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Nitrogen Fixation by Manganese Complexes – Waiting for the Rush?

Quentin Le Dé,[a] Dmitry A. Valyaev,*[a] and Antoine Simonneau*[a]

Manganese is currently experiencing a great deal of attention in homogeneous catalysis as a sustainable alternative to platinum group metals due to its abundance, affordable price and low toxicity. While homogeneous nitrogen fixation employing well-defined transition metal complexes has been an important part of coordination chemistry, manganese derivatives have been only sporadically used in this research area. In this contribution, the authors systematically cover manganese organometallic chemistry related to N_2 activation spanning almost 60 years, identify apparent pitfalls and outline encouraging perspectives for its future development.

1. Introduction

Nitrogen is a life-sustaining element found in inexhaustible amounts in the Earth's atmosphere. Often considered as an archetypal chemically inert molecule, N_2 is indeed difficult to transform as testified by the few systems that efficiently "fix" atmospheric nitrogen into ammonia: the biologically occurring nitrogenases[1] and the industrial Haber-Bosch process (HBP).[2] Both of them reduce dinitrogen at a high energetic expense on scales reaching hundreds Gt per year. Just as the nitrogenase-expressing microorganisms feed the biosphere with bioavailable ammonium, more than 75% of industrially produced ammonia is manufactured into fertilizers, reflecting its importance in sustaining the 20th century demographic growth.[3] At times where global warming threatens, the high amount of CO_2 emissions contribution of the HBP appears to be difficultly tenable on the long term,[4] especially considering the potential application of ammonia as a concurrent for dihydrogen as a carbon-free energy vector.[5] Trying to circumvent the drawbacks of the HBP is a challenge that has bolstered considerable research effort over last two decades. In particular, molecular complexes catalyzing homogeneous N_2 reduction have remarkably emerged as credible alternatives.[6] Being related to nitrogenases in terms of reaction mechanisms and operating conditions (ambient T and P), they may be suitable for future small-scale NH_3 production processes relying on intermittent renewable energies. Organometallic complexes of manganese, the third most abundant transition metal in the Earth's crust, have recently found a great success in catalytic (de)hydrogenation,[7] C–H activation,[8] CO_2 reduction[9] or hydrogen production processes.[10] However, manganese remains curiously absent from the homogenous N_2 reduction field, notwithstanding the fact that Haber himself mentioned in its Nobel lecture the remarkable activity of manganese in its early results of ammonia synthesis[11] and its emerging role in chemical looping ammonia synthesis.[12] Looking down group 7, there is expectedly little known for technetium,[13] whereas rhenium particularly stands out with a rich N_2 chemistry.[14] We would like herein to give a critical overview of molecular manganese-dinitrogen chemistry, underline the difficulties that seem to hamper its development and outline some perspectives.

As the above paragraph intimates, there are relatively few examples of known Mn(I) and Mn(0) dinitrogen complexes, whereas such species in the two common oxidation states of this metal (+II or +III) have not been yet reported probably due to apparently harder character of these cations and specific ligand field properties. In contrast to other transition metals, the reduction of Mn(II) halide precursors under an N_2 atmosphere has met limited success, affording only dinuclear complexes bearing diazene-diide (μ-N_2^{2-}) ligands (*vide infra*). For this reason, all mononuclear manganese N_2 complexes have been prepared either by the chemical modification of *N*-donor ligand or by the exchange of weakly coordinating ligands with N_2 under thermal or photochemical activation conditions.

2. Syntheses of Manganese-Dinitrogen Complexes by N-Ligand Transformations

Although carbonyl-containing complexes such as $[Mn_2(CO)_{10}]$, $[Mn(CO)_5Br]$ or $[CpMn(CO)_3]$ belong to the most common organometallic manganese precursors, the direct CO-to-N_2 substitution remains a highly challenging task (*vide infra*) due to the weaker σ-donor/π-acceptor properties of dinitrogen relative to CO. For this reason, the synthesis of the first Mn dinitrogen complex **2a**[15] (Scheme 1a) was achieved by the Sellmann group *via* low-temperature oxidation of hydrazine complex **1** by two equivalents of hydrogen peroxide in the

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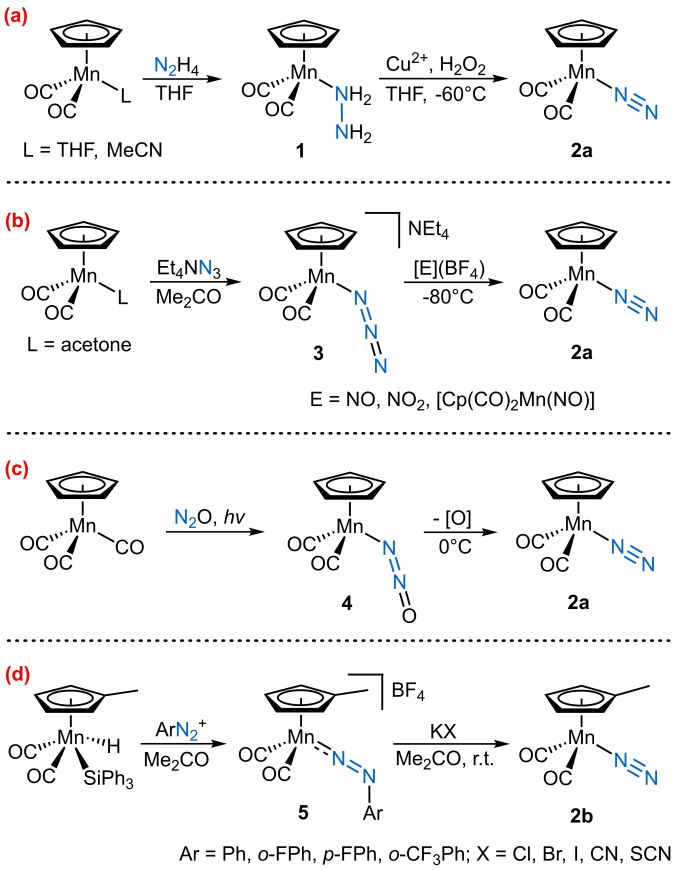

Scheme 1. Different routes to half-sandwich Mn(I) N_2 complexes *via* N-ligand transformation approach.

presence of copper salts, followed by careful sublimation under high vacuum. The key Mn(I) precursor **1** may be prepared either by the substitution of labile THF ligand in [Cp(CO)$_2$Mn(THF)], photochemically generated *in situ* from cymantrene or using thermal MeCN ligand displacement in isolable [Cp(CO)$_2$Mn-(MeCN)].[16,17] Despite its description more than 50 years ago, the crystal structure of **2a** was only reported recently[16] and exhibits a short N–N triple bond (1.1144(1) Å), which correlates well with a high-energy N≡N stretch (2162 cm^{-1}). Both parameters clearly indicate a weakly activated N_2 ligand, a common feature for all piano-stool Mn-N_2 complexes (*vide infra*). Later, Sellmann have shown that **2a** may also be prepared by treatment of the anionic azido-Mn(I) complex **3** with various electrophiles (Scheme 1b).[18] The decomposition of complex **4** (Scheme 1c) generated by the photolysis of [CpMn(CO)$_3$] in near-critical liquid N_2O afforded **2a** as a main product albeit the mechanism of oxygen atom loss remains unclear.[19] The related analogue **2b** bearing a monomethylated Cp ligand (Cp′) was also obtained by the Sutton group *via* reactions of Mn(I) aryldiazonium complexes **5** with a variety of anionic nucleophiles (Scheme 1d).[20] Finally, the Hermann group has reported that reactions of the THF adduct [CpMn(CO)$_2$(THF)] or its Cp′ congener with 1,1,1-trifluorodiazoethane led to the isolation in low yields of the first examples of Mn(I) dinuclear species bearing bridging N_2 ligand (**6a**–**b**, Scheme 1e).[21] The crystal structure of **6b** revealed only slight N–N bond elongation relative to that in its mononuclear analogue **2a** (1.118(7) *vs.* 1.1144(1) Å, respectively), reflecting the poor π-donation ability of the [Cp′Mn(CO)$_2$] fragment. Of note, Re-N_2 complexes were also prepared by the Chatt and Sutton groups through base/nucleophile/reduction-promoted degradation of benzoylazo[14a,c,g] or aryldiazenido ligands,[14f,h,i,j] respectively.

3. Syntheses of Manganese Dinitrogen Complexes by Thermal Ligand Exchange

After the seminal report of the synthesis of **2a**, alternative routes aiming at the uptake of gaseous N_2 through thermal ligand substitution and preparation of related complexes have been reported. Sellmann showed thereafter that **2a** can be prepared from [Cp(CO)$_2$Mn(THF)] under a high N_2 pressure (Scheme 2a).[22] Later, Poliakoff evidenced that the same N_2 complex can be readily obtained by dihydrogen ligand displacement in Mn(I) complex **7** generated in supercritical (sc) xenon or CO_2 (Scheme 2a).[23] The extension of this chemistry to pentamethylcyclopentadienyl (Cp*) Mn(I) derivative **2c** revealed a curious reversibility of the ethyl vinyl ether (EVE) ligand

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Antoine Simonneau obtained his PhD in 2011 from Sorbonne Université (Paris) under the supervision of Profs. M. Malacria and L. Fensterbank, and then move to Berlin for a postdoctoral stay with Prof. M. Oestreich. In 2015 he joined the Laboratoire de Chimie de Coordination du CNRS in Toulouse as Researcher. His research interests span synthetic inorganic and organometallic chemistry of early-to-mid transition metals and small molecule activation.

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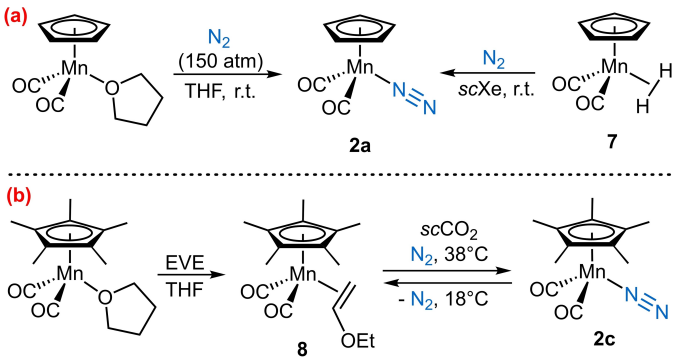
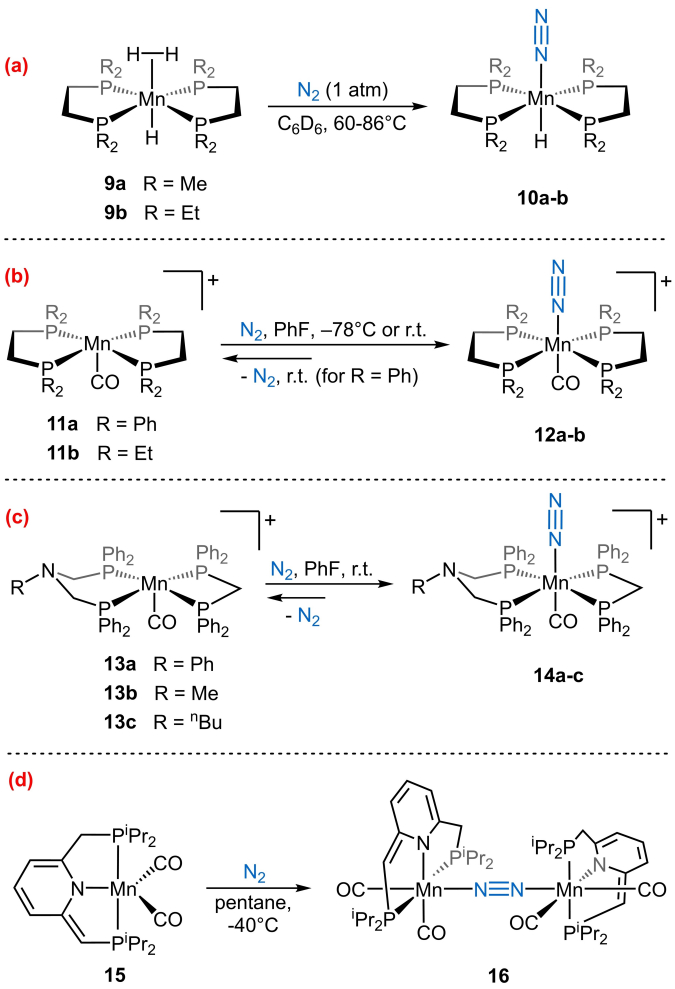


Scheme 2. Preparation of piano-stool Mn-N_2 complexes *via* thermal ligand displacement.

substitution process in complex **8** with dinitrogen in $scCO_2$ (Scheme 2b),[24] in which the equilibrium position may be entirely shifted within a narrow (20 °C) temperature range.

While all chemistry described above was dominated by half-sandwich complexes, thermal ligand displacement to dinitrogen in Mn(I) octahedral complexes was reported only during the 1990s. The synthesis of stable Mn(I) dinitrogen complexes **10a–b** bearing two highly electron-rich chelating diphosphine ligands by thermal η^2-H_2 ligand substitution under a dinitrogen atmosphere was reported by the Jones group (Scheme 3a),[25] and echoes the earlier work of the Chatt group on diphosphine supported Re(I)-N_2 complexes.[14a,c,g] According to IR spectroscopy ($\nu_{N\equiv N}$ 1947 cm^{-1}) and X-ray diffraction data (1.127(7) Å), the N–N bond in **10a** displays the highest activation degree for all known Mn-N_2 complexes. Structurally similar Mn(I) dinitrogen complexes **12** were prepared by the Kubas group from formally 16-electron cationic complexes **11** stabilized by multiple C–H agostic interactions (Scheme 3b).[26] While the formation of **12b** bearing alkyl-substituted diphosphine ligands is quantitative in fluorobenzene at room temperature, its analogue **12a** under the same conditions exists in equilibrium with the starting product **11a** that can be completely shifted towards the N_2 complex at −80 °C. The experimental N≡N stretching frequencies for **12a** (2167 cm^{-1}) and **12b** (2146 cm^{-1}) were significantly higher than for the hydride complexes **10**, presumably due to an overall positive charge and the presence of the π-accepting CO ligand in trans relationship. This chemistry was later extended by Bullock for complexes **13** bearing two different diphosphine ligands (Scheme 3c),[27] revealing the existence of Mn-N_2 species **14** as major components (71–78 %) at room temperature. Noteworthy, no N_2 binding on the metal in complex *trans*-$[(PCy_3)_2Mn(CO)_3]^+$ have been evidenced by ^{15}N NMR spectroscopy even at −60 °C thus showing the importance of a sufficient number of phosphine donors for Mn–N≡N bond stabilization.[28] The formation of binuclear complex **16** upon crystallization of unsaturated Mn(I) complex **15** bearing dearomatized PNP ligand was recently observed by Milstein (Scheme 3d).[29] X-ray diffraction data of this compound show a short N–N bond (1.1135(18) Å), comparable with those found in half-sandwich Mn(I) derivatives **2a** and **6b** (*vide supra*).



Scheme 3. Syntheses of octahedral Mn(I) N_2 complexes supported with diphosphines and PNP ligands.

Pump-probe experiments employing time-resolved IR spectroscopy have allowed the observation of labile Mn-N_2 complexes formed by the reaction of transient solvent-stabilized Mn(I) species with N_2. In particular, the Ford group has shown that laser-flash photolysis of $[Mn(CO)_5CH_3]$ in cyclohexane (CyH) initially forms the C–H agostic intermediate **17**, which reacts with N_2 to give presumably complex **18**, stable only for ~1 ms (Scheme 4a).[30] More recently, a similar experiment was performed jointly by the Fairlamb and Lynam groups for cyclometallated complex **19** in the context of mechanistic studies of C–H bond activation catalysis (Scheme 4b).[31] It was shown that the latter rapidly loses CO under UV irradiation (355 nm) in heptane (HeptH) to afford after solvent-to-N_2 displacement on the microsecond timescale complex **21**, exhibiting very high $\nu_{N\equiv N}$ value (2249 cm^{-1}).

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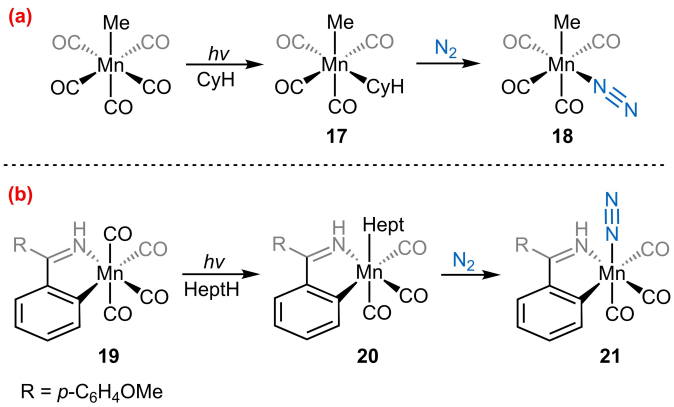
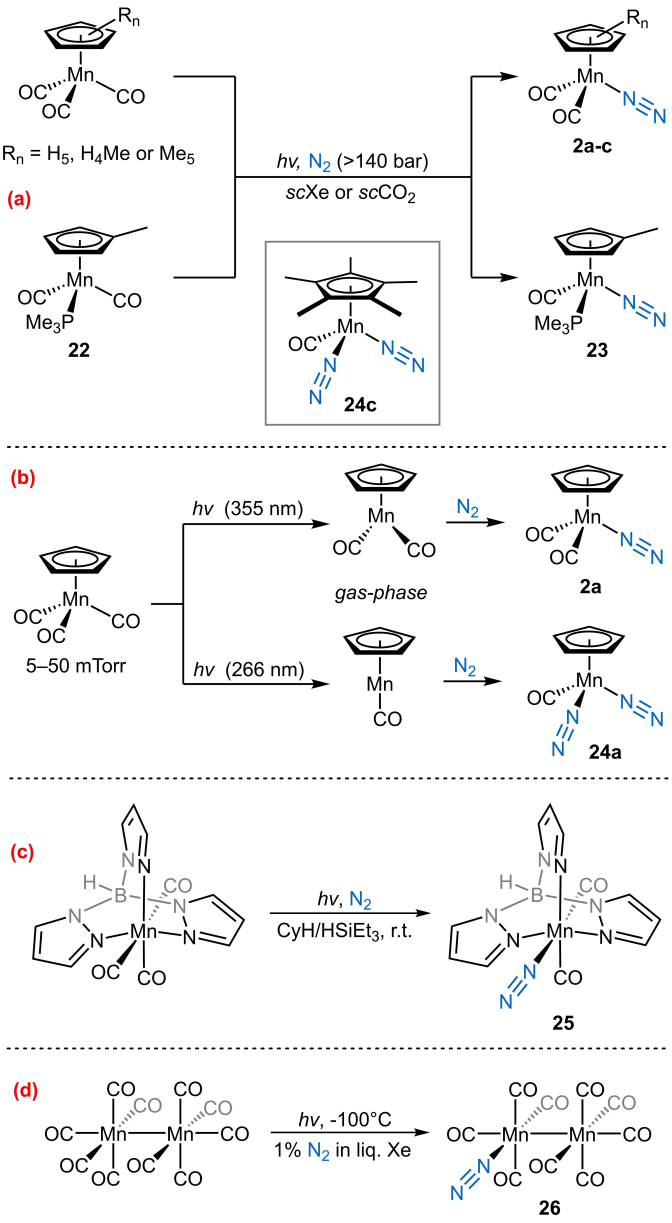


Scheme 4. Mn-N_2 complexes detected by time-resolved pump-probe IR spectroscopy experiments.

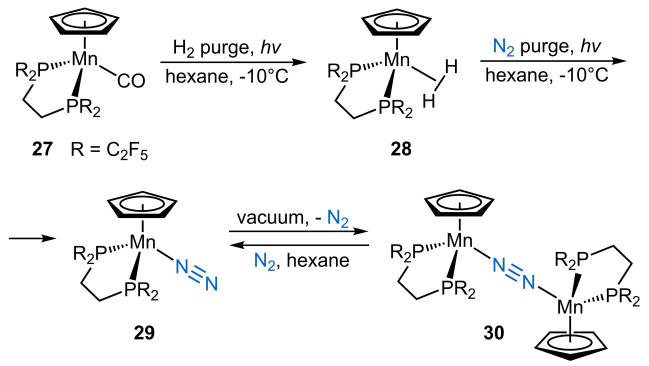
4. Syntheses of Manganese-Dinitrogen Complexes by Photolytic Ligand Exchange

Photochemically induced CO-to-N_2 ligand exchange on cymantrene and its methylated derivatives readily proceeds in *sc*Xe or *sc*CO_2 under high N_2 pressure (>140 bar) to give complexes **2a–c** (Scheme 5a).[32] Under these conditions even monocarbonyl complexes **23** or **24c** can be generated from phosphine complex **22** or [Cp*Mn(CO)$_3$], respectively. Later work by the Fu group explored the reactivity of unsaturated [CpMn(CO)$_2$] and [CpMn(CO)] species, generated in the gas phase by the irradiation of cymantrene at 355 and 266 nm, respectively, to afford Mn-N_2 complexes **2a** and **24a** (Scheme 5b).[33] The groups of Darensbourg and Bengali carried out time-resolved IR spectroscopic studies of [TpMn(CO)$_3$] under UV irradiation in the presence of Et_3SiH revealing the formation of N_2 complex **25** (Scheme 5c),[34] which contrasts with the behavior of [CpMn(CO)$_3$] that affords the σ-complex [Cp(CO)$_2$Mn(η^2-HSiEt$_3$)] under the same conditions. Despite stronger N_2 binding on this system *vs.* H_2, C_2H_4 or $HSiEt_3$, no attempts on the preparative isolation of this product have been performed. The unique example of a Mn(0) dinitrogen complex, **26**, was prepared upon photolysis of [$Mn_2(CO)_{10}$] in liquid Xe doped with 1% N_2. The N_2 ligand in **26** is likely to be found in equatorial position (Scheme 5d).[35] Similar results were obtained for [$Re_2(CO)_{10}$] and [$(CO)_5MnRe(CO)_5$].

The Roddick group used an indirect approach for the photochemical CO-to-N_2 substitution in Mn(I) diphosphine complex **27** (Scheme 6).[36] While its irradiation under nitrogen failed to produce the target species **29**, the latter may be obtained stepwise *via* the initial formation of dihydrogen complex **28** followed by photo-induced H_2-to-N_2 exchange. Upon concentration of a hexane solution, complex **29** bearing a terminal N_2 ligand reversibly transforms into dinuclear product **30**. As expected, the N_2 ligand in the latter is significantly more activated (2015 cm^{-1}) than in its mononuclear congener **29** (2113 cm^{-1}), but to a surprisingly lower extent than in the related dicarbonyl complex **6a** (1975 cm^{-1}).



Scheme 5. Syntheses of Mn-N_2 complexes *via* photolytic CO ligand exchange.



Scheme 6. Syntheses of Mn-N_2 complexes by photolytic H_2 ligand substitution.

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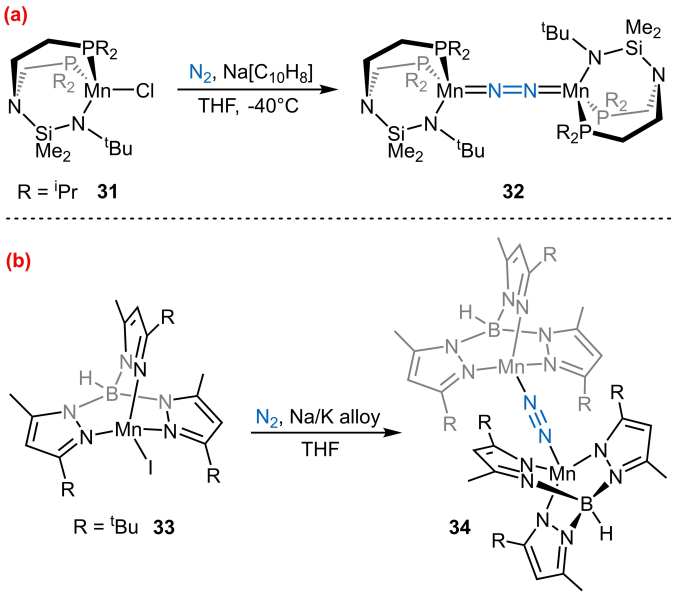
5. Syntheses of Manganese-Dinitrogen Complexes by Reduction of Halide Precursors

Reduction of metal halide precursors under an atmosphere of N_2 remains the most widely used method to prepare dinitrogen complexes. However, only two publications reported a successful synthesis of Mn-N_2 complexes using this strategy, leading in both cases to the isolation of dinuclear μ-η^1:η^1-diazene-diide (N_2^{2-}) complexes (Scheme 7). The Arnold group has prepared complex **32** by sodium naphthalenide reduction under an N_2 atmosphere of the Mn(II) chloride precursor **31** bearing tripodal diphosphineamide ligand (Scheme 7a).[37] Experimental N–N bond length in **32** (1.208(6) Å) is *ca.* 0.1 Å longer than those in related binuclear Mn(I) complexes **6b** and **16**, which is also consistent with the Raman spectra of **32** ($\nu_{N\equiv N}$ 1685 cm^{-1}), showing a low frequency shift compared to conventional binuclear Mn(I) species **6a** or **30**. These data point to an N_2^{2-} unit in complex **32** situated between two Mn(II) centers. Later, the Theopold group reported the reduction of the Mn(II) iodide complex **33** supported with substituted Tp ligand using sodium-potassium alloy (Scheme 7b)[38] to form the related product **34**, in which N_2 is also likely to be reduced to the diazene-diide stage according to N–N bond distance (1.196(5) Å).

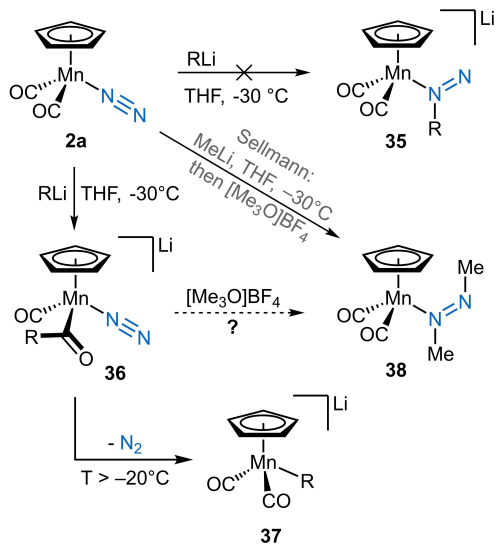
6. Reactivity of Manganese Complexes Relevant to Nitrogen Fixation

Few years after the synthesis of **2a**, the Sellmann group reported an intriguing reactivity for this compound, claiming it could undergo nucleophilic attack by organolithium reagents on its N_2 ligand, occurring at the proximal nitrogen atom and affording an anionic diazenido complex **35** (Scheme 8).[39] This unusual reactivity represents a sort of N_2 ligand "umpolung", since N_2 complexes across the d block are generally prone to electrophilic attack at the distal N. As a matter of comparison, Re-ligated N_2 was shown to react with organic electrophiles to lead to Re-diazenido compounds.[14d,r] The reactivity of the Re analogue of **2a**[14b,e] with lithium organyles was not examined. Coming back to Mn, the nucleophilic attack on coordinated N_2 was recently ruled out by a combined experimental and computational study[16] showing that the actual reactivity site of **2a** is a CO ligand to afford a thermally labile anionic Mn-N_2 acylate **36**. The latter cleanly rearranges into a manganate **37** upon N_2 loss. This latter species was erroneously formulated as the diazenide complex **35** by the Sellmann group. The key point pushing them to propose the nucleophilic attack on the N_2 ligand was the isolation of a neutral 1,2-dimethyldiazene complex **38** after sequential treatment of **2a** with MeLi and $[Me_3O]BF_4$ at low temperature.[40] In view of the recent re-examination of the reactivity of **2a**,[16] the mechanism leading to **38** remains unclear. Since it is unlikely that the final manganate **37** could produce a diazene complex, detailed investigation of the reactivity between manganese-dinitrogen acylate **36** and electrophiles is required to shed light on this puzzling chemistry. Once confirmed, that would make manganese quite unique in the homogenous N_2 chemistry landscape given the peculiarity of such a transformation.

A more classical transformation of N_2 under homogeneous conditions deals with its stoichiometric or catalytic reduction to ammonia or silylamines. While the reactivity of Mn-N_2 complexes with electrophiles is still virtually unexplored, two reports on catalytic dinitrogen reduction using Mn(II) halide precatalysts have recently appeared. The Murray group reported the reductive silylation of N_2 into $N(SiMe_3)_3$ mediated by a trinuclear manganese complex **39**, employing KC_8 as reductant and Me_3SiCl as an electrophile (Scheme 9a).[41] Systematic analysis of the performance for structurally similar complexes of different



Scheme 7. Syntheses of Mn-N_2 complexes under reducing conditions.



Scheme 8. Reactivity of piano-stool Mn-N_2 complex **2a** with organolithium reagents.

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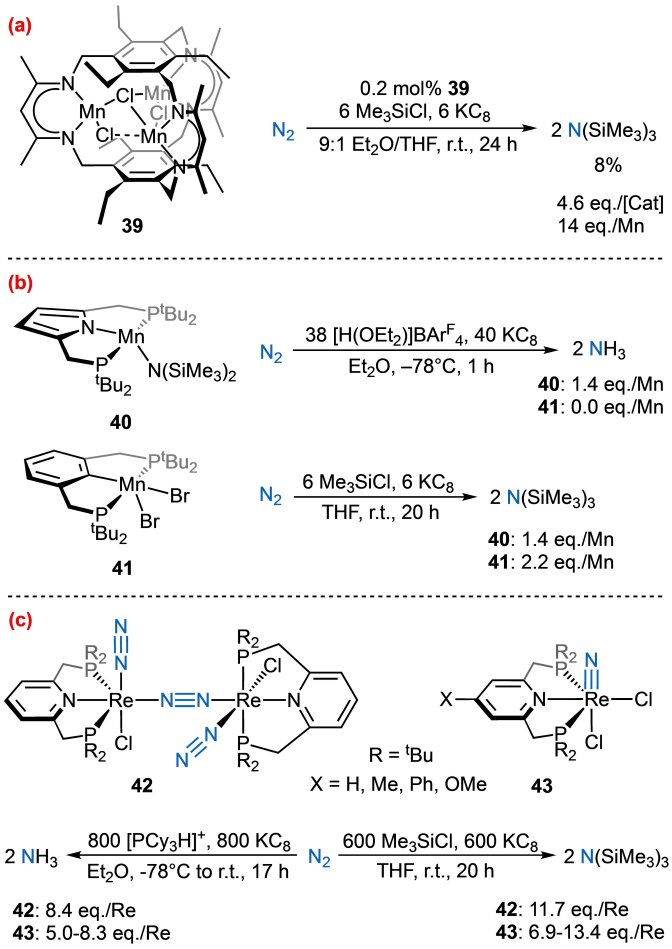
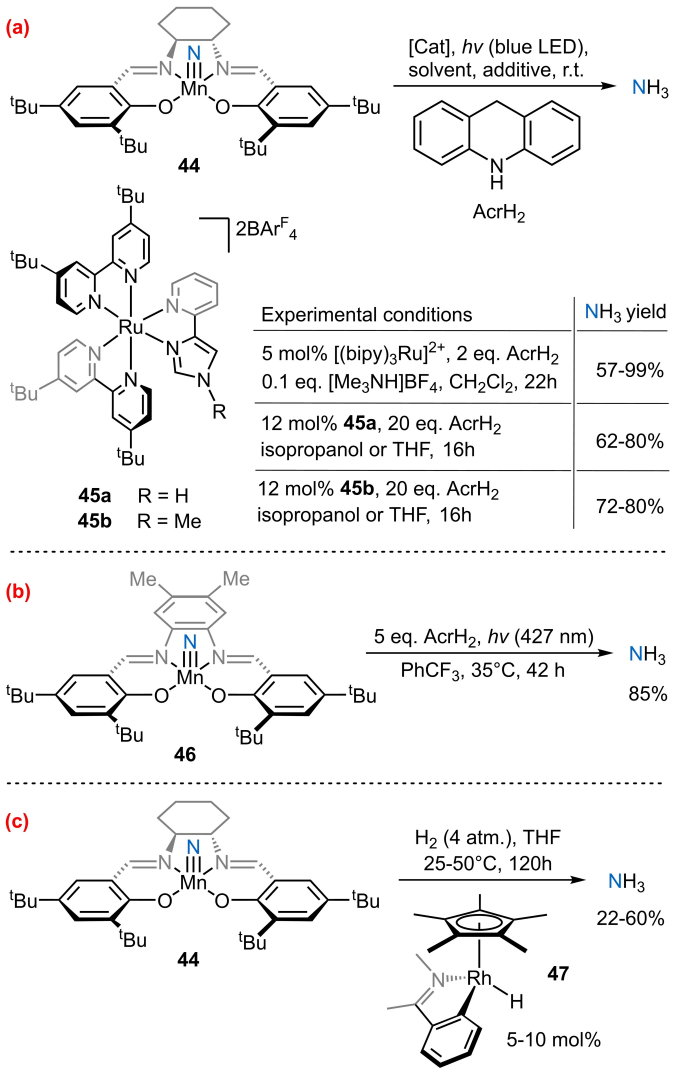


Scheme 9. Manganese and rhenium complexes in catalytic N_2-reduction reactions.

3d metals (Cr, Mn, Fe, Co and Ni) showed that the Mn one was the least efficient, providing 14 equivalents of amine per molecule of catalyst, the best value (77 equivalents) being obtained for Co. The catalytic activity of two pincer-type Mn(II) complexes was evaluated by the Nishibayashi group (Scheme 9b).[42] It was shown that PNP complex **40** reduces N_2 into NH_3 with a low efficiency (TON 1.4), probably due to the occurrence of proton reduction as a preferred pathway. Slightly higher NH_3 yields were obtained using the PCP-supported system **41** after the hydrolysis of tris(trimethylsilyl)amine formed under reductive silylation conditions. Looking down the group, dinuclear Re(I)-N_2 complex **42**[14p] (Scheme 9c) or mononuclear Re(V) nitrido[43] derivatives **43** bearing pyridine-based PNP pincer ligands were also evaluated as catalysts for these reductions and proved more efficient: up to 8.4 eq. of NH_3 and 13.4 eq. of $N(SiMe_3)_3$ were obtained after 15–20 h of reaction.

Metal nitrides are considered as key intermediates in the dinitrogen reduction cycle in both heterogeneous and homogenous processes, therefore their reduction into ammonia is a highly relevant process in the context of nitrogen fixation, especially if the reductant is dihydrogen. In 2019, the Knowles and Chirik groups jointly reported the formation of ammonia by the reduction of Mn(V) salen complex **44** under photoredox conditions, using dihydroacridine ($acrH_2$) as hydrogen donor (Scheme 10a).[44] The conventional photosensitizer $[Ru(bipy)_3](PF_6)_2$ in the presence of weak acid additives was found to be the best catalytic system affording up to 57% of ammonia yield, which can be improved to nearly quantitative by the liberation of coordinated NH_3 from the reduced manganese species with CO or *N,N'*-tetramethylethylenediamine (TMEDA).[44b] The use of Ru(II) photocatalysts **45** in polar solvents (Scheme 10a) allowed to avoid NH_3 complexation resulting in better yields even without post-treatment of Mn residues.[44a] Mechanistic studies revealed that the reaction proceeds *via* proton-coupled electron transfer (PCET) and ruled out any participation of the NH moiety in **45a**. Interestingly, the observation of small background NH_3 production in the absence of Ru(II) complexes allowed the authors to develop an efficient precious-metal-free protocol for the reduction of nitride complex **46** (Scheme 10b)[45] using acridine, readily obtained by photo-oxidation of $AcrH_2$, as organic photocatalyst. The Chirik group later reported the direct hydrogenation of Mn(V) nitride **44** catalyzed by Rh(III) complex **47** (Scheme 10c),[46] albeit the



Scheme 10. Catalytic reduction of manganese nitrides to ammonia.

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reduction proceeded more sluggishly compared to the photoredox approach.

7. Critical Outlook

Although known since the advent of homogeneous dinitrogen activation, Mn-N_2 complexes have not made a breakthrough in this discipline. A notable exception was the unique reactivity of [$CpMn(CO)_2(N_2)$] with carbon nucleophiles,[39,40] which was partially ruled out.[16] This situation contrasts greatly with molybdenum or iron, obviously concentrating early focus of the research community due to the presence of these metals in the nitrogenase's active site. However, it has to be mentioned that d^6 electronic configuration of Mn(I) center in the majority of its organometallic complexes is indeed the same as those in Mo(0) and Fe(II) compounds being two cornerstones of transition metal homogeneous N_2 reduction. So, what makes manganese so overlooked in N_2 chemistry?

The main reason seems to be a limited number of easily available and sufficiently stable Mn-N_2 systems. Even the access to the emblematic Sellmann's complex [$CpMn(CO)_2(N_2)$] (**2 a**) and related half-sandwich derivatives is not trivial and requires multistep synthesis with often low overall yields. According to our own experience, **2 a** is rather difficult to handle because of its rapid decomposition in solution at room temperature with N_2 loss, probably as a result of poor orbital overlap offered by the piano-stool geometry, as well as uncontrolled ligand redistribution affording highly thermodynamically stable [$CpMn(CO)_3$]. At the same time, the octahedral Mn(I) scaffold supported by two chelating diphosphines seems to offer more robust N_2 complexes especially if a strongly σ-donating hydride ligand is present in the trans position. Yet, even in this favorable case, no classical N_2-centered chemistry have been reported so far for these systems. Despite the existence of a multitude of Mn(II) halide complexes bearing bi- and tridentate ligands, only two examples of their reduction were reported in literature to form binuclear N_2 complexes (**32** and **34**, Scheme 7) supported with tripodal ligands. Although the μ-η^1:η^1-N_2 coordination mode in such species is not always optimal to test the reactions relevant to nitrogen fixation, this lets glimpse potential for provoking N_2 scission[47] to form terminal or bridging Mn-nitrides, provided judicious ligand sphere geometries and oxidation state combinations are chosen to ensure full N≡N cleavage.[48] The resulting nitrido complexes may then be further transformed into NH_3, as recently demonstrated by Chirik and Knowles.[44–46] Pincer-supported rhenium complexes have been shown to be particularly efficient at achieving N_2 cleavage in a variety of conditions,[14k,l–o,49] and follow-up reactivity studies have led to the formation of N_2-derived ammonia[14n] and nitriles.[14l,o,50]

Regardless many objective problems discussed above, the lack of systematic investigations in Mn-N_2 chemistry is still difficult to explain from a rational point of view. However, another recent example of such a completely irrational scenario may be pinpointed: organometallic Mn(I) complexes, previously considered as "black sheep" in homogeneous catalysis, have impressively broken through the domain of transition metal-mediated reduction during the last decade. The development of efficient and modular synthetic methods towards Mn-N_2 complexes obviously remains a key factor for the future of this chemistry. The application of conventional reductive approach to readily available Mn(I)/Mn(II) halide derivatives with half-sandwich or octahedral geometry seems in our opinion the most promising option taking into account some precedents for the preparation of isoelectronic V(–I)[51] or Cr(0)[52] analogues of Mn(I) diphosphine complexes. The implementation of strong σ-donating ligands is expected to boost back-donation to the N_2 ligand and potentially lead to complete N–N bond cleavage, still unknown for manganese. A special attention in this case should be paid to the influence of the ligand in *trans*-position to coordinated dinitrogen in octahedral complexes on the Mn–N_2 bond energy and reactivity of this moiety. Conversely, maintaining π-accepting ligands in metal coordination sphere may stabilize low-valent open-shell and/or anionic complexes *vs.* N_2 uptake.

We hope to convince our readers that a lot remains to do in the chemistry of Mn-N_2 complexes starting from the validation of Sellmann's diazene synthesis to structure/reactivity relationship studies relevant to nitrogen fixation chemistry and supported by the evaluation of key thermodynamic parameters (binding energies, redox potentials, barriers for N_2 scission, …). It is anticipated that this largely underdeveloped area may drain the interest of synthetic, physical and computational chemists in the near future.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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CONCEPT

In the context of nitrogen fixation, manganese complexes seem to be set back when compared to other early-to-mid transition metals. This does not reflect the rush this metal has experienced in homogeneous hydrogenation catalysis and related processes. Giving an overview of the relevant literature, the authors attempt to answer why this metal has not yet made its breakthrough in N_2 activation.

Dr. Q. Le Dé, Dr. D. A. Valyaev, Dr. A. Simonneau**

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Nitrogen Fixation by Manganese Complexes – Waiting for the Rush?

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