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Putting Chromium on the Map for N₂ Reduction: Production of Hydrazine and Ammonia. A Study of *cis*-M(N₂)₂ (M = Cr, Mo, W) Bis(diphosphine) Complexes

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The first complete structurally and spectroscopically characterized series of isostructural Group 6 N₂ complexes is reported. Protonolysis experiments on *cis*-[M(N₂)₂(P^Et^N^R^P^Et^)₂] (M = Cr, Mo, W; R = 2,6-difluorobenzyl) reveal that only Cr affords N₂H₅⁺ and NH₄⁺ from the reduction of the N₂ ligands.

Transition metal dinitrogen complexes have been studied for several decades, and have revealed a myriad of information relevant to the mechanism of ammonia formation in biological and heterogeneous N₂ reduction processes.[1] Large-scale ammonia synthesis from N₂ and H₂ by the Haber-Bosch process is critical for making fertilizers to maintain worldwide food production.[2] However, concerns over CO₂ emissions from this century-old process are motivating the development of alternative approaches.[3] For example, an electrocatalytic system for N₂ reduction via addition of protons and electrons, (akin to the mild reaction conditions employed by nitrogenase[4]) would provide a carbon-neutral approach to NH₃ production.

Seminal studies on zero-valent group 6 complexes have primarily focused on N₂ reactivity at Mo and W.[5] Moreover, reports deciphering N₂ reactivity on the basis of the identity of the metal and phosphine ligands examined only Mo and W,[6] as very few related Cr(N₂) complexes were known due to limited stability toward binding N₂.[7] Recently, in efforts to develop electrocatalysts for N₂ reduction, our group has made advances in understanding N₂ bonding and reactivity of Cr by studying mono- and bis(dinitrogen) complexes with cyclic 8-,[8] 12-,[9] and 16-membered[10] phosphine ligands containing pendant amines. While these unique Cr-N₂ complexes provided a qualitative assessment of spectroscopic and acid reactivity patterns between N₂

complexes of Cr, Mo, and W, the absence of an isolable series of complexes for *all* the group 6 metals with identical ligands has prevented an unambiguous comparison based *only* on metal identity.[7a, 11] Herein we report the first spectroscopic, electrochemical, and protonolysis study of a structurally identical series of group 6 bis(dinitrogen) complexes, *cis*-[M(N₂)₂(P^Et^N^R^P^Et^)₂] (M = Cr (**1**), Mo (**2**), W (**3**); R = 2,6-difluorobenzyl). The results of this metal-based comparison show the ability of zero-valent Cr to serve as an active metal for the reduction of N₂. Notably, of the group 6 metal complexes examined in this study, the Cr analogue exhibits the most activated N₂ ligands and is the only complex to produce N₂-derived hydrazine and ammonia upon the addition of excess acid.

Complexes **1-3** were prepared by Mg reduction of M^III/IV^ precursors in the presence of two equiv of the PNP diphosphine ligand in THF, Scheme 1. Importantly, the reaction time and temperature were critical parameters in the synthesis of **1** and **2**. Complex **1** was prepared at –5 °C, as the reduction carried out at room temperature resulted in nearly no formation of **1**. Stirring for 60 h afforded a (~9:1) mixture of **1** and *trans*-[Cr(N₂)₂(P^Et^N^2,6-F2-Bn^P^Et^)₂], *trans*-**1** (Fig. S1 and S2, ESI†). The isomers were separated by precipitating **1** from a THF solution by adding cold
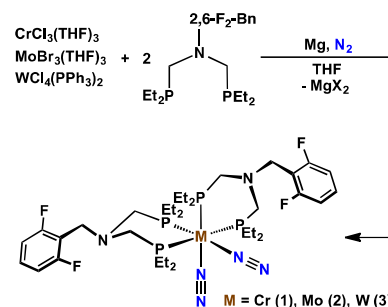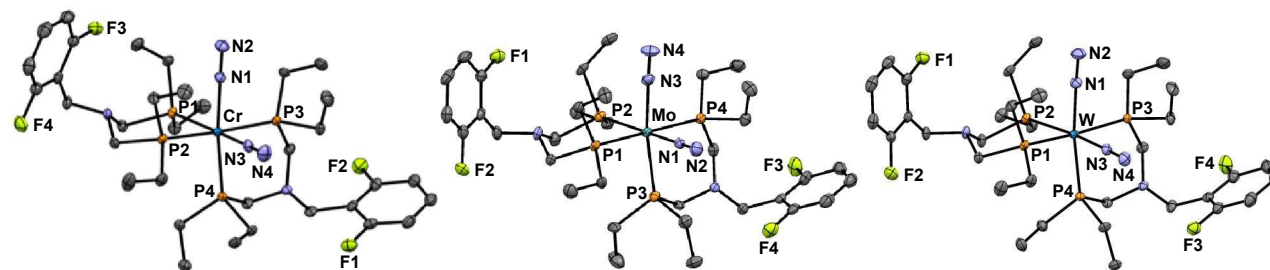

Scheme 1 Synthesis of *cis*-[M(N₂)₂(P^Et^N^2,6-F2-Bn^P^Et^)₂]; (M = Cr, Mo, W), X = Cl, Br. Conditions (temperature, reaction time): **1**, -5 °C, 72 h; **2**, -5 °C, 8 h; **3**, 25 °C, 24 h.

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Fig. 1 Molecular structures of complexes **1** (left), **2** (middle), and **3** (right). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Crystals of **2** and **3** contain two molecules per asymmetric unit with similar metric parameters; only one molecule is shown. Selected bond distances (Å): (**1**) Cr–N1 = 1.864(2); Cr–N3 = 1.871(2); N1–N2 = 1.132(2); N3–N4 = 1.130(2); (**2**) Mo–N1 = 2.027(7); Mo–N3 = 2.020(6); N1–N2 = 1.112(8); N3–N4 = 1.117(8); (**3**) W–N1 = 2.004(3); W–N3 = 1.991(3); N1–N2 = 1.125(4); N3–N4 = 1.134(4).

pentane. In solution, only the Cr isomers show reversible interconversion,[12] suggesting they are similar in energy. In THF at room temperature, a 3:1 mixture of *trans*-**1** to **1** isomerized to >90 % **1**, by IR and ^{31}P NMR spectroscopy (Fig. S3, S4 ESI†). Heating the same sample to 40 °C for 3 days results in partial conversion (ca. 20 %) back to *trans*-**1** with a small amount of free PNP ligand present (Fig. S5, ESI†). In the case of Mo, the reduction performed at –5 °C was vital to isolate **2**, the kinetic product, after 8 h of stirring. In a previous study, we reported the formation of *trans*-[Mo(N$_2$)$_2$(P^{Et}N$^{2,6\text{-}F2\text{-}Bn}$P^{Et})$_2$] by an analogous procedure after stirring for 20 h under a N$_2$ atmosphere at 25 °C.[13] In the present case, reaction times exceeding 8 h, even at –5 °C, result in partial isomerization to the thermodynamically favored trans isomer. In contrast to **1** and **2**, the synthesis of **3** was performed at 25 °C, and after 24 h of stirring, only the *cis* isomer was observed. Isolated yields of the *cis*-M(N$_2$)$_2$ products increase going down the group, ca. 4% for **1**, 41% for **2**, and 62% for **3**. The higher yields for Mo and W may reflect a greater affinity to bind N$_2$ at higher metal oxidation states during the reduction process.

Complexes **1-3** were characterized by X-ray crystallography, allowing for the first structural comparison of a full series of group 6 bis(dinitrogen) complexes with identical ligands. In each case, single crystals were obtained by evaporation of a concentrated Et$_2$O solution. The molecular structures, shown in Fig. 1, are essentially isostructural, exhibiting a 6-coordinate octahedral geometry at the metal, and dinitrogen ligands in the cis conformation. The P–M–P angle is ~86° consistently across the metal series. Metal-ligand bond lengths are similar for complexes **2** and **3**; the M–P and M–N bonds are ca. 2.45 Å and 2.01 Å, respectively. However, those for **1** are shorter at ca. 2.35 Å and 1.87 Å.

The N–N bond lengths for the entire series fall within the range 1.11–1.13 Å, consistent with an N≡N triple bond of the end-on bound N$_2$ ligands. This observed elongation of N$_2$, compared to free N$_2$ at 1.0975 Å, is analogous to other group 6 phosphine complexes with cis N$_2$ ligands.[8,14]

The variance in N–N bond lengths is quite small (ca. 0.02 Å). Distances for the N–N bonds in **1** and **3** are ca. 1.13 Å, and, the N–N distances in **2** are ca. 1.11 Å.

The N$_2$ stretching frequencies in the infrared spectra provide a more quantitative measure of the activation of the N$_2$ ligands. The IR spectra collected in THF contain two ν_{NN} bands for **1-3**, as shown in Fig 2. Although the energy of the ν_{NN} bands are expected to decrease going down the group on the basis of more electron-releasing dπ donation of the metal,[6, 15] complex **2** has the highest ν_{NN} bands at 2012, 1950 cm^{-1}. The ν_{NN} bands for **3** are 1987 and 1925 cm^{-1}, and notably, **1** exhibits ν_{NN} bands at 1990 and 1911 cm^{-1} and the lowest N-N force constant of the series (Table S1, ESI†).[16] **1** also displays slight asymmetry in the band intensities in THF, indicative of dissimilarity in the N-M-N bond angle compared to **2** and **3**. Thus, enhanced N$_2$ activation for **1** could be due to better dπ overlap with N$_2$ anti-bonding orbitals,[17] or based on our earlier bonding assessment of Cr-N$_2$ complexes, a stronger polarization of the N$_2$ ligand in **1** decreases the N-N vibrational frequency.[8]

Characterization of complexes **1-3** by ^{31}P and ^{15}N NMR spectroscopy afforded additional trends based on metal
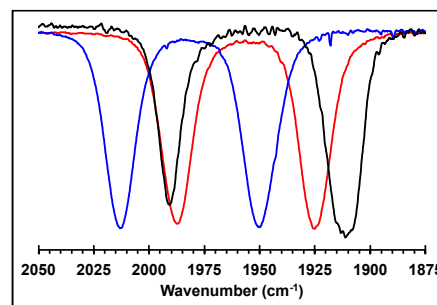
Fig. 2 Infrared spectra showing the ν_{NN} bands of *cis*-[M(N$_2$)$_2$(P^{Et}N$^{2,6\text{-}F2\text{-}Bn}$P^{Et})$_2$] recorded in THF at 25 °C: M = Cr (**1**), black, 1990, 1911; Mo (**2**), blue, 2012, 1950; W (**3**), red, 1987, 1925 cm^{-1}.

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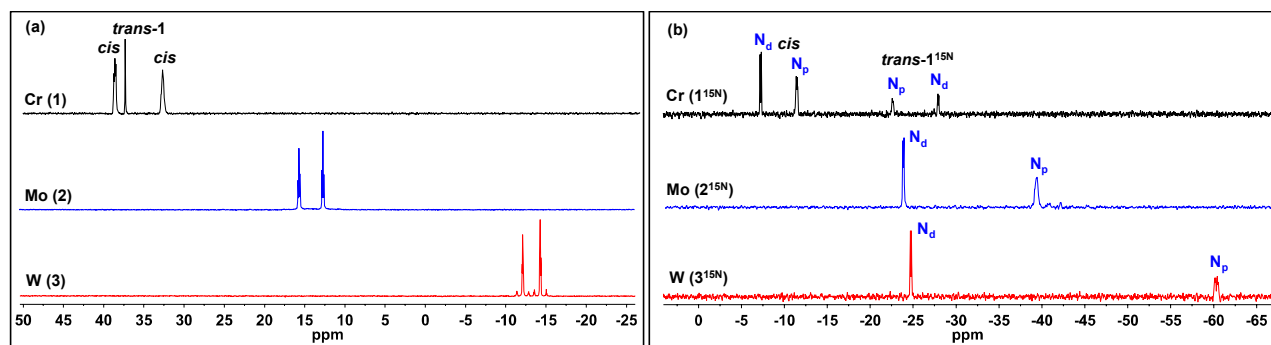
Fig. 3 (a) $^{31}P\{^1H\}$ NMR spectra (202.4 MHz) of complexes **1-3** recorded at 25 °C in THF-d_8. (b) $^{15}N\{^1H\}$ NMR spectra (50.7 MHz) of complexes **1^{15N}, 2^{15N} and 3^{15N}** recorded at 25 °C in THF-d_8. The selected ^{31}P and ^{15}N NMR spectra of **1** contain *trans*-**1** and *trans*-**1^{15N}**, respectively, for a comparison of data for the cis and trans stereoisomers.

identity. The ^{31}P and ^{15}N NMR spectra for complexes **1-3** is shown in Fig. 3a and 3b, respectively. In the $^{31}P\{^1H\}$ NMR spectra, each complex displays two multiplets of an AA'BB' pattern, as expected for two distinct phosphorus environments. Descending the group, the ^{31}P NMR resonances appear at higher field. Resonances for **1** appear at δ 37.9, 32.2, while *trans*-**1** shows a singlet at δ 37.1. The resonances for **3** have ^{183}W satellites, J_{PW} = 297 and 303 Hz.

The $^{15}N_2$-labelled isotopologues **1^{15N}, 2^{15N}**, and **3^{15N}** were prepared for ^{15}N NMR spectral studies by exposing a degassed THF-d_8 solution of the complex to a headspace of $^{15}N_2$ gas. N_2 ligand exchange was rapid in all cases, resulting in $^{15}N_2$ incorporation into the product within minutes. The $^{15}N\{^1H\}$ NMR spectrum for each complex displays two signals for the end-on bound $^{15}N_2$ ligands, a broad resonance (due to ^{31}P coupling) for the proximal nitrogen atoms (N_p), and a doublet ($J_{15N-15N}$ ca. 6-7 Hz) for the distal nitrogen atoms (N_d). As in the ^{31}P NMR spectra, the ^{15}N resonances appear upfield upon descending the group. For **1^{15N}**, the ^{15}N signals appear close together at δ −7.3, −11.5, for N_d and N_p, respectively. For comparison between isomers, the ^{15}N signals for N_d and N_p of *trans*-**1^{15N}** appear at higher field in opposite positions, at δ -28.0, -22.6, respectively. For **2^{15N}** and **3^{15N}** the N_d resonances are nearly identical, however the position of the signals differ for N_p at δ −39.1 for **2^{15N}** and δ −60.4 for **3^{15N}**. Thus, it is clear that the magnetic environment of the $^{15}N_2$ ligands display a periodic trend of increased magnetic shielding upon descending the group.[18] However, the trend in ^{15}N chemical shifts does not correlate to metal center basicity to release electron density[15b] to the N_2 ligands based on the values of the ν_{NN} bands.

Cyclic voltammetry (CV) experiments probed the metal oxidation potentials for this series of complexes to assess the trend of the electron density at the metal center with an identical ligand set. This trend could be correlated to the ν_{NN} stretching frequencies and acid reactivity at N_2. The CV of the $M^{I/0}$ couple for complexes **1-3** were recorded in THF at a scan-rate of 0.1 V s^{-1} (Fig. S6, ESI†). Complexes **2** and **3** exhibit quasi-reversible waves corresponding to the $Mo^{I/0}$

and $W^{I/0}$ redox couple with a half-wave potential, $E_{1/2}$ = −1.04 V and −1.03 V, respectively (vs $Cp_2Fe^{+/0}$). The $M^{I/0}$ waves of **2** and **3** are similar despite **3** having ν_{NN} bands that appear 25 cm^{-1} lower in energy. The quasi-reversible nature of the $M^{I/0}$ wave at low scan-rates, ca. 0.1 V s^{-1}, is likely due to N_2 ligand loss upon metal oxidation. The waves do not become reversible at faster scan rates, ca. υ = 1 V s^{-1}.

In contrast to **2** and **3**, complex **1** exhibits an irreversible, anodic wave corresponding to the $Cr^{I/0}$ oxidation, E_{pa} = −1.36 V. This wave is irreversible at all attempted scan rates (up to 20 V s^{-1}), even when the CV was performed at -30 °C. The irreversibility of the $Cr^{I/0}$ wave is analogous to the CV of *cis*-$[Cr(N_2)_2(P^{Ph}_2N^{Bn}_2)_2]$,[8] but differs from the quasi-reversible $Cr^{I/0}$ wave of *trans*-$[Cr(N_2)_2(P^{Ph}_4N^{Bn}_4)]$.[10] Irreversibility of this wave suggests that $[Cr^I(N_2)_2(PNP)_2]^+$ is unstable, and that N_2 ligand loss is rapid upon metal oxidation. Remarkably, the anodic peak potential, E_{pa}, for **1** is ca. 300 mV more negative than the $E_{1/2}$ of **2** and **3**. The position of the $Cr^{I/0}$ wave is likely due in part to a negative kinetic potential shift resulting from rapid N_2 loss upon Cr oxidation. Kinetic analysis suggests that the formal reduction potential ($E°'$) of **1** is also more negative than the $E_{1/2}$ values observed for **2** and **3**. For example, $E°'$ for **1** would be −1.12 V if the first-order rate constant for N_2 loss were 1 × 10^9 s^{-1} (Table S2, ESI†). Accordingly, these data are consistent with **1** being easier to oxidize than **2** and **3**.

Protonolysis experiments revealed the outcome of metal-dependence on the reduction of N_2 to ammonium (NH_4^+) and hydrazinium ($N_2H_5^+$) products. In a typical reaction, a THF-d_8 solution of complex **1**, **2**, or **3** was treated with 100 equiv of triflic acid (CF_3SO_3H) at −40 °C, according to Scheme 2. Results from five runs revealed complex **1** formed $N_2H_5^+$ (avg. 0.22 equiv $N_2H_5^+$ per Cr atom), and NH_4^+ (avg. 0.08 equiv NH_4^+ per Cr atom) from the protonation and reduction of the N_2 ligands (electrons originate from Cr), (Table S3, ESI†).[19] The yields of NH_4^+ and $N_2H_5^+$ were quantified by ^1H NMR spectroscopy using 1,3,5-trimethoxy-benzene as an internal integration standard (for additional details see ESI†). Acid addition to **1^{15N}** confirmed the

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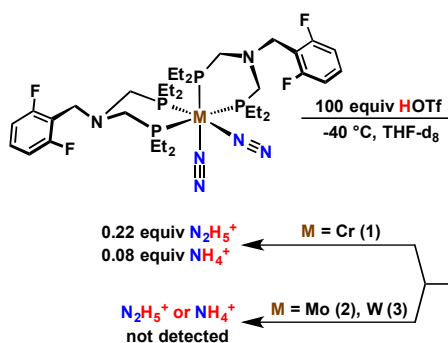
Scheme 2 Reaction of cis-[M(N$_2$)$_2$(P^{Et}N$^{2,6-F2-Bn}$P^{Et})$_2$] with excess HOTf.

products are derived from the dinitrogen ligands.[20] To obtain reduced N$_2$ products, low temperatures are required, as N$_2$H$_5^+$ and NH$_4^+$ were not formed in HOTf addition to **1** at 25 °C. In contrast, treatment of **2** and **3** with excess triflic acid at -40 °C did not produce any detectible amount of NH$_4^+$ or N$_2$H$_5^+$ by ^{1}H NMR.[21] Furthermore, treatment of a THF solution of complexes **1**, **2**, or **3** with 100 equiv H$_2$SO$_4$ at 25 °C did not form detectible amounts of NH$_4^+$ or N$_2$H$_5^+$.[22]

In conclusion, we prepared N$_2$ complexes of Cr, Mo, and W with identical ligands and examined their spectroscopic and electrochemical properties to more clearly understand the metal-dependent N$_2$ activation and reactivity. The Cr-N$_2$ complex contains the most activated N$_2$ ligands and the most negative oxidation potential of the series. Greater N$_2$ activation for **1** may reflect better dπ overlap with N$_2$ anti-bonding orbitals. Cr was the only complex to form NH$_4^+$ and N$_2$H$_5^+$ from reduction of the N$_2$ ligands upon addition of acid. Future studies aim to identify Cr-N$_x$H$_y$ intermediates in the N$_2$ reduction pathway, and to utilize Cr to develop an electrocatalytic system for N$_2$ reduction to N$_2$H$_4$ and NH$_3$.

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19. The peak area of N$_2$H$_5^+$ (broad singlet, 10.8 ppm) and NH$_4^+$ (1:1:1 triplet, 7.0 ppm, J_{HN} = 51 Hz) were determined by manual integration and by line-fitting analysis using the CRAFT NMR software program.
20. Protonolysis of **1^{15N}** afforded ^{15}N$_2$H$_5^+$ and ^{15}NH$_4^+$ by ^{15}N NMR at -326 ppm and -363 ppm, respectively. In addition, [HP^{Et}N$^{2,6-F2-Bn}$P^{Et}][OTf] was observed by ^{1}H and ^{31}P NMR spectroscopy.
21. The formation of M-H products for **2** and **3** was apparent based upon multiplet resonances (due to ^{31}P coupling) in the high-field region of the ^{1}H NMR spectra.
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