitrile,[7e] which is an attractive target as judged by the similar bond energies of C≡N and N≡N triple bonds. The reaction proceeds via rhenium mediated splitting of N_2, and subsequent functionalization of the resulting nitrides, by alkylation, deprotonation and ligand oxidation with *N*-chlorosuccinimide. Examination of this final oxidation step by stepwise 1-electron oxidation of ketimido intermediate $\mathbf{1^{Me}}$ (Scheme 1) gave an unprecedented rhenium(V) vinyl imido complex (**2**), i.e. a tautomer of the unobserved rhenium(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 vinylimide tautomerization. This observation raises the question whether nitriles that cannot tautomerize, such as arylnitriles ArCN, are also accessible through such a reaction sequence. We here present a full synthetic cycle for the direct synthesis of benzonitrile from dinitrogen via N_2 splitting into nitrides.

Chemical or electrochemical reduction of the rhenium pincer complexes [$ReCl_2$(PNP)] or [$ReCl_3$(PNP)] (**3**; PNP = $N(CH_2CH_2P\mathit{t}Bu_2)_2$) under N_2 (1 bar) affords the rhenium(V) nitride complex [Re(N)Cl(PNP)] (**4**).[7d,e,11] Starting from the rhenium(IV) chloride, isolated yields between 60-70% are obtained with Na/Hg as reductant in THF at room temperature (Scheme 2). The terminal nitride complex can be selectively alkylated at the nitride moiety with alkyltriflates ROTf (R = Me, Et) giving the imido complexes [Re(NR)Cl(PNP)]OTf (R = Me ($\mathbf{5^H}$), Et ($\mathbf{5^{Me}}$)).[7d,e] In contrast to these triflate reagents, benzyltriflate is not stable at room temperature. $PhCH_2OTf$ was therefore prepared *in situ* according to published procedures for other alkyltriflates from excess benzylbromide and AgOTf.[12] Unlike with methyl- and ethyltriflate, only the previously reported protonation product of **4**,[7d] i.e. the amine complex [Re(N)Cl{$HN(CH_2CH_2P\mathit{t}Bu_2)_2$}]OTf, was obtained almost quantitatively as indicated by comparison of the NMR spectra. The origin of the proton remains unclear at this point. However, nitride benzylation is obtained upon addition of a non-nucleophilic base. The benzylimido complex [Re(NCH_2Ph)Cl(PNP)]OTf ($\mathbf{5^{Ph}}$) is obtained in up to 90% yield with *in situ* generated benzyltriflate in the presence of ca. 2 eq of 2,6-di-*tert*-butyl-4-methylpyridine (Scheme 2).

The green benzylimido complex $\mathbf{5^{Ph}}$ exhibits C_s symmetry on the NMR timescale. The chemical shift of the $^{31}P\{^1H\}$ NMR signal ($\delta(C_6D_6)$ = 90.3 ppm) resembles the respective methyl- and ethylimido complexes $\mathbf{5^{Me}}$ ($\delta(C_6D_6)$ = 90.7 ppm) and $\mathbf{5^{Et}}$ ($\delta(C_6D_6)$ = 90.1 ppm), respectively.[7d,e] Similarly, the ^1H NMR signatures of their pincer ligands reveal closely related characteristics. The methylene protons of the benzylimido moiety (NCH_2Ph) of $\mathbf{5^{Ph}}$ 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 *t*Bu groups, yet not with pincer backbone protons. This observation confirms selective nitride rather than pincer amide benzylation.

Benzylimide complex $\mathbf{5^{Ph}}$ is quantitatively deprotonated by strong bases, such as KOtBu or $KN(SiMe_3)_2$. For example, with $KN(SiMe_3)_2$ the azavinylidene complex [Re(NCHPh)Cl(PNP)] ($\mathbf{1^{Ph}}$, Scheme 2) is obtained in about 80% isolated yield. ^{31}P, ^1H and ^{13}C NMR spectroscopic characterization indicates two full sets of

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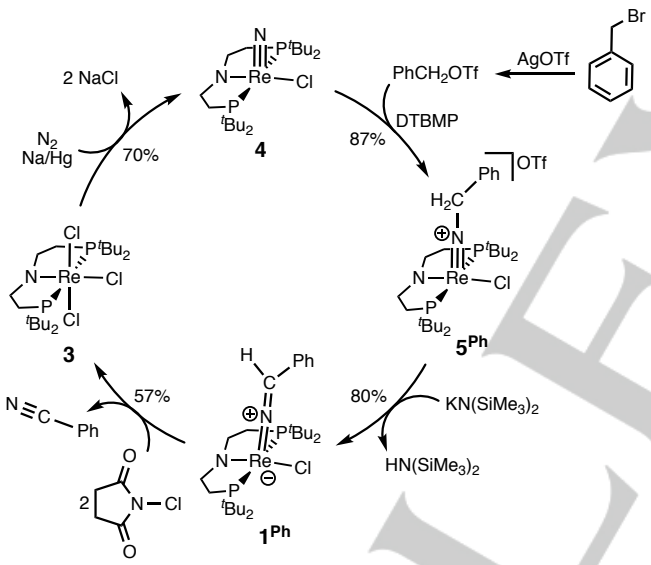
signals with a ratio of approx. 2:3 for ketimide **1^{Ph}**. As for the methylketimido complex **1^{Me}**,[7e] the two sets are assigned to the two stereoisomers that are interconverted by the hindered rotation around the C=N=Re azavinylidene core. The vinylic (PhC*H*N) protons of the two isomers are observed as signals at δ = 3.75 ppm and 5.47 ppm, respectively, both exhibiting coupling with the two pincer ^{31}P nuclei ($^4J_{HP}$ = 2.0 and 2.2 Hz). ^{1}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.



Scheme 2. Synthetic cycle for the synthesis of benzonitrile directly from N_2 (DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine).

Single crystals of **1^{Ph}** 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 (τ_5 = 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) °) of the benzylidene moiety are in agreement with the ketimide formulation. In the solid state, the phenyl ring is coplanar with the ketidmide moiety (C27-C22-C21-N2: 3.5(3) °) and the shortend C_{ipso}-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] **1^{Ph}** was tested towards generation of benzonitrile upon reaction with *N*-chlorosuccinimide (NCS). Addition of 2 eq. NCS to **1^{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*-methylbenzonitrile over five reaction steps starting from a cyclopentadienyl titanium(IV)chloride. [7f,14]

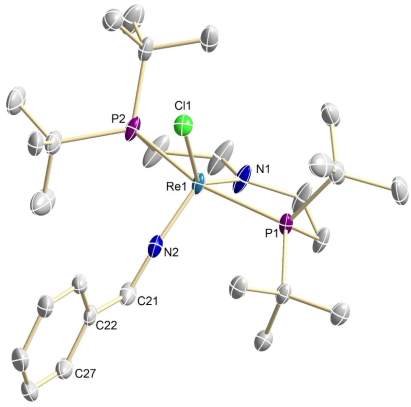


Figure 1. Molecular structure of complex **1^{Ph}** derived by single-crystal X-ray diffraction (one of two independent molecules in the asymmetric unit). ORTEP plots with anisotropic displacement parameters set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re1-N1 1.938(2), Re1-N2 1.798(2), Re1-Cl1 2.3964(6), N2-C21 1.289(3); N1-Re1-N2 114.54(10), N1-Re1-Cl1 137.19(8), 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, benzylation, deprotonation and oxidation of phenylketimido intermediate **1^{Ph}**. The putative nitrile complex that is formed form oxidation of **1^{Ph}** with NCS prior to product release is inherently not capable of nitrile (M–N≡C–CHR$_2$) / enimido (M=N–CH=CR$_2$) 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

Materials and methods. All experiments were carried out using standard Schlenk and glove-box techniques (Ar or N_2 atmospheres). Non-deuterated solvents were dried and deoxygenated using an MBraun solvent system. Deuterated solvents were obtained from Euriso-Top GmbH, dried over Na/K (C_6D_6 and d_8-THF), distilled by trap-to-trap transfer in vacuo, and degassed by three freeze-pump-thaw cycles, respectively. *N*-chlorosuccinimide (Acros Organics) was sublimed and benzylbromide (Sigma Aldrich) was stirred over CaH_2 and trap-to-trap distilled prior to use. $KN(SiMe_3)_2$ (Sigma Aldrich) was used as purchased. Complex **4** was synthesized as previously published.[7d] 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 (C_6D_6: δ_H = 7.16 ppm, δ_C = 128.39; d_8-THF: δ_H = 3.58 ppm). ^{31}P and ^{19}F chemical shifts are reported relative to external phosphoric acid and $CFCl_3$ (δ = 0.0 ppm). Signal multiplicities are abbreviated as: s (singlet), d (dublet), t (triplet), q (quartet), m (multiplet), br (broad). LIFDI mass spectrometry was carried out on a JEOL AccuTOF JMS-T100GCV spectrometer.

Syntheses. *[(PNP)Re(NCH$_2$Ph)Cl)]OTf (**5^{Ph}**)*. AgOTf (8.6 mg, 33.6 µmol, 1 eq) is dissolved in Et_2O 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*-butyl-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 nitride **4** (20.0 mg, 33.6 µmol, 1 eq) in Et_2O (1 mL). Storage at -40°C for 48-72 h affords a green precipitate, which is filtered off, washed with Et_2O, extracted with benzene and lyophilized. Yield: 24.4 mg (29.2 µmol, 87%). Anal. calcd.(found) for $C_{28}H_{51}ClF_3N_2O_3P_2ReS\cdot(C_6H_6)_{0.167}$ (%): C, 41.01 (41.04); H, 6.17 (6.23); N, 3.30 (3.32). ^1H NMR (300 MHz, C_6D_6), [ppm]): δ = 1.00 ($A_9XX'A'_9$, N = $|^3J_{HP} + {}^5J_{HP}|$ = 7.0 Hz, 18H, PC(CH_3)$_3$), 1.08 ($A_9XX'A'_9$, N = $|^3J_{HP} + {}^5J_{HP}|$ = 7.2 Hz, 18H, PC(CH_3)$_3$), 2.02 (m, 2H, PCH_2), 2.28 (m, 2H, PCH_2), 3.80 (m, 2H, NCH_2CH$_2$), 4.61 (s, 2H, NCH_2Ph), 4.70 (m, 2H, NCH_2CH$_2$), 7.00 (t, $^3J_{HH}$ = 7.4 Hz, 1H, CH_{para}), 7.13 (m, 2H, CH_{meta}, partially superimposed), 7.49 (d, $^3J_{HH}$ = 7.2 Hz, 2H, CH_{ortho}). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, [ppm]): δ = 24.3 ($AXX'A'$, N = $|\,^1J_{CP} + {}^3J_{CP}\,|$ = 11.3 Hz, PCH_2), 29.5 ($A_3XX'A'_3$, N = $|\,^2J_{CP} + {}^4J_{CP}\,|$ = 1.9 Hz, PC(CH_3)$_3$), 29.7 ($A_3XX'A'_3$, N = $|\,^2J_{CP} + {}^4J_{CP}\,|$ = 1.4 Hz, PC(CH_3)$_3$), 37.8 ($AXX'A'$, N = $|^1J_{CP} + {}^3J_{CP}\,|$ = 10.7 Hz, P*C*(CH_3)$_3$), 38.1 ($AXX'A'$, N = $|^1J_{CP} + {}^3J_{CP}\,|$ = 8.7 Hz, P*C*(CH_3)$_3$), 75.0 (s, NCH_2Ph), 76.2 ($AXX'A'$, N = $|^2J_{CP} + {}^3J_{CP}\,|$ = 2.7 Hz, NCH_2CH$_2$), 127.0 (s, C^{Ph}_{ortho}), 128.0 (s, C^{Ph}_{para}), 129.1 (s, C^{Ph}_{meta}), 134.8 (s, C^{Ph}_{ipso}). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, [ppm]): δ = 90.3 (s, P^{t}Bu$_2$). $^{19}F\{^1H\}$ NMR (376.5 MHz, d$_8$-THF, [ppm]): δ = -79.0 (s, CF_3). LIFDI$^+$ (toluene, m/z$^+$): 687.1 ($C_{27}H_{51}ClN_2P_2Re^+$).

*[Re(NCHPh)Cl(PNP)] (**1^{Ph}**)*. Complex **5^{Ph}** (26.5 mg, 31.7 µmol, 1 eq) and $KN(SiMe_3)_2$ (6.3 mg, 31.7 µmol, 1 eq) are suspended in benzene (4 mL) and stirred for 2 h at room temperature. The solvent is evaporated and the residue extracted with pentanes (3 x 2 mL). After lyophilization with benzene, the brown ketimido complex **1^{Ph}** is obtained as a mixture of two diastereomers, which was not further separated. Yield: 17.3 mg, 25.2 µmol, 80%. An assignment of all signals to distinct isomers was not possible. Anal. calcd. (found) for $C_{27}H_{50}ClN_2P_2Re$ (%): C, 47.25 (47.67); H, 7.46 (7.34); N, 4.08 (3.97). ^1H NMR (400 MHz, C_6D_6, [ppm]): δ = 1.16 ($A_9XX'A'_9$, N = $|^3J_{HP} + {}^5J_{HP}|$ = 6.3 Hz, 18H, PC(CH_3)$_3$), 1.18 ($A_9XX'A'_9$, N = $|^3J_{HP} + {}^5J_{HP}|$ = 6.5 Hz, 18H, PC(CH_3)$_3$), 1.24 ($A_9XX'A'_9$, N = $|^3J_{HP} + {}^5J_{HP}|$ = 6.0 Hz, 18H, PC(CH_3)$_3$), 1.29 ($A_9XX'A'_9$, N = $|^3J_{HP} + {}^5J_{HP}|$ = 6.2 Hz, 18H, PC(CH_3)$_3$), 1.65 (m, 4H, PCH_2), 1.80 (m, 2H, PCH_2), 1.95 (m, 2H, PCH_2), 3.42 (m, 4H, NCH_2CH$_2$), 3.54 ($ABCDXX'D'C'B'A'$, N = $|\,^3J_{HP} + {}^4J_{HP}\,|$ = 1.7 Hz, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.3 Hz, 2H, NCH_2CH$_2$), 3.75 (t, $^4J_{HP}$ = 2.0 Hz, 1H, N=C*H*Ph), 3.78 (m, 2H, NCH_2CH$_2$, partially superimposed), 5.47 (t, $^4J_{HP}$ = 2.2 Hz, 1H, N=C*H*Ph), 6.47 (br, 2H, CH_{ortho}), 6.65 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, CH_{para}), 6.73 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, CH_{para}), 7.18 (m, 2H, N=CH*Ph,* superimposed by benzene), 7.35 (m, 2H, N=CH*Ph*), 7.44 (m, 2H, N=CH*Ph*). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, [ppm]): δ = 27.4 ($AXX'A'$, N = $|^1J_{CP} + {}^3J_{CP}|$ = 8.3 Hz, PCH_2CH$_2$), 29.6 ($AXX'A'$, N = $|^1J_{CP} + {}^3J_{CP}|$ = 7.9 Hz, PCH_2CH$_2$), 30.3 (m, PC(CH_3)$_3$), 30.5 (m, PC(CH_3)$_3$), 36.5 ($AXX'A'$, N = $|^1J_{CP} + {}^3J_{CP}|$ = 7.0 Hz, P*C*(CH_3)$_3$), 37.2 ($AXX'A'$, N = $|^1J_{CP} + {}^3J_{CP}|$ = 7.0 Hz, P*C*(CH_3)$_3$), 38.7 ($AXX'A'$, N = $|^1J_{CP} + {}^3J_{CP}|$ = 8.9 Hz, P*C*(CH_3)$_3$), 39.2 ($AXX'A'$, N = $|^1J_{CP} + {}^3J_{CP}|$ = 8.5 Hz, P*C*(CH_3)$_3$), 74.0 ($AXX'A'$, N = $|^2J_{CP} + {}^3J_{CP}|$ = 4.4 Hz, NCH_2CH$_2$), 75.0 ($AXX'A'$, N = $|^2J_{CP} + {}^3J_{CP}|$ = 4.1 Hz, NCH_2CH$_2$), 124.2 (s, C^{Ph}_{para}), 124.8 (s, C^{Ph}_{para}), 127.5 – 129.0 (*Ph*, superimposed by benzene), 132.3 (s, C^{Ph}_{ipso}), 132.8 (s, C^{Ph}_{ipso}), 146.8 (t, $^3J_{CP}$ = 2.4 Hz, N=*C*HPh), 150.6 (t, $^3J_{CP}$ = 2.3 Hz, N=*C*HPh). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6, [ppm]): δ = 54.8 (s, P^{t}Bu$_2$), 56.5 (s, P^{t}Bu$_2$).

Release of benzonitrile. **1^{Ph}** (4.9 mg, 7.14 µmol, 1 eq) and hexamethylbenzene (1.2 mg, 7.14 µmol, 1 eq) as internal standard are dissolved in C_6D_6 in a *J*-Young 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. C_6Me_6) are confirmed by ^1H-NMR spectroscopy.

Crystallographic results. Suitable single crystals for X-ray structure determination of **1^{Ph}** were selected from the mother liquor under argon, transferred into protective perfluoro polyether 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 SAINT and a semi-empirical absorption correction was applied using SADABS. The structure was solved and refined using the Bruker SHELX 2014 software package.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 U_{eq} 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/products/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).

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Keywords: Rhenium • Pincer Ligand • Dinitrogen • Nitrile • N_2 Splitting

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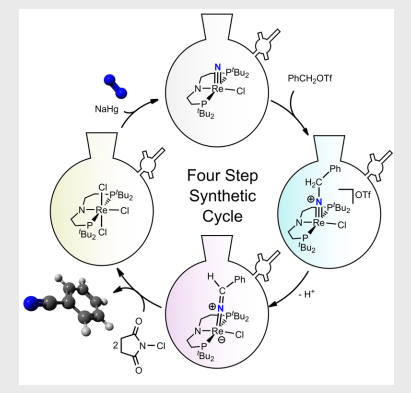
Entry for the Table of Contents

COMMUNICATION

The synthesis of benzonitrile directly from N_2 as nitrogen source in about 30% yield over four steps is presented. The reaction sequence proceeds via 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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