ORGANOMETALLICS

First-Row Transition Metal and Lithium Pyridine-ene-amide Complexes Exhibiting N- and C-Isomers and Ligand-Based Activation of Benzylic C–H Bonds

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Supporting Information



ABSTRACT: Ene-amines Z-3-(2-pyridyl)-1-aza(2,6-ⁱPr₂-Ph)propene, (pynac)H, and 2-(2-pyridyl)-1-aza(2,6-R,R'-Ph)propene, (pyEA-ArRR')H, were synthesized by condensation procedures; corresponding lithium or potassium ene-amides were prepared via standard deprotonation protocols. Addition of 2 equiv of (pynac)H to $\{(Me_3Si)_2N\}_2Fe(THF)$ or 2 Li(pynac) to FeBr₂(THF)₂ afforded (pynac)₂Fe (1), while treatment of CrCl₂(THF)₂, MnCl₂, FeBr₂(THF)₂, and CoCl₂py₄ with 2 equiv of (pyEA-ArⁱPr₂)K afforded pseudotetrahedral (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe) and (pyEA-ArⁱPr₂)₂Co-py (2-Co-py). Diamagnetic (κ -C,N-pyEA-ArⁱPr₂)₃Co (3) was prepared in low yield (~7%) from CoCl₂, and its Co-C(sp³) linkages are unusually low in field strength. Reactivity studies yielded little clean reactivity, but thermolysis of 2-Co-py afforded the bis-indolamide derivative { κ -N,N-N(C₆H₃(2-ⁱPr)CMe₂C(Me)(2-py)}₂Co (5-Co), and related thermolyses of 2-M (M = Cr, Mn, Fe), conducted on NMR tube scales, generated related 5-M (M = Cr, Mn, Fe) at roughly the same rates. This observation prompted thermolyses of (pyEA-ArRR')Li, which rearrange to their corresponding indolamides in >90% yields. Rate studies, accompanied by KIE and EIE observations, revealed that an initial hydrogen transfer is reversible and is likely to correspond to an anionic rearrangement, whereas C-C bond formation is rate-determining, as suggested by accompanying calculations. X-ray structure determinations of 1, 2-Fe, 2-Co-py, 3, and 5-Co were conducted.

INTRODUCTION

Transition metal compounds containing pyridine-imine $(PI)^{1-6}$ and pyridine-diimine $(PDI)^{7-19}$ moieties often exhibit redox noninnocent $(RNI)^{20-29}$ behavior due to multiple accessible charged states of the ligands. This capacity is most evident in first-row transition metals, where the ionic character of the metal–ligand bond limits charge distribution via covalency, and in early transition metals²⁹⁻³² that have limited redox capability. Ligands designed as PI variants consisting of 2-azaallyls, their precursors, or related chelates have led to intriguing carbon– carbon and C–X bond-forming reactions and afford examples of RNI, as illustrated in Figure 1.

Compounds containing 1,3-di-2-pyridyl-2-azaallyl (smif)³³ tridentate ligands exhibit reversible and irreversible C–C bond-forming reactions depending on steric factors (A),³⁴ while the generation of transient azaallyls within a tetradentate chelate have afforded [{Me₂C(CHNCH-2-py)₂}M]₂ (M = Cr, Co, Ni) dimers wherein three new carbon–carbon bonds have been formed around unique metal–metal bonds (B).³⁵ Incorporating PI precursors into a nacnac framework^{36–39} permitted the isolation of carbon radical

character, leading to C–C bond formation (C),⁴⁰ but in related tetradentate ligands, electrostatic stabilization of a 14e⁻ π -system afforded very stable Fe(II) complexes (D).^{41,42} Finally, a tetradentate di-PI ligand revealed five redox states (E) that were quite stable, while the metal formally remained Ni(II).⁶

The successful implementation of 2-azaallyls^{34,35,40,43} in bondforming processes^{44–47} prompted an investigation into corresponding 1-azaallyls,^{15,46–49} recognizing that such entities are ene-amides that can be readily prepared via condensation routes. Herein is described an initial study of 1-azaallyl ligands, with pyridine utilized in its usual supporting role in bidentate chelation.

RESULTS

Ligand Syntheses. The 1-azaallyl ligands used in this study were prepared as illustrated in Scheme 1. Treatment of 2,6-diisopropyl

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Figure 1. Pyridine-imine (PI) redox states (red box) and corresponding azaallyl ligand variations: (A) 1,3-di-2-pyridyl-2-azaallyl (smif) compounds exhibiting C–C bond couplings that can be construed as diradical couplings; (B) tetradentate precursors to 2-azaallyls are activated by metal diamides to afford three new C–C bonds and six stereocenters in the generation of metal–metal-bonded complexes; (C) incorporating oxidatively destabilized pyridine-imines within a nacnac group affords C–C coupling; (D) PIs within nacnacs are electrostatically stabilized by Fe(II) and through $(4n+2)e^{-\pi}$ -systems; and (E) electrostatically stabilizing pyridine-imines with Ni(II) inhibits reactivity.

Scheme 1



aniline with triethyl orthoformate afforded, upon thermolysis, the 2,6-diisopropyl-ethoxyimine as a colorless oil in 78% yield.⁵⁰ 2-Lithiomethylpyridine was generated via deprotonation of

2-picoline with LDA and treated with the 2,6-diisopropylethoxyimine⁵¹ to prepare Z-3-(2-pyridyl)-1-aza(2,6-ⁱPr₂-Ph)propene, (pynac)H, as a light brown solid in 98% yield.

Article

Scheme 2



Standard condensation procedures utilizing 2-acetylpyridine and 2,6-R,R'-anilines provided the pyridine-methylimines in good to very good yields, and subsequent deprotonation of a methylimine proton with LiHMDS or KH led to the lithium and potassium ene-amides, (pyEA-ArRR')Li (R, R' = Me, Et, ⁱPr; R = Me (CD₃), R' = H) and (pyEA-ArⁱPr₂)K, respectively. Somewhat surprisingly, the ene-amides possessed reproducible, vibrant colors depending on substituent and main group metal. While the spectral properties of the species were not studied, it is worthwhile noting that related di-2-pyridyl-2-azaallyl main group species are an intense maroon color whose larger crystals are bronze/gold.^{33,34} The 1-azaallyl species in Scheme 1 were not as intense, and their solid colors matched those in solution.

Synthesis of (pynac)₂**Fe (1).** The initial ligand entry into 1-aza-allyl complexes was the pyridyl-based nacnac analogue pynac. A ferrous derivative containing two pynac ligands was prepared via two metathesis routes: (1) protonation of $\{(Me_3Si)_2N\}_2Fe(THF)^{52}$ with the free ligand, $^{33-35,40-42}$ which afforded (pynac)₂Fe (1) in 85% yield, and (2) salt metathesis of FeBr₂(THF)₂ with Li(pynac), prepared *in situ* from (pynac)H and LDA, which provided 1 in 77% yield. The red complex was high spin (μ_{eff} (Evans's)⁵³ = 5.2(1) μ_B) and relatively devoid of substantive, clean reactivity, despite being exposed to numerous reagents. Incorporation of the azaallyl into a nacnac analogue was deemed counterproductive from a reactivity standpoint; hence a change to ene-amide coordination was warranted.

Structure of (pynac)₂**Fe (1).** A molecular view of (pynac)₂Fe (1) is given in Figure 2, along with pertinent interatomic metric parameters, and Table 1 lists selected data acquisition and refinement information. The complex is a highly distorted tetrahedron⁴⁰ caused by pynac bite angles (93.5(7)° av) that are substantially less than 109.5°. The bulky 2,6-diisopropylphenyl substituents cause the nitrogens of the pynac imines to splay apart at 128.63(6)°, whereas the nitrogens of the smaller py components are separated by only 92.67(6)°. The remaining N_{im}–Fe-N_{py} angles average 122.4(47)°; hence the structure is roughly C₂-symmetric. The Fe–N distances corresponding to the pyridines (2.069(2) Å av) and imines (1.976(2) Å av) are normal in comparison to related ligands and are consistent with the high-spin ferrous environment.

Syntheses of Ene-amides (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe, Co-py). The shift to ene-amide-pyridine derivatives was accomplished by salt metathesis, and Scheme 3 summarizes the results. $CrCl_2(THF)_2$, $MnCl_2$, and $FeBr_2(THF)_2$ were treated with 2 equiv of the bulky potassium diisopropyl-eneamide, (pyEA-ArⁱPr₂)K, in THF, and pseudotetrahedral (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe) were prepared in 61–68% yields. All derivatives were high spin according to magnetic measurements using Evans's method,⁵³ with near spin-only μ_{eff} values of 4.7(1), 5.5(1), and 5.2(1) μ_B for 2-Cr, 2-Mn, and 2-Fe, respectively. Interestingly, treatment of CoCl₂ with potassium or lithium ene-amides failed to cleanly provide the bis-chelate derivatives obtained for the other



Figure 2. Molecular view of $(pynac)_2Fe(1)$ and selected interatomic distances (Å) and angles (deg): Fe1–N1, 2.0678(15); Fe1–N2, 1.9777(15); Fe1–N3, 2.0707(15); Fe1–N4, 1.9743(14); N1–C5, 1.358(2); C5–C6, 1.414(3); C6–C7, 1.370(3); N2–C7, 1.348(2); N2–C8, 1.434(2); N3–C24, 1.354(2); C24–C25, 1.420(3); C25–C26, 1.367(3); N4–C26, 1.335(2); N4–C27, 1.441(2); N1–Fe1–N2, 94.00(6); N1–Fe1–N3, 92.67(6); N1–Fe1–N4, 119.06(6); N2–Fe1–N3, 125.68(6); N2–Fe1–N4, 128.63(6); N3–Fe1–N4, 93.01(6).

metals, but a red-brown pyridine adduct was generated in 57% yield when $CoCl_2py_4$ was utilized as the starting material. Its μ_{eff} was 3.9(1) μ_{B} , consistent with an S = 3/2 ground state, and it is depicted in Scheme 3 as a trigonal bipyramid, as its structural study indicates.

Structure of (pyEA-ArⁱPr₂)₂Fe (2-Fe). Data acquisition and refinement parameters for (pyEA-ArⁱPr₂)₂Fe (2-Fe) are listed in Table 1, and its molecular view in Figure 3, with accompanying metric values, shows a distorted tetrahedral⁴⁰ arrangement similar to $(pynac)_2$ Fe (1). Bite angles of the pyridine ene-amide average $79.5(2)^{\circ}$, which allows the nitrogens of the bulky 2,6diisopropylphenylamide components to be $136.70(7)^{\circ}$ apart, while those of the pyridines are $100.94(7)^{\circ}$. The remaining N_{py} -Fe- N_{am} angles average 130.6(35)°, as the small bite angles permit a greater value than in 1, and all core angles are in accord with a C2-structure. Iron-nitrogen distances corresponding to the pyridines and amides average 2.114(12) and 1.948(7) Å, respectively, and are typical for a high-spin environment. There is little evidence of imine character to the ene-amides, as d(C6-C7) and d(C24-C25) are 1.340(3) and 1.345(3) Å, respectively, consistent with standard carbon-carbon double bonds adjacent to nitrogen.⁵⁴ Likewise, the N_{am}C distances of 1.374(3) Å are in line with $N(sp^2)-C(sp^2)$ bond lengths, ⁵⁴ as are the N_{am} - C_{ar} distances of 1.429(2) and 1.425(2) Å.

Structure of $(pyEA-Ar^{i}Pr_{2})_{2}Co-py$ (2-Co-py). Data acquisition and refinement information for $(pyEA-Ar^{i}Pr_{2})_{2}Co-py$ (2-Co-py) are provided in Table 1, while structural metrics are given in the caption to Figure 4, which contains a molecular view

Table 1. Select Crystallographic and Refinement Data for $(pynac)_2$ Fe (1), $(pyEA-Ar^iPr_2)_2$ Fe (2-Fe), $(pyEA-Ar^iPr_2)_2$ Co-py (2-Co-py), $(\kappa$ -C,N-pyEA-ArⁱPr_2)_3Co (3), and $\{\kappa$ -N,N-N(C₆H₃(2-ⁱPr)CMe₂C(Me)(2-py)\}_2Co (5-Co)

| | 1 | 2-Fe | 2 -Co-py ^{<i>a</i>} | 3 | 5 -Co |
|---|---|---|---|---|---|
| formula | C ₃₈ H ₄₆ N ₄ Fe | $C_{38}H_{46}N_4Fe$ | C47H61N5OCo | $C_{57}H_{69}N_6Co\cdot(C_6H_6)_{0.5}$ | C ₃₈ H ₄₆ N ₄ Co |
| fw | 614.64 | 614.64 | 770.94 | 936.17 | 617.72 |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | R3 | $P\overline{1}$ |
| Ζ | 4 | 4 | 4 | 6 | 4 |
| <i>a,</i> Å | 10.6647(10) | 12.0967(8) | 11.3721(5) | 19.691(2) | 9.7996(7) |
| <i>b,</i> Å | 14.9567(14) | 14.8011(11) | 23.8329(11) | 19.691(2) | 9.8387(7) |
| c, Å | 21.981(2) | 20.1037(14) | 16.3006(7) | 24.631(3) | 38.267(3) |
| α , deg | 90 | 90 | 90 | 90 | 87.205(4) |
| β , deg | 101.760(4) | 107.236(3) | 101.587(2) | 90 | 83.381(4) |
| γ, deg | 90 | 90 | 90 | 120 | 89.069(4) |
| <i>V</i> , Å ³ | 3432.6(6) | 3437.8(4) | 4327.9(3) | 8271.2(16) | 3660.3(5) |
| $ ho_{\rm calc}$ g cm ⁻³ | 1.189 | 1.188 | 1.183 | 1.128 | 1.121 |
| μ , mm ⁻¹ | 0.470 | 0.469 | 0.436 | 0.353 | 0.498 |
| temp, K | 173(2) | 213(2) | 203(2) | 203(2) | 173(2) |
| λ (Å) | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| <i>R</i> indices $[I > 2\sigma(I)]^{b,c}$ | $R_1 = 0.0359$ | $R_1 = 0.0463$ | $R_1 = 0.0370$ | $R_1 = 0.0508$ | $R_1 = 0.0598$ |
| .,_ | $wR_2 = 0.0873$ | $wR_2 = 0.1109$ | $wR_2 = 0.0923$ | $wR_2 = 0.1193$ | $wR_2 = 0.1251$ |
| R indices (all data) ^{b,c} | $R_1 = 0.0517$ | $R_1 = 0.0786$ | $R_1 = 0.0539$ | $R_1 = 0.1254$ | $R_1 = 0.0702$ |
| | $wR_2 = 0.0971$ | $wR_2 = 0.1267$ | $wR_2 = 0.1015$ | $wR_2 = 0.1710$ | $wR_2 = 0.1287$ |
| GOF^d | 1.021 | 1.022 | 1.012 | 1.067 | 1.166 |
| Contains Et ₂ O of solvation. ¹ | ${}^{b}R_{1} = \sum F_{1} - F_{2} / \sum$ | $ F_1 $, ${}^c w R_2 = [\sum w (F_1)]$ | $(- F_{1})^{2}/\sum w F_{1}^{2} T_{1}^{1/2}$ | $GOF(all data) = [\Sigma w(F_{\cdot})]$ | $- F_{1} ^{2}/(n-p)^{1/2}$ |

n = number of independent reflections, p = number of parameters.

Scheme 3



of the C₂-symmetric compound. The N1–Co–N3 angle of 172.64(4)° and corresponding N2–Co–N4 angle of 135.83(4)° lead to an Addison parameter of $\tau = 0.61$,⁵⁵ a value consistent with a distorted trigonal bipyramidal geometry where the pyridine and two amides lie in the equatorial plane and the two chelate-pyridines are axial. Amide Co–N distances of 1.968(4) Å (av), chelate-pyridine Co–N bond lengths of 2.183(4) Å (av), and the

pyridine d(Co-N) of 2.1148(11) Å are normal for Co(II) in a high-spin environment. There is a slight twist to the axial axis due to 77.91(11)° (av) chelate bite angles and corresponding N2–Co–N3 and N1–Co–N4 angles of 99.05(4)° and 99.55(4)°, respectively. The nitrogen of the unique equatorial pyridine is 93.7(3)° (av) and 112.1(22)° (av) from the nitrogens of the axial chelate-pyridines and equatorial amides, respectively.

D



Figure 3. Molecular view of $(pyEA-Ar^{i}Pr_{2})_{2}Fe$ (2-Fe) and selected interatomic distances (Å) and angles (deg): Fe1–N1, 2.1050(17); Fe1–N2, 1.9532(16); Fe1–N3, 2.1221(17); Fe1–N4, 1.9427(15); N1–C5, 1.342(3); C5–C6, 1.489(3); C6–C7, 1.340(3); N2–C6, 1.374(3); N2–C8, 1.429(2); N3–C24, 1.348(3); C24–C25, 1.482(3); C25–C26, 1.345(3); N4–C25, 1.374(3); N4–C27, 1.425(2); N1–Fe1–N2, 79.66(7); N1–Fe1–N3, 100.94(7); N1–Fe1–N4, 128.05(7); N2–Fe1–N3, 133.07(7); N2–Fe1–N4, 136.70(7); N3–Fe1–N4, 79.37(6).



Figure 4. Molecular view of $(pyEA-Ar^{i}Pr_{2})_{2}$ Co-py (2-Co-py) and selected interatomic distances (Å) and angles (deg): Co-N1, 2.1864(10); Co-N2, 1.9648(10); Co-N3, 2.1802(10); Co-N4, 1.9709(10); Co-N5, 2.1148(11); N2-C6, 1.3718(16); C6-C7, 1.356(2); C5-C6, 1.4881(18); N1-C5, 1.3481(16); N4-C25, 1.3750(15); C25-C26, 1.3566(18); C24-C25, 1.4878(18); N3-C24, 1.3467(16); N1-Co-N2, 77.95(4); N1-Co-N3, 172.64(4); N1-Co-N4, 99.55(4); N1-Co-N5, 93.48(4); N2-Co-N3, 99.05(4); N2-Co-N4, 135.83(4); N2-Co-N5, 110.55(4); N3-Co-N4, 77.83(4); N3-Co-N5, 93.87(4); N4-Co-N5, 113.61(4); N2-C6-C7, 126.65(13); N2-C6-C5, 113.28(11); C5-C6-C7, 120.06(13); N4-C25-C26, 126.60(12); N4-C25-C24, 113.17(10); C24-C25-C26, 120.23(12).

As in 2-Fe, the chelate bond distances are descriptive of 1-aza-allyls with clear C=C bonds.⁵⁴

Synthesis of $(\kappa$ -*C*,*N*-**pyEA**-**Ar**ⁱ**Pr**₂)₃**Co (3).** When CoCl₂ was used as the starting material, a persistent diamagnetic product was isolated as a red-purple precipitate—despite its low yield $(\sim 7\%)$ —due to its lesser solubility in hydrocarbons. ¹H NMR spectroscopic studies revealed a single type of ene-amide ligand with diastereotopic methylene hydrogens and four distinct isopropyl methyl groups. With consideration of its solubility, the NMR spectrum hinted at a highly symmetric aggregate structure or a rigid, mononuclear Co(I) or Co(III) species. An X-ray diffraction structural examination of the complex showed it to be a C₃-symmetric monomer containing three Co–C bonds, which are a consequence of the linkage isomerization available to the ene-amide ligand. Formally a Co(III) tri-sp³-alkyl, (κ -C,*N*-pyEA-ArⁱPr₂)₃Co



(3), is an uncommon species in coordination chemistry, as

the vast majority of organometallic Co(III) alkyls are supported by additional strong-field carbon-based ligands such as cyclo-

Figure 5. UV–vis spectrum of $(\kappa$ -*C*,*N*-pyEA-ArⁱPr₂)₃Co (3) taken in THF. Concentrations are 10 μ M (blue), 100 μ M (red), and 200 μ M (green).

Shown in Figure 5, the UV-vis spectrum of (κ -C,N-pyEA- $Ar^{i}Pr_{2}_{3}Co(3)$ exhibits two bands at 370 and 493 nm that have relatively strong intensities of 5600 and 3400 M^{-1} cm⁻¹, respectively. Normally such intensities would be attributable to MLCT or LMCT transitions, but a TDDFT calculation on a truncated model of 3 (ArⁱPr₂ replaced by Me) supports their tentative assignments as the ${}^{1}A \rightarrow {}^{1}(A,E)$ absorptions that correlate to the ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ d-d bands in an octahedral complex. All CT absorptions are calculated to be at much higher energy (>35 000 cm^{-1}). The lower symmetry, which renders both transitions electric dipole-allowed, and significant intensity stealing from the tail of an MLCT band in the ultraviolet region are responsible for their rather high extinction coefficients. Since each axis in the molecule is identical, Δ_{oct} and *B* values for **3** were estimated from interpolation of a d⁶ Tanabe–Sugano diagram.⁵⁶ From a Δ/B ratio of ~45, Δ_{oct} is ~22 000 cm⁻¹ and B is ~483 cm⁻¹, which is 44% of the Co³⁺ free ion value of 1100 cm⁻¹ and fully consistent with the high covalency expected for a complex containing three Co–C bonds. The Δ_{oct} for a hypothetical $Co(py)_6^{3+}$ complex can be estimated as ~24000 cm⁻¹;⁵⁶ hence application of the rule of average environment would suggest that the field strength of the sp3-

alkyls in 3 would amount to $\Delta_{oct} \approx 20\ 000\ \text{cm}^{-1}$ for "CoR₆^{3–}". **Structure of (\kappa-C,N-pyEA-ArⁱPr₂)₃Co (3).** A molecular view of (κ -C,N-pyEA-ArⁱPr₂)₃Co (3) and its accompanying metric parameters are given in Figure 6, and selected information regarding data acquisition and refinement is available in Table 1. The compound crystallizes in the hexagonal system and has the space group R3, which translates into having one unique κ -C,NpyEA-ArⁱPr₂ ligand and C₃ local symmetry. The cobalt–carbon distance is 1.963(4) Å, and the $d(Co-N_{py})$ is 2.001(3) Å, values that are consistent with the diamagnetic ground state accorded Co(III). The bite angle for κ -C,N-pyEA-ArⁱPr₂ is 89.39(16)°, the N–Co–N angle is 95.80(11)°, and the C–Co–C angle is



Figure 6. Molecular view of (*κ*-*C*,*N*-pyEA-ArⁱPr₂)₃Co (3), whose isopropyl methyl groups have been removed for clarity, and selected interatomic distances (Å) and angles (deg): Co1–N1, 2.001(3); Co1–C6, 1.963(4); N1–C5, 1.342(5); N1–C1, 1.365(4); C1–C7, 1.476(5); C6–C7, 1.502(5); N2–C7, 1.282(4); N1–Co1–N1, 95.80(11); C6–Co1–C6, 89.30(18); N1–Co1–C6 (bite angle), 89.39(16); N1–Co1–C6, 85.37(14); N1–Co1–C6, 174.53(17); Co1–N1–C1, 114.6(2); N1–C1–C7, 114.3(3); C1–C7–N2, 117.0(3); C1–C7–C6, 115.5(3); C6–C7–N2, 127.5(3); Co1–C6–C7, 109.8(3).

89.30(18)°, rendering the molecule nearly octahedral. The Co–C–C angle of 109.8(3)°, the C6–C7 distance of 1.502(5) Å, and the 360° sum of the angles about C7 are consistent with a C(sp²)–C(sp³)–Co linkage in the chelate.⁵⁴ The C7–N2 distance of 1.282(4) Å is short and ascribed to an imine, and d(C1-C7) = 1.476(5) Å, in line with an sp²–sp² connection.⁵⁴ In summary, the cobalt–carbon interaction appears to be purely sigma and corresponds to an α -imino-carbyl.

Reactivity of Ene-amides (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe, Co-py). The transfer of a hydrogen atom (HAT) to the ene-amide methylene group would generate a pyridine-imine that is likely to be a radical anion, as this ligand is known for its redox noninnocent behavior in stabilizing pseudotetrahedral M(II) complexes.¹ The feasibility of HAT to (pyEA-ArⁱPr₂)₂Fe (2-Fe) was assessed by calculation (primes) and tested by experiment, as illustrated in Scheme 4. A hypothetical, stepwise

Scheme 4

addition of dihydrogen to the methylene functionality of 2'-Fe showed each step to be slightly favorable, with the first $\Delta G = -7.2$ kcal/mol and the second equal to -2.4 kcal/mol. The enthalpy changes (BDE(H₂) = 104 kcal/mol)⁵⁷ suggest that the first C–H bond formed has a bond dissociation energy (BDE) of ~63 kcal/mol, and the second is ~59 kcal/mol, modest values that reflect disruption of the pyridine-imine RNI character upon HAT. For comparison, note that the BDE of H–CH₂C==O(R)⁵⁷ and, presumably, a corresponding imine is ~94 kcal/mol. How much of the roughly 30 kcal/mol decline in BDE is due to RNI vs the effects of coordination is unknown, but it is significantly attenuated. Numbers for the analogous Co compound, 2'-Co, are similar, although the second HAT is endoergic.

The calculations suggested that dehydrogenation of 9,10dihydroanthracene by $(pyEA-Ar^iPr_2)_2Fe$ (2-Fe) is slightly downhill, although the first HAT is likely to be ~15 kcal/mol unfavorable; yet no observed transfer of H₂ was noted upon extended thermolysis. The same rough thermodynamics apply to HAT from HSnⁿBu₃, and this reagent was unreactive as well. While it is possible that the degradation noted upon thermolysis, later recognized as a rearrangement, was promoted by HAT, no byproducts were observed that support this contention, and stable bis-pyridine-imine Fe(II) complexes have been prepared.¹

One reaction that appeared promising was the thermolysis of $(pyEA-Ar^iPr_2)_2Fe$ (2-Fe) in the presence of ^tBuI, which afforded a mixture of paramagnetic material (4) and isobutylene, consistent with the elimination of HI. It is conceivable that the products resulted from HAT,^{18,19,58} yet thermolyses of 2-Fe and ^tBuX (X = Cl, Br) failed to elicit related products, prompting a study of the thermal stabilities of 2-M.

Thermolyses of Ene-amides (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe, Co-py). In testing the thermal stability of eneamides (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe, Co-py), a surprising rearrangement occurred as illustrated in eqs 1 and 2. High-temperature extended thermolysis of 2-Co-py affected the addition of two methine C–H bonds across the carbon–carbon double bonds of the ene-amides, affording the bis-indolamide { κ -N,N-NC₆H₃(6-ⁱPr)CMe₂C(Me)(2-py)}₂Co (5-Co, eq 1), in



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an essentially clean (>95%) conversion. Related thermolyses of **2**-M (M = Cr, Mn, Fe), performed on NMR tube scales in C_6D_6 or THF- d_8 , gave evidence of similar transformations to $\{\kappa$ -N,N- $NC_6H_3(6$ - ^{1}Pr)CMe₂C(Me)(2-py) $\}_2$ M (5-M; M = Cr, Mn, Fe, eq 2), according to NMR spectroscopy and aqueous quenching studies. After 36 h at 140 °C in benzene, the Cr, Mn, and Fe complex rearrangements were estimated to have occurred to 83%, 80%, and 44% conversion, according to aqueous quenching studies.

The generic nature of the rearrangement and observations of similar C–H additions across ligands with related characteristics^{59–62} prompted an investigation into corresponding lithium ene-amides, as eq 3 indicates. Ene-amides with 2,6-R,R'-aryl



(R, R' = Me, Et, ⁱPr; R = Me (CD₃), R' = H) substitution proved to rearrange on similar time scales, and each generated an indolamide with a quaternary center adjacent to the amide nitrogen, which renders the transformation potentially useful. Since the product amide can serve as a base to deprotonate an imine, the rearrangement to the indoline can be catalyzed, and $LiN(SiMe_3)_2$ can be used as indicated in eq 4. Unfortunately, the reaction is quite sluggish at 140 °C, and since generating pure lithium ene-amide is inexpensive, the stoichiometric reaction is preferable. Attempts to expand the scope of the cyclization were made via replacement of the pyridine with an aryl group. Clean rearrangements were no longer observed, and while withdrawing groups other than pyridine may be effective, they have not been assessed.

Structure of { κ -N,N-NC₆H₃(6-ⁱPr)CMe₂C(Me)(2-py)}₂Co (5-Co). Information pertaining to data acquisition and refinement for { κ -N,N-NC₆H₃(6-ⁱPr)CMe₂C(Me)(2-py)}₂Co (5-Co) are given in Table 1, while molecular views of both enantiomers of 5 are illustrated in Figure 7, accompanied by selected interatomic

distances and angles. The distorted tetrahedral C_2 core of **5** is related to those of $(pynac)_2Fe(1)$ and $(pyEA-Ar^iPr_2)_2Fe(2-Fe)$, again reflecting the bite angle of the pyridine-amide chelate $(82.21(11)^\circ, 82.44(11)^\circ)$. Nitrogens of the pyridine ligands are closer to each other $(N1-Co1-N3 = 111.37(12)^\circ)$ than those of the amides $(N2-Co1-N4 = 148.41(12)^\circ)$, presumably due to the same steric factors that affect the similarly distorted structures of **1** and **2**-Fe. The disparity is somewhat greater, probably because of the tertiary carbon center resulting from C–H bond activation by the ene-amide. All of the carbon–carbon and carbon–nitrogen bonds within the chelate are normal, as are the $d(N_{py}-Co)$ and $d(N_{am}-Co)$ of 2.051(3) and 1.908(3) Å, respectively.

Table 2. Kinetics of Li(pyEA-ArRR') (ArRR' = 2,6-R₂-C₆H₃ (R = ⁱPr, Et, Me), 2-Me-C₆H₄) and (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe, Co-py) Rearrangement to Corresponding Indolamides Li{ κ -N,N-NC₆H₃(6-R)CR'R"C(Me)(2-py)) (R = ⁱPr, R' = R" = Me; R = Et, R' = H, R" = Me; R = Me, R' = R" = H; R = R' = R" = H) and { κ -N,N-NC₆H₃(6-ⁱPr)CMe₂C(Me)(2-py)}₂M (5-M, M = Cr, Mn, Fe, Co)

| | , | T | k | ΔG^{\ddagger} |
|--|---------------------------|--------------|----------------------------------|-----------------------|
| cmpd | solv | $(C(\pm 1))$ | $(\times 10^{+} \text{ s}^{-1})$ | (kcal/mol) |
| $Li(pyEA-ArMe_2)^a$ | $\mathrm{THF}\text{-}d_8$ | 100 | 0.072(1) | 30.8(1) |
| $Li(pyEA-ArMe_2)^a$ | $\mathrm{THF}\text{-}d_8$ | 120 | 0.47(1) | 31.0(1) |
| $Li(pyEA-ArMe_2)^a$ | $\mathrm{THF}\text{-}d_8$ | 130 | 1.2(1) | 31.1(1) |
| $Li(pyEA-ArMe_2)^a$ | $\mathrm{THF}\text{-}d_8$ | 140 | 2.7(1) | 31.2(1) |
| $Li(pyEA-ArMe_2)^a$ | $THF-d_8$ | 150 | 5.9(1) | 31.3(1) |
| Li(pyEA-ArEt ₂) | $\mathrm{THF}\text{-}d_8$ | 130 | 6.3(1) | 29.7(1) |
| Li(pyEA-Ar ⁱ Pr ₂) | $\mathrm{THF}\text{-}d_8$ | 130 | 0.019(1) | 34.4(1) |
| Li(pyEA- <i>o</i> -tol) ^b | $\mathrm{THF}\text{-}d_8$ | 130 | 0.29(1) | 32.2(1) |
| $Li(py(EA-o-tol)-d_5)^b$ | $\mathrm{THF}\text{-}d_8$ | 130 | 0.25(1) | 32.3(1) |
| Li(pyEA- <i>o</i> -tol) ^c | $\mathrm{THF}\text{-}d_8$ | 130 | 0.33(1) | 32.1(1) |
| $Li(pyEA-o-tol-d_3)^c$ | $\mathrm{THF}\text{-}d_8$ | 130 | 0.27(1) | 32.3(1) |
| $(pyEA-Ar^{i}Pr_{2})_{2}Cr (2-Cr)^{d}$ | $\mathrm{THF}\text{-}d_8$ | 130 | 0.040(4) | 33.8(1) |
| $(pyEA-Ar^{i}Pr_{2})_{2}Mn (2-Mn)^{d,e}$ | $\mathrm{THF}\text{-}d_8$ | 130 | | |
| $(pyEA-Ar^{i}Pr_{2})_{2}Fe (2-Fe)^{d}$ | $\mathrm{THF}\text{-}d_8$ | 130 | 0.06(2) | 33.5(3) |
| $(pyEA-Ar^{i}Pr_{2})_{2}Co-py (2-Co-py)^{d_{f}}$ | $THF-d_8$ | 130 | 0.13(1) | 32.8(1) |
| | $\mathrm{THF}\text{-}d_8$ | 130 | $0.034(6)^{g}$ | $33.9(2)^{g}$ |

^{*a*}From an Eyring plot, $\Delta H^{\ddagger} = 26.9(2)$ kcal/mol, $\Delta S^{\ddagger} = -10.3(5)$ cal/mol·K. ^{*b*}Tandem runs: $k_{\rm H}/k_{\rm D5} = 1.16(9)$. ^{*c*}Tandem runs: $k_{\rm H}k_{\rm D3} = 1.22(9)$. ^{*d*}Analytical problems associated with NMR spectral integration of paramagnetic substances hampered accuracies. ^{*e*}Overlapping, broad resonances prevented analysis by ¹H NMR integration. ^{*f*}For **5**-Co, py inhibits the rate of rearrangement, indicating that its dissociation is not rate-determining. ^{*g*}Conducted with 10 equiv of py present.

Ene-amide (Li(pyEA-ArR₂) (R = Me, Et, ⁱPr) and (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe, Co-py)) Rearrangement Kinetics. Kinetics of the Li(pyEA-ArR₂) (R = Me, Et, ⁱPr) rearrangement to the corresponding indolamide eq 3 were conducted in THF-*d*₈ after efforts in C₆D₆ revealed biexponential decays that hinted at potential aggregation issues or interference from the product. In THF-*d*₈, the kinetics exhibited smooth first-order decays, and the rate constants are given in Table 2. A study of the temperature dependence of the rearrangement from 100 to 150 °C afforded activation parameters of $\Delta H^{\ddagger} = 26.9(2)$ kcal/mol and $\Delta S^{\ddagger} = -10.3(5)$ eu, indicative of substantial bond breaking in a transition state that is moderately ordered.

Calculations (*vide infra*) prompted an investigation into the kinetic isotope effect (KIE) for the rearrangement, and the rate of Li(pyEA-*o*-tol) was measured relative to $(2\text{-py})C(=CD_2)NLi-(C_6H_4-o-CD_3)$ in a tandem kinetics experiment (k_H/k_{D5} , eqs 5, 6). Somewhat surprisingly, the k_H/k_{D5} obtained was 1.16(9), a value



commensurate with a secondary KIE.⁶³ A value substantially larger was expected for a mechanism in which hydrogen atom, hydride, or proton transfer was rate-determining. In support, the rearrangement of $(2\text{-py})C(=CH_2)NLi(C_6H_4\text{-}o-CD_3)$ was also

Scheme 5

measured relative to the all-protio material. As Scheme 5 reveals, scrambling was detected between the *o*-CD₃-tolyl and the methylene of the eneamide, and the overall phenomenological $k_{\rm H}/k_{\rm D3}$ was ~1.22(9).

A rough analysis of the equilibrium isotope effect (EIE)⁶³ was conducted by ¹H (0.89 H in $=C(H/D)_2$ vs 1.11 H in *o*-Me) and ²D (1.1 D in =C(H/D)₂ vs 1.9 D in *o*-Me) NMR spectral integration of the starting material once equilibrium was established during the course of rearrangement. The values deviate from those predicted from a purely statistical distribution $(A:B:C = 1:6:3; 0.8 \text{ H in} = C(H/D)_2 \text{ vs } 1.2 \text{ H in } o\text{-Me}; 1.2 \text{ D in}$ $=C(H/D)_2$ vs 1.8 D in o-Me) and lead to an EIE (z/z') in Scheme 5) of 1.20, which was calculated assuming secondary isotope effects are negligible and that the methylene positions were indistinguishable. The data show that transfer of hydrogen is unlikely to be the rate-determining step. Unfortunately, the intrinsic KIE associated with the hydrogen transfer cannot be assessed because intramolecular KIE experiments (i.e., 2,6- CH_3 , CD_3 - C_6H_3) that would provide the number are upset by the scrambling process.



Figure 7. (a) Enantiomeric { κ -N,N- $NC_6H_3(6^{-i}Pr)CMe_2C(Me)(2-py)$ }₂Co (5-Co (S,S), upper left, and (R,R), lower right) molecules in the asymmetric unit. (b) Molecular view of 5-Co (S,S) and selected interatomic distances (Å) and angles (deg): Co1-N1, 2.051(3); Co1-N2, 1.908(3); Co1-N3, 2.050(3); Co1-N4, 1.907(3); N1-C5, 1.339(4); N3-C24, 1.342(4); C5-C6, 1.515(5); C24-C25, 1.524(5); C6-C14, 1.538(4); C25-C33, 1.538(5); N2-C6, 1.492(4); N4-C25, 1.481(4); N2-C13, 1.385(4); N4-C32, 1.385(4); N1-Co1-N2, 82.21(11); N1-Co1-N3, 111.37(12); N1-Co1-N4, 116.19(11); N2-Co1-N3, 116.07(12); N2-Co1-N4, 148.41(12); N3-Co1-N4, 82.44(11).

Scheme 6



The nature of the hydrogen transfer is hidden by its occurrence within the preequilibrium; hence the varied rates (130 °C) corresponding to the aryl substituents (e.g., Et ($\Delta G^{\ddagger} = 29.7(1)$) kcal/mol) > Me (ΔG^{\ddagger} = 31.1(1) kcal/mol) \gg ⁱPr (ΔG^{\ddagger} = 34.4(1) kcal/mol)) cannot be attributed to a clear trend. It is tempting to conclude that steric factors are important, given the higher activation energy for the isopropyl, but the observation of Et > Me may invoke additional factors. In examining HAT vs H⁺ vs H⁻ transfer mechanisms, it becomes clear that conjugation within the system leads to the same intermediates in each case (vide infra), which likely obscures any particular character of the transfer. For the reversible transfer of the hydrogen, the perpendicular orientation of the ArR₂ plane relative to the LiN, N_{pv} plane suggests that the o-Me \tilde{C} -H bond is already directed toward the methylene unit; hence a large reorganization energy is not necessary. Since the reversible hydrogen exchange between = CH₂ and - CH₃ is unlikely to possess a significant entropy change, the ΔS^{\ddagger} of -10.3(5) eu likely reflects the orientation required for C-C bond formation.

The transition metal rearrangements are slightly more sluggish than those with lithium, and the ΔG^{\ddagger} 's are roughly 33.4(5) kcal/mol. The data are fairly crude, as overlapping resonances in the paramagnetic compounds hampered the accuracy of NMR spectral integrations, and that of (pyEA-ArⁱPr₂)₂Co-py (2-Co) was shown to be inhibited by added pyridine, consistent with reversible dissociation of py prior to rearrangement steps. Note that no intermediates were detected in the transition metal rearrangements, suggesting that the second ene-amide to indolamide rearrangement occurs faster than the first. No obvious trend is evident, and it is reasonable to assume that the transition metal is not particularly relevant to what is intrinsically the rearrangement of an anion.

DISCUSSION

A Cobalt(III) Tris-alkyl, (κ -C,N-pyEA-ArⁱPr₂)₃Co (3). The synthesis of several ene-amide complexes was readily affected via metathesis methods, and the most interesting was a low-yield product, (κ -C,N-pyEA-ArⁱPr₂)₃Co (3). Diamagnetic 3 is formally Co(III) by virtue of three bidentate ligands bound as C,Nisomers that generate the C₃-symmetric pseudo-octahedral product. Aside from organometallic examples involving ligands such as cyclopentadienyls and/or phosphines, 3 is a rare example of a cobalt tris-hydrocarbyl species. Berben and Long have prepared Co(CCSiMe₃)₆³⁻⁶⁴ and via analysis of its UV–vis spectrum concluded that $\Delta_{oct} = 32500 \text{ cm}^{-1}$ and $B \approx 516 \text{ cm}^{-1}$, which is 47% of the Co³⁺ free ion value (1100 cm⁻¹). The hexaacetylide approaches Co(CN)₆³⁻ in field strength ($\Delta_{oct} = 34000 \text{ cm}^{-1}$) and is fairly similar in nepelauxetic character ($B = 430 \text{ cm}^{-1}$).⁶⁴

Successful application of the Tanabe–Sugano diagram to the UV–vis features of (κ -C,N-pyEA-ArⁱPr₂)₃Co (3) in Figure 4 supports the assignment of the 493 and 370 nm bands as d–d transitions, but the field strength of ~20 000 cm⁻¹ thus derived is significantly lower than that of Co(CCSiMe₃)₆^{3–}. An sp³-alkyl might be expected to impart a stronger field on the basis of a better energy match with the cobalt 3d-orbitals—assuming all carbon-based σ -orbitals are lower than those of the cobalt—than the sp-hybridized alkynyl ligand, but this is not the case. Note that the $d(Co^{III}-C)$ for Co(CCSiMe₃)₆^{3–} is 1.908(3) Å, the $d(Co^{III}-C(sp^2))$ for Co(ppz)₃ (ppz = 2-phenylpyrazolato) is 1.921(6) Å,⁶⁵ and the values of more traditional organometallic $d(Co^{III}-C(sp^2))$ average 1.950(15) Å.⁶⁶ Since field strength typically correlates with metal–ligand distance, the value of 20 000 cm⁻¹ affiliated with the sp³-alkyl of 3 is in line with its 1.963(4) Å distance.

Ene-amide to Indoline Rearrangement. One reaction of consequence, and potentially useful in the construction of indoline fragments containing quaternary centers, was the rearrangement of the ene-amides to indolamides (eqs 1–6). Similar types of rearrangements have been observed in systems that feature PDI and nacnac ligands that are known to support RNI reactivity. Scheme 6 illustrates a PDI rhodium azide⁵⁹ that ultimately generates an indoline ring via a purported isopropyl radical attack at one imine. In a related case, the 2,6-ⁱPr₂-Ar substituent of an iron nacnac chelate is attacked at an imine position by a similarly disposed isopropyl radical.⁶⁰ The RNI character of PDI and nacnac implicated radical character in these rearrangements, but there is no direct evidence that these processes cannot have considerable hydride-transfer character, as might be expected for anionic ligands.

Consider the rearrangement of the lithium ene-amides featured and the initial preequilibrium in which the hydrogen





Figure 8. Calculations of $Li(pyEA-ArMe_2)$ rearrangement conducted at MP2 and M06 levels of theory at 403.15 K. Note that the C-C bond-forming step is rate-determining because the intermediate azapentadienyl anion is at a high energy.

is reversibly transferred. Scheme 7 shows that the conjugation in the system does not permit ready differentiation between hydrogen atom, proton, or hydride transfer character. Since the transfer is not rate-determining, variation in the *ortho*-substituents on the phenyl ring provides limited information and does not implicate any of the three limiting processes.

Calculation of the Li-ene-amide Rearrangement. Calculations were performed on the rearrangement of Li(pyEA-ArMe₂) at 403.15 K, and the results are depicted in Figure 8. The experimental ΔG^{\ddagger} of 31.1(1) kcal/mol is bracketed by values of 28.7 and 35.5 kcal/mol, respectively, from the M06 and MP2 methods utilized. Using either M06 or MP2 techniques,^{67–70} the highest transition state is predicted to correspond to the C–C bond-forming step, in concert with the observed methylene/*o*-methyl H/D scrambling, and the low, experimental KIE of 1.16(9). The preequilibrium in which hydrogen transfer is reversibly affected relates the starting eneamide to an azapentadienyl anion (labeled *intermediate*) that is quite high in energy; hence its ΔH° is the primary component of the experimental ΔH^{\ddagger} of 26.9(2) kcal/mol measured for the overall process. As a consequence, while the barrier to C–C bond formation is modest at 4.3 (MP2) and 12.4 (M06) kcal/mol, its transition state (TS^2) is the highest in the system.

There is another calculated intermediate, labeled as rotamer, in which C-N bond rotation occurs to afford a species with the newly formed CH₂ bound to Li in addition to imine- and pyridine-N coordination. There is no experimental support for this complex, which is calculated to be considerably lower in energy than the first-formed intermediate generated via the hydrogen transfer (TS^1) , and there is some question whether it would form in competition with THF solvation. Attempts to model the rearrangement with two THF molecules coordinated (e.g., (THF)₂Li(pyEA-ArMe₂)) led to similar free energy values for ene-amide and indolamide ground-state species and nearly equal free energies for the intermediate and rotamer, but transition-state geometries could not be located. Calculations of a single THF-bound lithium ene-amide (e.g., (THF)Li(pyEA-ArMe₂)) afforded related results, including undiscovered transition-state conformations.

Calculation of the EIEs pertaining to the isotopomers in Scheme 5 was conducted by using the energies for Li(pyEA-ArMe₂) and ignoring one of the methyl groups, since the experiments were conducted on Li(pyEA-*o*-tol). The static geometry of Li(pyEA-ArMe₂) was used, H's were appropriately replaced with D's for the calculations, and the energies of rotational isomers were averaged. The approximation was deemed appropriate since the positioning of the deuteria among the three methyl positions in $-CH_2D$ and $-CHD_2$ did not substantially change the energy of each isotopomer, nor did changes in the =CHD positions. The calculated EIE values pertaining to $A \rightleftharpoons B$ and $B \rightleftharpoons C$ of Scheme 5 were 1.08 and 1.09, respectively, in good agreement with experiment.

Since H/D scrambling between o-Me and methylene groups was observed, the KIE (d_0 vs d_5 , eqs 5 and 6) for rearrangement of 1.16(9) must correspond to a preequilibrium between eneamide and the intermediate or rotamer, followed by ratedetermining C-C bond formation. In support of this statement, the calculated KIE for formation of the intermediate (i.e., barrier TS¹) is $k_{\rm H}/k_{\rm D5} \approx 2.95$. The experimental overall KIE is then the product of the EIE for the preequilibrium along the reaction coordinate and the KIE for C-C bond formation, which likely reflects two α -secondary and three β -secondary isotope effects.⁶³ EIEs calculated for Li(pyEA-ArMe₂) to the intermediate and rotamer are 1.00 and 1.04, respectively, While it is not feasible to experimentally verify which equilibrium is consequential, the intermediate is most likely along the reaction coordinate, and the calculated KIE (using TS^2 in Figure 8) is 1.06, consistent with experiment.

CONCLUSIONS

Ene-amide coordination complexes, alternatively described as 1-azaallyls, have been synthesized via metathetical procedures. While the reactivity of high-spin (pynac)₂Fe (1) and (pyEA-ArⁱPr₂)₂M (2-M, M = Cr, Mn, Fe, Co-py)) is limited, 2-M (M = Cr, Mn, Fe, Co-py) exhibited rearrangements to bis-indolamide complexes { κ -N,N-NC₆H₃(6-ⁱPr)CMe₂C(Me)(2-py)}₂M (5-M, M = Cr, Mn, Fe, Co). The same rearrangement was found for the corresponding Li species, Li(pyEA-ArR₂/R) (ArR₂/R = 2,6-R₂-C₆H₃ (R = ⁱPr, Et, Me), 2-Me-C₆H₄), which afforded Li{ κ -N,N-NC₆H₃(2-R)CR'R"C(Me)(2-py)} (R = ⁱPr, R' = R" = Me; R = Et, R' = Me, R" = H; R = Me, R' = R" = H; R = R' = R" = H). The reaction, which may be a useful way to prepare the indoline ring system with one or two quarternary centers, has a reversible

hydrogen transfer prior to a rate-determining C–C bondforming reaction. Related transition metal rearrangements in pyridine-diimine and nacnac systems have invoked radical character, but anionic, etc., alternative paths may also be plausible. $(\kappa$ -C,N-pyEA-ArⁱPr₂)₃Co (3), a low-yielding diamagnetic byproduct of metathesis, possesses Co–C(sp³) bonds that have an anomalously low field strength.

EXPERIMENTAL SECTION

General Considerations. Qualitative descriptions of the synthetic experiments and crystallographic data collection and refinements are given in the schemes and tables. For the kinetics experiments, ¹H NMR spectroscopy was used to monitor the progress of the reactions. For details concerning procedures, NMR spectroscopy, kinetics, and calculations, ^{67–70} consult the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Experimental details regarding syntheses, reactivity studies, kinetics measurements and KIE derivations, single-crystal X-ray structure determination, and computations. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00385.

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Notes

The authors declare no competing financial interest.

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DEDICATION

This paper is dedicated to the memory of Gregory L. Hillhouse, friend, colleague, collaborator, and an innovative and significant organometallic chemist.

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