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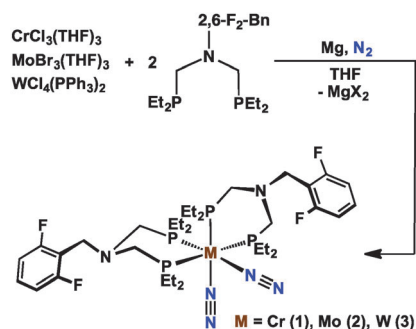
The first complete structurally and spectroscopically characterized series of isostructural Group 6 N₂ complexes is reported. Protonolysis experiments on *cis*-[M(N₂)₂(P^{Et}N^RP^{Et})₂] (M = Cr, Mo, W; R = 2,6-difluorobenzyl) reveal that only Cr affords N₂H₅⁺ and NH₄⁺ from the reduction of the N₂ ligands.

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 nitrogenase⁴) 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-membered¹⁰ 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^RP^{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 pentane. In solution, only the Cr isomers show reversible interconversion,¹² suggesting they are similar in energy.



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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