# **Inorganic Chemistry**

# Oxidatively Triggered Carbon–Carbon Bond Formation in Ene-amide Complexes

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**Supporting Information** 

**ABSTRACT:** Ene-amides have been explored as ligands and substrates for oxidative coupling. Treatment of  $CrCl_2$ ,  $Cl_2Fe(PMe_3)_2$ , and  $Cl_2Copy_4$  with 2 equiv of  $\{(2,6^{-i}Pr_2C_6H_3)-(1^{-c}Hexenyl)N\}Li$  afforded pseudosquare planar  $\{\eta^3 - C, N-(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2Cr$  (1-Cr, 78%), trigonal  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2Fe(PMe_3)$  (2-Fe, 80%), and



tetrahedral { $(2,6^{-i}Pr_2C_6H_3)$ (1-<sup>c</sup>Hexenyl)N}<sub>2</sub>Co(py)<sub>2</sub> (3-Co, 91%) in very good yields. The addition of CrCl<sub>3</sub> to 1-Cr, and FeCl<sub>3</sub> to 2-Fe, afforded oxidatively triggered C–C bond formation as *rac*-2,2'-di(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=)<sub>2</sub>dicyclohexane (EA<sub>2</sub>) was produced in modest yields. Various lithium ene-amides were similarly coupled, and the mechanism was assessed via stoichiometric reactions. Some ferrous compounds (e.g., 2-Fe, FeCl<sub>2</sub>) were shown to catalyze C-arylation of { $(2,6^{-i}Pr_2C_6H_3)$ (1-<sup>c</sup>Hexenyl)N}Li with PhBr, but the reaction was variable. Structural characterizations of 1-Cr, 2-Fe, and 3-Co are reported.

# 1. INTRODUCTION

Recent investigations in these laboratories have focused on transition metals that exhibit C-C and C-X bond formations derived from ligands that have redox noninnocent capability.<sup>1</sup> In most cases, the azaallyl functionality,<sup>8</sup> or a related nacnac framework,9 was the ligand segment involved in bond formation, as Figure 1 illustrates. For example, metal-amide deprotonation of an azaallyl precursor led to the production of  $[{Me_2C(CHNCHpy)}M]_2$  (M = Cr, Co, Ni), in which three new carbon-carbon bonds are formed and six new stereocenters are set, encapsulating metal-metal bonds in the process.<sup>10</sup> C-C bonds formed reversibly via the coupling of the smif ligand of (smif)FeN(TMS)<sub>2</sub> (B),<sup>11</sup> while orthomethylation of smif enabled a single CC bond formation that linked two pyridine-imine radical anions about iron(II) (C).<sup>12</sup> In a related pyridylmethyl-nacnac ligand system, dehydroaminations were triggered oxidatively and via carbonylation, initiating CC coupling (D) and CN bond-forming (E) events, respectively.<sup>13</sup> Finally, bis-ene-amide complexes, { $\kappa$ -N,N-N- $(2_{6}-^{i}Pr_{2}C_{6}H_{3})C(=CH_{2})-2$ -pyridyl)M (M = Cr, Mn, Fe, Co(py)), were found to cyclize to form indolamide complexes (F), and corresponding lithium cyclizations suggested anionic character.14

The aforementioned ene-amide cyclizations<sup>14</sup> prompted their possible use in oxidatively triggered CC bond formations, but the orientation of the C==CH<sub>2</sub> functionality within these chelates is not ideal for intramolecular couplings. Bulkier ene-amides, or 1-azaallyls, were envisaged to promote bond formation by positioning the relevant carbons via sterics. There is ample precedent for synthesis of such low-coordinate amide complexes,<sup>15–26–30</sup> whose synthesis and reactivity constitute a forefront area of first row transition metal research. In addition, iron species are emerging as targets for catalytic or stoichiometric applications toward organic synthesis,<sup>31,32</sup> and

present a logical target as base metal, inexpensive reagents. Herein are reported ene-amide complexes of Cr, Fe, and Co, including some that generate CC bonds via oxidation and disproportionation.

# 2. RESULTS

**2.1. Ligand Synthesis.** Standard condensation procedures were employed in the synthesis of various imines, as shown in Scheme 1. In certain instances, TsOH catalysis was employed, whereas other efforts simply required utilization of 4 Å molecular sieves. Imine deprotonations were conducted with either <sup>n</sup>BuLi, without significant interference from attack at the C=N unit, or LDA, and reasonable yields were typically found.

**2.2.** {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}<sub>2</sub>Cr (1-Cr). 2.2.1. Synthesis. Treatment of chromous chloride with 2 equiv of {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}Li in diethyl ether at -78 °C led to the generation of dark green {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-(1-<sup>c</sup>Hexenyl)N}<sub>2</sub>Cr (1-Cr) upon warming to 23 °C over 24 h.<sup>15-17,20</sup> As Figure 2 illustrates, the complex was isolated in 78% yield, and Evans' method<sup>33</sup> measurements provided a  $\mu_{eff}$  of 4.7  $\mu_{B}$ , consistent with an S = 2 center whose spin-only moment is slightly attenuated due to spin-orbit coupling.<sup>34</sup>

2.2.2. Structure. Figure 2 illustrates a molecular view of  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2Cr$  (1-Cr), which has a  $C_2$  di-1-azaallyl structure reminiscent of  $Cr^{II}(allyl)_2$  species.<sup>35–37</sup> Pertinent crystallographic information is given in Table 1, while metric parameters may be found in the caption of Figure 2. The Cr–N distances average 2.017(6) Å, while the adjacent Cr–C distances are 2.295(13) Å (av), which is slightly longer than the end-carbon chromium bond lengths of 2.262(2) Å (av). Conjugation of the ene-amide is evident in N–C bond lengths

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Figure 1. Previous examples of CC and CX bond formation derived from 2- and 1-azaallyls in smif (di-2,3-(2pyridyl)-2-azapropenyl) and nacnac fragments, and as ene-amides.

#### Scheme 1





seems reasonable, given the nature of a high-spin chromous center, that any increase is best construed as a consequence of  $\sigma$ -donation. It is tempting to argue that steric factors of the 2,6-<sup>i</sup>Pr<sub>2</sub>-phenyl groups pertaining to the C<sub>2</sub>-symmetric molecule cause the N1-Cr-N2 angle to open (124.75(4)°) relative to  $\angle$ C6-Cr-C20 = 105.91(5)°, but the difference is mostly due



Figure 2. Synthesis and molecular view of  $\{(2,6^{-i}Pr_2C_6H_3)-(1^{-c}Hexenyl)N\}_2Cr$  (1-Cr), which crystallizes in a triclinic lattice; a monoclinic polymorph is reported in Supporting Information. Interatomic distances (Å) and angles (deg): Cr–N1, 2.0131(11); Cr–N2, 2.0217(11); Cr–C1, 2.3040(13); Cr–C6, 2.2622(14); Cr–C19, 2.2859(13); Cr–C20, 2.2619(14); N1–C1, 1.3527(17); C1–C6, 1.3884(19); N2–C19, 1.3637(16); C19–C20, 1.3766(19); N1–C7, 1.4238(16); N2–C25, 1.4156(16); N1–Cr–N2, 124.75(4); N1–C1–C6, 116.17(12); N1–Cr–C19, 158.52(5); N1–Cr–C20, 165.62(5); N2–C19–C20, 17.23(12); N2–Cr–C1, 158.14(5); N2–Cr–C6, 165.68(5); C1–Cr–C19, 165.10(5); C1–Cr–C20, 131.46(5); C6–Cr–C19, 131.11(5); C6–Cr–C20, 105.91(5).

to the disparity in Cr–N versus Cr–C bond lengths, and the azaallyls are only twisted by  $\sim 19.8^{\circ}$ .

2.2.3. Coupling Reactions. Efforts at oxidatively triggered C–C bond formation<sup>13,36</sup> were initiated with  $\{(2,6-Pr_2C_6H_3)-(1-Pr_2C_6H_3)-$ 

Table 1. Select Crystallographic and Refinement Data



products showed that  $CrCl_2(THF)_2$  was the byproduct, as compared with an independently prepared sample. In eq 2, treatment of  $CrCl_3$  with  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}Li$  resulted in 1-Cr and half an equivalent of  $EA_2$ , consistent with observations that a tris-ene-amide complex of Cr(III) could not be prepared under these conditions. If  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2CrCl$  is formed under these

	1-Cr	<b>2</b> -Fe	3-Co	EA <sub>2</sub>
formula	$C_{36}H_{52}N_2Cr$	$C_{39}H_{61}N_2PFe$	$C_{46}H_{62}N_4Co$	$C_{36}H_{52}N_2$
formula wt	564.80	644.72	729.93	512.80
space group	$P\overline{1}$	$P\overline{1}$	$P2_1/n$	C2/c
Z	2	4	4	4
a, Å	11.320(2)	10.3180(5)	10.6653(10)	15.550(6)
b, Å	11.5351(19)	18.3944(10)	36.834(4)	9.151(5)
<i>c,</i> Å	13.336(3)	22.0796(11)	21.080(2)	24.380(11)
$\alpha$ , deg	87.146(8)	68.324(3)	90	90
$\beta$ , deg	82.848(9)	78.952(3)	97.136(4)	107.24(3)
γ, deg	70.288(7)	86.630(3)	90	90
<i>V</i> , Å <sup>3</sup>	1626.5(5)	3821.7(3)	8217.1(13)	3313(3)
$ ho_{ m calc}$ g cm $^{-3}$	1.153	1.121	1.180	1.028
$\mu$ , mm <sup>-1</sup>	0.377	0.463	0.453	0.059
temp, K	233(2)	223(2)	223(2)	296(2)
$\lambda$ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
R indices	R1 = 0.0388	R1 = 0.0443	R1 = 0.0575	R1 = 0.0413
$[I > 2\sigma(I)]^{a,b}$	wR2 = 0.0904	wR2 = 0.0950	wR2 = 0.1234	wR2 = 0.1019
R indices <sup>b</sup>	R1 = 0.0569	R1 = 0.0863	R1 = 0.1316	R1 = 0.0688
(all data) <sup>a</sup>	wR2 = 0.0998	wR2 = 0.1169	wR2 = 0.1622	wR2 = 0.1181
GOF <sup>c</sup>	1.034	1.009	1.068	1.002

 ${}^{a}\text{R1} = \sum ||F_o| - |F_c|| / \sum |F_o|. {}^{b}\text{wR2} = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}. {}^{c}\text{GOF} \text{ (all data)} = [\sum w(|F_o| - |F_c|)^2 / (n-p)]^{1/2}, n = \text{number of independent reflections}, p = \text{number of parameters}.$ 

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circumstances, it is likely that disproportionation occurs. In concert with these arguments, the treatment of  $\{(2,6-Pr_2C_6H_3)(1-Pexenyl)N\}$ Li with CrCl<sub>3</sub> leads to the coupled product, EA<sub>2</sub>, in 55% isolated yield. Various oxidants were explored in an attempt to render the coupling catalytic in Cr, but most were ineffective, and CrCl<sub>3</sub> is quite inexpensive and worked best.

NMR spectra of  $\mathbf{EA}_2$  were consistent with either the *rac-* or *meso-*form of coupled ene-amide, and due to hydrolysis problems (*vide infra*), correlation with the corresponding diketone could not be accomplished. The  $C_2$ -stereochemistry was proven via X-ray crystal structure, and its metrical data can be found in the Supporting Information. No indication of the  $C_i$  isomer was found by NMR analysis in any of the coupling reactions studied.

Some additional couplings were tested to probe the generality of the process. In each case, after an appropriate time period, the solvent was removed, and the products were taken up in  $CH_2Cl_2$  and washed with water to remove chromous byproduct(s). The products were simply assayed by NMR spectroscopy, typically generated in >90% purity, and not purified further. As eq 4 illustrates, Cr(III) oxidation of



{ $(2,6^{-i}Pr_2C_6H_3)(1^{-Pentenyl})N$ }Li afforded the coupled product as a tan powder in 68% yield, similar to the cyclohexenyl species (EA<sub>2</sub>) illustrated in eq 3. Certain acyclic species could be coupled, as the 2,6-<sup>i</sup>Pr-phenyl-ene-amide from acetophenone in eq 5 reveals, but extensions to other substrates caused hydrolysis issues. When a less hindered imine was used in coupling of a cyclohexenyl ene-amide, the aqueous workup afforded the dicyclohexyl-phenyl pyrrole shown in eq 6 as a yellow oil in 54% yield. Similarly, the coupling of the phenylene-amide derived from ethyl-phenyl-ketone shown in eq 7 afforded its corresponding pyrrole upon workup in the presence of water. For the protected ene-amides, typically those derived from 2,6-<sup>i</sup>Pr<sub>2</sub>-phenylamine, hydrolysis could not be accomplished unless forcing conditions were used, and the stereochemical regularity gained via the coupling was lost in the



process of pyrrole formation, as eq 8 reports. These cyclizations to give pyrrole are simple variants of Paal–Knorr pyrrole syntheses,  $^{39-43}$  and are difficult to circumvent.



**2.3.** {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}<sub>2</sub>FePMe<sub>3</sub> (2-Fe). 2.3.1. Synthesis. Treatment of  $(Me_3P)_2FeCl_2^{44}$  with 2 equiv of {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}Li in benzene at room temperature afforded red crystals of {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-(1-<sup>c</sup>Hexenyl)N}<sub>2</sub>FePMe<sub>3</sub> (2-Fe) in 80% yield as, Figure 3 illustrates.<sup>15-17,22-25</sup> Evans' method<sup>33</sup> measurements on 2-Fe generated a  $\mu_{eff}$  of 5.1  $\mu_B$ , slightly greater than the spin-only value, which is expected for a system with some spin-orbit coupling.<sup>34</sup>

2.3.2. Structure. The structure of  $\{(2,6^{-i}Pr_2C_6H_3)-(1^{-c}Hexenyl)N\}_2$ FePMe<sub>3</sub> (2-Fe) is illustrated in Figure 3, and pertinent metric data is listed in the caption. Select data collection and refinement information is presented in Table 1. A symmetric X<sub>2</sub>YM situation results in a nonorbitally degenerate  ${}^{5}A_{2}$  state in  $C_{2\nu}$  symmetry, but deviations can still



Figure 3. Synthesis and view of one of two inequivalent  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2FePMe_3$  (2-Fe) molecules in the asymmetric unit, chosen because of its lack of disorder. Interatomic distances (Å) and angles (deg): Fe2–N3, 1.920(2); Fe2–N4, 1.927(2); Fe2–P2, 2.4490(9); N3–C40, 1.402(4); N3–C51, 1.427(3); C40–C41, 1.502(4); C40–C45, 1.329(4); N4–C58, 1.401(3); N4–C64, 1.423(3); C58–C59, 1.334(4); C58–C63, 1.508(4); N3–Fe2–N4, 136.53(10); N3–Fe2–P2, 110.59(7); N4–Fe2–P2, 112.84(7); Fe2–N3–C40, 124.23(18); Fe2–N3–C51, 118.06(18); C40–N3–C51, 116.9(2); Fe2–N4–C58, 127.19(18); Fe2–N4–C64, 115.26(16); C58–N4–C64, 117.5(2).

provide additional stability if the rotational symmetry is lost, or if a plane of symmetry is removed. In this instance, the angular distortion is minor as two of the three core angles are roughly equivalent:  $\angle N3$ -Fe-N4 = 136.52(10)° >  $\angle N4$ -Fe-P2 = 112.84(7)° >  $\angle N3$ -Fe-P2 = 110.60(8)°. The ene-amides are twisted relative to one another by 39.4°, a distortion from  $C_{2\nu}$ symmetry that is quite significant. The d(Fe-N) values average 1.924(3) Å, and unlike 1-Cr, the iron-carbon distances of the ene-amide are beyond (>2.95 Å) a reasonable bonding limit. The C-C bond lengths in the ene-amides average 1.331(4) Å, a value quite close to that of a double bond,<sup>38</sup> while the C-N distances of 1.402(4) and 1.401(4) Å indicate a significant attenuation of the delocalization observed in the chromium case (1-Cr), as they approach the 1.426(4) average of the  $d(N-C_{Ar})$ .

2.3.3. Ene-amide Couplings. As in the prior chromium case, C–C bond formation<sup>36</sup> was initially probed via reactions with  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2FePMe_3$  (2-Fe), as eq 9



indicates. Analogous to the chromium oxidations, treatment of **2**-Fe with FeCl<sub>3</sub><sup>45-50</sup> affected a 65% conversion to *rac*-2,2′di(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=)<sub>2</sub>-dicyclohexane (**EA**<sub>2</sub>) after only 2 h at room temperature, according to monitoring by <sup>1</sup>H NMR spectroscopy. When {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}Li was treated with FeCl<sub>3</sub>, as shown in eq 10, the yield of coupled product was attenuated (42%), and the process required 2 days in refluxing THF. Since an Fe(III) intermediate of the type {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}<sub>2</sub>FeCl was anticipated as a



precursor, it seemed plausible that solubility issues could be affecting the process. Addition of 5 mol %  $FeCl_2$  to the product mixture of eq 10 failed to elicit much more material after another day (44%), but the addition of 5 mol % 2-Fe, as shown in eq 11, shortened the process to roughly 1 day, consistent



with the greater availability of iron for amidation. Conversions seemed to be generally limited to 40-65%, and were less wellbehaved than the Cr system; hence, this study was limited to the ene-amide shown. Since an outer sphere oxidant,  $[Cp_2Fe]PF_6$ , caused the formation of  $EA_2$  in 38% yield, it is plausible that C–C bond formation is occurring via reduction of Fe(III) to Fe(I), followed by disproportionation. Various oxidants were again explored in an attempt to render the coupling catalytic, but stoichiometric ferric chloride proved to be the best and cheapest, although some unusual chemistry was discovered in the survey of oxidants.

2.3.4. Catalytic Ene-amide  $\beta$ -Arylation. In testing oxidants for the triggered coupling of the ene-amides on  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2FePMe_3$  (2-Fe), arylation at the  $\beta$ -carbon of the  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}$  ligand was observed as illustrated in eq 13. This time the product was



correlated with the known 2-phenylcyclohexanone via hydrolysis (eq 14) to ensure that arylation did not occur at the



nitrogen. Since the arylation is likely to be accompanied by iron reduction, and PhBr is a potential oxidant, catalysis of the cyclohexane ene-amide arylation was attempted with 10 mol % **2**-Fe, and 44% ( $\sim$ 4 TO) conversion to arylation product was observed (eq 15) in THF-d<sub>8</sub>. Since **2**-Fe was prepared from



 $FeCl_2(PMe_3)_2$ , it was utilized in 5 mol %, and catalysis was noted, as 47% (~9 TO) of the arylated ene-amine was produced (eq 16). While the arylation was reproducible, the



yields were variable, and an increase in the catalyst concentration to 10% had little effect, affording 53% (~5 TO) of product. Extended reaction times did not affect production of arylated product.

Different metal sources were employed in attempted catalytic arylations, with no positive results. A switch to  $\text{FeBr}_2(\text{PMe}_3)_2^{44}$  elicited no conversion, and neither did  $\text{FeBr}_3$ , nor the pseudo-Fe(0) species, "Fe(PMe<sub>3</sub>)<sub>4</sub>",<sup>51</sup> although in the latter case conversion to the parent imine was indicated. The addition of excess PMe<sub>3</sub> proved deleterious to the catalysis of eq 16, as did the use of excess PhBr, although the iron was shown to be necessary, as a control experiment without iron catalyst gave no product. PhI gave arylation product, but the yield was half (~22% at 10 mol % 2-Fe) that of the bromide.

Since excess  $PMe_3$  appeared to slow the reaction, anhydrous ferrous chloride was tested, and the arylated imine was produced in 54% (~5 TO) yield, as indicated by eq 17. Use



of FeCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub> as a potential catalyst showed no arylation product, but hydrolysis of the lithium ene-amide was noted, as the parent imine was produced. In all successful cases, ~50% conversion was noted, suggesting limited turnover by the iron catalyst, perhaps independent of loading.Since the catalysis was modest, no further investigations were conducted. Any mechanistic discussion was deemed speculative, but there are ample investigations of iron cross-coupling reactions<sup>52–64</sup> that mostly invoke radical paths related to those initially suggested by Kochi.<sup>65</sup> Furthermore, Pd-catalyzed arylations of ketones are well-established,<sup>66–70</sup> and recent, related catalytic vinylations of ketones have been reported.<sup>71</sup>

**2.4.** {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}<sub>2</sub>Copy<sub>2</sub> (3-Co). 2.4.1. Synthesis. CoCl<sub>2</sub> or phosphine-ligated equivalents failed to elicit a clean product when treated with {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-(1-<sup>c</sup>Hexenyl)N}Li, but use of CoCl<sub>2</sub>py<sub>4</sub><sup>72</sup> enabled the synthesis of {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}<sub>2</sub>Copy<sub>2</sub> (3-Co) in 91% yield, as shown in Scheme 2.<sup>15-17,26,28</sup> The violet compound was assessed by Evans' method measurements<sup>33</sup> and was shown to have a  $\mu_{eff}$  of 4.1  $\mu_{B}$ , consistent with an S = 3/2 center that has a substantial spin-orbit contribution, as is typical for Co(II) pseudotetrahedral species.<sup>34</sup>

Scheme 2



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**Figure 4.** Views of two inequivalent {(2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-'Hexenyl)N}<sub>2</sub>Copy<sub>2</sub> (3-Co) molecules in the asymmetric unit. Interatomic distances (Å) and angles (deg): Co1–N1, 1.954(5); Co1–N2, 2.145(5); Co1–N3, 1.941(5); Co1–N4, 2.108(6); N1–C1, 1.427(7); N3–C24, 1.421(8); N1–C13, 1.429(7); N3–C36, 1.422(7); C13–C14, 1.332(8); C13–C18, 1.486(8); C36–C37, 1.346; C36–C41, 1.495(8); N1–Co1–N2, 102.3(3); N1–Co1–N3, 135.2(2); N1–Co1–N4, 107.2(2); N2–Co1–N3, 106.6(2); N2–Co1–N4, 95.5(2); N3–Co1–N4, 103.3(2); Co1–N1–C1, 114.7(4); Co1–N1–C13, 132.2(4); C1–N1–C13, 113.0(5); Co1–N3–C24, 116.9(4); Co1–N3–C36, 130.5(4); C24–N3–C36, 112.3(5); Co2–N5, 1.963(5); Co2–N6, 1.949(4); Co2–N7, 2.093(5); Co2–N8, 2.122(5); N5–C59, 1.391(7); N5–C47, 1.436(7); C59–C60, 1.340(8); C59–C64, 1.491(8); N6–C65, 1.397; N6–C71, 1.422(7); C65–C66, 1.494(8); C65–C70, 1.338(8); N5–Co2–N6, 131.5(2); N5–Co2–N7, 113.1(2); N5–Co2–N8, 104.4(2); N6–Co2–N7, 99.03(19); N6–Co2–N8, 106.4(2); N7–Co2–N8, 97.6(2); Co2–N5–C47, 115.1(4); Co2–N5–C59, 131.7(4); C47–N5–C59, 113.0(5); Co2–N6–C65, 124.6(4); Co2–N6–C71, 120.5(4); C65–N6–C71, 114.9(5).





2.4.2. Structure. Two molecules of  $\{(2,6^{-i}Pr_2C_6H_3)-(1-Hexenyl)N\}_2Copy_2$  (3-Co) are contained in the asymmetric unit, and each has a particular conformation, as illustrated in Figure 4. Pertinent metric parameters may be found in its caption, and data collection and refinement details are recorded in Table 1. In the conformer containing Co1, the

CNC fragments of the ene-amides are roughly eclipsed, and the 2,6- $^{1}Pr_{2}C_{6}H_{3}$  and  $^{c}$ Hexenyl substituents are disposed in a  $C_{2}$  arrangement. In the alternate conformer containing Co2, the CNC portions of the ene-amides are staggered, although the substituents are also in essentially a  $C_{2}$  relationship. The eclipsed configuration opens up N1–Co1–N3 to 135.2(2)°

#### Scheme 4



over the corresponding N5–Co2–N6 angle of 131.5(2)°, and the related N2–Co1–N4 angle is compressed by a few degrees relative to N7–Co2–N8 (95.5(2)° vs 97.6(20°)). The remaining core angles exhibit significant differences between the conformers, likely due to subtle steric differences. As for the distances, the configurations are quite similar, with  $d(\text{Co-N}_{am})$ and  $d(\text{Co-N}_{py})$  averaging 1.952(9) and 2.117(22) Å, respectively.

Ene-amide C=C bond lengths average 1.339(6) Å, but the related C-N bonds are slightly shorter in the Co2 conformer (1.394(4) (av) vs 1.426(5) (av) Å). With the eclipsed CNC orientation in the Co1 conformer, the ene-amide N(p)-orbitals compete for donation into the same  $Co(d\pi)$ -orbital(s), whereas in the Co2 conformer, the staggered ene-amide disposition permits the related interactions to occur with two different  $Co(d\pi)$ -orbitals. While it is tempting to invoke slightly greater NCC conjugation in Co1 as a consequence, the Co-N bond lengths do not really support this argument, as the d(Co2-N)values are slightly longer than those corresponding to Co1, and all the distances are within  $3\sigma$ . Localized geometric differences in the conformers are likely a consequence of subtle electronic factors, but are too small to support substantive arguments, and the fact that both conformations exist in the asymmetric unit reflects their overall similar energies. It must be noted that the structure is of low resolution, and metric parameters are less reliable than normal; hence, the arguments are intrinsically limited.

2.4.3. Coupling Attempts. All efforts at inducing coupling reactions via  $\{(2,6-{}^{i}Pr_{2}C_{6}H_{3})(1-{}^{c}Hexenyl)N\}_{2}Copy_{2}$  (3-Co) and various oxidants failed, with the parent imine observed as a product with several reagents under varied conditions.

#### 3. DISCUSSION

3.1. Mechanism of Cr-Based Ene-amide Coupling. Scheme 3 illustrates a probable mechanism for the formation of  $EA_2$  from {(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(1-<sup>c</sup>Hexenyl)N}<sub>2</sub>Cr (1-Cr). Note that NMR spectroscopic monitoring was limited due to the broad resonances in this system and in the subsequent iron case. As portrayed, the generation of  $\{(2,6^{-i}Pr_2C_6H_3)\}$ - $(1-^{c}Hexenyl)N_{2}CrCl$  from  $CrCl_{3}$  and 2 equiv of  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenvl)N\}$  enables a subsequent chlorine atom transfer to afford  $\{(2,6-iPr_2C_6H_3)(1-cHexenyl)N\}CrCl_2$ . The atom transfer is envisaged to occur via a  $\{(2,6^{-i}Pr_2C_6H_3)$ - $(1-^{c}Hexenyl)N_{2}Cr(\mu-Cl)_{2}CrCl_{2}$  binuclear complex that can break apart into CrCl<sub>2</sub> and the Cr(IV) transient. Oxidative coupling from the Cr(IV) center ensues, providing  $EA_2$  and  $Cr_2(THF)_2$ . It is plausible that other complexities, such as the disproportionation of  $\{(2,6^{-1}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2$ CrCl to the Cr(IV) intermediate and 1-Cr, can happen, but the latter species was not directly observed during the process; hence, its conversion to Cr(II) and EA<sub>2</sub> must be rapid if invoked.

**3.2. Mechanism of Fe-Based Ene-amide Coupling.** For the ene-amide coupling derived from  $\{(2,6^{-i}Pr_2C_6H_3)-(1^{-c}Hexenyl)N\}_2FePMe_3$  (2-Fe), shown in eq 9, a plausible mechanism is given in Scheme 4. The process could operate in a pathway directly analogous to that of Cr, but an Fe(I)/Fe(III) path is favored instead on the basis of the fact that ferrecinium oxidation of 2-Fe induces coupling, yet this oxidant is unlikely to afford an Fe(IV) species related to the Cr(IV) complex of Scheme 4. Ferric chloride oxidation of 2-Fe is likely to produce  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-c}Hexenyl)N\}_2FeCl$ , or a PMe<sub>3</sub>/solvent adduct, and it oxidatively couples its bound ene-amides to afford EA<sub>2</sub> and FeCl, which can redistribute with another equivalent of FeCl<sub>3</sub> to produce 2 equiv of FeCl<sub>2</sub>. The process also seems viable in the context of eq 10, in which  $\{(2,6-Pr_2C_6H_3)(1-Pr_2C_6H_3)($ 

# 4. CONCLUSIONS

Low-coordinate ene-amide complexes,  $\{(2,6^{-i}Pr_2C_6H_3)-(1^{-}Hexenyl)N\}_2Cr (1-Cr) and <math>\{(2,6^{-i}Pr_2C_6H_3)(1^{-}Hexenyl)-N\}_2FePMe_3 (2-Fe)$ , exhibit different hapticities, but both generate rac- $\{2,2'-di(2,6^{-i}Pr_2C_6H_3N=)$ -dicyclohexane $\}$  **EA**<sub>2</sub> when oxidatively triggered by CrCl<sub>3</sub> and FeCl<sub>3</sub>, respectively. Tetrahedral  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-}Hexenyl)N\}_2Copy_2 (3^{-}Co)$ , in contrast, did not generate any coupled product when subjected to oxidants. An unusual imine arylation occurred when **2**-Fe was treated with PhBr, and while some catalysis of the arylation of  $\{(2,6^{-i}Pr_2C_6H_3)(1^{-}Hexenyl)N\}_L$ i was achieved, low turnover numbers (4-9) and sporadic reactivity may hamper any significant application.

#### 5. EXPERIMENTAL SECTION

Reasonable details have been given in the equations, figures, and schemes, and a detailed experimental section, including procedural and spectroscopic details is given as Supporting Information.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02990.

Full experimental details, including procedures, and X-ray structural details, such as metric data pertaining to the monoclinic polymorph of 1-Cr, and EA<sub>2</sub> (PDF) Crystallographic details (CIF)

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#### Notes

The authors declare no competing financial interest.

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