

Conversion of Dinitrogen into Acetonitrile under Ambient Conditions

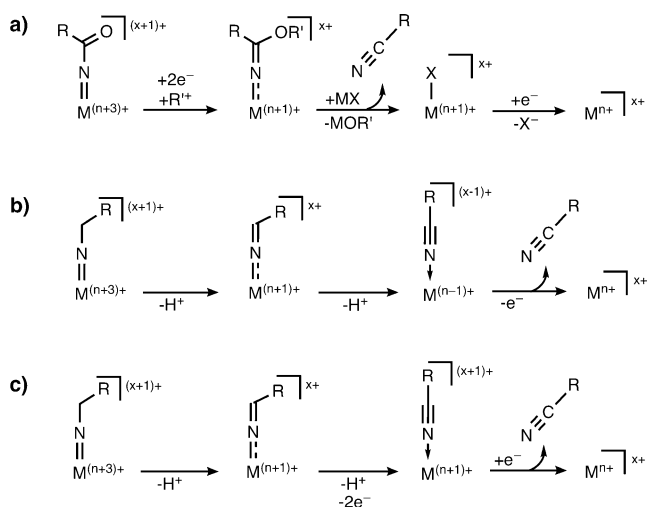
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Abstract: About 20 % of the ammonia production is used as the chemical feedstock for nitrogen-containing chemicals. However, while synthetic nitrogen fixation at ambient conditions has had some groundbreaking contributions in recent years, progress for the direct conversion of N_2 into organic products remains limited and catalytic reactions are unknown. Herein, the rhenium-mediated synthesis of acetonitrile using dinitrogen and ethyl triflate is presented. A synthetic cycle in three reaction steps with high individual isolated yields and recovery of the rhenium pincer starting complex is shown. The cycle comprises alkylation of a nitride that arises from N_2 splitting and subsequent imido ligand centered oxidation to nitrile via a 1-azavinylidene (ketimido) intermediate. Different synthetic strategies for intra- and intermolecular imido ligand oxidation and associated metal reduction were evaluated that rely on simple proton, electron, and hydrogen-atom transfer steps.

Synthetic nitrogen fixation at ambient conditions underwent tremendous advances in the past years.^[1] Several molecular catalysts for NH_3 -formation are known.^[2] Turn-over numbers (TONs) over 60 currently define the most efficient system.^[3] Similarly, catalytic N_2 silylation with large excess of $ClSiMe_3$ and alkali reductants saw some remarkable progress, but remains mechanistically less well defined.^[4] While the lion's share of ammonia is used for fertilizers, around 20 % serves as feedstock for chemical synthesis, for example, of amines, nitro compounds, or nitriles. However, catalysts for the direct introduction of N_2 into organic products remain elusive and even stoichiometric systems are scarce. Pioneering work demonstrated transformations of coordinated N_2 , such as four-electron reductions to hydrazido ligands with C-electrophiles.^[5] But hydrazines apparently are less-promising synthetic targets, owing to the weak N–N single bond. More recent work evaluated pathways for E–N (E = C, Si, B) bond formation accompanied by full N_2 splitting, for example, with heterocummulenes,^[6] CO,^[7] silyl,^[8] alkyl,^[9] or boryl groups.^[10]

According to thermochemical arguments, nitriles are attractive targets as the formation of strong $C\equiv N$ bonds ($D^0(HC\equiv N) = 937 \text{ kJ mol}^{-1}$) facilitates offsetting the large N_2 bond energy (941 kJ mol^{-1}).^[11] Cummins and co-workers reported elegant synthetic cycles for the six-electron transformation of N_2 to nitriles mediated by Mo and Nb

complexes.^[12] The routes start with initial dinitrogen splitting,^[13] followed by nitride acylation with silyltriflate and acyl chloride. Subsequent stepwise three-electron reduction requires further silyltriflate and Lewis acid ($SnCl_2$ or $ZnCl_2$) for oxygen removal with nitrile release in up to 38 % yield over all five steps.^[12b] In this synthetic scheme re-reduction of the (formal) catalyst is a purely metal-centered process (Scheme 1 a).



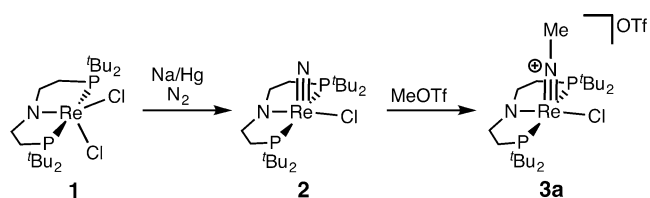
Scheme 1. Schematic pathways of nitrile synthesis after N_2 -splitting and functionalization: Through nitride acylation established by Cummins et al. (a)^[12b] or through nitride alkylation (b and c) evaluated herein.

This work inspired us to evaluate new ways of N_2 into nitrile conversion, which rely on intramolecular electron transfer: The interconversion of imido and nitride ligands via 1-azavinylidenes (or ketimides) by simple double de/protonation (Scheme 1 b) was previously reported, but not applied to N_2 fixation.^[14] Importantly, both deprotonation steps are associated with formal metal/ligand two-electron redox steps offering new strategies for metal reduction within a (pseudo)-catalytic N_2 functionalization cycle (Schemes 1 b/c). Following these strategies, we herein report several routes for the conversion of N_2 into acetonitrile via rhenium-mediated N_2 splitting, nitride alkylation, and ligand oxidation leading up to a synthetic cycle in three steps in over 50 % yield per cycle.

We recently reported dinitrogen splitting upon reduction of rhenium(III) pincer complex $[ReCl_2(PNP)]$ (**1**, $PNP = N(CH_2CH_2PtBu_2)_2$) with Na/Hg or $CoCp^*_2$ and methylation of the resulting rhenium(V) nitride $[Re(N)Cl(PNP)]$ (**2**) to methylimido complex **3a** (Scheme 2).^[15] In analogy, the ethylimido complex **3b** is obtained upon reaction of nitride **2** with ethyl triflate in essentially quantitative isolated yield.^[16] The NMR spectroscopic features of **3b** are close to **3a**,

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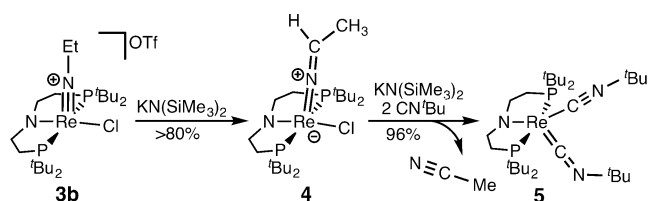
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Scheme 2. Rhenium-mediated dinitrogen splitting and alkylation.^[15]

suggesting square-pyramidal geometry with the imide in the apical position as confirmed by X-ray diffraction for **3a**.^[15]

Ethylimide **3b** is deprotonated quantitatively with KN(SiMe₃)₂ giving the red-brown 1-azavinylidene rhenium(III) complex [Re(N=CHCH₃)Cl(PNP)] (**4**; Scheme 3).^[16] The synthesis of **4** can also be carried out as a one-pot reaction directly from **2** by successive ethylation and deprotonation in



Scheme 3. Synthesis of acetonitrile upon double deprotonation of N₂-derived ethylimide **3b**.

benzene with almost quantitative spectroscopic and over 80% isolated yield. Spectroscopic characterization of complex **4** indicates the presence of two isomers in about 60:40 ratio with diagnostic ¹H, ¹³C, and ¹⁵N NMR signals for the azavinylidene ligands, respectively.^[16] This observation is in line with the formation of two stereoisomers as a result of hindered 1-azavinylidene rotation about the Re=N and N=C double bonds owing to strong Re→N back bonding. The N=C double bond stretching vibration of the ketimide can be assigned to a weak band in the vibrational spectrum at 1594 cm⁻¹, which shifts by 22 cm⁻¹ upon ¹⁵N-labelling.

The structural assignment of **4** is confirmed by single-crystal X-ray diffraction (Figure 1 a). The coordination geometry around the rhenium ion is close to that in the methyl imide **3a**^[15] and all N-Re-N and N-Re-Cl bond angles of the two structures are the same within 5°. However, the almost linear Re-N-C moiety of **4** exhibits considerably longer Re-N (Δ*d* = +0.12 Å) and shorter C-N (Δ*d* = -0.17 Å) bonds than **3a**, in line with the changes in Re-N and C-N bond orders and with the only other structurally characterized rhenium 1-azavinylidene complex reported.^[17]

The ketimido complex **4** can be further deprotonated if the resulting rhenium(I) ion is stabilized by strong π-acceptor ligands. For example, the reaction of **4** with KN(SiMe₃)₂ and *tert*-butylisocyanide (2 equiv) gives the bis-isonitrile complex [Re(CNtBu)₂(PNP)] (**5**) in almost quantitative yield with concomitant release of acetonitrile.^[16] While **5** has C_{2v} symmetry in solution on the NMR time-scale, in the crystal (Figure 1 b) this compound features one strongly bent isocyanide ligand (C26-N3-C27: 134.2(4)°) while the other

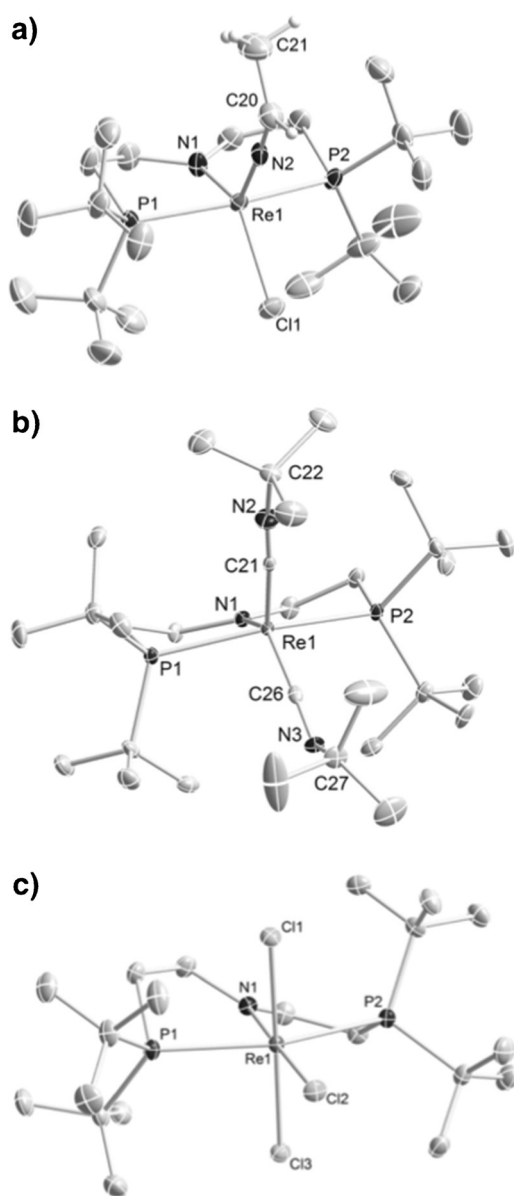
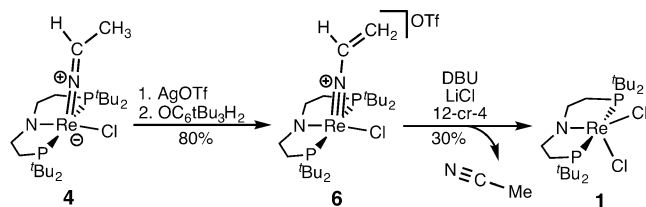


Figure 1. Molecular structures of complexes **4** (a), **5** (b), and **7** (c) derived by single-crystal X-ray diffraction. ORTEP plots with anisotropic displacement parameters set at 50% probability. Hydrogen atoms except for the azavinylidene ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: **4**: Re1–N1 1.948(5), Re1–N2 1.822(4), Re1–Cl1 2.3962(14), N2–C20 1.273(7), C20–C21 1.489(10); N1–Re1–N2 120.5(2), N1–Re1–Cl1 135.07(15), N2–Re1–Cl1 104.39(16), P1–Re1–P2 162.01(5), Re1–N2–C20 174.3(5), N2–C20–C21 125.7(7). **5**: Re1–N1 2.028(3), Re1–C21 1.937(4), Re1–C26 1.906(4), C21–N2 1.181(6), C26–N3 1.222(5); N1–Re1–C21 131.76(15), N1–Re1–C26 140.30(15), Re1–C21–N2 171.9(4), Re1–C26–N3 168.9(3), C21–N2–C22 168.7(5), C26–N3–C27 134.2(4). **7**: Re1–N1 1.9038(16), Re1–Cl1 2.3893(5), Re1–Cl2 2.4024(5), Re1–Cl3 2.3700(5); N1–Re1–Cl1 91.50(5), N1–Re1–Cl2 178.69(5), N1–Re1–Cl3 91.59(5), P1–Re1–P2 160.046(16), Cl1–Re1–Cl2 88.090(17), Cl1–Re1–Cl3 176.471(16).

isonitrile remains almost linear (C21–N2–C22: 168.7(5)°). Such a strong bending is rare and indicates an unusually high degree of Re→C π-back bonding as a consequence of the electron-rich nature of the {Re^I(PNP)} fragment.^[18] Accordingly, the C26–N3 bond (1.222(5) Å) of the bent

isonitrile is considerably longer than in the linear isonitrile moiety (C21–N2: 1.181(6) Å). The electronic asymmetry is also resolved in the IR spectrum, which features bands in two regions at around 1960 cm⁻¹ and 1760 cm⁻¹, respectively, assignable to the linear and bent isonitriles.^[16] The low-energy stretching mode reflects the strongly reduced character of the bent isonitrile. Both bands are split into two, respectively, which can be rationalized with conformational isomers, as was previously reported for complexes with mixed linear/bent isonitriles.^[18]

Hence, intramolecular four-electron charge transfer from the ethylimido ligand to the metal by double deprotonation (Scheme 1 b) is in fact feasible if the electron-rich {Re(PNP)} fragment is trapped by π -accepting ligands, such as isonitriles. However, regeneration of parent **1** on this route was unsuccessful, so far. Therefore, conversion of **4** by oxidative functionalization of the azavinylidene ligand was examined. Cyclic voltammetry (CV) reveals reversible oxidation of **4** at low potential ($E_0 = -0.58$ V) and an irreversible oxidation wave beyond +0.6 V.^[16] Accordingly, chemical oxidation with one equivalent of AgOTf in CH₂Cl₂ results in the formation of a red, paramagnetic product.^[16] While this compound could not be isolated because of its slow degradation, in situ hydrogen-atom transfer (HAT) with 2,4,6-tri-*tert*-butylphenoxy radical (after preceding oxidation of **4** with AgOTf) gives the vinylimido complex [Re(N-CH=CH₂)Cl(PNP)]⁺ (**6**) in spectroscopic yields beyond 80 % (Scheme 4).^[16] The vinyl substituent in **6** is unequivocally identified by its ¹H NMR signature,^[16] while the signals for the pincer ligand exhibit only small differences from those of the imido and ketimido complexes **3a/b** and **4**. Notably, without preceding oxidation of **4** (with AgPF₆ or AgOTf) no reaction is observed with 2,4,6-tri-*tert*-butylphenoxy radical.

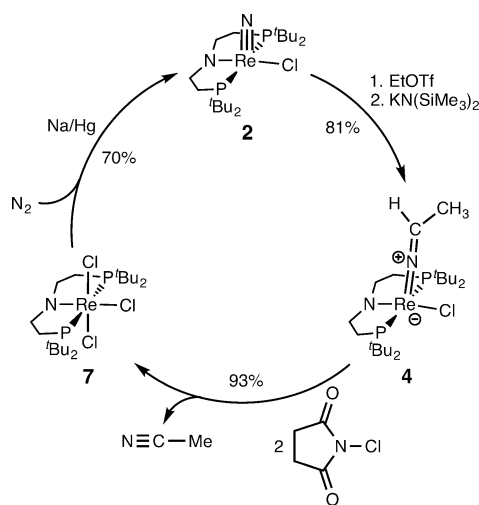


Scheme 4. Synthesis of acetonitrile upon oxidation of N₂-derived ketimide **4**.

Hence, formal hydride abstraction from **4** by stepwise one-electron oxidation and subsequent HAT favors the formation of an unusual rhenium(V) vinyl imide over the rhenium(III) acetonitrile tautomer. This observation again emphasizes the distinct tendency of the electron-rich {ReCl-(PNP)} core for M→N back bonding. However, the nitrile isomer [Re(NCMe)Cl(PNP)]⁺ was computed to exhibit a triplet ground state that lies only around $\Delta G^0 = +16$ kJ mol⁻¹ higher than **6**.^[16] This result suggests that acetonitrile elimination might be accessible on the rhenium(III) stage by trapping of the {ReCl(PNP)}⁺ fragment. Accordingly, the reaction of **6** with LiCl, crown ether (12-cr-4) and substoichiometric amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) results in formation of parent **1** and acetonitrile

(Scheme 4), closing a full synthetic cycle.^[16] Without DBU no reaction is observed and the non-nucleophilic base presumably facilitates proton transfer for vinyl-group tautomerization. Albeit the spectroscopic yield in **1** and MeCN is only around 30 % (internal ¹H NMR standard naphthalene) besides several other unidentified products, these results define the requirements for oxidative acetonitrile release from **4**: A two-electron oxidant and a base for formal hydride removal in combination with a chloride source to stabilize rhenium(III).

To raise the overall yield of the synthetic cycle, several reagents were screened that fulfill the aforementioned requirements. For example, **4** reacts with a mixture of CuCl₂ (2 equiv) and DBU (1 equiv) to give **1** in around 20 % spectroscopic yield (³¹P NMR). However, best results were obtained with *N*-chlorosuccinimide (NCS). Reaction of **4** with 2 equiv NCS (Scheme 5) gives free acetonitrile in over 90 %



Scheme 5. Most efficient synthetic cycle for acetonitrile synthesis from N₂.

yield by ¹H NMR (internal standard hexamethylbenzene).^[16] Besides that, rhenium(IV) complex [ReCl₃(PNP)] (**7**) is obtained almost quantitatively according to comparison of the ¹H NMR ($\delta_{\text{H}}(\text{tBu}) = 10.7$ ppm) and UV/Vis spectra with an authentic sample. Complex **7** was independently prepared by oxidation of **1** with 1 equivalent NCS and fully characterized.^[16] Determination of the molecular structure by single-crystal X-ray diffraction (Figure 1c) reveals octahedrally coordinated rhenium with some distortion mainly arising from the pincer bite angle. The magnetic moment in solution at room temperature from Evans' method (1.5 μ_{B}) is in agreement with a d³ low-spin configuration resulting from the strong pincer π -donation and some orbital contribution to the magnetic moment that leads to reduction of the magnetic moment with respect to the spin-only value. The facile synthesis of rhenium(IV) complex **7** from parent rhenium(III) dichloride **1** and NCS (1 equiv)^[16] indicates that **1** could in fact be an intermediate in the oxidation of **4** with NCS.

Finally, the synthetic cycle could be closed by reduction of **7** with Na/Hg (2 equiv) under dinitrogen (1 bar) at room

temperature (Scheme 5).^[16] The nitride **2** is obtained in over 70 % spectroscopic yield. This full cycle of N₂ conversion into acetonitrile was further confirmed with a ¹⁵N-labeled sample producing ¹⁵N labeled acetonitrile. The reaction of **7** with only one equivalent of reductant (CoCp*₂) under argon quantitatively gives complex **1** as determined by ¹H and ³¹P NMR spectroscopy,^[16] indicating that N₂-splitting starting from **7** might also pass through rhenium(III) complex **1** as an intermediate.

In summary, a new route for the pseudo-catalytic synthesis of acetonitrile is presented directly utilizing N₂ and ethyl triflate as N- and C-sources, respectively. The best synthetic cycle is composed of three simple reaction steps with 52 % overall yield. The present results describe a new strategy for dinitrogen functionalization to valuable chemicals beyond ammonia. Besides the thermochemical attractiveness of forming C≡N triple bonds after N₂ splitting, this work also offers mechanistic implications regarding the restoration of low-valent rhenium after N₂ splitting. We demonstrate that the alkylimide to nitrile ligand oxidation can be partially coupled with metal re-reduction. Such proton-coupled metal-ligand redox processes are therefore of particular relevance for future efforts to design truly (electro-)catalytic variants of N₂ transformation to organic compounds.

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Keywords: acetonitrile · nitrogen fixation · pincer ligands · rhenium · small-molecule activation

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