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Evaluating Molecular Cobalt Complexes for the Conversion of N_2 to NH_3

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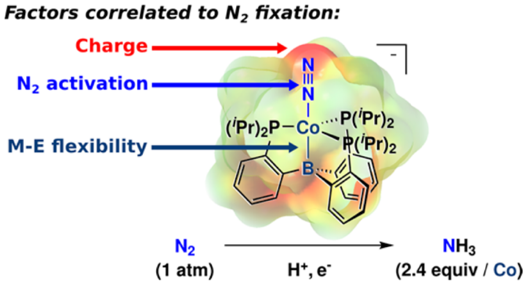
Ⓢ *Supporting Information*

ABSTRACT: Well-defined molecular catalysts for the reduction of N_2 to NH_3 with protons and electrons remain very rare despite decades of interest and are currently limited to systems featuring molybdenum or iron. This report details the synthesis of a molecular cobalt complex that generates superstoichiometric yields of NH_3 (>200% NH_3 per Co−N_2 precursor) via the direct reduction of N_2 with protons and electrons. While the NH_3 yields reported herein are modest by comparison to those of previously described iron and molybdenum systems, they intimate that other metals are likely to be viable as molecular N_2 reduction catalysts. Additionally, a comparison of the featured tris(phosphine)borane Co−N_2 complex with structurally related Co−N_2 and Fe−N_2 species shows how remarkably sensitive the N_2 reduction performance of potential precatalysts is. These studies enable consideration of the structural and electronic effects that are likely relevant to N_2 conversion activity, including the π basicity, charge state, and geometric flexibility.



INTRODUCTION

The conversion of dinitrogen (N_2) to ammonia (NH_3) is integral for life.[1] Despite extensive study, there are many unanswered questions regarding the rational design of molecular N_2-to-NH_3 conversion catalysts. It may be that the ability of a complex to activate terminally bound N_2 (as reported by the N−N stretching frequency) relates to the propensity of that complex to functionalize the N_2 moiety. For example, $HCo(N_2)(PPh_3)_3$ (ν_{N-N} = 2088 cm^{-1}) quantitatively releases N_2 upon treatment with acid, with no evidence of N_2 functionalization;[2,3] however, if this cobalt complex is deprotonated to generate the more activated complex $[(PPh_3)_3Co(N_2)][Li(Et_2O)_3]$ (ν_{N-N} = 1900 cm^{-1}), treatment with acid does produce some NH_3 and N_2H_4 (0.21 and 0.22 equiv, respectively).[3] Extensive efforts have been made to study the activation and functionalization of N_2 bound to metal centers of varying electronic properties.[4] In some cases, systems have been shown to activate bound N_2 to the extent that the N−N bond is fully cleaved.[5] In other cases, it has been shown that the treatment of strongly activated N_2 complexes with acid or H_2 leads to reduced nitrogenous products.[2−4] However, this guiding principle alone has been insufficient in the design of many synthetic species capable of catalyzing the conversion of N_2 to NH_3.[6−8] In this regard, it is prudent to study the few systems known to catalyze this reaction with an emphasis on identifying those properties critical to the observed N_2 reduction activity.

We have recently reported that a tris(phosphino)borane-ligated iron complex is capable of catalyzing the conversion of N_2 to NH_3 at −78 °C.[7] We have postulated that the success of this system in activating N_2 stoichiometrically and mediating its catalytic conversion to NH_3 may arise from a highly flexible Fe−B interaction.[9,10] Such flexibility, trans to the N_2 binding site, may allow a single Fe center to access both trigonal-bipyramidal and pseudotetrahedral coordination geometries, alternately stabilizing π-acidic or π-basic nitrogenous moieties sampled along an N_2 fixation pathway.[4d,11] Consistent with this hypothesis, we have studied isostructural P_3E-ligated Fe systems and found a measurable dependence of activity on the identity of the E atom, with the least flexible E = Si system furnishing divergently low NH_3 yields and the more flexible E = C or B systems affording moderate yields of NH_3.[7,8] However, the lower NH_3 production by the E = Si precursor may alternatively be attributed to other factors. Potential factors include (i) a lesser degree of N_2 activation than that observed in the E = C or B species (vide infra), (ii) faster poisoning of the E = Si system, for example, by more rapid formation of an inactive terminal hydride,[7,8] and (iii) faster degradation of the E = Si system, for example, by dechelation of the ligand.

To complement our previous ligand modification studies, we chose to alter the identity of the transition metal. Moving from iron to cobalt predictably modulates the π basicity and electronic configuration of the metal center while maintaining the ligand environment. In principle, this allows the extrication of electronic effects, such as π-back-bonding, from structural features, such as geometric flexibility, via a comparison of the iron and cobalt systems. We therefore sought to explore the N_2 reduction activity of cobalt complexes of $[o\text{-}({}^iPr_2P)C_6H_4]_3B$ (TPB), $[o\text{-}({}^iPr_2P)C_6H_4]_3Si$ (SiP_3), and $[o\text{-}({}^iPr_2P)C_6H_4]_3C$ (CP_3). While correlating NH_3 yields with molecular structure is no doubt informative in terms of understanding the behavior of

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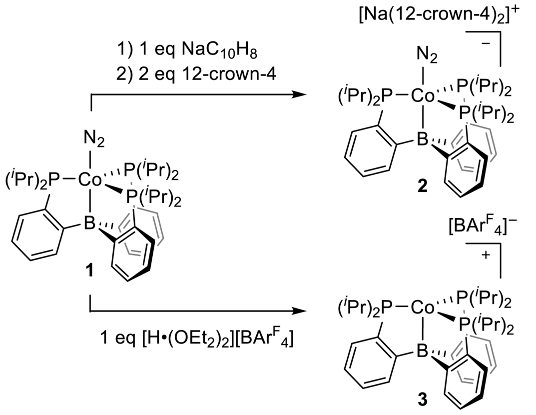
nitrogen-fixing systems, correlation does not imply causation, and the results described herein should be read with that in mind.

■ RESULTS AND DISCUSSION

The previously reported[12] (TPB)Co(N_2) complex (Scheme 1, **1**) provided a logical entry point to study the N_2 chemistry of (TPB) Co complexes. The cyclic voltammogram of **1** in tetrahydrofuran (THF) displays a quasi-reversible reduction wave at −2.0 V vs Fc/Fc$^+$ and a feature corresponding to an oxidation process at −0.2 V vs Fc/Fc$^+$ (Figure 1). These features are reminiscent of the cyclic voltammogram of (TPB)Fe(N_2), which shows a reduction event at −2.2 V vs Fc/Fc$^+$ and an oxidation event at −1.5 V vs Fc/Fc$^+$.[10]

Scheme 1. Chemical Oxidation and Reduction of 1



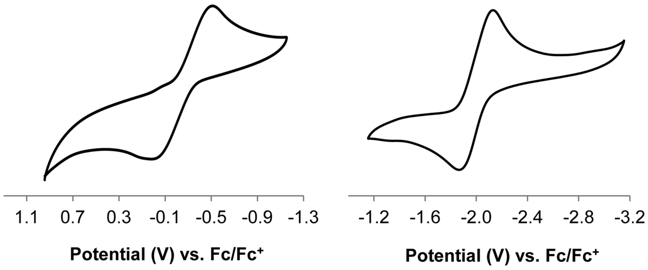


Figure 1. Cyclic voltammagram of **1** scanning oxidatively (left) and reductively (right) at 100 mV s^{-1} in THF with a 0.1 M TBAPF$_6$ electrolyte.

Treatment of **1** with 1 equiv of NaC$_{10}$H$_8$ followed by 2 equiv of 12-crown-4 (12-c-4) generates diamagnetic [Na(12-c-4)$_2$)]-[(TPB)Co(N_2)] as red crystals (Scheme 1, **2**). The ν_{N-N} stretch of **2** is lower in energy than that of **1** (Table 1), and the solid-state structure of **2** (Figure 2, left) displays contracted Co−N, Co−B, and Co−P distances compared to **1**, consistent with increased back-bonding to each of these atoms. The one-electron oxidation of **1** can be achieved by the addition of 1 equiv of [H·(OEt$_2$)$_2$][BAr$^F_4$] at low temperature followed by warming, which generates red-purple [(TPB)Co][BAr$^F_4$] (Scheme 1, **3**; BAr$^F_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate). The structure of **3** (Figure 2, right) confirms that it does not bind N_2 in the solid state. The lack of N_2 binding at room temperature for **3** is consistent with the behavior of the isostructural iron complex [(TPB)Fe][BAr$^F_4$].[13] SQUID magnetometry measurements indicate that **3** is high-spin (S = 1) in the solid state with no evidence for spin crossover (Figure 3).

Table 1. Select Characterization Data for (P$_3$E)M Complexes (M = Co, Fe; E = B, C, Si)

entry	complex	M—E (Å)	ν_{N-N} (cm^{-1})[a]
A[b]	(TPB)Co(N_2) (**1**)	2.319(1)	2089[c]
B	[(TPB)Co(N_2)]$^-$ (**2**)	2.300(3)	1978
C	[(TPB)Co]$^+$ (**3**)	2.256(2)	
D[b]	(SiP$_3$)Co(N_2) (**4**)	2.2327(7)	2063
E	(CP$_3$)Co(N_2) (**5**)	2.135(4)	2057
F	[(CP$_3$)Co(N_2)]$^+$ (**6**)	2.054(2)	2182
G[b]	(TPB)CoBr	2.4629(8)	
H[d]	(TPB)FeBr	2.458(5)	
I[d]	(TPB)Fe(N_2)		2011
J[d]	[(TPB)Fe(N_2)]$^-$	2.293(3)	1905
K[e]	[(CP$_3$)Fe(N_2)]$^+$	2.081(3)	2128
L[e]	(CP$_3$)Fe(N_2)	2.152(3)	1992
M[e]	[(CP$_3$)Fe(N_2)]$^-$	2.165(2)	1905
N[f]	[(SiP$_3$)Fe(N_2)]$^-$	2.236(1)	1920

[a] IR from solid-state samples. [b] From ref 12. [c] From ref 14. [d] From ref 10. [e] From ref 8. [f] From ref 15.

The synthesis of (SiP$_3$)Co(N_2) (**4**) was reported previously.[14] The isoelectronic alkyl species (CP$_3$)Co(N_2) (**5**) was obtained in 83% yield as a deep-red solid from the reaction of CP$_3$H, CoCl$_2$·1.5THF, and MeMgCl under an N_2 atmosphere (Scheme 2). Complex **5** (ν_{N-N} = 2057 cm^{-1}) is diamagnetic, possesses C_3 symmetry in solution and binds N_2, as confirmed by a solid-state structure. The cyclic voltammogram of **5** in THF displays a quasi-reversible oxidation wave at −1.1 V vs Fc/Fc$^+$ (Figure 4, left). Treatment of **5** with 1 equiv of [Fc][BAr$^F_4$] at low temperature allowed for isolation of the one-electron oxidation product [(CP$_3$)Co(N_2)][BAr$^F_4$] (**6**; ν_{N-N} = 2182 cm^{-1}) in 86% yield after recrystallization (Scheme 2). The coordinated N_2 ligand of **6** is labile and can be displaced under vacuum (Figure 4, middle) to generate a vacant or possibly solvent-coordinated [(CP$_3$)Co(L)]$^+$ species. The electron paramagnetic resonance (EPR) spectrum of **6** at 80 K under N_2 is consistent with an S = $^1/_2$ species (Figure 4, right).

Consideration of the M−E interatomic distances presented in Table 1 reveals that the (TPB)Co platform exhibits a significant degree of flexibility of the M−B interaction, similar to that observed for the (TPB)Fe platform. Within each platform, the M−B distance varies by >0.16 Å between the neutral halide (Table 1, G and H) and anionic N_2 complexes (B and J). Likewise, the M−C interaction among (CP$_3$)Co complexes exhibits flexibility comparable to that of the analogous iron series. For both platforms, the M−C distance increases by ~0.07 Å upon one-electron reduction of the cationic N_2 complexes (Table 1, F to E and K to L).

A comparison of the trends in interatomic metrics between the isoelectronic $\{(TPB)Co(N_2)\}^n$ and $\{(CP_3)Co(N_2)\}^n$ redox series reveals divergent geometric behavior. Upon reduction from **1** to **2**, the Co−B distance decreases by 0.02 Å, resulting in a significant decrease in the pyramidalization about cobalt ($\Delta\tau$ = 0.13).[16] The opposite is true for the reduction of **6** to **5**, which results in an increase in the Co−C distance and an increase in the pyramidalization ($\Delta\tau$ = −0.13). A plausible rationale is that the Z-type borane ligand in (TPB)Co complexes enforces a trigonal-bipyramidal geometry upon reduction, by drawing the Co atom into the P$_3$ plane with an attractive Co−B interaction. The X-type alkyl ligand in (CP$_3$)

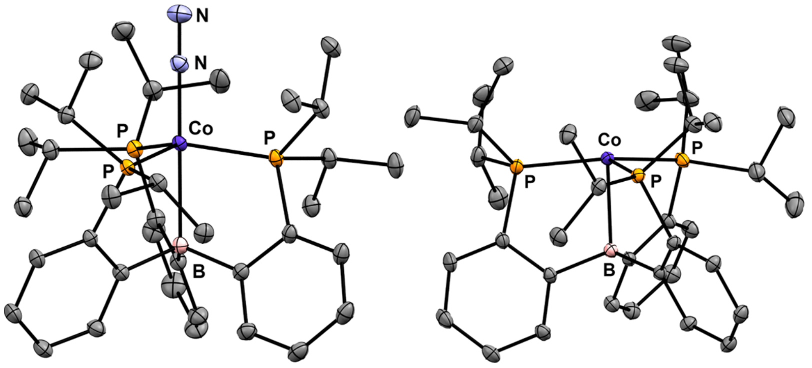


Figure 2. Solid-state crystal structures of **2** (left) and **3** (right; also see the SI). Thermal ellipsoids are shown at 50% probability. Counterions, solvent molecules, and H atoms are omitted for clarity.

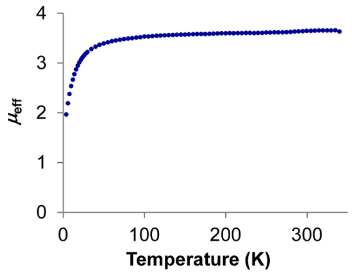
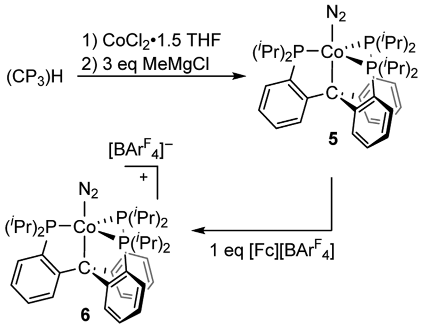


Figure 3. Temperature dependence of the magnetic susceptibility of **3** as measured by SQUID magnetometry.

Scheme 2. Synthesis and Oxidation of 5



Co complexes instead causes a distortion away from a trigonal-pyramidal geometry upon reduction, with a comparatively repulsive Co–C interaction forcing the Co atom above the P_3 plane.

The reactivity of these (P_3E)Co complexes with sources of protons and electrons in the presence of N_2 was investigated. In analogy to the [Na(12-c-4)$_2$][(TPB)Fe(N$_2$)] complex, treatment of a suspension of **2** in Et_2O at −78 °C with excess [H·(OEt$_2$)$_2$][BAr$^F_4$] followed by excess KC_8 under an atmosphere of N_2 leads to the formation of 2.4 ± 0.3 equiv of NH_3 (240% per Co; the average of six independent runs using a single batch of **2**, acid, and reductant with independent NH_3 yields of 2.3, 2.1, 2.2, 2.5, 2.8, and 2.2 equiv (Table 2, A); independently prepared batches of **2** also reliably afford NH_3 yields slightly greater than 2.0 equiv per Co). Yields of NH_3 were determined by the indophenol method;[17] no hydrazine was detected by a standard UV–vis quantification method.[18] While we acknowledge that the NH_3 yields are close to stoichiometric, we underscore that the yields are reproducibly above 2.1 equiv. While such yields are only modestly suggestive of bona fide catalysis, they are consistently greater than 200% NH_3 normalized to cobalt in **2** and represent an order of magnitude improvement over the only previous report of N_2 to NH_3 conversion mediated by well-defined cobalt complexes (NH_3 yield ≤0.21 equiv per Co–N_2 vide supra).[3,19]

Notably, no NH_3 is formed when either **2**, [H·(OEt$_2$)$_2$]-[BAr$^F_4$], or KC_8 is omitted from the standard conditions, indicating that all three components are necessary for NH_3 production. In an effort to study the fate of **2** under the reaction conditions, we treated **2** with 10 equiv of [H·(OEt$_2$)$_2$][BAr$^F_4$] and 12 equiv of KC_8 and observed signs of ligand decomposition by ^{31}P NMR (see the Supporting Information, SI). If the observed reactivity indeed represents modest catalysis, ligand decomposition under the reaction conditions provides a plausible rationale for the limited turnover number. As a control, free TPB ligand was subjected to the standard conditions as a precatalyst, leading to no detectable NH_3 production.

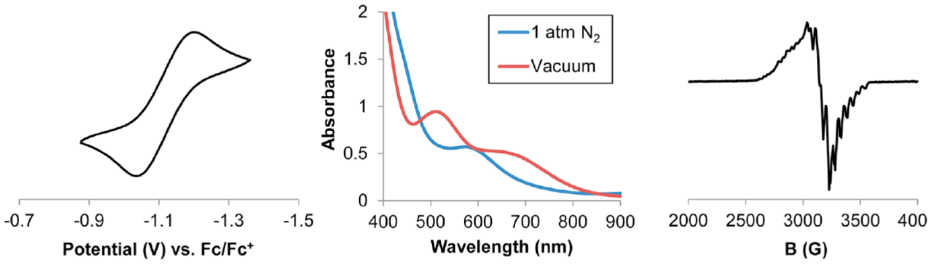


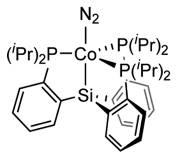
Figure 4. (left) Cyclic voltammagram of **5** scanning oxidatively at 100 mV s^{-1} in THF with a 0.1 M TBAPF$_6$ electrolyte. (middle) UV–vis spectra of **6** under 1 atm of N_2 (solid line) and under static vacuum (dotted line: after three freeze–pump–thaw cycles). Spectra were collected on a 1 mM solution of **6** in THF at 298 K. (right) X-band EPR spectrum of **6** collected under 1 atm of N_2 in 2-Me–THF at 80 K. No low-field features were detected.

Table 2. NH_3 Generation from N_2 Mediated by Cobalt Precursors[a]

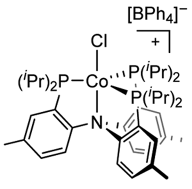
$$N_2\ (1\ \text{atm}) + \text{xs}\ KC_8 + \text{xs}\ [H\bullet(Et_2O)_2][BAr^F{}_4] \xrightarrow[-78\ ^\circ C,\ Et_2O]{\text{Co complex}} NH_3$$

entry	cobalt complex	NH_3 equiv per Co
A	$[(TPB)Co(N_2)][Na(12\text{-}c\text{-}4)_2]$ (**2**)	2.4 ± 0.3^b
B	$(TPB)Co(N_2)$ (**1**)	0.8 ± 0.3
C	$[(TPB)Co][BAr^F{}_4]$ (**3**)	1.6 ± 0.2
D	(TPB)CoBr	0.7 ± 0.4
E	$(SiP_3)Co(N_2)$ (**4**)	<0.1
F	$(CP_3)Co(N_2)$ (**5**)	0.1 ± 0.1
G	$[(NArP_3)CoCl][BPh_4]$	<0.1
H	$(PBP)Co(N_2)$	0.4 ± 0.2
I	$Co(PPh_3)_2I_2$	0.4 ± 0.1
J	$CoCp_2$	0.1 ± 0.1
K	$Co_2(CO)_8$	<0.1

[a] Cobalt precursors at −78 °C under an N_2 atmosphere treated with an Et_2O solution containing 47 equiv of $[H\cdot(OEt_2)_2][BAr^F{}_4]$, followed by an Et_2O suspension containing 60 equiv of KC_8. Yields are reported as an average of three iterations; data for individual experimental iterations are presented in the SI. [b] Average of six iterations.



E (4)



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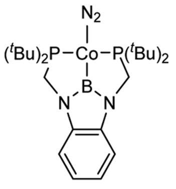


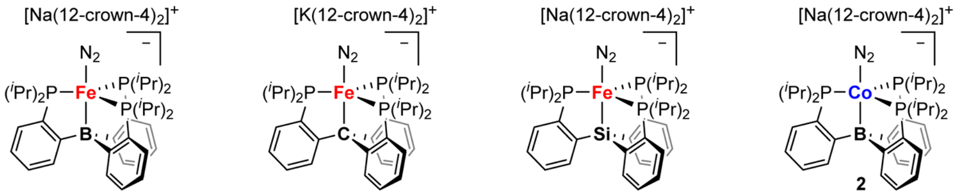
H

Interestingly, although anionic **2** and cationic **3** both generated substantial NH_3 under the standard conditions, submitting neutral **1** to these conditions provided attenuated yields of NH_3, comparable to the yields obtained with (TPB)CoBr (Table 2, B–D). Furthermore, complexes **4** and **5**, which are isoelectronic to **2**, are not competent for the reduction of N_2 with protons and electrons, producing ≤0.1 equiv of NH_3 and no detectable hydrazine under identical conditions (Table 2, E and F). This result appears to underscore the importance of the nature of the M–E interaction in facilitating N_2 fixation by $(P_3E)M$ complexes.

To further explore the generality of N_2 conversion activity for cobalt complexes under these conditions, we screened a number of additional cobalt species. We targeted, for instance, a cobalt complex of the tris(phosphino)amine ligand $[2\text{-}({}^iPr_2P)\text{-}4\text{-}(CH_3)\text{-}C_6H_3]_3N$ ($NArP_3$).[20] The synthesis of a $(NArP_3)Co$ complex completes a family of tris(phosphino)cobalt complexes featuring L-, X-, and Z-type axial donors. $[(NArP_3)CoCl][BPh_4]$ (Table 2, G) was isolated as purple crystals in 90% yield from the reaction of the $NArP_3$ ligand with $CoCl_2$ and $NaBPh_4$. An X-ray diffraction study revealed a pseudotetrahedral geometry at the Co center, with minimum interaction with the apical N atom of the ligand (d = 2.64 Å). As expected for tetrahedral cobalt(II), $[(NArP_3)CoCl][BPh_4]$ is high-spin ($S = {}^3/_2$), with a solution magnetic moment of 3.97 μ_B in CD_2Cl_2 at 23 °C. We also tested the known bis(phosphino)boryl Co–N_2 complex[21] (Table 2, H), as well as various other common cobalt complexes (Table 2, I–K). Interestingly, of all of the cobalt precursors subjected to the standard conditions, only TPB-ligated cobalt complexes generated >0.5 equiv of NH_3 per metal center. At this point, we can begin to delineate the structural/electronic factors correlated to NH_3 production by $(P_3E)M$ complexes.

Among $(P_3E)Fe$ complexes, NH_3 production appears to be correlated both with the flexibility of the M–E interaction and with the degree of N_2 activation, with more flexible and more activating platforms providing greater yields of NH_3. Moving from Fe to Co, the degrees of N_2 activation are systematically lower, which is expected because of the decreased spatial extent of the Co 3d orbitals (due to increased Z_{eff}).[22] Nevertheless, NH_3 production is still correlated among these $(P_3E)Co$ complexes with N_2 activation. However, comparing the iron and cobalt complexes demonstrates that, in an absolute sense, the degree of N_2 activation is not predictive of the yield of NH_3 (Figure 5). For example, $[Na(12\text{-}c\text{-}4)_2][(SiP_3)Fe(N_2)]$ shows a higher degree of N_2 activation than **2**, yet **2** demonstrates higher N_2-to-NH_3 conversion activity. The relative activity of these two complexes *is* predicted, on the other hand, by the flexibility of the M–E interactions trans to bound N_2. Indeed, among the factors considered here, only M–E interaction flexibility appears to predict the comparatively high N_2 conversion activity of **2**.

The potentials at which the anionic states of the complexes depicted in Figure 5 are achieved do not follow a clear trend regarding their relative N_2 conversion activity. However, a comparison of the iron and cobalt systems does demonstrate that the accessibility of highly reduced, *anionic* $[(P_3E)M(N_2)]^-$ complexes is favorably correlated to NH_3 production. It may be the case that the relative basicity of the β-N atom (N_β) plays an important role in N_2 conversion activity, with anionic species being appreciably more basic. Considering complexes **2** and **5**, neutral **5** affords <5% NH_3 per Co–N_2 subunit under the standard reaction conditions, whereas the isoelectronic and isostructural, yet anionic **2** produces >200% NH_3 (Table 2). The enhanced basicity of N_β in the anion would, in turn, favor



$\nu_{(N\text{-}N)}$ (cm^{-1}) [a]	1905	1905	1920	1978
$E_{1/2}$ (V vs. Fc/Fc$^+$) [b]	-2.19	-2.55	-2.20	-2.00
NH_3 equiv/M	7.0 ± 1.0	3.5 ± 0.3	0.8 ± 0.4	2.4 ± 0.3

Figure 5. Vibrational spectroscopy, electrochemistry, and catalytic competence data for select $[(P_3E)M(N_2)]^-$ complexes. Data for M = Fe and E = B are from refs 7 and 10, data for M = Fe and E = C are from ref 8, data for M = Fe and E = Si are from refs 8 and 15, and data for M = Co and E = B are from this work. [a] IR from solid-state samples. [b] Oxidation potentials determined by cyclic voltammetry in THF. Note: NH_3 yields based on the addition of ~50 equiv of $[H\cdot(OEt_2)_2][BAr^F{}_4]$ and ~60 equiv of KC_8 in Et_2O (see refs provided for specific details).

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protonation to produce a "Co(N_2H)" intermediate relative to other reaction pathways. We have performed calculations [density functional theory (DFT); see the SI for details] to compare the theoretically predicted electrostatic potential maps of **2** and **5**. As shown in Figure 6, N_β in anionic **2** shows a far greater degree of negative charge relative to the same atom in neutral **5**.

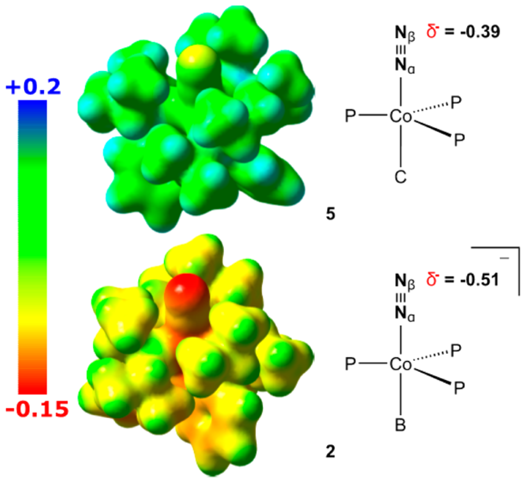

Figure 6. Electrostatic potential maps of anionic **2** and neutral **5** (isovalue = 0.015, color map in hartrees) and atomic charges for N_β.

CONCLUSION

We have demonstrated the ability of a molecular Co−N_2 complex to facilitate the conversion of N_2 to NH_3 at −78 °C in the presence of proton and electron sources (2.4 equiv of NH_3 generated per Co center on average). Prior to this report, the only well-defined molecular systems (including nitrogenase enzymes) capable of directly mediating the catalytic conversion of N_2 to NH_3 contained either molybdenum or iron. While the measured NH_3 production by the featured cobalt complex is very modest with respect to bona fide catalysis, the measured yields consistently indicate that some degree of catalysis is viable. The propensity of the (P_3E)M complexes that we have studied to perform productive N_2 fixation does not appear to depend solely on the ability of the precursor complex to activate N_2. The observations collected herein indicate that the anionic charge and hence the basicity of the bound N_2 ligand, in addition to flexibility of the M−E interaction trans to the bound N_2 ligand, correlate with more favorable NH_3 production. Of course, correlation does not presume causation, and the factors that lead to different NH_3 yields may be numerous. While some of the design features important to consider in catalysts of the (P_3E)M(N_2) type have been highlighted here, other factors, including the comparative rates of H_2 evolution and catalyst degradation/poisoning rates, warrant further studies.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an N_2 atmosphere. Solvents were deoxygenated and dried by thoroughly sparging with N_2, followed by passage through an activated alumina column in a solvent purification system by SG Water, USA LLC. Nonhalogenated solvents were tested with sodium benzophenone ketyl in tetrahydrofuran (THF) in order to confirm the absence of oxygen and water. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3-Å molecular sieves prior to use.

[$H(OEt_2)_2$][$BAr^F{}_4$],[23] KC_8,[24] (TPB)Co(N_2) (**1**),[12] (TPB)CoBr,[12] (SiP_3)Co(N_2) (**4**),[14] $NArP_3$,[20] (PBP)Co(N_2),[21] CP_3H,[8] and Co(PPh_3)$_2I_2$[25] were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Et_2O for NH_3 generation reactions was stirred over Na/K (≥2 h) and filtered before use.

Physical Methods. Elemental analyses were performed by Midwest Microlab, LLC (Indianapolis, IN). ^1H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane, using ^1H and ^{13}C resonances from a residual solvent as internal standards. ^{31}P chemical shifts are reported in ppm relative to 85% aqueous H_3PO_4. Solution-phase magnetic measurements were performed by the method of Evans.[26] IR measurements were obtained as solutions or thin films formed by the evaporation of solutions using a Bruker Alpha Platinum ATR spectrometer with *OPUS* software. Optical spectroscopy measurements were collected with a Cary 50 UV−vis spectrophotometer using a 1 cm two-window quartz cell. Electrochemical measurements were carried out in a glovebox under an N_2 atmosphere in a one-compartment cell using a CH Instruments 600B electrochemical analyzer. A glassy carbon electrode was used as the working electrode, and platinum wire was used as the auxiliary electrode. The reference electrode was Ag/$AgNO_3$ in THF. The ferrocene couple (Fc/Fc^+) was used as an internal reference. THF solutions of the electrolyte (0.1 M tetra-*n*-butylammonium hexafluorophosphate, $TBAPF_6$) and analyte were also prepared under an inert atmosphere. X-band EPR spectra were obtained on a Bruker EMX spectrometer.

X-ray diffraction (XRD) studies were carried out at the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a Bruker three-circle SMART diffractometer with a SMART 1K CCD detector. Data were collected at 100 K using Mo Kα radiation (λ = 0.71073 Å). Structures were solved by direct or Patterson methods using *SHELXS* and refined against F^2 on all data by full-matrix least squares with *SHELXL-97*. All non-H atoms were refined anisotropically. All H atoms were placed at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all H atoms were fixed at 1.2 (1.5 for methyl groups) times U_{eq} of the atoms to which they are bonded.

*[Na(12-c-4)$_2$][(TPB)Co(N_2)] (**2**).* To a −78 °C solution of (TPB)CoBr (70.5 mg, 0.0967 mmol) in THF (2 mL) was added a freshly prepared solution of $NaC_{10}H_8$ (23.5 mg of $C_{10}H_8$, 0.222 mmol) in THF (3 mL). The solution was brought to room temperature and allowed to stir for 6 h. The addition of 12-c-4 (51.1 mg, 0.290 mmol) and removal of solvent in vacuo provided a dark-red solid. Et_2O was added and subsequently removed in vacuo. The residue was suspended in C_6H_6 and filtered, and the solids were washed with C_6H_6 (2 × 2 mL) and pentane (2 × 2 mL) to furnish a red solid (68.8 mg, 0.0660 mmol, 68%). Single crystals were grown by vapor diffusion of pentane onto a THF solution of the title compound that had been layered with Et_2O. ^1H NMR (400 MHz, THF-d_8): δ 7.41 (3H), 6.94 (3H), 6.66 (3H), 6.44 (3H), 3.64 (32H), 2.29 (br), 1.37 (6H), 1.20 (6H), 0.93 (6H), −0.26 (6H). ^{11}B NMR (128 MHz, THF-d_8): δ 9.32. ^{31}P NMR (162 MHz, THF-d_8): δ 62.03. IR (thin film, cm^{-1}): 1978 (N_2). Anal. Calcd for $C_{52}H_{86}BCoN_2NaO_8P_3$: C, 59.32; H, 8.23; N, 2.66. Found: C, 59.05; H, 7.99; N, 2.47.

*[(TPB)Co][$BAr^F{}_4$] (**3**).* To a −78 °C solution of **1** (91.5 mg, 0.135 mmol) in Et_2O (2 mL) was added solid [$H(OEt_2)_2$][$BAr^F{}_4$] (134.0 mg, 0.132 mmol). The reaction was brought to room temperature and vented to allow for the escape of H_2. The purple-brown solution was stirred for 1 h. The solution was layered with pentane (5 mL) and stored at −35 °C to furnish red-purple single crystals of the title compound (162.9 mg, 0.0952 mmol, 82%), which were washed with pentane (3 × 2 mL). ^1H NMR (400 MHz, C_6D_6): δ 26.25, 23.80, 8.64, 8.44 ([$BAr^F{}_4$]), 7.88 ([$BAr^F{}_4$]), 6.33, −2.16, −3.68. UV−vis [Et_2O; λ, nm (ϵ, L cm^{-1} mol^{-1})]: 585 (1500), 760 (532). Anal. Calcd for $C_{68}H_{66}B_2CoF_{24}P_3$: C, 53.99; H, 4.40. Found: C, 53.94; H, 4.51.

*(CP_3)Co(N_2) (**5**).* (CP_3)H (100 mg, 0.169 mmol) and $CoCl_2$·1.5 THF (40 mg, 0.169 mmol) were mixed at room temperature in THF

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(10 mL). This mixture was allowed to stir for 1 h, yielding a homogeneous cyan solution. This solution was chilled to −78 °C, and a solution of MeMgCl in THF (0.5 M, 0.560 mmol) was added in three 370 μL portions over 3 h. The mixture was allowed to warm slowly to room temperature and then was concentrated to ca. 1 mL. 1,4-Dioxane (2 mL) was added, and the resultant suspension was stirred vigorously for at least 2 h before filtration. The filtrate was concentrated to a tacky red-brown solid, which was extracted with 1:1 C_6H_6−pentane (10 mL), filtered over Celite, and lyophilized to yield the product as a red powder (96 mg, 0.141 mmol, 83%). Crystals suitable for XRD were grown via the slow evaporation of a pentane solution. ^{1}H NMR (300 MHz, C_6D_6): δ 7.28 (br, 3H), 6.82 (m, 9H), 2.82 (oct, −C*H*, 3H), 2.09 (sept, −C*H*, 3H), 1.49 (m, 18H), 1.06 (dd, −CHC*H*$_3$, 9H), 0.30 (dd, −CHC*H*$_3$, 9H). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 47.39. IR (thin film, cm^{-1}): 2057 (N_2). Anal. Calcd for $C_{37}H_{54}CoN_2P_3$: C, 65.48; H, 8.02; N, 4.13. Found: C, 64.14; H, 8.36; N, 4.03.

[(CP$_3$)Co(N$_2$)][BAr^F$_4$] ***(6)***. **5** (75 mg, 0.11 mmol) and $[Cp_2Fe][BAr^F{}_4]$ (122 mg, 0.12 mmol) were dissolved separately in diethyl ether (ca. 3 mL each), and the ethereal solutions were cooled to −78 °C. The chilled solution of $[Cp_2Fe][BAr^F{}_4]$ was added dropwise to the solution of **5**, and the resultant mixture was allowed to stir at low temperature for 1 h. At this point, the mixture was allowed to warm to room temperature before filtration over Celite and concentration to ca. 2 mL. The concentrated filtrate was layered with pentane and placed in a freezer at −35 °C to induce crystallization. Decanting the mother liquor off crystalline solids and washing thoroughly with pentane yields **6** as dark-green-brown crystals (147 mg, 0.095 mmol, 86%). Crystals suitable for XRD were grown by the slow diffusion of pentane vapors into an ethereal solution of **6** at −35 °C. μ_{eff} (5:1 toluene-d_8−THF-d_8, Evans' method, 23 °C): 3.49 μ_B. ^{1}H NMR (300 MHz, C_6D_6): δ 17.22, 9.94, 8.24 ($[BAr^F{}_4]$), 7.72 ($[BAr^F{}_4]$), 3.13, 2.57, +1.5 to −2 (br, m), −3.68. IR (cm^{-1}): 2182 (N_2, thin film), 2180 (N_2, solution). Elemental analysis shows low values for N consistent with a labile N_2 ligand. Anal. Calcd for $C_{69}H_{66}BCoF_{24}N_2P_3$: C, 53.75; H, 4.31; N, 1.82. Found: C, 53.86; H, 4.31; N, 0.27. Note: The magnetic moment for **6** in solution may be complicated by some degree of solvent exchange for N_2 at the Co center, as described in the text.

[(NArP$_3$)CoCl][BPh$_4$]. THF (5 mL) was added to a solid mixture of $NArP_3$ (58 mg, 91.2 mmol), $CoCl_2$ (12 mg, 92.4 mmol), and $NaBPh_4$ (31 mg, 90.6 mmol). The reaction was stirred for 4 h at room temperature, during which the color evolved from yellow to green to purple. The solvent was removed in vacuo, and the residue was taken up in dichloromethane. The suspension was filtered over a plug of Celite, and the filtrate was dried, yielding a purple powder (86 mg, 82.1 mmol, 90%). Single crystals were grown by the slow evaporation of a saturated solution of $[(NArP_3)CoCl][BPh_4]$ in diethyl ether−dichloromethane (1:2, v/v). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 177.77, 37.50, 23.78, 13.48, 12.96, 7.37, 7.08, 6.92, 4.41, 1.50, −3.60, −9.81. UV−vis [THF; λ, nm (ϵ, L cm^{-1} mol^{-1})]: 564 (452), 760 (532). μ_{eff} (CD_2Cl_2, Evans' method, 23 °C): 3.97 μ_B. Anal. Calcd for $C_{63}H_{80}BClCoNP_3$: C, 72.10; H, 7.68; N, 1.33. Found: C, 71.97; H, 7.76; N, 1.30.

NH_3 Quantification. A Schlenk tube was charged with HCl (3 mL of a 2.0 M solution in Et_2O, 6 mmol). Reaction mixtures were vacuum transferred into this collection flask. Residual solid in the reaction vessel was treated with a solution of [Na][O-*t*-Bu] (40 mg, 0.4 mmol) in 1,2-dimethoxyethane (1 mL) and sealed. The resulting suspension was allowed to stir for 10 min before all volatiles were again vacuum-transferred into the collection flask. After completion of the vacuum transfer, the flask was sealed and warmed to room temperature. The solvent was removed in vacuo, and the remaining residue was dissolved in H_2O (1 mL). An aliquot of this solution (20 μL) was then analyzed for the presence of NH_3 (present as $[NH_4][Cl]$) by the indophenol method.[17] Quantification was performed with UV−vis spectroscopy by analyzing the absorbance at 635 nm.

Standard NH_3 Generation Reaction Procedure with 2. $[(TPB)Co(N_2)][Na(12\text{-}c\text{-}4)_2]$ (2.2 mg, 0.002 mmol) was suspended in Et_2O (0.5 mL) in a 20 mL scintillation vial equipped with a stir bar. This suspension was cooled to −78 °C in a cold well inside of an N_2 glovebox. A solution of $[H\cdot(OEt_2)_2][BAr^F{}_4]$ (95 mg, 0.094 mmol) in Et_2O (1.5 mL) similarly cooled to −78 °C was added to this suspension in one portion with stirring. Residual acid was dissolved in cold Et_2O (0.25 mL) and added subsequently. This mixture was allowed to stir for 5 min at −78 °C, before being transferred to a precooled Schlenk tube equipped with a stir bar. The original reaction vial was washed with cold Et_2O (0.25 mL), which was added subsequently to the Schlenk tube. KC_8 (16 mg, 0.119 mmol) was suspended in cold Et_2O (0.75 mL) and added to the reaction mixture over the course of 1 min. The Schlenk tube was then sealed, and the reaction was allowed to stir for 40 min at −78 °C before being warmed to room temperature and stirred for 15 min.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, spectroscopic data, experimental details, additional data for NH_3 production experiments, and XRD tables. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00645.

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Notes

The authors declare no competing financial interest.

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