

Catalytic Dinitrogen Silylation



Evaluating Metal Ion Identity on Catalytic Silylation of Dinitrogen Using a Series of Trimetallic Complexes

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Abstract: We report catalytic silylation of dinitrogen to tris(trimethylsilyl)amine by a series of trinuclear first row transition metal complexes (M = Cr, Mn, Fe, Co, Ni) housed in our tris(β diketiminate) cyclophane (L^{3-}). Yields are expectedly dependent on metal ion type ranging from 14 to 199 equiv. NH₄⁺/

complex after protonolysis for the Mn to Co congeners, respectively. For the series of complexes, the observed trend for the number of turnovers as a function of metal ion type is Co > Fe > Cr > Ni > Mn, consistent with prior reports of greater efficacy of Co over Fe in other ligand systems for this reaction.

Introduction

The industrial production of ammonia from N₂ and H₂ pioneered by Haber and commercialized by Bosch in the early 20th century represents one of the most important technological advances of that century.^[1-4] Notably, this process, which is vital to support current agricultural output and industrial chemical processes, has remained largely unchanged since its implementation. Despite the high energy efficiency and yields of this process, significant interest has focused on addressing the drawbacks, such as the reliance on fossil fuels as the H₂ source and the need for highly centralized and large scale production facilities. The pursuit of novel catalytic systems for N₂ fixation methods to alleviate these issues remains an area of active research. Significant advances have been made with respect to N_2 conversion to NH_3 and N_2H_4 under ambient conditions.^[5] For homogeneous systems, the majority employ iron or molybdenum centers and derive their inspiration from the ironmolybdenum cofactor, which is the active site for nitrogen fixation in molybdenum-dependent nitrogenases. Notable examples in this regard are the first report of stepwise conversion of N₂ to NH₃ for multiple cycles, catalytic N₂ fixation by an iron complex in the presence of protons and reducing agents, and the recent reports of Fe and Mo catalysts that effect N₂ fixation using PCET reagents.^[6-13] Impressively, the molybdenum catalyst reported by Nishibayashi and co-workers generates up to 4,350 equivalents of NH₃ using Sml₂ and alcohols or water. Examples have been reported for other metal centers;^[14] however, a systematic approach to evaluating the role of metal ion type on N₂ fixation has yet to be reported.

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Given that demetalation, hydrogen production, or both can compete with N₂ fixation by homogeneous catalysts in the presence of protons and chemical reductants, use of a silyl cation source as a proton surrogate provides a complementary approach to examine N₂ fixation by coordination compounds. The resultant silylamine products from such catalytic silylation experiments can be readily decomposed to NH₄⁺ using a strong mineral acid. Catalytic silylation has been demonstrated by complexes of Ti, V, Cr, Fe, Mo, W, Co, and Rh, with single run yields as high as 195 equiv. N(SiMe₃)₃ reported by Lu and coworkers.^[15–33] Two observations are notable for this series, however. First, the supporting ligands typically differ across these complexes; in some cases, Co and Fe congeners are evaluated, but examples extending such series to include to Cr, Mn, or Ni remain absent from the literature. The only systematic study is that from Shiina wherein catalytic N₂ fixation by various metal chloride salts is examined and CrCl₃ noted as the most efficacious with 5.4 equiv. N(SiMe₃)₃ per equivalent of the metal salt.^[34] Other first row transition metal ions in that survey included chloride salts of Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II}. Second, standard approaches have not been employed, and particularly with respect to mol-% of catalyst or electron equivalents. The latter prevents a faithful comparison of the yields of fixed nitrogen as a function of metal ion type.

Previously, our group demonstrated that a family of triiron complexes housed in our tris(β -diketiminate) cyclophane (L³⁻) is competent for the catalytic reduction of N₂ to N(SiMe₃)₃ using KC₈ and Me₃SiCl as the reductant and electrophile, respectively.^[35] The maximum yield reported under those conditions was 83 equiv. N(SiMe₃)₃ per complex for Fe₃Br₃L, which was determined by ¹H-NMR spectroscopic quantification of the NH₄⁺ generated after quenching the reaction with acid. Notably, this yield corresponds to conversion of 50 % of the added electrons into fixed nitrogen species – the highest reported for any catalyst of this reaction to date. For these triiron complexes, a general trend is apparent in which complexes bearing π -basic ligands (e.g., sulfide and bromide) afford higher number of turnovers of fixed nitrogen as compared to those with strong σ

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donors and/or π -acidic donors (viz. hydride and carbonyl, respectively). Indeed, changing one hydride in Fe₃H₃L to a formate in Fe₃H₂(O₂CH)L restores the number of turnovers to levels comparable to that of the bromide complex. We speculate that this trend results from more facile dissociation of the ancillary ligands upon reduction by KC₈, which creates a vacant coordination site for N₂ binding and subsequent activation. Given we can access isostructural complexes of L³⁻ wherein metal ion type is varied, our system provides a unique opportunity to evaluate the effect of metal ion type on N₂ fixation by polynuclear metal complexes. Herein, we report catalytic silylation of N₂ by a family of M₃X₃L complexes in which M = Cr, Mn, Fe, Co, or Ni, and X = CI or Br (Scheme 1). Our results highlight the superiority of Co for this reaction, which has been previously noted by others.



Scheme 1. Dinitrogen silylation catalysed by M₃X₃L complexes.

Results and Discussion

Synthesis of M₃X₃L (M/X = Cr/Cl, Ni/Br)

Given our prior success at generating trimetallic complexes of Mn, Fe, Co, Cu, and Zn, we extended a similar methodology to the syntheses of the related chromium(II) and nickel(II) complexes. The synthetic scheme bears resemblance to that previously reported for $Mn_3Br_3L^{[36]}$ with the following exceptions. First, the THF adducts of $CrCl_2$ and NiBr₂ were used as these starting materials have improved solubility in THF as compared to the desolvated anhydrous metal dihalides and react more readily with the deprotonated ligand. Second, initial metalation of the deprotonated ligand was conducted at -34 °C followed by stirring at room temperature for an extended period. Yields of the target tri-chromium(II) and -nickel(II) complexes at 35 % and 34 %, respectively, are low in comparison to other congeners.

The solid-state structure of Cr₃Cl₃L reveals a comparable ladder-like pseudo $C_{2\nu}$ arrangement of the $[M_3X_3]^{3+}$ cluster as observed for a number of other complexes of this ligand, including the tri-manganese(II) and -iron(II) tri(chloride) complexes of this ligand (Figure 1). The metal centers in Cr₃Cl₃L are most consistent with Cr1 and Cr2 in trigonal pyramidal coordination ($\tau_4 = 0.74-0.81$)^[37] whereas the bond metrics around Cr3 indicate a planar 3-coordinate metal center (Cr3–Cl1 or Cl2 = 2.76 or 2.87 Å). Other bond metrics, such as the N–M–N angles and M–(μ_3 -Cl) bond lengths, are comparable for Cr₃Cl₃L, Mn₃Cl₃L, and Fe₃Cl₃L. Combustion analysis and other spectroscopic characterization are consistent with the formulation of Cr₃Cl₃L. Spectroscopic data on the trinickel(II) tri(bromide) congener agrees with the expected C_{2v} symmetry and the proposed formulation.



Figure 1. Side-view (left) and top-view (right) of solid-state structure of Cr_3Cl_3L . Cr1 and Cr2 are best described as trigonal pyramidal, whereas Cr3 is consistent with a trigonal planar Cr^{II} center with Cr3···Cl1 or Cl2 distances being > 2.76Å. Cr, Cl, C, and N atoms are depicted as maroon, lime green, grey, and blue ellipsoids at 70 % probability maps, respectively. Solvent molecules and H atoms are omitted for clarity.

Catalytic Silylation of Dinitrogen

With the series comprising the trinuclear chromium, manganese, iron, cobalt, and nickel compounds in hand, we then sought to evaluate the effect of metal ion type on the catalytic silvlation of dinitrogen. We intended to employ the conditions reported in our prior study; however, Mn₃Cl₃L is poorly soluble in toluene or toluene/ether mixtures. Consequently, we determined the turnover for catalytic silvlation of dinitrogen by these complexes, including Fe₃Br₃L, in a 9:1 mixture of Et₂O and THF (Scheme 2). Under these conditions, all complexes proved to be competent precatalysts for the catalytic silylation of N₂. Including mercury in the catalytic reaction did not result in a significant effect on the number of turnovers, strongly suggesting that trace heterogeneous species are not responsible for the observed catalysis.^[38] In addition, experiments in which the precatalyst is subjected to catalytic conditions and, following consumption of KC_8 and $\mathsf{Me}_3\mathsf{SiCl},$ the reaction is refreshed with more equivalents to continue catalysis were performed for Co₃Br₃L. This portion wise addition method gives a similar yield to a single addition of reductant and electrophile. Taken together, these experiments demonstrate that the active species is likely homogeneous and recyclable (Table S1). From these results, the trend observed is that Co > Fe > Cr > Ni > Mn. Insofar as our species are discrete trimetallic complexes, our data are reported per complex rather than per metal ion and our comparisons to prior articles based on number of turnovers per complex.

N₂ + 500 KC₈ + 500 Me₃SiCl
$$\xrightarrow{precatalyst}$$
 (Me₃Si)₃N $\xrightarrow{xs \text{ HCl}}$ NH₄Cl
9:1 Et₂O/THF
rt, 24 h

Scheme 2. Catalytic silylation of N₂.

 Cr_3Cl_3L affords up to 41(5) N(SiMe_3)_3 per complex using KC₈ and Me₃SiCl as the electron and silyl cation sources, respectively (Table 1, Entry 1). This yield is comparable to that previously



reported by Mock and co-workers for a chromium complex of a macrocyclic tetraphosphine ligand (**A**, Table S2).^[17] Optimized conditions for the Mock system yield 10.6 equiv. N(SiMe₃)₃ in a single run and up to 34.1 equiv/complex when catalytic reactions are recharged with additional equivalents of reductant and Me₃SiCl. Yin, et al. reported N₂ reduction to N(SiMe₃)₃ by anionic chromium(0)-bis(dinitrogen) complexes using K and Me₃SiCl, with yields of up to 26 equiv. N(SiMe₃)₃/complex (**B**, Table S2).^[18] In both prior examples of Cr catalysts, the supporting ligands disfavor metal ion dissociation during redox cycling, likely improving catalyst lifetime and resulting in the observed yields. Similarly, stabilization of the complex towards substitution and demetalation may be operative in our system as well.^[39]

Table 1. Silylation of $N_{\rm 2}$ catalyzed by a family of trimetallic cyclophanates.

Entry	Precatalyst	N(SiMe ₃) ₃ /complex ^[a]	Yield [%] ^[b]
1	Cr ₃ Cl ₃ L	41 ± 5	25
2	Mn ₃ Cl ₃ L	14 ± 2	8
3	Fe ₃ Br ₃ L	56 ± 6	34
4 ^[c]	Fe ₃ Br ₃ L	57 ± 7	34
5	Co ₃ Br ₃ L	77 ± 9	46
6 ^[c]	Co ₃ Br ₃ L	97 ± 2	58
7 ^[c,d]	Co ₃ Br ₃ L	199	40
8	Ni ₃ Br ₃ L	24 ± 4	14
9 ^[e]	No catalyst	0	0

[a] Reaction conditions unless stated otherwise: 0.66 μ mol precatalyst (in THF), 330 μ mol KC₈ and Me₃SiCl, 9:1 Et₂O/THF, r.t., 24 h, and 1 atm N₂. Quantified after acid hydrolysis by ¹H NMR and reported as mol N(SiMe₃)₃/mol precatalyst averaged over 3 trials. [b] Yield based on reducing equivalents (KC₈). [c] Stock solution of precatalyst in PhMe and the final solution is 9:1 Et₂O/PhMe. [d] KC₈ and Me₃SiCl increased to 990 μ mol and the time increased to 54 h. [e] Standard reaction conditions. An equal volume of neat THF was used instead of a THF solution of catalyst.

To the best of our knowledge, this report is only the second example of dinitrogen reduction and functionalization by a molecular manganese species, with the first being from Sellmann and co-workers.^[19] Our trimanganese(II) cyclophanate affords 14(2) equiv. N(SiMe₃)₃/complex, which is the lowest of our reported systems (Table 1, Entry 2). The fact that this yield is the lowest of all other metals tested, however, is consistent with lack of substantial precedent for dinitrogen coordination and activation at Mn centers.^[40] The spherical electron distribution of the d^5 Mn^{II} ion results in ligand substitution reactivity and bonding interactions analogous to *s*-block metal ions.^[41] We postulate that the enhanced stability towards redox cycling afforded by our ligand is integral to the presumed N₂ binding and reduction to tristrimethylsilylamine by Mn₃Cl₃L.

Use of Fe_3Br_3L as the precatalyst affords yields of $N(SiMe_3)_3$ which are within error from our prior reported values,^[35] implying minimal effect of the solvent composition change wherein PhMe is replaced with THF (Table 1, Entries 3 and 4). However, a solvent dependence has been observed under catalytic silylation conditions in our system and others; in particular, solutions in which THF is the major solvent component (e.g., 1:9 mixture of PhMe/THF) results in a 3-fold decrease in the yield of $N(SiMe_3)_3$ when Fe_3Br_3L is employed as precatalyst. The reason for this solvent effect on catalysis is unclear; however, competing reactions involving THF under reducing conditions, such

as ring-opening, polymerization, and demetalation, have been documented by others and may compete with N_2 reduction in THF-rich solutions. $^{[17,21,23,31]}$

 Co_3Br_3L is the best complex for effecting catalytic silvlation of dinitrogen of the suite of complexes reported here with 77(9) equiv. N(SiMe₃)₃/complex and a 46 % yield based on reducing equivalents (Table 1, Entry 5). This result is strikingly similar to prior reports from others, in which the cobalt complex outperforms the iron congener for this reaction (Figure 2). The greater electronegativity of cobalt vs. iron balances the metal-nitrogen σ -bonding interactions with the extent of π -donation to the N₂ ligand. Specifically, traversing the catalytic cycle requires stability of the various multimetallic complexes across the sampled oxidation states as well as the ability to activate N₂. We opine that the extent of activation of the coordinated N₂ is reflected in the electronegativity of the metal ion wherein the energy difference between the metal d_{π} orbitals and N₂ π^* orbitals influences the extent of charge accumulation on the N₂ fragment, which leads to the nucleophilic character needed for silylation (e.g., comparison of the N-N vibration for Ti₂N₂ vs. isovalent Fe₂N₂ complexes).^[42,43] In contrast, the metal-ligand bond lability with respect to the cyclophane β -diketiminate donors, which are weak field ligands, can be described by the Irving-Williams series with Mn^{II} complexes being more kinetically labile as compared to the Ni^{II} congeners.^[44] Indeed, we speculate that the deleterious effect noted when the reaction solvent is rich in THF results from metal-ion dissociation and complex dissolution from the cyclophane ligand. We suggest then that the metal-cyclophanate bond lability and extent of charge accumulation on the dinitrogen ligand (i.e., formally anionic N₂ species) are competing factors across the series explored here, with the best compromise at Fe and Co. Such an analysis, however, posits a mechanism wherein silvl-radicals are not catalytically relevant. Future studies, such as DFT calculations or freeze-quench experiments, will be necessary to provide further insight into the mechanism of this reaction. Although few isostructural examples are known, comparison of Co and Fe towards N₂ reduction to ammonia may follow the reverse trend of catalytic silvlation. This change in order as a function of electrophile



Figure 2. Relationship between Pauling electronegativity of the metal in the precatalyst employed and the yield of NH_4^+ from catalytic silylation.



likely reflects the relative strengths of the Me_3Si/H–N and Me_3Si/H–M (M = Fe or Co) bonds.

The tricobalt precatalyst yields fewer turnovers when THF is used as the cosolvent instead of PhMe, contrasting the insensitivity for this solvent change noted above for the triiron analogs. For a single addition of reductant and silyl electrophile, yields of tris(trimethylsilyl)amine per complex dramatically increase from 77(9) equiv. for the THF-containing reaction to 97(2) equiv. for reactions performed in 9:1 Et₂O/toluene (Table 1, Entry 6). Moreover, increasing the reaction time and decreasing the mol-% of Co₃Br₃L (but not the catalyst concentration) in the Et₂O/PhMe solvent system results in an impressive yield of 199 equivalents of the amine per complex (Table 1, Entry 7). These yields are comparable to other molecular cobalt catalysts in the literature, which have emerged as some of the most effective catalysts for this reaction. For example, Fryzuk and Masuda's Co^I complex binds N_2 at -40 °C with minimal activation and is an effective catalyst at this temperature for N₂ silylation with 200 ± 20 equiv. N(SiMe₃)₃/complex after 10 d (**D**, Table S2). A more appropriate comparison, however, is of their catalyst at room temperature; their reported yield of 100 equiv. NH₄Cl (post hydrolysis of the tris-silylamine) after 24 h is comparable to our value here. A notable difference is the substantially higher yield based on KC₈ at 58 % for our complex as compared to their value, which we calculate as 20 % based on their reported conditions.

The final comparison is to the dicobalt catalyst reported by Lu, which affords 195 equiv. N(SiMe₃)₃/complex and a 30 % yield relative to KC₈ in a single run at room temperature after only 12 h (C, Table S2).^[21] This value is one of the highest number of turnovers reported for any catalyst of this reaction to date. Interestingly the second cobalt, although potentially redox active, is presumed not to participate directly in N₂ binding and reduction but rather acts as a ligand for the catalytically active Co center. The importance of metal-metal interactions or cooperative metal-ligand effects (e.g., bridging ligands) to effect dinitrogen fixation are a developing theme from the assembled data. Specifically, we surmise that multiple metal centers improve electron efficiency for N₂ reduction potentially by providing a means of storing reducing equivalents and reducing deleterious side reactions. Our system demonstrates the ability of three metal centers, regardless of metal ion identity or type, to facilitate N₂ binding and functionalization.

For Ni₃Br₃L, we observe fewer turnovers with only 24(4) equiv. N(SiMe₃)₃/complex and a 14 % yield based on reducing equivalents (Table 1, Entry 8). Dinitrogen complexes of Group $10^{[45-47]}$ and $11^{[48,49]}$ metals are relatively rare, although a growing number of nickel(I) and nickel(0) dinitrogen adducts are being reported. In general, however, the extent of activation of the bound N₂ is significantly less than that of the Fe or Co congeners, in agreement with the expected weaker π -backdonation from Ni to N₂ as compared to Fe or Co if formal oxidation state is held constant. Expectedly then, no examples of N₂ cleavage on a nickel complex have been reported, with dinitrogen dissociation typically preferred over functionalization.^[47,50-52] To the best of our knowledge, Ni₃Br₃L represents the first example of catalytic dinitrogen reduction by a molec-

ular Ni complex. The ability to execute catalytic silylation of dinitrogen using our trinickel complex – albeit in low yield and number of turnovers-may arise from metal-metal cooperative effects. Specifically, the additive effect of multiple Ni centers allows for sufficiently strong interactions with N₂ to allow for charge transfer and N–N bond scission, whereas such activation is absent in isolated or aggregated monometallic species. Our prior report of a tricopper-dinitrogen species reinforces this hypothesis.^[48]

Conclusions

In summary, a family of homotrimetallic cyclophanates were demonstrated to be competent for catalyzing dinitrogen reduction under ambient conditions using KC₈ and Me₃SiCl as the electron and electrophile sources, respectively. The number of turnovers range from 14 to 199 equiv. N(SiMe₃)₃/complex with some of the highest reported yields based on electrons added (58 % for Co₃Br₃L). These results include seminal examples of a molecular manganese and molecular nickel catalyst for N₂ reduction as well as the most turnovers in a single run by a chromium catalyst to date. The yield of fixed N correlate with differences in the electronegativities of the metals utilized in each complex, which balances the σ and π metal-dinitrogen covalency. In addition, our trinucleating cyclophane ligand likely serves to stabilize the catalyst to metal ion dissociation during redox cycling.

Experimental Section

General Considerations: All manipulations were performed in an Ar filled Vigor Tech glovebox or an N₂ filled Innovative Technologies alovebox. Solvents were purchased from Sigma-Aldrich, dried using an Innovative Technologies solvent purification system, and stored over 3 Å molecular sieves in the gloveboxes. Dimethyl sulfoxide- d_6 ([D₆]DMSO) was purchased from Cambridge Isotope Laboratories, degassed, dried by stirring over activated basic alumina under an Ar atmosphere, filtered, and stored over 3 Å molecular sieves in the glovebox. [D₆]Benzene was purchased from Cambridge Isotope Laboratories, dried by refluxing over CaH₂, distilled and degassed, and then stored over 3 Å molecular sieves in the glovebox. H_3L , $\mathsf{Mn}_3\mathsf{Cl}_3\mathsf{L},\ \mathsf{Fe}_3\mathsf{Br}_3\mathsf{L},\ \mathsf{and}\ \mathsf{Co}_3\mathsf{Br}_3\mathsf{L}$ were synthesized using published literature procedures.^[36,53,54] Me₃SiCl was purchased from Sigma-Aldrich and stored in the gloveboxes. KC₈ was prepared under Ar by the solid state reaction of K metal and graphite at 150 °C under vacuum with vigorous mechanical stirring until a golden-brown powder was obtained. BnK was synthesized as reported by Schlosser.^[55] THF adducts of metal halide salts were prepared via Soxhlet extraction of the anhydrous material under N_2 . ¹H Nuclear Magnetic Resonance (¹H NMR) spectra were recorded on a Varian Inova 500 MHz spectrometer or a Mercury operating at 300 MHz equipped with a three-channel 5 mm indirect detection probe with *z*-axis gradients. Chemical shifts were reported in δ (ppm) and were referenced to solvent resonances $\delta H = 7.16$ ppm and 2.50 ppm for [D₆]benzene and [D₆]dimethyl sulfoxide, respectively.

CCDC 1972558 (for Cr_3Cl_3L) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



Cr₃Cl₃L: A 20 mL scintillation vial was charged with H₃L (200 mg, 0.289 mmol) and THF (10 mL). The suspension was cooled to -34 °C for 30 min. To the cold suspension was added BnK (118 mg, 0.906 mmol) and, upon dissolution, CrCl₂·2THF (242 mg, 0.906 mmol). The viscous, blood red suspension was stirred at -34 °C for 30 min followed by 3 h of stirring at room temperature. THF was removed under reduced pressure and replaced with benzene (15 mL). The mixture was stirred overnight at 80 °C and then vacuum filtered through a pad of Celite to yield a brick red solution. The filtrate immediately precipitated the product as an analytically pure, brick red microcrystalline powder (96 mg, 35 %). Single crystals suitable for X-ray diffraction were grown by slow cooling of a saturated benzene solution. ¹H NMR (500 MHz, C_6D_6): $\delta = -57.4$, -28.1, -20.4, 82.1, 88.2 ppm. ATR-IR (cm⁻¹): 2947, 1521, 1461, 1431, 1395, 1371, 1325, 1066, 1013, 724. C45H63N6Cr3Cl3•2C6H6: calcd. C 61.867, H 6.831, N 7.594; found C 61.388, H 6.834, N 7.736.

Ni₃Br₃L: A 20 mL scintillation vial was charged with H₃L (200 mg, 0.289 mmol) and THF (10 mL). The suspension was cooled to -34 °C for 30 min. To the cold mixture was added BnK (118 mg, 0.906 mmol) followed by NiBr₂•2THF (329 mg, 0.906 mmol) upon dissolution. The suspension was stirred at -34 °C for 30 min and then 3 h at room temperature during which time the reaction gradually turned dark green. The THF was removed under reduced pressure and replaced with benzene (15 mL). The suspension was stirred overnight at 80 °C and then vacuum filtered through a pad of Celite to yield a dark green filtrate. The solvent was removed under reduced presduced pressure to yield analytically pure material (110 mg, 34 %). ¹H NMR (500 MHz, C₆D₆): $\delta = -65.6$, 9.5, 19.5 ppm. ATR-IR (cm⁻¹): 2948, 2921, 1526, 1429, 1392, 1370, 1275, 1216, 1009, 728. C₄₅H₆₃Ni₃Br₃•0.5C₄H₈O: calcd. C 49.524, H 5.925, N 7.373; found C 49.204, H 5.897, N 6.844.

Standard Procedure for the Catalytic Conversion of N₂ to N(SiMe₃)₃: KC₈ (45.0 mg, 330 µmol) was suspended in Et₂O (1.80 mL) in a 20 mL scintillation vial equipped with a glass stir bar. Chlorotrimethylsilane (42.0 µL, 330 µmol) was added, followed by the respective precatalyst as a solution in THF (200 µL, 3.3 mM, 0.66 µmol). The reactions were stirred at room temperature for 24 h after which they were filtered through a plug of Celite into a vial containing HCl as a 2 m solution in Et₂O (200 µL). The Celite plug and reaction vial were rinsed with 2 mL of Et₂O. The resulting filtrate was allowed to react for a minimum of 10 min before removing the solvent under reduced pressure. The resulting white solids were dissolved in dry [D₆]DMSO with 1,3,5-trimethoxybenzene as an internal standard. The ammonium was quantified using ¹H NMR. The experiments were performed in triplicate.

Mercury Poisoning Test: To a 20 mL scintillation vial containing KC₈ (45.0 mg, 330 µmol) was added Et₂O (1.8 mL) followed by chlorotrimethylsilane (42.0 µL, 330 µmol) and a solution of precatalyst in THF (200 µL, 3.3 mM, 0.66 µmol). To the suspension was added mercury (50.0 mg, 0.249 mmol). The reaction was allowed to stir at room temperature for 24 h followed by filtration through a Celite plug and quenching with 2 m HCl in Et₂O (200 µL). N(SiMe₃)₃ was quantified as described above.

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- A. Mittasch, W. Frankenburg, in *Adv. Catal.* (Eds.: W. G. Frankenburg, V. I. Komarewsky, E. K. Rideal), Academic Press, **1950**, pp. 81–104.
- [2] "The Nobel Prize in Chemistry 1918," can be found under https:// www.nobelprize.org/prizes/chemistry/1918/haber/lecture/.
- [3] G. Prieto, F. Schüth, Angew. Chem. Int. Ed. 2015, 54, 3222–3239; Angew. Chem. 2015, 127, 3268.
- [4] V. Smil, Nature 1999, 400, 415-415.
- [5] Y. Nishibayashi, Inorg. Chem. 2015, 54, 9234–9247.
- [6] K. Arashiba, Y. Miyake, Y. Nishibayashi, Nat. Chem. 2011, 3, 120–125.
- [7] J. S. Anderson, J. Rittle, J. C. Peters, Nature 2013, 501, 84-87.
- [8] D. V. Yandulov, R. R. Schrock, Science 2003, 301, 76-78.
- [9] S. Kuriyama, K. Arashiba, K. Nakajima, Y. Matsuo, H. Tanaka, K. Ishii, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2016**, *7*, 1–9.
- [10] M. M. Rodriguez, E. Bill, W. W. Brennessel, P. L. Holland, Science 2011, 334, 780–783.
- [11] Y. Lee, F. T. Sloane, G. Blondin, K. A. Abboud, R. García-Serres, L. J. Murray, Angew. Chem. Int. Ed. 2015, 54, 1499–1503; Angew. Chem. 2015, 127, 1519.
- [12] P. J. Hill, L. R. Doyle, A. D. Crawford, W. K. Myers, A. E. Ashley, J. Am. Chem. Soc. 2016, 138, 13521–13524.
- [13] T. D. Lohrey, R. G. Bergman, J. Arnold, Dalton Trans. 2019, 48, 17936– 17944.
- [14] Z.-J. Lv, Z. Huang, W.-X. Zhang, Z. Xi, J. Am. Chem. Soc. 2019, 141, 8773– 8777.
- [15] P. Ghana, F. D. van Krüchten, T. P. Spaniol, J. van Leusen, P. Kögerler, J. Okuda, Chem. Commun. 2019, 55, 3231–3234.
- [16] R. Imayoshi, K. Nakajima, Y. Nishibayashi, Chem. Lett. 2017, 46, 466-468.
- [17] A. J. Kendall, S. I. Johnson, R. M. Bullock, M. T. Mock, J. Am. Chem. Soc. 2018, 140, 2528–2536.
- [18] J. Yin, J. Li, G.-X. Wang, Z.-B. Yin, W.-X. Zhang, Z. Xi, J. Am. Chem. Soc. 2019, 141, 4241–4247.
- [19] D. Sellmann, W. Weiss, Angew. Chem. Int. Ed. Engl. 1977, 16, 880–881; Angew. Chem. 1977, 89, 918.
- [20] Y. Ohki, Y. Araki, M. Tada, Y. Sakai, Chem. Eur. J. 2017, 23, 13240-13248.
- [21] R. B. Siedschlag, V. Bernales, K. D. Vogiatzis, N. Planas, L. J. Clouston, E. Bill, L. Gagliardi, C. C. Lu, J. Am. Chem. Soc. 2015, 137, 4638–4641.
- [22] Y. Gao, G. Li, L. Deng, J. Am. Chem. Soc. **2018**, 140, 2239–2250.
- [23] R. Imayoshi, H. Tanaka, Y. Matsuo, M. Yuki, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Chem. Eur. J.* 2015, *21*, 8905–8909.
- [24] T. Suzuki, K. Fujimoto, Y. Takemoto, Y. Wasada-Tsutsui, T. Ozawa, T. Inomata, M. D. Fryzuk, H. Masuda, ACS Catal. 2018, 8, 3011–3015.
- [25] R. Kawakami, S. Kuriyama, H. Tanaka, K. Arashiba, A. Konomi, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Chem. Commun.* **2019**, https://doi.org/ 10.1039.C9CC06896A.
- [26] D. E. Prokopchuk, E. S. Wiedner, E. D. Walter, C. V. Popescu, N. A. Piro, W. S. Kassel, R. M. Bullock, M. T. Mock, *J. Am. Chem. Soc.* **2017**, *139*, 9291– 9301.
- [27] A. D. Piascik, R. Li, H. J. Wilkinson, J. C. Green, A. E. Ashley, J. Am. Chem. Soc. 2018, 140, 10691–10694.
- [28] G. Ung, J. C. Peters, Angew. Chem. Int. Ed. 2015, 54, 532–535; Angew. Chem. 2015, 127, 542.
- [29] R. Araake, K. Sakadani, M. Tada, Y. Sakai, Y. Ohki, J. Am. Chem. Soc. 2017, 139, 5596–5606.
- [30] A. Cavaillé, B. Joyeux, N. Saffon-Merceron, N. Nebra, M. Fustier-Boutignon, N. Mézailles, Chem. Commun. 2018, 54, 11953–11956.
- [31] H. Tanaka, A. Sasada, T. Kouno, M. Yuki, Y. Miyake, H. Nakanishi, Y. Nishibayashi, K. Yoshizawa, J. Am. Chem. Soc. 2011, 133, 3498–3506.
- [32] K. Komori, H. Oshita, Y. Mizobe, M. Hidai, J. Am. Chem. Soc. 1989, 111, 1939–1940.
- [33] Y. Tanabe, Y. Nishibayashi, Coord. Chem. Rev. 2019, 389, 73-93.
- [34] K. Shiina, J. Am. Chem. Soc. 1972, 94, 9266-9267.
- [35] R. B. Ferreira, B. J. Cook, B. J. Knight, V. J. Catalano, R. García-Serres, L. J. Murray, ACS Catal. 2018, 8, 7208–7212.



- [36] G. L. Guillet, F. T. Sloane, D. M. Ermert, M. W. Calkins, M. K. Peprah, E. S. Knowles, E. Čižmár, K. A. Abboud, M. W. Meisel, L. J. Murray, *Chem. Commun.* **2013**, 49, 6635–6637.
- [37] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, J. Chem. Soc., Dalton. Trans. 1984, 1349–1356.
- [38] R. H. Crabtree, Chem. Rev. 2012, 112, 1536-1554.
- [39] R. B. Ferreira, L. J. Murray, Acc. Chem. Res. 2019, 52, 447-455.
- [40] E. A. Ison, in *Transit. Met.-Dinitrogen Complexes*, John Wiley & Sons, Ltd, 2019, pp. 271–284.
- [41] R. A. Layfield, Chem. Soc. Rev. 2008, 37, 1098-1107.
- [42] H. Seino, Y. Kajita, in *Transit. Met.-Dinitrogen Complexes*, John Wiley & Sons, Ltd, **2019**, pp. 79–158.
- [43] A. D. Piascik, A. E. Ashley, in *Transit. Met.-Dinitrogen Complexes*, John Wiley & Sons, Ltd, **2019**, pp. 285–335.
- [44] H. Irving, R. J. P. Williams, J. Chem. Soc., Resumed 1953, 3192-3210.
- [45] R. B. Ferreira, L. J. Murray, in *Transit. Met.-Dinitrogen Complexes*, John Wiley & Sons, Ltd, **2019**, pp. 403–439.
- [46] S. Pfirrmann, C. Limberg, C. Herwig, R. Stößer, B. Ziemer, Angew. Chem. Int. Ed. 2009, 48, 3357–3361; Angew. Chem. 2009, 121, 3407.
- [47] S. Pfirrmann, S. Yao, B. Ziemer, R. Stösser, M. Driess, C. Limberg, Organometallics 2009, 28, 6855–6860.

- [48] L. J. Murray, W. W. Weare, J. Shearer, A. D. Mitchell, K. A. Abboud, J. Am. Chem. Soc. 2014, 136, 13502–13505.
- [49] S. Zhang, H. Fallah, E. J. Gardner, S. Kundu, J. A. Bertke, T. R. Cundari, T. H. Warren, *Angew. Chem. Int. Ed.* **2016**, *55*, 9927–9931; *Angew. Chem.* **2016**, *128*, 10081–10085.
- [50] P. Holze, B. Horn, C. Limberg, C. Matlachowski, S. Mebs, Angew. Chem. Int. Ed. 2014, 53, 2750–2753; Angew. Chem. 2014, 126, 2788.
- [51] B. Horn, C. Limberg, C. Herwig, B. Braun, Chem. Commun. 2013, 49, 10923–10925.
- [52] R. C. Cammarota, J. Xie, S. A. Burgess, M. V. Vollmer, K. D. Vogiatzis, J. Ye, J. C. Linehan, A. M. Appel, C. Hoffmann, X. Wang, et al., *Chem. Sci.* **2019**, *10*, 7029–7042.
- [53] K. J. Anderton, D. M. Ermert, P. A. Quintero, M. W. Turvey, M. S. Fataftah, K. A. Abboud, M. W. Meisel, E. Čižmár, L. J. Murray, *Inorg. Chem.* **2017**, *56*, 12012–12022.
- [54] Y. Lee, K. J. Anderton, F. T. Sloane, D. M. Ermert, K. A. Abboud, R. García-Serres, L. J. Murray, J. Am. Chem. Soc. 2015, 137, 10610–10617.
- [55] M. Schlosser, J. Hartmann, Angew. Chem. Int. Ed. Engl. 1973, 12, 508–509; Angew. Chem. 1973, 85, 544.

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