# **ORGANOMETALLICS**

# Square-Planar Cobalt Complexes with Monodentate N-Heterocyclic Carbene Ligation: Synthesis, Structure, and Catalytic Application

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Supporting Information

**ABSTRACT:** The unique cobalt(I)-NHC complex  $[Co(IEt)_4]$  $[BPh_4](1)$  (IEt = 1,3-diethyl-4,5-dimethylimidazole-2-ylidene) and its analogues employing outer carbonic horizont pared by the reactions of  $[Co(PPh_3)_3Cl]$  with free carbone Me Me and its analogues employing other carbene ligands were preligands followed by anion exchange. X-ray diffraction revealed 1 features a homoleptic cation  $[Co(IEt)_4]^+$  with square-planar geometry. Electrochemical studies showed the square-planar complexes support the redox series  $[Co(IEt)_4]^{+/2+/3+}$ , of



which the divalent cation has been synthesized and structurally characterized as in  $[Co(IEt)_4][BF_4]_2$  (2). Both EPR and DFT studies indicated 2 has a low-spin Co(II) center. 1 can efficiently catalyze the oxidative homocoupling reactions of aryl Grignard reagents. Investigations on the stoichiometric reactions of 1 with organic halides and 2 with aryl Grignard reagents established an interesting radical mechanism involving the  $[Co(IEt)_4]^{+/2+}$  redox shuttle for these cobalt-NHC complex catalyzed homocoupling reactions.

# INTRODUCTION

The cobalt-catalyzed coupling reaction is one of the traditional yet very efficient methods for C-C bond construction.<sup>1</sup> Since the pioneer work by Kharasch,<sup>2</sup> continuing efforts in this field by Cahiez, Gosmini, Oshima, et al. have led to the emergence of versatile coupling methods,<sup>1,3</sup> in which simple cobalt salts in combination with amine or phosphine ligands are generally applied as the catalysts. In addition to these catalyst systems, recently, N-heterocyclic carbenes (NHCs) have been introduced to cobalt catalysis.<sup>4</sup> Although still in its infancy, it has been well established that the utilization of NHCs could dramatically influence both the reactivity and selectivity of the catalyzed reactions.<sup>4h</sup> Successful applications of NHCs in cobalt-catalyzed reactions include the cross-coupling reaction of aryl halide with aryl Grignard reagent,<sup>4a</sup> dehydrohalogenation of alkyl halides with Grignard reagent,<sup>4c</sup> sequential cyclization/cross-coupling of 6-halo-1-hexene derivatives with Grignard reagent,<sup>4e</sup> intramolecular [2+2+2] cycloaddition of enediynes,4b and so on.

In view of the fine performance of NHC-promoted cobalt catalysis and in association with our interest in late 3d transition metal-NHC chemistry,<sup>5</sup> we are curious about the chemistry of cobalt-NHC complexes. Cobalt complexes bearing NHC ligands are known, but most of the previous studies were focused on complexes with complicated coordination environments.<sup>6</sup> Distinct from those studies, we report here the synthesis, structure, and catalytic application of a new category of cobalt-NHC complexes with exclusively monodentate NHC ligation. Not only do these cobalt-NHC complexes represent rare examples of homoleptic cobalt compounds having square-planar geometry,<sup>7</sup> but more

importantly, they are efficient catalysts to mediate the homocoupling reactions of aryl Grignard reagents, in which a unique radical-type mechanism based on a Co(I)/Co(II) redox shuttle has been disclosed.

#### RESULTS AND DISCUSSION

**Homoleptic Cobalt(I)-NHC Complex.** The unique cobalt(I)-NHC complex  $[Co(IEt)_4][BPh_4]$  (1) (IEt = 1,3-diethyl-4,5dimethylimidazole-2-ylidene) was prepared as a blue crystalline solid in 80% yield from the reaction of  $[Co(PPh_3)_3Cl]^8$  with four equivalents of IEt<sup>9</sup> and one equivalent of NaBPh<sub>4</sub> in THF (Scheme 1).<sup>10</sup> 1 is air- and moisture-sensitive and soluble in polar solvents such as THF and acetonitrile. Its <sup>1</sup>H NMR spectrum in *d*<sub>8</sub>-THF displays seven sets of peaks, at 0.39, 1.98, 3.74, 5.50, 6.65, 6.85, and 7.28 ppm, with the corresponding integral ratio of 6:6:2:2:1:2:2, suggesting a 4:1 ratio of the carbene ligands to the borate anion  $[BPh_4]^-$ . The resonances at 3.74 and 5.50 ppm are corresponding to the two methylene protons on the same ethyl group, indicative of the restricted rotation of ethyl groups. 1 forms a green solution in THF. Its UV-vis spectrum shows three absorption bands around 406 ( $\varepsilon = 3823 \text{ M}^{-1} \text{ cm}^{-1}$ ), 586 ( $\varepsilon =$ 8924  $M^{-1}$  cm<sup>-1</sup>), and 650 ( $\varepsilon$  = 3710  $M^{-1}$  cm<sup>-1</sup>) nm, which are typical of many square-planar d<sup>8</sup> complexes (Figure 1).<sup>7a,11</sup>

The molecular structure of 1 has been confirmed by singlecrystal X-ray diffraction study. As shown in Figure 2, the cation

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 $[Co(IEt)_4]^+$  has pseudo- $D_4$  symmetry in which the cobalt center is bound to four carbene ligands in a square-planar geometry with

Scheme 1. Preparation of Homoleptic Co(I)-NHC Complexes





the Co–C(carbene) bond distances ranging from 1.923(3) to 1.936(3) Å (Table 1). These Co–C(carbene) separations are close to those observed in the pincer complexes [(CNC)CoX] (X = Me, Br),<sup>6e</sup> but shorter than the ones in the tetrahedral complex [(TIMEN)Co(CO)]Cl.<sup>6f</sup> Interestingly, due to steric repulsion among the ethyl groups, the four imidazole planes are not perpendicular to the idealized coordinate plane (Co(1)–C(1)–C(2)–C(3)–C(4)) but have dihedral angles from 60.6° to 63.3°. It is worth mentioning that, although cobalt(I) complexes are not scarce, 1 represents one of the few examples of homoleptic ones adopting square-planar geometry.<sup>7a–c</sup>

The redox property of 1 has been examined by cyclic voltammetry study. Its voltammogram shows three oxidation processes, two quasi-reversible ones with  $E_{1/2}^{+/2+} = -1.26$  V and  $E_{1/2}^{2+/3+} = 1.37$  V corresponding to the redox processes of the cation, and an irreversible one near 0.90 V correlated to the oxidation of the borate anion,<sup>12</sup> and no reduction out to -2.0 V was observed (Figure 3). The potential for the  $[Co(IEt)_4]^{+/2+}$  couple is lower than that for the Co(I)/Co(II) couple of vitamin  $B_{12}^{-13}$  but close to those observed for other square-planar cobalt macrocycles.<sup>14</sup>

**Homoleptic Cobalt(II)-NHC Complex.** In light of the stability of the divalent species  $[Co(IEt)_4]^{2+}$  over a broad potential window, the divalent complex  $[Co(IEt)_4][BF_4]_2$  (2) has been synthesized via either the oxidation reaction or direct interaction of  $CoCl_2$  with IEt and  $NaBF_4$  (Scheme 2). 2 has been fully characterized by various spectroscopic methods. Its <sup>1</sup>H NMR

Table 1. Selected Structural Parameters of  $[Co(IEt)_4]^{+, 2+}$  from X-ray Diffraction and Computational Studies

	$[Co(IEt)_4]^+$		[Co(IEt) <sub>4</sub> ] <sup>2+</sup>	
	X-ray	calcd	X-ray	calcd
Co–C distance (Å) $^{a}$	1.935(3) 1.936(3) 1.928(3) 1.923(3)	1.991	1.947(7) 1.964(7) 1.981(7) 1.969(6)	2.028
$\alpha$ (deg) <sup>b</sup>	60.6 to 63.3	61.5	60.4 to 61.7	62.7

<sup>*a*</sup> Co-C(carbene) distances. <sup>*b*</sup> Dihedral angles between the Co-C(1)-C(2)-C(3)-C(4) plane and the four imidazolylidene planes.



Figure 2. Structures of cations  $[Co(IEt)_4]^{+,2+}$  in 1 and 2, showing 30% probability ellipsoids and the partial atom-numbering scheme.



**Figure 3.** Cyclic voltammogram (50 mV/s) of ca. 1 mM THF solution prepared from  $[Co(IEt)_4][BPh_4]$  (1). Waves marked by asterisks are caused by the redox process of tetraphenylborate anion.

Scheme 2. Preparation of Homoleptic Co(II)-NHC Complex



spectrum in CD<sub>3</sub>CN displays four broad peaks in the range -1.62 to 8.10 ppm, revealing its paramagnetism. The complex has its solution magnetic moment  $\mu_{\rm eff} = 2.4 \ \mu\text{B}$  at room temperature, <sup>15</sup> characteristic for four-coordinate low-spin Co(II) complexes.<sup>7d,16</sup> Differing from that of the d<sup>8</sup> complex [Co(IEt)<sub>4</sub>]<sup>+</sup>, the absorption spectrum of **2** shows no absorption band in the visible region (Figure 1), suggestive of its low-spin d<sup>7</sup> metal center.

X-ray crystallography study revealed the dication  $[Co(IEt)_4]^{2+}$ in **2** retains the pseudo- $D_4$  symmetry (Figure 2) with dimensions similar to those of the univalent cation in **1** (Table 1). The geometrical resemblance might result from the joint effects of electronic and steric factors since the oxidation from  $[Co(IEt)_4]^+$ to  $[Co(IEt)_4]^{2+}$  should remove only an electron from the



Figure 4. EPR spectrum of  $[Co(IEt)_4][BF_4]_2$  (2) recorded in a frozen acetonitrile solution at 4 K.

nonbonding  $3d_{z^2}$  orbital of the univalent cation (*vide supra*), and steric repulsion between those ethyl groups might prevent further shortening of the Co–C(carbene) bonds. Recently, Spicer and Murphy reported a closely related tetrahedral cobalt-(II) complex bearing a cyclic tetradentate carbene ligand.<sup>6</sup><sup>j</sup> Because the ligand field stabilization energies for these two tetracarbene ligand sets should be approximately the same, steric factors might account for the distinct coordination geometries. It is worth mentioning that four-coordinate Co(II) complexes under a monodentate ligand environment usually are tetrahedral, but **2** is among the few having square-planar structure.<sup>7d,17</sup>

The electronic structure of  $[Co(IEt)_4]^{2+}$  was investigated by EPR spectroscopy. The EPR spectrum of  $[Co(IEt)_4][BF_4]_2$  (2) recorded at 4 K in frozen CH<sub>3</sub>CN glass is presented in Figure 4. The spectrum exhibits axial symmetry with well-resolved eightline patterns with  $g_{\perp} = 2.95$ ,  $A_{\perp} = 160$  G and  $g_{\parallel} = 2.02$ ,  $A_{\parallel} = 249$  G, similar to those found for a variety of low-spin Co(II) complexes.<sup>18</sup> The eight-line splitting pattern of the EPR spectrum, arising from interaction of an unpaired electron with a single <sup>59</sup>Co (I = 7/2) nucleus, clearly proves the presence of a low-spin  $d^7$ -Co(II) center. The presence of a Co(II) center in  $[Co(IEt)_4]^{2+}$ was further supported by computational study. The optimized structures show good agreement with crystallography studies (Table 1).

Theoretical calculations indicated the singlet cation  $[Co(IEt)_4]^+$ is a formal Co(I) complex, and its LUMO and HOMO are composed mainly by the 4p<sub>z</sub> and 3d<sub>z<sup>2</sup></sub> orbitals of the metal center, respectively (Figure 5). The one-electron oxidation of  $[Co(IEt)_4]^+$ generates the doublet dication  $[Co(IEt)_4]^{2+}$ , which holds a Co(II) center with its spin density residing primarily on the metal's 3d<sub>z<sup>2</sup></sub> orbital (Figure 6), being in strong contrast to its isoelectronic nickel complex  $[Ni(crown-carbene)]^{3+}$ , which was predicted to have a formal Ni(II) center bonded with a tetradentate crown carbene radical cation.<sup>19</sup>

Homoleptic Cobalt-NHC Complex Catalyzed Homocoupling Reactions. Cobalt(I) species are prominent in electron transfer chemistry, which has been well documented by the redox chemistry of coenzyme B<sub>12</sub>, cobalt-corrins, and their derivatives.<sup>20</sup> However these studies were generally performed on Co(I) species generated *in situ*. The well-defined square-planar Co(I)



Figure 5. HOMO and LUMO orbitals of  $[Co(IEt)_4]^+$ , depicted using isodensity at 0.03 au.



**Figure 6.** Spin density population  $(\alpha - \beta)$  for  $[Co(IEt)_4]^{2+}$  (*S* = 1/2) by DFT(B3LYP/6-311+G\*\*/cc-pVTZ) calculation.

complex 1 provides an excellent opportunity to study its redox reactions. As illustrated in eq 1 (Scheme 3), the univalent cation  $[Co(IEt)_4]^+$  is prone to oxidation, as it can be readily oxidized by common organic halides, such as 3,5-dimethylphenyl iodide, benzyl bromide, and 2-methyl-1,2-dichloropropane, to yield the dication  $[Co(IEt)_4]^{2+}$  and the corresponding organic radicals that subsequently undergo dimerization or H-abstraction reactions. On the other hand, unexpected redox reaction of the divalent cation  $[Co(IEt)_4]^{2+}$  with aryl Grignard reagent (*p*-tolylmagnesium bromide) was observed, which gave the univalent cation  $[Co(IEt)_4]^+$  and biaryl in high yield (eq 2 in Scheme 3). No reaction was noticed when treating either  $[Co(IEt)_4]^+$  with aryl Grignard reagent or  $[Co(IEt)_4]^{2+}$  with the organic halides. These stoichiometric reactions demonstrated that square-planar complexes are adept at one-electron redox reactions.

According to these, a catalytic method employing the homoleptic cobalt-NHC complexes as catalysts for biaryl synthesis was developed. As depicted in Table 2, 1 is very efficient in catalyzing the homocoupling reactions of various aryl Grignard reagents with 2-methyl-1,2-dichloropropane as the oxidant.<sup>21</sup> Several Scheme 3. Redox Conversions between  $[Co(IEt)_4]^+$  and  $[Co(IEt)_4]^{2+}$ 

(1)  $[Co(IEt)_4]^{1+} + RX \xrightarrow{THF} [Co(IEt)_4]^{2+} + R^{\bullet} + X^{-}$ 

(2) 
$$[Co(IEt)_4]^{2+} + p-MeC_6H_4MgBr \xrightarrow{\text{THF}}$$
  
 $[Co(IEt)_4]^{1+} + 0.5 p-MeC_6H_4-C_6H_4-Me-p + Mg^{2+} + Br^{-1}$ 

unique features for this reaction are worth noting. First, the reaction can proceed efficiently with a very low catalyst load of 1%. Second, the catalysis is applicable to aryl Grignard reagents with both electron-donating and electron-withdrawing groups in good yields. What's more, high-yield conversions of *ortho*-substituted aryl Grignard reagents can be achieved (entries 3, 4, and 6), which normally gave coupling products in low yields under other catalyst systems.<sup>22</sup>

Based on these understandings, a radical-type mechanism involving the redox shuttle between  $[Co(IEt)_4]^+$  and  $[Co(IEt)_4]^{2+}$  has been proposed for these cobalt-catalyzed coupling reactions. As rationalized in Scheme 4, the catalytic cycle might start from the electron transfer (ET) reaction between the univalent cation  $[Co(IEt)_4]^+$  and the organic halide (RX), through which the divalent speceis  $[Co(IEt)_4]^{2+}$  and an alkyl radical  $(R \cdot)$  will be generated. The alkyl radical might subsequently be deactivated via either H-atom abstraction or dimerization, while the Co(II) complex could further interact with the Grignard reagent to yield an aryl radical (Ar  $\cdot$  ) and the univalent cation  $[Co(IEt)_4]^+$ . Further dimerization of the aryl radical will furnish the biaryl (Ar-Ar). Meanwhile, the regenerated cation  $[Co(IEt)_4]^+$  will join a new cycle upon its interaction with another organic halide molecule. It should be mentioned that due to steric repulsion the involvement of five-coordinate intermediate  $[ArCo(IEt)_4]^+$  or  $[ClCo(IEt)_4]^+$  in this catalytic cycle is very unlikely. Hence, these probable transitional species are better to be viewed as loosely bound ion pairs  $[\operatorname{Ar} \cdots \operatorname{Co}(\operatorname{IEt})_4]^+$  and  $[\operatorname{Cl} \cdots \operatorname{Co}(\operatorname{IEt})_4]^+$ .<sup>23</sup> Notably, the radicaltype pathway with a Co(I)/Co(II) redox shuttle disclosed here is distinct from the traditional organometallic mechanisms,<sup>1,2,22</sup> but an unambiguous understanding on the mechanism of carbonhalogen bond cleavage and carbon-carbon bond formation steps needs further investigation.

## CONCLUSION

We have demonstrated that the ligation of monodentate N-heterocyclic carbene ligands to a cobalt center can lead to the formation of unprecedented homoleptic cobalt complexes  $[Co(NHC)_4]^{+,2+}$  with square-planar geometry. These homoleptic cobalt-NHC complexes are adept at electron transfer reactions and can be used as catalysts to mediate the oxidative homocoupling reactions of various aryl Grignard reagents, demonstrating a unique radical-type mechanism via a Co(I)/Co(II) redox shuttle.

## EXPERIMENTAL SECTION

**General Procedures.** All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. [(PPh<sub>3</sub>)<sub>3</sub>CoCl],<sup>8</sup> 2,5-diisopropyl-3,4-dimethylimidazol-1-ylidene (IPr),<sup>9</sup> 2,5-diethyl-3,4-dimethylimidazol-1-ylidene (IEt),<sup>9</sup> and 2,3,4,5-tetramethylimidazol-1-ylidene (IMe)<sup>9</sup> were prepared according to literature methods. All chemicals were purchased from

 Table 2. [Co(IEt)<sub>4</sub>][BPh<sub>4</sub>]-Catalyzed Oxidative Homocoupling of Aryl Grignard Reagents<sup>a,b,c</sup>



<sup>*a*</sup> All reactions were carried out using aryl Grignard reagents (1.0 mmol), 1,2-dichloroisobutane (0.50 mmol), and a catalytic amount of  $[Co(IEt)_4][BPh_4]$  (1% mol) in THF (10 mL). <sup>*b*</sup> Isolated yield after column chromatography. <sup>*c*</sup> 5% mol  $[Co(IEt)_4][BPh_4]$  was used.

either Strem or J&K Chemical Co. and used as received unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer. All chemical shifts were reported in  $\delta$ units with references to the residual protons of the deuterated solvents for proton chemical shifts and the <sup>13</sup>C of deuterated solvents for carbon chemical shifts. Mass spectra were recorded with a HP-5989 instrument. GC/MS was performed on a Shimadzu GCMS-QP2010 Plus spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured at 23 °C by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub> standard.<sup>15</sup> Absorption spectra were recorded with a Hitachi U-3310 UV-vis spectrophotometer. Cyclic voltammetry measurements were made with a CHI 600D potentiostation in THF solutions using a sweep rate of 50 mV/s, a glassy carbon working electrode, 0.1 M (Bu<sub>4</sub>N)(PF<sub>6</sub>) supporting electrolyte, and a SCE reference electrode. Under these conditions,  $E_{1/2} = 0.55$  V for the  $[Cp_2Fe]^{0,+}$  couple. X-Band EPR spectra were recorded on a Bruker EMX EPR spectrometer equipped with a variable-temperature helium flow cryostat system (Oxford Instruments).

**X-ray Structure Determinations.** The structures of the four compounds in Table S1 were determined. Diffraction-quality crystals were obtained as  $1 \cdot 0.5$ THF  $\cdot$  toluene,  $[Co(IMe)_4][BPh_4]$ ,  $[Co(IPr)_4][BPh_4]$  in THF/toluene, and  $2 \cdot$ THF in THF. Crystallizations were performed at room temperature. Crystals were coated with Paratone-N oil and mounted on a Bruker APEX CCD-based diffractometer equipped with an Oxford low-temperature apparatus. Data were collected with scans of 0.3 s/frame for 30 s. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS.<sup>24</sup> Space groups were

Scheme 4. Possible Mechanism for  $[Co(NHC)_4]^+$ -Catalyzed Homocoupling Reaction of Aryl Grignard Reagent with Organic Halides As Oxidant



assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.<sup>25</sup> Metal and first coordination sphere atoms were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement cycles, and during final cycles were refined anisotropically. Hydrogen atoms were placed in calculated positions employing a riding model. Final crystal parameters and agreement factors are reported in Table 3.

**Preparation of [Co(IEt)**<sub>4</sub>][**BPh**<sub>4</sub>] (1). To a THF (15 mL) solution of 1,3-diethyl-4,5-dimethylimidazolin-2-ylidene (0.608 g, 4.0 mmol) was slowly added Co(PPh<sub>3</sub>)<sub>3</sub>Cl (0.881 g, 1.0 mmol) at room temperature. The reaction mixture was stirred for half an hour, and NaBPh<sub>4</sub> (0.342 g)1.0 mmol) was then added. After stirring overnight and removal of the solvent, the residue was washed with *n*-hexane (5 mL) and extracted with THF (5 mL). The blue extraction was filtrated and added to a small portion of toluene (1 mL). Slow evaporation of THF afforded 1.0.5THF.toluene as a bluish-green crystalline solid (0.816 g, 80%). <sup>1</sup>H NMR (300 MHz,  $d_8$ -THF):  $\delta$  0.39 (t, <sup>3</sup>J(H,H) = 7.2 Hz, 24H, NCH<sub>2</sub>CH<sub>3</sub>), 1.98 (s, 24H, NCCH<sub>3</sub>), 3.74 (m, 8H, NCH<sub>2</sub>CH<sub>3</sub>), 5.50 (m, 8H, NCH<sub>2</sub>CH<sub>3</sub>), 6.65 (m, 4H, p-C<sub>6</sub>H<sub>5</sub>), 6.85 (t, J = 7.2 Hz, 8H, m-C<sub>6</sub>H<sub>5</sub>), 7.28 (m, 8H, o-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (75 MHz,  $d_8$ -THF):  $\delta$  8.32 (NCH<sub>2</sub>CH<sub>3</sub>), 13.31 (NCCH<sub>3</sub>), 42.56 (NCH<sub>2</sub>CH<sub>3</sub>), 121.0 (C<sub>6</sub>H<sub>5</sub>), 123.9 (NCCH<sub>3</sub>), 124.8 (C<sub>6</sub>H<sub>5</sub>), 136.5 (C<sub>6</sub>H<sub>5</sub>), 164.7 (C<sub>6</sub>H<sub>5</sub>), 198.6 (br, C-Co carbene). Anal. Calcd for  $C_{62}H_{88}BCoN_8O_{0.5}$  (1 + 0.5THF): C, 72.78; H, 8.67; N, 10.95. Found: C, 72.40; H, 8.54; N, 10.37.

**Preparation of [Co(IMe)<sub>4</sub>][BPh<sub>4</sub>].** This complex was obtained (0.740 g, 85%) as a bluish-green crystalline solid by the reaction of 1,3dimethyl-4,5-dimethyl imidazolin-2-ylidene (0.500 g, 4.0 mmol) with Co(PPh<sub>3</sub>)<sub>3</sub>Cl (0.881 g, 1.0 mmol) and NaBPh<sub>4</sub> (0.342 g, 1.0 mmol) in THF (15 mL) using a procedure similar to that for 1. <sup>1</sup>H NMR (300 MHz, *d*<sub>8</sub>-THF): δ 1.91 (s, 24H, NCCH<sub>3</sub>), 3.38 (s, 24H, NCH<sub>3</sub>), 6.68 (m, 4H, *p*-C<sub>6</sub>H<sub>5</sub>), 6.82 (t, *J* = 6.9 Hz, 8H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.27 (m, 8H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (100 MHz, *d*<sub>8</sub>-THF): δ 9.27 (NCCH<sub>3</sub>), 34.07 (NCH<sub>3</sub>), 121.9 (*C*<sub>6</sub>H<sub>5</sub>), 123.9 (NCCH<sub>3</sub>), 125.8 (*C*<sub>6</sub>H<sub>5</sub>), 137.3 (*C*<sub>6</sub>H<sub>5</sub>), 165.4 (*C*<sub>6</sub>H<sub>5</sub>), 201.3 (br, C-Co carbene). Anal. Calcd for C<sub>52</sub>H<sub>68</sub>BCoN<sub>8</sub>: C, 71.39; H, 7.83; N, 12.81. Found: C, 71.73; H, 7.83; N, 12.30.

**Preparation of [Co(IPr)<sub>4</sub>][BPh<sub>4</sub>].** This complex was obtained (0.836 g, 76%) as a bluish-green crystalline solid by the reaction of 1,3diisopropyl-4,5-dimethyl imidazolin-2-ylidene (0.720 g, 4 mmol) with  $Co(PPh_3)_3Cl$  (0.881 g, 1.0 mmol) and  $NaBPh_4$  (0.342 g, 1.0 mmol) in THF (15 mL) using a procedure similar to that for 1. <sup>1</sup>H NMR

	$1 \cdot 0.5 \text{THF} \cdot \text{toluene}$	2.THF	[Co(IMe) <sub>4</sub> ][BPh <sub>4</sub> ]	$[Co(IPr)_4][BPh_4]$
formula	C <sub>69</sub> H <sub>95.5</sub> BCoN <sub>8</sub> O <sub>0.5</sub>	C40H72B2C0F8N8O	C <sub>52</sub> H <sub>68</sub> BCoN <sub>8</sub>	C <sub>68</sub> H <sub>100</sub> BCoN <sub>8</sub>
cryst size (mm)	0.30  imes 0.25  imes 0.20	$0.21 \times 0.13 \times 0.10$	0.30  imes 0.25  imes 0.20	$0.32\times0.28\times0.24$
fw	1114.8	913.6	874.88	1099.3
cryst syst	triclinic	trigonal	triclinic	monoclinic
space group	$P\overline{1}$	P3(2)	$P\overline{1}$	$P2_{1}/c$
<i>a,</i> Å	11.5698(3)	11.4224(4)	11.5569(3)	19.043(2)
<i>b,</i> Å	16.3321(4)	11.4224(4)	18.8089(5)	19.781(2)
<i>c,</i> Å	17.6166(4)	32.1421(2)	23.9386(6)	19.401(2)
α, deg	89.199(1)	90	103.176(1)	90
$\beta$ , deg	84.057(1)	90	97.061(1)	116.133(1)
γ, deg	82.613(1)	120	92.145(1)	90
<i>V</i> , Å <sup>3</sup>	3283.5(1)	3631.8(3)	5016.6(2)	6560.9(9)
Ζ	2	3	4	4
$D_{\rm calcd}$ , Mg/m <sup>3</sup>	1.128	1.253	1.158	1.113
radiation ( $\lambda$ ), Å	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
2 heta range, deg	2.4 to 50.1	3.8 to 50.9	1.9 to 50.1	2.4 to 52.0
$\mu$ , mm <sup>-1</sup>	0.307	0.424	0.384	0.306
F(000)	1203	1455	1872	2384
no. of obsd reflns	11 587	8964	17 671	12 755
no. of params refnd	788	550	1303	727
goodness of fit	0.971	0.792	0.998	1.008
R1	0.052	0.057	0.056	0.047
wR2	0.144	0.099	0.108	0.133

Table 3. Crystal Data and Summary of Data Collection and Refinement for  $1 \cdot 0.5$  THF  $\cdot$  toluene,  $2 \cdot$ THF,  $[Co(IMe)_4][BPh_4]$ , and  $[Co(IPr)_4][BPh_4]$ 

(300 MHz,  $d_8$ -THF):  $\delta$  0.51 (d,  ${}^3J(H,H) = 6.9$  Hz, 24H, NCH(CH<sub>3</sub>)<sub>2</sub>), 1.52 (d,  ${}^3J(H,H) = 6.9$  Hz, 24H, NCH(CH<sub>3</sub>)<sub>2</sub>), 2.09 (s, 24H, NCCH<sub>3</sub>), 6.15 (m, 8H, NCH(CH<sub>3</sub>)<sub>2</sub>), 6.68 (m, 4H, *p*-C<sub>6</sub>H<sub>5</sub>), 6.82 (t, *J* = 6.6 Hz, 8H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.25 (m, 8H, *o*-C<sub>6</sub>H<sub>5</sub>).  ${}^{13}$ C NMR (75 MHz,  $d_8$ -THF):  $\delta$ 10.80 (NCCH<sub>3</sub>), 20.88 (NCH(CH<sub>3</sub>)<sub>2</sub>), 21.31 (NCH(CH<sub>3</sub>)<sub>2</sub>), 52.99 (NCH(CH<sub>3</sub>)<sub>2</sub>), 121.8 ( $C_6$ H<sub>5</sub>), 125.7 (NCCH<sub>3</sub>), 126.2 ( $C_6$ H<sub>5</sub>), 137.3 ( $C_6$ H<sub>5</sub>), 165.4 ( $C_6$ H<sub>5</sub>), 199.3 (br, C-Co carbene). Anal. Calcd for C<sub>68</sub>-H<sub>100</sub>BCoN<sub>8</sub>: C, 74.29; H, 9.17; N, 10.19. Found: C, 74.38; H, 9.34; N, 10.44.

Preparation of [Co(IEt)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> (2). Method A. To a THF  $(15 \mbox{ mL})$  solution of 1,3-diethyl-4,5-dimethylimidazolin-2-ylidene (0.608 g, 4.0 mmol) were slowly added Co(PPh<sub>3</sub>)<sub>3</sub>Cl (0.881 g, 1.0 mmol) and NaBF<sub>4</sub> (0.109 g, 1.0 mmol). After stirring overnight, [Cp<sub>2</sub>Fe][BF<sub>4</sub>] (0.300 g, 1.1 mmol) was added, and the reaction mixture was further stirred for 24 h. After filtration and concentration, n-hexane (10 mL) was added to the concentrated filtrate (ca. 6 mL), which led to the precipitation of a pale blue solid. Recrystallization of this solid in THF (5 mL) afforded 2. THF as an off-white crystalline solid (0.476 g, 52%). The <sup>1</sup>H NMR spectrum of this paramagnetic complex displayed four characteristic peaks in the range -1.62 to 8.10 ppm. <sup>1</sup>H NMR (CD<sub>3</sub>-CN):  $\delta - 1.62$ , 1.96, 3.40, 8.10. Anal. Calcd for C<sub>40</sub>H<sub>72</sub>B<sub>2</sub>CoF<sub>8</sub>N<sub>8</sub>O (2 + THF): C, 52.59; H, 7.94; N, 12.27. Found: C, 52.76; H, 8.09; N, 11.63. Method B. To a THF (15 mL) solution of 1,3-diethyl-4,5-dimethylimidazolin-2-ylidene (0.608 g, 4.0 mmol) was slowly added CoCl<sub>2</sub> (0.130 g, 1.0 mmol) and NaBF<sub>4</sub> (0.218 g, 2.0 mmol) at room temperature. The reaction mixture was further stirred for 12 h. After filtration and concentration, *n*-hexane (10 mL) was added to the concentrated filtrate (ca. 6 mL), which led to the precipitation of a pale blue solid. Recrystallization of the solid in THF (5 mL) afforded 2. THF as an off-white crystalline solid (0.682 g, 75%). The <sup>1</sup>H NMR spectrum of this material was identical with that of the product from method A.

**Reaction of 1 with 4-Methylbenzyl Bromide.** To a solution of  $[Co(IEt)_4][BPh_4]$  (98.7 mg, 0.1 mmol) in THF (5 mL) was slowly added 4-methylbenzyl bromide (18.5 mg, 0.1 mmol) at -116 °C. The

mixture was warmed to room temperature and stirred for 6 h. Addition of *n*-hexane (10 mL) to the reaction mixture led to the precipitation of a pale blue solid. After filtration, the filtrate was quenched with a 1.0 M aqueous HCl solution (0.5 mL). The organic phase was separated and analyzed by GC-MS with hexamethylbenzene (8.1 mg, 0.05 mmol) as an internal standard. The reaction yielded (determined by GC) (*p*-CH<sub>3</sub>-PhCH<sub>2</sub>)<sub>2</sub> (90%) and *p*-xylene (10%). The <sup>1</sup>H NMR spectrum of the pale blue solid in CD<sub>3</sub>CN shows all the characteristic <sup>1</sup>H NMR peaks of  $[Co(IEt)_4]^{2+}$  in **2**.

**Reaction of 1 with 1,3-Dimethyl-5-iodobenzene.** To a solution of  $[Co(IEt)_4][BPh_4]$  (98.7 mg, 0.1 mmol) in THF (5 mL) was slowly added 1,3-dimethyl-5-iodobenzene (23.2 mg, 0.1 mmol) at -116 °C. The mixture was warmed to room temperature and stirred for 6 h. Addition of *n*-hexane (10 mL) to the reaction mixture led to the precipitation of a pale blue solid. After filtration, the filtrate was quenched with a 1.0 M aqueous HCl solution (0.5 mL). The organic phase was separated and analyzed by GC-MS with hexamethylbenzene (8.1 mg, 0.05 mmol) as an internal standard. The reaction yielded 1, 3-dimethylbenzene quantitatively. The <sup>1</sup>H NMR spectrum of the pale blue solid in CD<sub>3</sub>CN shows all the characteristic <sup>1</sup>H NMR peaks of  $[Co(IEt)_4]^{2+}$  in 2.

**Reaction of 1 with 2-Methyl-1,2-dichloropropane.** To a solution of  $[Co(IEt)_4][BPh_4]$  (197.4 mg, 0.2 mmol) in THF (5 mL) was slowly added 2-methyl-1,2-dichloropropane (11.6  $\mu$ L, 0.1 mmol) at -116 °C. The mixture was warmed to room temperature and stirred for 24 h. Addition of *n*-hexane (10 mL) to the reaction mixture led to the precipitation of pale blue solid. The <sup>1</sup>H NMR spectrum of the pale blue solid in CD<sub>3</sub>CN shows all the characteristic <sup>1</sup>H NMR peaks of  $[Co(IEt)_4]^{2+}$  in 2. 2-Methylpropene was presumably formed as the byproduct similar to some iron-catalyzed oxidative coupling reactions.<sup>26</sup>

**Reaction of 2 with** *p*-Me-PhMgBr. To a solution of [Co-(IEt)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> (168 mg, 0.2 mmol) in THF (5 mL) was slowly added *p*-Me-PhMgBr (0.2 mL, 1.0 M in THF) at -116 °C. The mixture was

then warmed to room temperature and stirred for 12 h. After filtration, part of the filtrate (ca. 2 mL) was quenched with a 1.0 M aqueous HCl solution (0.5 mL). The organic phase was separated and analyzed by GC-MS using hexamethylbenzene as an internal standard, which indicated the quantitative formation of 4,4'-dimethylbiphenyl. The other portion of the filtrate (ca. 3 mL) was concentrated, and a small portion of toluene (0.5 mL) was added. Slow evaporation of THF afforded a bluish-green crystalline solid, which shows identical <sup>1</sup>H NMR spectrum to that of  $[Co(IEt)_4]^+$  in 1.

General Procedure for Cobalt-NHC Complex-Catalyzed Homocoupling of Grignard Reagents. To a frozen solution of [Co-(IEt)<sub>4</sub>][BPh<sub>4</sub>] (9.9 mg, 0.01 mmol) in THF (10 mL) was added Grignard reagent<sup>27</sup> (1.0 mmol) and 2-methyl-1,2-dichloropropane (58  $\mu$ L, 0.5 mmol) at -116 °C. The mixture was then warmed to room temperature or heated to 50 °C (Table 2) and stirred for 6 h. After quenching with a 1.0 M aqueous HCl solution (5 mL), the mixture was extracted with Et<sub>2</sub>O (5 mL × 3), and the combined organic portions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the resulting residue was subjected to column chromatographic separation (SiO<sub>2</sub>, 300-400 mesh) to give the following biaryls as colorless solids. All the isolated yields are given with respect to the Grignard reagents. The <sup>1</sup>H NMR spectra of these biaryls are consistent with those reported in the literature.<sup>27</sup>

*Biphenyl.* Yield: 86%. Colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d, *J* = 7.5 Hz, 4H, *o*-C<sub>6</sub>H<sub>5</sub>), 7.44 (t, *J* = 7.2 Hz, 4H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.34 (t, *J* = 7.2 Hz, 2H, *p*-C<sub>6</sub>H<sub>5</sub>).

4,4'-Dimethlbiphenyl. Yield: 83%. Colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 7.5 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.23 (d, *J* = 7.5 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 2.38 (s, 6H, CH<sub>3</sub>).

2,2'-Dimeth/biphenyl. Yield: 81%. Colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.18 (m, 6H, C<sub>6</sub>H<sub>4</sub>), 7.03 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 1.98 (s, 6H, CH<sub>3</sub>).

2,2'-4,4'-6,6'-Hexamethlbiphenyl. Yield: 75%. Colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.85 (s, 4H, C<sub>6</sub>H<sub>2</sub>), 2.25 (s, 6H, *p*-CH<sub>3</sub>), 1.78 (s, 12H, m-CH<sub>3</sub>).

4,4'-Dichlorobiphenyl. Yield: 74%. Colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.39–7.49 (m, 8H, C<sub>6</sub>H<sub>4</sub>).

2,2'-Dimethoxybiphenyl. Yield: 74%. Colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.26 (t, *J* = 7.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.17 (d, *J* = 7.2 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 6.93 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 3.70 (s, 6H, OCH<sub>3</sub>).

4,4'-Dimethoxybiphenyl. Yield: 84%. Colorless solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.41 (d, *J* = 8.7 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 6.89 (d, *J* = 8.7 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 3.77 (s, 6H, OCH<sub>3</sub>).

**Calculation Details.** To have a better understanding of the structure of the Co complexes, density functional theory  $(DFT)^{28}$  studies have been performed with the Gaussian09<sup>29</sup> program using the BS-B3LYP<sup>30</sup> method. The 6-311+G<sup>\*\*</sup> basis set was used for the C, H, and N atoms, and the cc-PVTZ basis set was used for the Co atom. The structures of [Co-(IEt)<sub>4</sub>]<sup>+</sup> and [Co(IEt)<sub>4</sub>]<sup>2+</sup> with  $D_4$  symmetry were fully optimized. Calculations were performed assuming a singlet electronic ground state for [Co(IEt)<sub>4</sub>]<sup>+</sup> and a doublet state for [Co(IEt)<sub>4</sub>]<sup>2+</sup>.

## ASSOCIATED CONTENT

**Supporting Information.** X-ray crystallographic files in CIF format, cyclic voltammogram of the cobalt complexes, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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