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Direct Manipulation of Metal Imido Geometry: Key Principles to Enhance C–H Amination Efficacy

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ABSTRACT: We report the catalytic C–H amination mediated by an isolable Co^{III} imido complex (^{Tr}L)Co(NR) supported by a sterically demanding dipyrromethene ligand (^{Tr}L = 5-mesityl-1,9-(trityl)dipyrrin). Metalation of (^{Tr}L)Li with CoCl₂ in THF afforded a high-spin (S = 3/2) three-coordinate complex (^{Tr}L)CoCl. Chemical reduction of (^{Tr}L)CoCl with potassium graphite yielded the high-spin (S = 1) Co^I synthm (^{Tr}L)Co which is stabilized through an intramolecular η^6 -arene interaction. Treatment of (^{Tr}L)Co (NAd) as confirmed by single-crystal X-ray diffraction, revealing a rare trigonal pyramidal geometry with an acute Co–N_{imido}–C angle 145.0(3)°. Exposure of 1-10 mol% of (^{Tr}L)Co to linear alkyl azides (RN₃) resulted in catalytic formation of substituted N-heterocycles via intramolecular C–H amination of a range of C–H bonds, including primary C–H bonds. The mechanism of the C–N bond formation was probed via initial rate kinetic analysis and kinetic isotope effect experiments [$k_{\rm H}/k_{\rm D} = 38.4(1)$], suggesting a stepwise H–atom abstraction followed by radical recombination. In contrast to the previously reported C–H amination mediated by (^{Ar}L)Co(NR) (^{Ar}L = 5-mesityl-1,9-(2,4,6-Ph₃C₆H₂)dipyrrin), (^{Tr}L)Co(NAd) exhibits an extremely low one-electron reduction potential (E°_{red} = -1.98 V vs. [Cp₂Fe]^{+/0}) indicating that the highly basic terminal imido unit contributes to the driving force for H–atom abstraction.

1. INTRODUCTION

The development of a cost-effective and efficient transition-metal catalyst for direct C–H functionalization has been of interest to synthesize value-added commodity chemicals from simple hydrocarbon feedstocks.¹⁻² To this end, the use of bioinspired transition metal complexes featuring metal-ligand multiple bonds (MLMBs) has emerged as an appealing C–H functionalization methodology.³⁻⁵ In this regard, the iron-oxo complex (compound I) of Cytochrome P450 demonstrates nature's key strategy to render the iron-oxo multiple bond highly reactive, and thereby enhancing its O–atom transfer efficacy.⁶ Specifically, the open-shell electronic configuration, high oxidation state of compound I, and highly basic oxo unit of its one-electron reduced form have been proposed as leading features enabling facile C–H hydroxylation at ambient conditions.⁷⁻⁸

As such, the isoelectronic synthetic analogues, metalnitrenoid complexes (e.g., imido, M(NR²⁻);^{4, 9-11} iminyl, M(²NR⁻);¹²⁻¹⁹ nitrene adducts, M(³NR)²⁰⁻²²) have received great attention as viable N–group transfer reagents into unactivated C–H bonds. In particular, late, first-row transition metal-based nitrenoid complexes have been extensively studied for direct C–N bond formation (Mn,²³ Fe,^{18-19, 24-33} Co,³⁴⁻⁴² Ni,^{10-11, 43-44} and Cu⁴⁵⁻⁴⁶). Among the structurally characterized metal-nitrenoid complexes, however, only a few manifest productive C–H amination due to the typically strong MLMBs between the metal ion and nitrene unit.^{32-33, 37-38, 43, 45} Thus, in order to improve the efficacy of C–H amination, understanding the key factors governing the lability of the terminal nitrenoid moiety is necessary. Akin to the enzymatic C–H hydroxylation, assessing redox potentials and basicity of relevant species (e.g., imides or amides) involved in C–H amination processes operating via H–atom abstraction (HAA) is essential to comprehend the thermodynamic and kinetic properties of the desired transformations.⁴⁷⁻⁵³

From a synthetic perspective, these properties (E°_{red} and pK_a) can be tuned by various elements such as identity or oxidation state of a metal center(s),⁵⁴ electronic configuration of metal-nitrenoid complexes,^{19, 32, 55} and the local geometry of the terminal nitrenoid moiety.⁵⁶ Previously, we have demonstrated that manipulation of the spin state of the metal imide³² and the spin density at the nitrogen atom of the nitrenoid unit¹⁹ can serve as synthetic approach to weaken the MLMBs and enable facile C–H amination.

In contrast, the direct manipulation of the geometry of a metal nitrenoid and its effect on C–H amination efficacy is relatively less explored. Nonetheless, Holland and co-workers have proposed that the geometry of the terminally bound imido unit can alter the basicity of the metal imido complex. They found enhanced C–H activation reactivity from the β -diketiminate Fe^{III} imido complex upon pyridine coordination.⁵⁶⁻⁵⁸ The pyridine-bound iron imide was proposed as more bent and basic compared to the pyridine-free iron imide. However, structural characterization of the bent imido is absent, and thus, a direct correlation between the bent imido geometry and its basicity is lacking.

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Scheme 1. Ligand and Metal Complex Syntheses

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Recently, our group showcased that the geometry of the imido unit can also affect the rate of C-H amination.³⁷ We have demonstrated the intramolecular C-H amination mediated by $(^{Ar}L)Co(NR)$ (^{Ar}L) = 5-mesityl-1,9-(2,4,6-Ph₃C₆H₂)dipyrrin) and found that addition of pyridine improves both yields and rates of C-H amination. Exogenous pyridine coordinates to the trigonal planar (ArL)Co(NR) to generate the pyridine-bound imide (ArL)Co(NR)(py) providing steric protection to circumvent formation of a catalytically inactive cobalt tetrazido complex. More importantly, the rate of C-H amination was accelerated in the presence of pyridine as cocatalyst. We have ascribed the enhanced rate of C-H amination from (ArL)Co(NR)(py) to the bent and attenuated MLMB (Co-NR) as suggested by density functional theory (DFT) calculations, yet isolation of the bent (^{Ar}L)Co(NR)(py) was hampered due to the weak binding affinity of pyridine.

Motivated by these precedents, we postulated that generating a metal-bound nitrenoid unit in a bent geometry can be an alternative strategy to engender a more reactive MLMB and thus improve C-H amination efficacy both kinetically and thermodynamically.⁵¹ Towards this, we sought to design a ligand that would enable synthesis of a cobalt imido complex featuring a significantly bent nitrenoid unit in the absence of exogenous ligands (e.g., pyridine). Specifically, we sought to investigate the following questions: (1) can we synthesize a dipyrrinato Co^{III} imido complex featuring a bent nitrenoid unit by modifying the substituents on the dipyrrin scaffold? If possible, (2) is the imide competent for catalytic C-H amination to afford substituted N-heterocycles? And (3) how does the geometry of the metal-bound nitrenoid moiety alter the efficacy and reactivity profile for C-H amination with respect to yields, rates, and reaction scope?

Towards this goal, we report herein the synthesis of a trityl-substituted dipyrromethene platform (^{Tr}L) (^{Tr}L = 5-mesityl-1,9-(trityl)dipyrrin) that provides access to a robust Co^I catalyst (^{Tr}L)Co and the corresponding bent Co^{III} imido complex (^{Tr}L)Co(NR), enables a facile Co^{IIII} catalytic C–H amination. Detailed mechanistic studies on the C–H amination processes establish the improved C–H amination efficacy of (^{Tr}L)Co(NR), demonstrating the importance of modulating the primary coordination sphere to effect more reactive and synthetically applicable C–H amination catalysis.

2. RESULTS AND DISCUSSTION

2.1. Synthesis and Characterization of Cobalt Synthons. As discussed in the introduction, the ligand design principle to synthesize a bent Co^{III} imide was informed by the previously studied ligand-accelerated C-H amination processes mediated 5-mesityl-1,9-(2,4,6- $(^{Ar}L)Co(NR)$ (^{Ar}L by = Ph₃C₆H₂)dipyrrin).³⁷ Specifically, we sought to emulate the primary coordination environment of (ArL)Co(NR)(py) by modifying the flanking groups of the dipyrrin scaffold. To this end, trityl moieties were considered to be more voluminous ligand flanking units than the 2,4,6-triphenylphenyl substituents of (^{Ar}L). Thus, we envisioned that the steric profile of the trityl groups may enforce a bent geometry on the nitrenoid unit and eliminate formation of cobalt tetrazido complexes even in the absence of exogenous pyridine. Additionally, we proposed that one of the phenyl rings of the trityl substituents may stabilize the low-coordinate cobalt center via an intramolecular η^6 interaction affording a roboust Co^I synthon akin to the previously reported iron and cobalt synthons such as (ArL)Fe³² and (ArL)Co.37

With these design principles in mind, we first prepared 2trityl-1H-pyrrole via Friedel-Crafts alkylation of excess pyrrole with trityl chloride to avoid bis-alkylation. Following literature procedures,¹⁸ subsequent condensation with mesitylaldehyde dimethyl acetal followed by oxidation with 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded (^{Tr}L)H (Scheme 1a). Subsequent deprotonation of (^{Tr}L)H with PhLi yielded the lithiated scaffold (^{Tr}L)Li. Metalation of (^{Tr}L)Li with CoCl₂ in THF for 20 hours at room temperature afforded a three-coordinate complex (^{Tr}L)CoCl (1) (Scheme 1b). Single crystals of 1 suitable for X-ray diffraction were grown from a layered 1:2 benzene/hexanes solution at room temperature. In contrast to the previously reported trigonal planar Co^{II} complex (^{Ar}L)CoBr, **1** adopts a trigonal pyramidal geometry, displaying an n^1 -arene interaction between the cobalt and one of the ortho carbons from the trityl substituents (Figure 1a). The discrete η^1 -arene interaction [Co-C_{ortho} = 2.345(7) Å] is of note as it occupies the equatorial position of the dipyrrin plane positioning the chloride on the axial site. Solid-state magnetic susceptibility of 1 was measured with superconducting quantum interference device magnetometry (SQUID) and is consistent with a high-spin ground state (S =3/2) (Figure 2a).

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Figure 1. Solid-state structures of (a) (^{Tr}L)CoCl (1), (b) (^{Tr}L)Co (2), and (^{Tr}L)Co(NAd) (3) at 100 K with thermal ellipsoids set at 50% probability (hydrogen atoms and solvent molecules are omitted for clarity; Co aquamarine, C gray, N blue, Cl green). Selected bond lengths (Å) and angles (deg) for 1: Co–C_{ortho}, 2.345(7); 3: Co–C_{ortho}, 2.756; Co–N, 1.636(3); \angle Co–N–C = 145.0(3).



Figure 2. Variable-temperature susceptibility data of (a) (^{Tr}L)CoCl (1) and (b) (^{Tr}L)Co (2) collected at 1.0 T from 5 to 300 K. (Inset) Reduced magnetization data collected at three fields (1, 4, 7 T) over the temperature range 1.8–10 K. Magnetization fit parameters obtained with PHI:⁵⁹ for 1, S = 3/2, g = 2.4, D = -48.1 cm⁻¹, |E/D|= 0.11 and for 2, S = 1, g = 2.03, D = 25.98 cm⁻¹, |E/D|= 0.085. (c) Variable-temperature susceptibility data of (^{Tr}L)Co(NAd) (3) collected at 0.5 T and 1.0 T upon heating and cooling (5 to 300 K and 300 to 5 K).

Chemical reduction of 1 with KC₈ in a thawing benzene solution cleanly furnished the reduced species (^{Tr}L)Co (2), which exhibits an intramolecular η^6 -interaction between the cobalt and one of the phenyl groups of the trityl substituents (Scheme 1b, Figure 1b). Solid-state magnetic susceptibility of 2 is consistent with an S = 1 high-spin ground state (Figure 2b). The cyclic voltammogram of 2 measured in a non-

coordinating solvent 1,2-difluorobenzene reveals two sequential one-electron oxidations ($E_{1/2} = -0.80$, 0.75 V vs. $[Cp_2Fe]^{+/0}$) and a single one-electron reduction (– 2.1 V, Figure 3a). The observed redox potentials are almost identical with the ones observed for its congener (^{Ar}L)Co, suggesting that **2** is a suitable alternative Co^I synthon to further explore two-electron oxidative group transfer reactivity (Figure 3b).



Figure 3. Cyclic voltammograms of (a) 2 and (b) (^{Ar}L)Co obatined in 1,2-difluorobenzene at room temperature using 0.1 M [^{*n*}BuN₄][PF₆] electrolyte. Potentials were referenced to [Cp₂Fe]^{+/0} couple. Scan rate = 100 mV/s.

2.2. Synthesis and Characterization of $({}^{Tr}L)Co(NAd)$. With the $({}^{Tr}L)Co{}^{I}$ synthon in hand, we sought to investigate its reactivity towards organoazides. Treating a benzene- d_6 solution of 2 with a stoichiometric amount of 1-azidoadamantane (AdN₃) immediately furnished a diamagnetic species as verified by 1 H and 13 C NMR spectroscopies. Single crystals of the product obstained from a 1:1 benzene/hexanes mixture stored at room temperature were analyzed by single crystal X-ray diffraction to reveal formation of a three-coordinate Co^{III} imido complex (${}^{Tr}L$)Co(NAd) (3) (Scheme 2 and Figure 1c-d).

Scheme 2. Reactivity Assessment of 2.



Notably, **3** exhibits a unique distorted trigonal pyramidal geometry with a significantly bent imido moiety $[\angle \text{Co}-\text{N}-\text{C} = 145.0(3)^\circ]$. Akin to **1**, a releatively long η^1 -arene interaction between the cobalt and one of the *ortho* carbons from the trityl groups is present (Co-C_{ortho} = 2.756 Å) orienting the nitrenoid unit orthogonal to the dipyrrin plane. Furthermore, the sterically encumbered trityl substituents shield the *trans* position of the nitrenoid moiety, enforcing an acute $\angle \text{L}-\text{Co}-\text{NAd}$ (119.7°) as well as blocking the fourth-coordination site of **3** as further evidenced by the space-filling model (Figure S-28). Consequently, no bimolecular reactivity affording the four-

coordinate tetrazido complex was detected upon heating a benzene- d_6 solution of **3** with excess amount of AdN₃ (Scheme 2).

We note that only a handful of structurally characterized metal imides display a substantially bent nitrenoid unit. For first-row transition metals, a four-coordinate late. bis(pyrrolyl)pyridine Fe^{IV} imide⁶⁰ and five-coordinate Fe^{IV} imide⁶¹ supported by a tetradentate N-heterocyclic (NHC) ligand display an Fe-N-C angle of 140.5(3)° and 150.07(10)°, respectively. Hillhouse and co-workers have shown the synthesis of a three-coordinate nickel imide featuring a bent nitrenoid moiety $[\angle Ni-N-C = 127.3(3)^{\circ}]$ using a sterically encumbered aryl azide (e.g., 2,5-dimesitylphenylazide, 2,6bis(2,6-diisopropylphenyl)phenylazide).44 Given that those bent M-N-C linkages were induced by either multidentate chelating ligands or steric properties of the R substituents on the metal-bound imido (NR) group, furnishing the bent imido complex 3 via direct manipulation of the primary coordination enviroment with the low-coordinate bidentate dipyrrin ligand is significant.

Having isolated the bent imido **3**, we sought to understand its electronic structure. As discussed, the diamagnetic spin ground state of **3** is further supported by the temperatureindependent susceptibility data (Figure 2c), which is consistent with the vast majority of Co^{III} imides including the analogous dipyrrin alkyl Co^{III} imide (^{Ar}L)Co(NR) reported by our group.³⁶⁻⁴² However, unlike (^{Ar}L)Co(NR), no thermal population of spin excited states (e.g., $S = 0 \rightarrow 2$) was observed (Figure 2c inset).³⁶

To further elucidate the frontier molecular orbital interactions in **3**, DFT calculations were conducted (SI-59).⁶²⁻⁶³ Interestingly, owing to the bent geometry, HOMO, HOMO–1, and HOMO–2 of **3** display almost non-bonding or significantly disrupted π^* interactions with respect to the imido unit. Instead, σ^* or π^* contributions from the dipyrrin become dominant. The non-bonding interaction with $3d_x^2-y^2$ and the slight π -overlap between the 2p orbitals of the N_{imido} and Co $3d_z^2$, $3d_{yz}$ and $3d_{xy}$ are illustrated in Figure 4.



Figure 4. Frontier molecular orbital description of 3.



Figure 5. (a) Double-reciprocal plot with 10 mol% of **2** at varying concentrations of pyridine- d_5 at 25 °C. (b) Job plot analysis between **2** and pyridine in benzene- d_6 at 25 °C. (c) Solid-state structures of (^{Tr}L)Co(py) (4) at 100 K with thermal ellipsoids set at 50% probability (hydrogen atoms and solvent molecules are omitted for clarity; Co aquamarine, C gray, N blue). Selected bond lengths (Å): Co–C_{ortho}, 2.050(8); Co–C_{meta}: 2.239(8).



Figure 6. (a) Full reaction progression with 10 mol% of 2 at 50 °C in benzene- d_6 . (b) Zeroth-order dependence on the concentration of 5 at 25 °C in benzene- d_6 . (Inset) Initial stages of reaction showing the concentration of 7 is constant. A dashed line indicates the region less than 10% of 6. (c) First-order dependence on the concentration of 7 at 25 °C benzene- d_6 .

2.3. Catalytic C-H Amination.

2.3.1. Steric protection from (^{Tr}L) leads to higher yields of C-H amination. Encouraged by the distorted MLMB of **3** and its steric shielding to prevent the catalyst degradation, we speculated that analogous (TrL)Co(NR) species featuring a linear alkyl moiety would greatly benefit the intramolecular C-H amination to afford N-hetetrocycles. To test this hypothesis, (4-azido-4-methylpentyl)benzene (5) was exposed to 10 mol% of 2 in benzene- d_6 . Gratifyingly, the desired product 2,2-dimethyl-5-phenylpyrrolidine (6)was quantitatively obtained at room temperature along with regenerated catalyst 2 (Figure S-2). We note that under the same conditions ([5] = 85.0 mM at 25 °C), 10 mol% of (^{Ar}L)Co yielded only 13% of **6** due to concomitant formation of a catalytically inactive tetrazido complex (^{Ar}L)Co(κ^2 -N₄R₂, $R = C(CH_3)_2(CH_2)_3Ph)$,³⁷ highlighting that absence of the offcycle pathway is critical to improve the yields of C-H amination. As a result, even with 1 mol% of 2 in benzene- d_6 , 6 was obtained in 91% yield at 80 °C.

The steric protection of the trityl substituents is further supported by the effect of pyridine on the rates of catalytic C– H amination. Given that the fourth-coordination site of **3** is blocked by the trityl substituents, we hypothesized that pyridine would behave as an inhibitor as opposed to an accelerant in contrast with the C–H amination mediated by (^{Ar}L)Co(NR).

Indeed, unlike (ArL)Co(NR), which binds one equivalent of pyridine in solution,³⁷ **3** showed no binding affinity towards pyridine. Moreover, at 25 °C, slower rates of C-H amination were observed when exposing 5 to 10 mol% of 2 at higher concentrations of pyridine-d5 (Figure S-7). A doublereciprocal plot suggests that pyridine- d_5 and 5 compete for the same coordination site of 2,64 and thus, the desired C-H amination is hampered in the presence of pyridine- d_5 (Figure 5a and Figure S-9). Job plot analysis further supports that 2 readily binds pyridine in benzene- d_6 to furnish the (^{Tr}L)Co(py) (4) adduct (Scheme 2 and Figure 5b).65 Furthermore, singlecrystal X-ray diffaction analysis of 4 verifies that pyridine occupies the same axial position as the imido moiety of 3 (Figure 5c). The solid-state structure of 4 displays an η^2 -arene interaction with one of the ortho and meta carbons from the trityl groups $[Co-C_{ortho} = 2.0520(8) \text{ Å and } Co-C_{meta} = 2.239(8)$ Å]. These results are in line with the aforementioned steric enviroment of 3 suggesting that the fourth coordination site of (^{Tr}L)Co(NR) is no longer available.

Thus, by simply switching the flanking groups of the Co^{I} catalyst from the 2,4,6-triphenylphenyl to trityl, pyridine becomes a competitive inhibitor as opposed to a cocatalyst for the desired C–H amination. These results demonstrate that the pyridine ligation effect precluding tetrazene formation, which is observed for the previously studied amination catalysis with

the (^{Ar}L) scaffold is successfully incorporated within the (^{Tr}L) ligand. Furthermore, considering that many other attempted N–group transfer reactions utilizing organoazides as a nitrene source are hampered by the reductive coupling of organoazides furnishing tetrazene^{36-37, 66} or hexazene⁶⁷ complexes, we believe that the study described herein provides a ligand design to circumvent loss of reactive metal-nitrenoid intermediates.

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2.3.2. Mechanism of the C–H amination. Next, we sought to investigate the mechanism of C–H amination mediated by $(^{Tr}L)Co(NR)$ and explore how the unusual geometry of the cobalt imide affects its C–H amination reactivity as compared to that of $(^{Ar}L)Co(NR)$.



Figure 7. Kinetic isotope effect experiments with 10 mol% of **2** at 25 °C in benzene- d_6 .

To this end, the reaction progression was monitored by ¹H NMR spectroscopy (Figure 6a). In the presence of 10-fold excess amount of azide substrate **5**, (^{Tr}L)Co (**2**) immediately converted to the corresponding Co^{III} imide (7) at 25 °C as verified by the diagnostic ¹H NMR chemical shifts (Figure S-2). At early stages of the reaction, imido **7** is the resting species as the concentration of azide **5** is sufficient to continuously oxidize **2** as soon as **7** generates pyrrolidine **6** (Figure 6b inset). Indeed, the rate of the azide consumption (-d[5]/dt) is almost identical to the rate of product formation (d[6]/dt) at initial statges of the catalytic reaction (SI-17). Thus, while the concentration of **7** is constant at early stages of the reaction (**6** < 10%), the rate of formation of **6** is zeroth order in [**5**] and first order in [**7**], corroborating that **7** is competent for C–H amination in a unimolecular fashion (Figure 6b-c).

Furthermore, a kinetic isotope effect (KIE) value was evaluated by comparing the initial rates of 10 mol% of **2** with **5** and (4-azido-4-methylpentyl-1,1-*d*₂)benzene (**5**-*d*₂). The observed ratio of the rate constants ($k_{\rm H}/k_{\rm D}$) was determined to be 38.4(1) at 25 °C (Figure 7), consistent with a rate-determining homolytic C–H bond cleavage.⁶⁸ Given all the kinetic data, we propose the following Co^{VIII} catalytic cycle (Scheme 3): fast oxidation of **2** by an alkyl azide affords a Co^{III} imide which undergoes intramolecular HAA; subsequent radical recombination of the resulting Co^{II} amide affords the cyclized products. However, we note that a direct C–H insertion pathway from the Co imido complex cannot be fully excluded.

Scheme 3. Proposed Catalytic Cycle.



2.3.3. Enhancement in rates of C-H amination. Surprisingly, the rate of C-H amination mediated by (TrL)Co(NR) is significantly faster compared to (ArL)Co(NR). Specifically, the rate constant (k) for the benzylic C-H amination mediated by 7 to afford 6 is 0.063 min⁻¹ at 25 °C, whereas the same magnitude of $k = 0.062 \text{ min}^{-1}$ was observed for the analogous (^{Ar}L)Co(NR) at 50 °C.³⁷ We propose the faster conversion is a result of the bent imido moiety of 7 (as observed for 3) that likely resembles the transition state geometry for HAA more closely than the linear (ArL)Co(NR). Therefore, the enhanced C-H amination rate of 7 supports our original hypothesis, where a bent nitrenoid unit may enhance the rate of C-H amination as less structural rearrangement is required for HAA. Overall, these results highlight that a bent MLMB linkage, which is enforced by the (TrL) scaffold, is critical to enhance the rate of C-H amination, thus kinetically improving the overall C-H amination process.

2.3.4. Scope of C-H amination. In addition to the enhanced rates, (TrL)Co(NR) is capable of functionalizing a range of C-H bonds, even primary C-H bonds in a catalytic fashion (Table 1). Previously, we were only able to functionalize benzylic C-H bonds from the analogous three-coordinate metal imides M(NR²⁻): (^{Ar}L)Fe(NAd)³² and (^{Ar}L)Co(NR).³⁷ Thus, the ability of (^{Tr}L)Co(NR) to functionalize C-H bonds stronger than a benzylic C-H bond catalytically is noteworthy. As such, we sought to address the elements rendering (^{Tr}L)Co(NR) a more potent oxidant relative to the analogous (^{Ar}L)Co(NR). Given that both imides (^{Tr}L)Co(NR) and (ArL)Co(NR) accomplish intramolecular C-H amination via an initial rate-limiting HAA step, as suggested by the measured KIE values,³⁷ we attempted to evaluate thermodynamic parameters such as E°_{red} and pK_a as described in eq 1, where the constant C represents the standard potential for proton reduction in aprotic solvent.⁴⁸ We hypothesized that the difference in driving force for HAA from the respective imides is proportional to the difference in bond dissociation energies 1

(BDEs) of the N–H bonds of the corresponding Co^{II} amide complexes (Scheme 4).

Table 1. Catalytic C–H amination using 2 and alkyl azides^a



^{*a*}Isolated yields from reactions conducted with 85.0 mM of azide substrate. ^{*b*}1mol% of 2. ^{*c*}5 mol% of 2. ^{*d*}10 mol% of 2.

BDE of N-H (kcal/mol) =
$$23.06E^{\circ}_{red} + 1.37pK_a + C$$
 (eq 1)

Scheme 4. Thermodynamic Square Scheme for HAA from Co^{III} Imides 3 and 8.



To this end, we used **3** and its isolable congener (^{Ar}L)Co(NAd) (**8**) as model complexes to probe their oneelectron reduction potentials (E°_{red} values for Co^{III/II} couples) via electrochemical analysis. Cyclic voltammetry experiments of **3** and **8** were conducted using 0.1 M ["BuN][PF₆] electrolyte in the non-coordinating solvent 1,2-difluorobenzene to obviate exogenous ligand coordination that may affect the E°_{red} . Interestingly, both **3** and **8** display reversible one electron reductions at E_{1/2} of -1.98 V and -1.93 V (vs. [Cp₂Fe]^{+/0}), respectively (Figure 8).

The observed low reduction potentials suggest that the driving force for HAA can be ascribed to the high basicity of the one-electron reduced anionic imides $[LCo(NR)]^-$, which are equivalent to the conjugate base of amides [LCo(NHR)] **3a** and **8a**, respectively (Scheme 4).⁵⁴ Furthermore, given the almost identical E°_{red} values of **3** and **8**, we believe that the greater oxidizing power of $(^{Tr}L)Co(NR)$ compared to

 $(^{Ar}L)Co(NR)$ arises from a more basic imido moiety of its oneelectron reduced form $[(^{Tr}L)Co(NR)]^{-}$.



Figure 8. Cyclic voltammograms of **3** and **8** obtained in 1,2difluorobenzene at room temperature using 0.1 M [*n*BuN4][PF6] electrolyte. Potentials were referenced to $[Cp_2Fe]^{+/0}$ couple. Scan rate = 100 mV/s.

Unfortunately, our attempts to directly probe the pK_a of the respective amide complexes (TrL)Co(NHAd) (3a) and (ArL)Co(NHAd) (8a) were unsuccessful due to their high propensity for subsequent HAA resulting in formation of 1adamantylamine.⁵¹ Instead, the difference in pK_a between **3a** and 8a was estimated by accounting for the difference in BDEs of the C-H bonds (6 kcal/mol) that can be activated by the respective imides intramolecularly at 25 °C. Specifically at 25 °C, (TrL)Co(NR) accomplishes amination of secondary C-H bonds (96 kcal/mol, $R = C(CH_3)_2(CH_2)_3CH_3$) affording 2,2,5-trimethylpyrrolidine, whereas (ArL)Co(NR) can only functionalize benzylic C-H bonds (90 kcal/mol, R = $C(CH_3)_2(CH_2)_3Ph$) to afford 6. Accordingly, the conjugate base of $3a \left[\left({^{Tr}L} \right) Co(NR) \right]^{-}$ is estimated to be about 10⁵ times more basic than the conjugate base of 8a [(ArL)Co(NR)]⁻. The observed difference in pK_a is further supported by DFT calculations,⁵¹ yet evaluation of the absolute pK_a of each amide complex needs to be further examined (SI-41).

This observed trend in basicity is in agreement with literature reports proposing that a bent imido moiety is more basic compared to a linear one.⁵⁶ Thus, these results demonstrate that altering the local geometry of the terminally bound metal imido unit subsequently affects its basicity as well, and thereby enhances its oxidizing power and broadens its C–H amination reaction scope.

3. CONCLUSIONS

The foregoing results illustrate how rational ligand design allowed the synthesis of a robust Co^{I} catalyst and isolation of a bent Co^{III} imide that promotes facile catatlytic C–H amination. The previously studied pyridine-accelerated C–H amination process mediated by (^{Ar}L)Co(NR) informed the design principles for the synthesis of a dipyrromethene ligand (^{Tr}L) featuring sterically encumbered trityl substituents. The subtle modification of the supporting ligand drastically altered the primary coordination environment of a Co^{III} imide to force the terminal imido unit perpendicular to the dipyrrin ligand plane, imposing a bent geometry. Kinetic and thermodynamic analyses of the C–H amination mediated by either (^{Tr}L)Co(NR) or (^{Ar}L)Co(NR) highlight that the unique structure of (^{Tr}L)Co(NR) is key for the significantly enhanced C–H amina-

tion efficacy as manifested in yields, rates, and oxidizing power. In particular, the sterically demanding trityl substituents prevent catalyst degradation (via tetrazene formation), contributing to higher yields of C-H amination. More importantly, the atypical trigonal pyramidal geometry of the CoIII imide with a significantly bent imide resembles the transition state for HAA more closely, and thereby, (TrL)Co(NR) displays enhanced rates of C-H amination compared to the trigonal planar (ArL)Co(NR) possessing a linear imido geometry. Lastly, the more bent, and thus more basic, one-electron reduced species of (^{Tr}L)Co(NR) provides a greater thermodynamic driving force for HAA enabling C-H amination with a broader substrate scope at milder conditions. We believe that this study provides an alternative synthetic strategy to generate highly reactive metal imido complexes via direct manipulation of the geometry of MLMBs to accomplish more applicable catalytic transformations.

EXPERIMENTAL SECTION

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General experimental considerations, synthesis and spectroscopic characterizations, X-ray diffraction techniques, kinetic analysis, electrochemistry measurements, and DFT results are all provided in Supporting Information.

Preparation of (^{Tr}L)CoCl (1). In an oven-dried 20 mL vial, anhydrous CoCl₂ (0.105 g, 0.81 mmol, 1.2 equiv) was dissolved in THF and frozen in a liquid nitrogen cooled coldwell. To a frozen solution, a solution of (TrL)Li (0.52 g, 0.68 mmol, 1 equiv) in THF was added and stirred for 20 hours at room temperature. The resulting dark red reaction mixture was filtered through a coarse glass frit with Celite to remove LiCl and the excess CoCl₂. The Celite was washed with an additional 20 mL benzene. The collected filtrate was frozen and benzene was removed by sublimation in vacuo to afford 1 as a dark red powder (0.52 g, 90%). Crystals suitable for X-ray diffraction were grown from a 2:1 n-hexane/benzene layered solution at room temperature. ¹H NMR (600 MHz, 295 K, C₆D₆): δ/ppm 68.14, 23.15, 20.56, 4.70, 0.64, -1.16, -10.13, -37.86. Anal. Calc. for C56H45ClCoN2: C 80.04, H 5.40, N 3.33; Found: C 80.00, H 5.29, N 3.45.

Preparation of (^{Tr}L)Co (2). In an oven-dried 20 mL vial, 1 (0.4 g, 0.476 mmol, 1 equiv) was dissolved in 10 mL of benzene and added to a frozen solution of potassium graphite (KC₈, 0.071 g, 0.524 mmol, 1.1 equiv). The reaction mixture was slowly warmed up to room temperature and stirred for 3 hours at room temperature. The dark red-orange mixture was filtered through a coarse glass frit with Celite to remove graphite. The Celite was washed with an additional 20 mL benzene. The collected filtrate was frozen and benzene was removed by sublimation *in vacuo* to afford **2** as a dark orange powder. (0.3 g, 78%). Crystals suitable for X-ray diffraction were grown from a 1:1 n-hexane/benzene mixture at room temperature. ¹H NMR (600 MHz, 295 K, C₆D₆): δ/ppm 49.82, 21.04, 14.90, 5.84, 5.16, 4.54, 0.96, -2.51. Anal. Calc. for C56H45CoN2: C 83.56, H 5.64, N 3.48; Found: C 83.45, H 5.50, N 3.39.

Preparation of (^{Tr}L)Co(NAd) (3). In an oven-dried 20 mL vial, a solution of 1-azidoadamantane (22 mg, 0.12 mmol, 1.0 equiv) in benzene was added to a stirring solution of 2 (100 mg, 0.12 mmol, 1.0 equiv) in benzene to observe an immediate color change from dark red to dark purple. After stirring for 30 min at room temperature, the reaction mixture was frozen and benzene was removed by sublimation *in vacuo* to

afford **3** as a purple powder (109 mg, 92%). Crystals suitable for X-ray diffraction were grown from a 1:1 *n*-hexane/benzene mixture at room temperature. ¹**H** NMR (600 MHz, 295 K, C₆D₆): δ /ppm 7.94 (d, 12 H), 7.23 (d, 2 H), 6.97 (t, 6 H), 6.84 (s, 2 H), 6.67 (t, 11 H), 6.03 (d, 2 H), 2.26 (s, 5 H), 2.20 (s, 3 H), 1.80 (s, 3 H), 1.63 (t, 6 H), 1.08 (s, 6 H). ¹³C{¹H} NMR (125 MHz, C₆D₆): δ /ppm 192.23, 153.36, 151.26, 146.88, 137.28, 135.37, 134.93, 132.14, 129.57, 128.59, 125.51, 124.41, 69.27, 61.65, 61.12, 37.54, 33.30, 31.03, 21.25, 20.69. Anal. Calc. for C₆₆H₆₀CoN₃: C 83.08, H 6.34, N 4.40; Found: C 82.72, H 6.52, N 4.71.

ASSOCIATED CONTENT

Supporting Information. General experimental considerations and procedures, multinuclear NMR data, electrochemistry data, kinetic analysis, magnetometry data, solid state molecular structures, computational details, crystallographic CIF files, and crystallography data.

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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