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# Bis(dinitrogen)cobalt(-I) Complexes with NHC Ligation: Synthesis, **Characterization and Their Dinitrogen Functionalization Reactions Affording Side-On Bound Diazene Complexes**

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ABSTRACT: Late transition-metal-based catalysts are widely used in N<sub>2</sub> fixation reactions, but the reactivity of late transitionmetal N<sub>2</sub> complexes, besides of iron N<sub>2</sub> complexes, remained poorly understood as their N<sub>2</sub> complexes were thought labile and hard to be functionalized. By employing a monodentate N-heterocyclic carbene (NHC), 1.3-dicyclohexyl-imidazol-2-ylidene (ICy) as ligand, the cobalt(0)- and cobalt(-1)-N<sub>2</sub> complexes,  $[(ICy)_3Co(N_2)]$  (1) and  $[(ICy)_2Co(N_2)_2M]_n$  (M = K, 2a; Rb, 2b; Cs, 2c), respectively, were synthesized from the stepwise reduction of  $(ICy)_{3}$ CoCl by the corresponding alkaline metals under a  $N_{2}$ atmosphere. Complexes 2a-2c in their solid states adopt polymeric structures. The N-N distances (1.145(6) to 1.162(5) Å) and small N-N infrared stretchings (ca. 1800 and 1900 cm<sup>-1</sup>) suggest the strong N<sub>2</sub> activation of the end-on N<sub>2</sub> ligands in **2a-2c**. One electron oxidation of 1 by  $[Cp_2Fe][BF_4]$  gave the cobalt(I) complex devoid of  $N_2$  ligand  $[(ICy)_3Co][BF_4]$  (3). The bis(dinitrogen)cobalt(-1) complexes 2a-2c undergo protonation reaction with triflic acid to give  $N_2H_4$  in 24-30% yields (relative to cobalt). Complexes 2a-2c could also react with silv halides to afford diazene complexes [(ICy)<sub>2</sub>Co( $\eta^2$ -R<sub>3</sub>SiNNSiR<sub>3</sub>)] (R = Me, 6a; Et, **6b**) that are the first diazene complexes of late transition-metals prepared from  $N_2$ -functionalization. Characterization data, in combination with calculation results, suggest the electronic structures of the diazene complexes as low-spin cobalt(II) complexes containing dianionic ligand  $[\eta^2 - R_3 SINNSiR_3]^2$ . Complexes 1, 2a-2c, 6a, 6b, and (ICy)<sub>2</sub>CoCl<sub>2</sub> proved effective catalysts for the reductive silvlation of N<sub>2</sub> to afford N(SiMe<sub>3</sub>)<sub>3</sub>. These NHC-cobalt catalysts display comparable turnover numbers (ca. 120) that exceed the reported 3d metal catalysts. The fine performance of the NHC-cobalt complexes in the stoichiometric and catalytic N<sub>2</sub>functionalization reactions points out the utility of low-valent low-coordinate group 9 metal species for N<sub>2</sub>-fixation.

# Introduction

The exploration on new catalysts for N<sub>2</sub> fixation in the recent decades<sup>1, 2</sup> has let cobalt stand out after iron, ruthenium, and molybdenum as the essential component of some effective catalysts of N<sub>2</sub> fixation.<sup>3</sup> As the notable examples, bariumpromoted cobalt catalysts supported on carbon are known to exhibit higher ammonia production activity and lower ammonia inhibition than the commercial iron catalyst,<sup>3a</sup> Lu's cobalt complexes supported by double-decker triamido-triphosphine ligand can catalyze the reductive silvlation reaction of N<sub>2</sub> under ambient conditions to give N(SiMe<sub>3</sub>)<sub>3</sub> up to 98 equivalents cobalt-N<sub>2</sub> and the per Co. complexes [(2,5- $[(B(C_6H_4PPr_2)_3)Co(N_2)][Na(12-C-4)_2]$ and  $(Bu_2^tPCH_2)_2C_4H_2N)Co(N_2)$  reported by Peters <sup>3i</sup> and Nishibayashi, <sup>3j</sup> respectively, promote the reduction of N<sub>2</sub> into NH<sub>3</sub> at  $-78^{\circ}$ C using [H(OEt<sub>2</sub>)<sub>2</sub>][BAr<sup>F</sup><sub>4</sub>] as the proton source and KC<sub>8</sub> as reducing reagent with the yield of NH<sub>3</sub> up to 16 equiv... These intriguing progresses hint at the potential of cobaltbased catalysts in promoting new N<sub>2</sub> fixation reactions with high atom-economical and less energy-intensive features.

Along with the emergence of these cobalt catalysts, fundamental question as to the reactivity of cobalt-N<sub>2</sub> species has remained poorly understood. Even since the first report of cobalt-N<sub>2</sub> complex [(Ph<sub>3</sub>P)<sub>3</sub>Co(N<sub>2</sub>)(H)] in 1967,<sup>4a, 4b</sup> a plenty of cobalt-N<sub>2</sub> complexes featuring versatile supporting ligands are known.<sup>4</sup> However, the bound N<sub>2</sub> ligands of these cobalt-N<sub>2</sub>

complexes are general recognized as labile and hard to be functionalized. To our knowledge, only two successful studies of N<sub>2</sub>-functionalization with well-defined cobalt-N<sub>2</sub> complexes are known, namely, the protonation reactions of the cobalt(-1)- $N_2$  complexes  $(Ph_3P)_3Co(N_2)M(solv)_3$  (M = Li, Na) to give ammonia and hydrazine 4c and the reactions of the cobalt(0)- $N_2$  complex [(PhB(CH<sub>2</sub>PPr<sup>i</sup><sub>2</sub>)<sub>3</sub>)Co(N<sub>2</sub>)]<sub>2</sub>Mg(THF)<sub>4</sub> with elecproduce trophiles diazenido complexes to  $[(PhB(CH_2PPr_2^i)_3)Co(NNR)]$  (R = Me, SiMe<sub>3</sub>).<sup>4f</sup> Notably, these are also the only known examples of N2 functionalization of late transition-metal N2 complexes besides of the studies with group 8 metal complexes.<sup>1,5</sup> The status quo urges exploration on the chemistry of late transition-metal N2 complexes.

In this context, we report herein the exploration on cobalt-N<sub>2</sub> complexes with N-heterocyclic carbene (NHC) ligation. Utilizing 1,3-dicyclohexyl-imidazol-2-ylidene (ICy) as ligand, novel bis(dinitrogen)cobalt(-1) complexes [(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>M]<sub>n</sub> (M = K, Rb, Cs) have been synthesized and fully characterized. Benefited from the low-valent nature of the metal center and strong  $\sigma$ -donating nature of NHCs,<sup>6</sup> the N<sub>2</sub> ligands of the cobalt(-1)-N<sub>2</sub> complexes are strongly activated and the complexes can react with acids and silvl halides to give N<sub>2</sub>H<sub>4</sub> and the diazene complexes  $[(ICy)_2Co(\eta^2 R_3SiNNSiR_3$ ] (R = Me, Et), respectively. Diazene imtermediates are proposed in the alternating pathway of N<sub>2</sub>reduction reactions catalyzed by nitrogenases and transition-ACS Paragon Plus Environment from a late transition-meal N<sub>2</sub> complex has never been observed. Thus, the conversion of the cobalt(-1)-N<sub>2</sub> complex to the diazene complexes [(ICy)<sub>2</sub>Co( $\eta^2$ -R<sub>3</sub>SiNNSiR<sub>3</sub>)] provides the first examples of the kind. Moreover, these NHC-cobalt complexes found effective in catalyzing the reductive silylation of N<sub>2</sub> to afford N(SiMe<sub>3</sub>)<sub>3</sub> with turnover numbers reaching 120 per cobalt. The achievement of these cobaltmediated N<sub>2</sub>-functionalization reactions point out the potential usage of low-coordinate low-valent group 9 metal complexes in N<sub>2</sub> functionalization after well-studied iron complexes.

#### **Results and Discussion**

+ Na[BF<sub>4</sub>]

width lw = 60 G.

THE

NaCl

Synthesis and Characterization of the Cobalt(0)-N<sub>2</sub> Complex [(ICy)<sub>3</sub>Co(N<sub>2</sub>)]. Previously, we found that the monodentate NHC ligand, ICy, supports tetrahedral iron(I) and iron(0) complexes in the forms of  $[(ICy)_3Fe(N_2)][BPh_4]$ and  $[(ICy)_3Fe(N_2)]$ , respectively, which are among the rare examples of isolable high-spin iron-N<sub>2</sub> complexes.<sup>8</sup> The introduction of this NHC ligand to cobalt complexes then proved the accessibility of analogue cobalt(0) complex. Treatment of the cobalt(I) complex  $[(ICy)_3CoCI]$  with one equiv. of KC<sub>8</sub> in THF under a N<sub>2</sub> atmosphere gave a red solution, from which the cobalt(0)-N<sub>2</sub> complex  $[(ICy)_3Co(N_2)]$ (1) was isolated in 87% yield as a red crystalline solid (Scheme 1).

#### Scheme 1. Synthetic Routes for the Cobalt-N<sub>2</sub> Complexes

+ KC<sub>8</sub>

THE

KCI, - graphite

1) M, N<sub>2</sub>, in THF

СуĊу

M = K, 2a; Rb, 2b; Cs, 2c

2) recrystal

in toluene

+ [Cp<sub>2</sub>Fe][BF<sub>4</sub>]

THE

h

- Cp<sub>2</sub>Fe

Figure 1. Molecular Structure of  $[(ICy)_3Co(N_2)]$  (1, left), and its EPR spectrum measured at 103 K in a toluene glass. Instrumental parameters for EPR measurement: v = 9.082 GHz, modulation frequency = 100 kHz, modulation amplitude = 2 G, microwave power = 0.998 mW, time constant = 30 ms, sweep time = 30 s. Simulation parameters: S = 1/2,  $g_1 = 2.16$ ,  $g_2 = 2.14$ ,  $g_3 = 1.99$ ;  $A_Co_1 = 207$  MHz,  $A_Co_2 = 160$  MHz,  $A_Co_3 = 115$  MHz; line

240

Complex 1 has a solution magnetic moment of 2.6(1)  $\mu_B$  (measured by Evans' method in C<sub>6</sub>D<sub>6</sub>) that exceeds the spin-

only value for S = 1/2 system, probably due to the contribution of orbital moment.<sup>9</sup> The X-band EPR spectrum of 1 recorded in a toluene glass at 103 K displys apparent <sup>59</sup>Co (I = 7/2) nuclear hyperfine splitting, and can be nicely simulated as an S =1/2 system with small g-value and large <sup>59</sup>Co nuclear hyperfine constants (Figure 1). The g value is in line with those of the cobalt(0) phosphine complexes  $Co(dppf)_2$  (dppf = 1,1'bis(diphenylphosphino)ferrocene) <sup>10</sup> and  $Co(troppph)_2$ (tropph = tropylindene phosphane).<sup>11</sup> The molecular structure of 1 established by a single-crystal X-ray diffraction study confirmed its distorted tetrahedral coordination geometry (Figure 1). Its end-on N<sub>2</sub> ligand sits in the pocket composed by three cyclohexyl groups, and has the Co-N distance of 1.798(5) Å and N-N distance of 1.051(5) Å. Despite of the short N-N distance, low energy N-N stretching vibrations (1917 and 1921 cm<sup>-1</sup> in KBr and THF, respectively) were observed on the IR spectra (Figures S18-S20). These wavenumbers are smaller than those of the cobalt(0)- $N_2$  complexes supported by phosphine-based ligands, e.g.  $[((2-Pr_2^iPC_6H_4)_3B)Co(N_2)]$  $(2089 \text{ cm}^{-1})^{4h}$  and [AltraPhosCo(N<sub>2</sub>)] (2081 cm<sup>-1</sup>),<sup>4q</sup> suggesting more pronounced N<sub>2</sub> activation in the NHC-Co(0)-N<sub>2</sub> complex caused by the strong  $\sigma$ -donating nature of the ICy ligands in 1. The  ${}^{15}N_2$ -labled sample of 1, which was prepared by exposing the solid sample of 1 to a  ${}^{15}N_2$  (2 atm.) at room temperature, shows a <sup>15</sup>N-<sup>15</sup>N stretching vibration at 1854 cm<sup>-1</sup>, being consistent with the mass difference of  ${}^{15}N_2$  to  ${}^{14}N_2$ .



Figure 2. Cyclic voltammogram of  $[(ICy)_3Co(N_2)]$  (1) measured in 0.1 M THF solution of  $[Bu_4^nN][PF_6]$  under a N<sub>2</sub> atmosphere with a scan rate of 100 mV/s.

Synthesis and Characterization of the Cobalt(-1)-N<sub>2</sub> Complexes M[(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>] (M = K, Rb, Cs). The cyclic voltammogram of 1 measured in THF under N<sub>2</sub> atmosphere features two sequential quasi-reversible one-electron redox waves with half-wave potentials at -2.10 and -0.34 V (*vs. SCE*, Figure 2), which are tentatively assigned to the redox couples of [(ICy)<sub>3</sub>Co(N<sub>2</sub>)]<sup>1-/0</sup> and [(ICy)<sub>3</sub>Co(N<sub>2</sub>)]<sup>0/1+</sup>, respectively. The half-wave potential of [(ICy)<sub>3</sub>Co(N<sub>2</sub>)]<sup>0/1+</sup>, respectively. The half-wave potential of [(ICy)<sub>3</sub>Co(N<sub>2</sub>)]<sup>1-/0</sup> is shifted cathodically *ca.* 0.6 V and 1.7 V, respectively, over those of the redox processes of [(((2-Pr<sup>*i*</sup><sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>B)Co(N<sub>2</sub>)]<sup>1-/0</sup> <sup>4h</sup> and [Altra-PhosCo(N<sub>2</sub>)]<sup>1-/0</sup>, <sup>4q</sup> signifying the strongly electron-donating nature of the tris(NHC) ligand set as compared to the trisphosphine ligands bearing additional Z-type site. Aiming to access the reduced species, chemical reduction of 1 by alkali metals was tried. Stirring the THF solutions of 1 with K, Rb, or Cs (1.2 equiv.) at room temperature gave reddish brown solutions. After further workup and recrystallization,



Figure 3. Structures of  $[(ICy)_2Co(N_2)_2K]_n$  (2a). (a) Ball-stick presentation of the polymer chain of 2a, (b) the structure of the unit of the polymer chain, and (c) the anion  $[(ICy)_2Co(N_2)_2]^-$  in 2a showing 30% probability ellipsoids. Balls in grey, light bule, blue, and purple correspond to carbon, nitrogen, cobalt, and potassium atoms, respectively. For simplicity, all the hydrogen atoms are ommited.

<b>Fable 1. Selected in</b>	iteratomic distance	(A)	and	N-N	stretches	(cm <sup>-1</sup> )	of	the	Co-N <sub>2</sub>	complexes.
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	1	2a	2b	2c	4 <sup>c</sup>
N-N	1.051(5)	1.154(2)	1.151(5)	1.145(6)	1.148(4)
		to 1.159(3)	to 1.162(5)	to 1.159(6)	1.161(4)
Co-N	1.798(5)	1.752(2)	1.747(4)	1.748(5)	1.752(3)
		to 1.758(2)	to 1.760(4)	to 1.765(4)	1.766(3)
$M \cdots N^{a}$		2.785(2)	2.928(4)	3.097(5)	2.766(4)
		to 3.214(2)	to 3.315(4)	to 3.434(5)	
Co-C	1.966(5)	1.968(2)	1.957(4)	1.954(5)	1.945(3)
	to 1.977(5)	to 1.984(2)	to 1.984(4)	to 1.967(5)	1.959(4)
$v_{\text{N-N}}{}^{b}$	1917	1807, 1881	1804, 1888	1811, 1882	1812, 1892
	(1921)	(1817, 1890)	(1816, 1891)	(1817, 1894)	(1828, 1906)

<sup>*a*</sup> M = K, Rb, Cs, and K for **2a-2c**, and **4**, respectively. <sup>*b*</sup> Data measured on solid samples and THF solutions (parenthesized), respectively. <sup>*c*</sup> Distances are the data in average from two crystallographically independent molecules in the unit cell.

the bis(dinitrogen)cobalt(-1) complexes  $[(ICy)_2Co(N_2)_2M]_n$  (M = K, **2a**; Rb, **2b**; Cs, **2c**), instead of mono(dinitrogen)cobalt(-1) complexes  $(ICy)_3Co(N_2)M$ , were isolated in 37%, 42%, and 64% yields, respectively, as red crystals (Scheme 1). The attempts to prepare  $[(ICy)_2Co(N_2)_2Na]_n$  using sodium metal and sodium amalgam as reducing reagents were unsuccessful. Complexes **2a-2c** have been characterized by various spectroscopic methods and their structures were established by X-ray diffraction studies. Their chemical composition as compared to **1** indicates the formation of ICy as by-product in their preparation. The latter, indeed, was isolated in high yields. The trial to prepare the one-electron oxidized species  $[(ICy)_3Co(N_2)]^{1+}$  *via* the reaction of **1** with  $[Cp_2Fe][BF_4]$  led to the isolation of the three-coordinate cobalt(I) complex devoid of N<sub>2</sub>-ligation  $[(ICy)_3Co][BF_4] (3) (Scheme 1). Alternatively, 3 is prepared from the salt elimination reaction of [(ICy)_3CoCl] with NaBF_4. The failure to access the cobalt(I)-N_2 complex [(ICy)_3Co(N_2)][BF_4] might be related to the weak N_2-affinity of high-spin cobalt(I) species as compared to high-spin iron(I) species, since analog high-spin iron(I)-N_2 complex [(ICy)_3Fe(N_2)][BAr_4] proved accessible.<sup>8</sup>$ 

In their solid states, **2a-2c** are iso-structural, presenting as one-dimensional polymers formed by interactions of the alkali metal cations  $M^+$  with the N<sub>2</sub> and imidazole moieties of the anion [(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>]<sup>-</sup>. As the representative, Figure 3 depicts the polymeric structure of **2a**. The structures of **2b** and **2c** are shown in Figures S3-S6. The key bond distances of **2a-2c** are listed in Table 1. Comparing the structure data indicated that,

irrelevant to their cations, the structures of the anions  $[(ICy)_2Co(N_2)_2]$  in **2a-2c** are nearly identical, in which the cobalt center coordinates with two ICy ligands and two end-on N<sub>2</sub> ligands, forming a distorted tetrahedral geometry (Figure 3c). In addition to the interaction with the cobalt center, the two N<sub>2</sub> ligands are further coordinating with alkaline metal ions with one in an  $\eta^2: \eta^2$ -fashion  $M^{1+}(\eta^2: \eta^2-N_2)M^{1+}$ , and the other in an  $\eta^1$ : $\eta^2$ -fashion  $M^{1+}(\eta^1:\eta^2-N_2)M^{1+}$  (Figure 3a). The long M<sup>1+</sup>...N separations (Table 1) as compared those of their counterparts in  $[M'_2(N_2)M_2(nacnac)_2]$  (M' = K, Rb, Cs; M = Fe,<sup>12</sup> Co,<sup>4j</sup> Ni <sup>13</sup>),  $[K(N_2)Co(PMe_3)_3]_6$ ,  $^{4e}$  [(Et<sub>2</sub> $cAAC)_{2}Fe(N_{2})][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]]]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]]]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]]]][K(18-C-6)],^{14} and [AltraPhosFe(N_{2})]]]][K(18-C-6)],^{14} and [AltrAPhosFe(N_{2})]]]][K(18-C-6)],^{14$ 6)]<sup>4p</sup> suggest the ionic nature of these complexes. Irrespective of the different alkali metal ions, the Co-N distances in these complexes are also close and locate in a narrow range (1.747(4))to 1.765(4) Å). The N-N distances are also in the short range (1.145(6) to 1.162(5) Å). The shorter Co-N and longer N-N distances when comparing with their counterparts in  $[(ICy)_3Co(N_2)]$  (1) imply stronger N<sub>2</sub> activation of the cobalt(-1) complexes. On the other hand, when comparing with the reported Co(-1)-N<sub>2</sub> complexes, the N-N distances in 2a-2c are between  $(PPh_3)_3Co(N_2)M(solv)_n$  (M = Li, Na; 1.16-1.19 Å)<sup>4c</sup> and the Z-ligand-anchored trisphosphine-Co(-1)-N<sub>2</sub> complexes Å),<sup>4p</sup> [AltraPhosCo(N<sub>2</sub>)][Li(crypt-222)] (1.12)[((2-Å),<sup>3i</sup>  $Pr_{2}^{i}PC_{6}H_{4}_{3}B)Co(N_{2})[Na(12-C-4)_{2}]$ and (1.13) $[(THF)Zr(MesNPPr_{2})_{3}Co(N_{2})]$  (1.13 Å).<sup>41</sup> Accordingly, the N-N stretching frequencies of the solid samples of 2a-2c (1807 and 1881 cm<sup>-1</sup>, 1804 and 1888 cm<sup>-1</sup>, and 1811 and 1882 cm<sup>-1</sup> respectively) (Figures S21, S24, and S27) also lay between those of  $(PPh_3)_3Co(N_2)M(solv)_n$  (M = Li, Na, et al; ca. 1900 cm<sup>-1</sup>) <sup>4c</sup> and the Z-ligand-anchored trisphosphine-Co(-1)-N<sub>2</sub> complexes (*ca.* 2000 cm<sup>-1</sup>). <sup>4i, 3p, 41</sup> As NHCs are stronger  $\sigma$ donors than phosphine ligands,<sup>6</sup> the shorter N-N distances and larger stretching vibration numbers of 2a-2c over those of  $(PPh_3)_3Co(N_2)M(solv)_n$  should be related to the cation effect. The difference observed between 2a-2c and the Z-type ligandanchored trisphosphine-Co(-1)-N<sub>2</sub> complexes could be attributed to the different electron-donating ability of the ligands.

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Figure 4. IR spectra of **2a** and  ${}^{15}N_2$ -**2a** (left), and the  ${}^{15}N$  NMR spectra of  ${}^{15}N_2$ -enrich **2a** and **2c** (right). The peaks at *ca.* -70.8 ppm in the NMR spectra arise from free  ${}^{15}N_2$ .

Complexes **2a-2c** are diamagnetic. Their <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra measured in THF- $d_8$  exhibit only one set of signals for the ICy ligands, suggesting an idealized  $C_2$  symmetry for these complexes in the solution phase. The infrared resonance spectra of **2a-2c** measured on their THF solutions dis-

play two N-N stretching vibrations with the wavenumbers close to those of the solid samples (Table 1, and Figures 4 and S21-S29). Despite of the low-valent nature of the cobalt center. the  $N_2$  ligands in these cobalt(-1)- $N_2$  complexes **2a-2c** are still labile as exposing the THF solutions of **2a-2c** to  ${}^{15}N_2$  atmosphere at room temperature readily led to  ${}^{14}N_2$ - ${}^{15}N_2$  exchange. The resulting <sup>15</sup>N<sub>2</sub>-labeled species show two characteristic stretches (ca. 1760 and 1830 cm<sup>-1</sup>, Figures 4, S23, S26, and S29). The two bands observed in these infrared resonance spectra are assigned to the symmetric and asymmetric stretches of the tetrahedral anion  $[(ICy)_2Co(N_2)_2]$ . The pattern is similar to the infrared resonace spectra of the bis(dinitrogen)titanium complexes reported by Chirik.15 In supportive to this assignation, the <sup>15</sup>N NMR spectra of these cobalt(-1)-N<sub>2</sub> complexes only show one set of  $^{15}$ N NMR signals assignable to cobalt-bound N<sub>2</sub> (-33.23 and -55.53 ppm for 2a. and -31.96 and -56.23 ppm for 2c. Figure 4). Careful examination of the NMR spectra revealed the decoalescence of the signals at ca. -56 ppm (Figures S37 and S42), which might be caused by the subtle difference of interaction of alkaline metal cations with the two N<sub>2</sub> ligands in  $[(ICy)_2Co(N_2)_2]^{-1}$ . This speculation gains support from the isolation of  $[(ICy)_2Co(N_2)_2K(18-C-6)]$  (4) from the reactions of 2a with 18-crown-6. An X-ray diffraction study revealed that the key structure parameters of the anion  $[(ICy)_2Co(N_2)_2]$  in 4 are similar to those of 2a, having one N<sub>2</sub> ligand bonding with the cobalt center solely and the other N<sub>2</sub> ligand bridging between the cobalt center and the crowned potassium ion (Figure 5). The N-N stretches of 4 in the infrared spectra also appear at similar wavenumbers as those of 2a (Table 1, and Figures S30-S32). As the bis(dinitrogen)cobalt(-1) complexes decompose quickly in the THF solution of [NBu<sup>n</sup><sub>4</sub>][BPh<sub>4</sub>] (0.1 M) as evidenced by fast color change of the solution from red to the cyclic voltammograms brown. of these bis(dinitrogen)cobalt(-1) complexes have not been obtained.



Figure 5. Molecular Structure of  $[(ICy)_2Co(N_2)_2K(18-C-6)]$  (4), showing 30% probability ellipsoids.



Figure 6. HOMO and HOMO-1 orbitals of  $[(ICy)_2Co(N_2)_2]^-$  at its S = 0 state.

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Low-valent late transition-metal species are thought to have low affinity toward N<sub>2</sub> as compared to low-valent earlier metal species due to the lower energy of their 3d orbitals being worse at  $\pi$ -backdonating to N<sub>2</sub>.<sup>16</sup> This point is reflected by the rarity of late transition-metal complexes that bind two or more N<sub>2</sub> molecules and a plenty of such complexes are known for the group 4-8 metals.<sup>17</sup> As for the later transition-metals, the square planar complex *trans*-[(IMes)<sub>2</sub>Ir(N<sub>2</sub>)<sub>2</sub>][BAr<sup>CF3</sup><sub>4</sub>] <sup>18</sup> is the only precedent. The access of the bis(dinitrogen)cobalt complexes 2a-2c and 4, thus, is significant, which revealed the high N<sub>2</sub>-affinity of the bis(NHC)cobalt(-1) fragment  $[(ICy)_2Co]^{1-}$ . In addition with the low-valent nature of the Co(-1) center, the high N<sub>2</sub>-affinity might should also benefit from the strong  $\sigma$ -donating nature of the NHC ligand, noting that the phosphine-Co(-1)-N<sub>2</sub> complexes are known only for the type of mono(dinitrogen) complex  $(R_3P)_3Co(N_2)M^{4c-4e}$  The combination of the two factors would generate a very electronrich metal center that incurs pronounced metal-to-N2 backdonation. Electronic structure calculations on  $[(ICy)_2Co(N_2)_2]^{-1}$ (S = 0) indicated that, in spite of the tetrahedral coordination geometry, the electron-richness of the  $d^{10}$  cobalt(-1) center has non-negligible Co(3d)-to- $N_2(\pi^*)$  back-donation that is discernible from the orbital composition of the HOMO and HOMO-1 orbitals (47% Co(3d) + 20% N(2p) and 49% Co(3d) + 13%N(2p), respectively, Figures 6 and S50), and also from the negative Mulliken atomic charges (-0.32 and -0.33) on the two distal N atoms. The charges are higher than that of the distal N atom of  $[(ICy)_3Co(N_2)]$  (-0.30) even though the latter contains only one  $\pi$ -accepting N<sub>2</sub> ligand.

Table 2. Yields of hydrazine and ammonia formed in the protonation reactions of cobalt- $N_2$  complexes.

cobalt-N <sub>2</sub>	complex + HX (16 equiv	$.) \xrightarrow{Et_2O} N_2H_4$	+ NH <sub>3</sub> + CoX <sub>2</sub> + H <sub>2</sub>
Co-N <sub>2</sub>	НХ	Yield of $N_2H_4$ (%)	Yield of NH <sub>3</sub> (%)
1	triflic acid	5(1)	<1
1	HCl <sup>b</sup>	<1	<1
2a	triflic acid	27(3)	<1
2a	HCl <sup>b</sup>	31(3)	<1
2b	triflic acid	23(2)	<1
2c	triflic acid	24(1)	<1
4	triflic acid	27(1)	<1
5 <sup>c</sup>	triflic acid	3(1)	<1
5 <sup>c</sup>	HCl <sup>b</sup>	18(3)	<1

<sup>*a*</sup> Yields are relative to *per* mol cobalt, and are the averaged data of 2 runs. <sup>*b*</sup> 7.6 M HCl in Et<sub>2</sub>O. <sup>*c*</sup> **5** denoted for  $[(Ph_3P)_3Co(N_2)Li(OEt_2)_3]$  prepared based on the reported procedures of ref. 4c.

**N<sub>2</sub>-Functionalization Reactions of the Cobalt-N<sub>2</sub> Complexes.** Noting the strong N<sub>2</sub>-activation in these NHC-cobalt-N<sub>2</sub> complexes, their N<sub>2</sub>-functionalization reactions were explored. Examining their reactions with anhydrous acids revealed that the cobalt(-1)-N<sub>2</sub> complexes **2a-2c** and **4** can react with an excess amount of triflic acid or HCl at -78 °C in Et<sub>2</sub>O to yield hydrazine (23-31% yields per cobalt atom) as determined by *p*-dimethylaminobenzaldehyde colorimetry (Table 2). The similar absorption spectra of the resultant cobalt species in their aqueous solutions as that of aqueous solution of

CoCl<sub>2</sub> suggests the formation of cobalt(II) species in these protonation reactions. Moreover, GC analysis on the gas formed in the protonation reaction indicated the formation of  $H_2$  (Figure S54). While the yields of hydrazine are far from stoichiometry, they are higher than those of the protonation reactions of some isolable late 3d metal-N2 complexes. For examples, the reaction of  $[(N(CH_2CH_2PPh_2)_3)Fe(N_2)]$  with HBr was reported to afford hydrazine in 11% yield,<sup>19</sup> the reaction of  $[(Si(C_6H_4PPh_2)_3)Fe(N_2)]$  with HBF<sub>4</sub> afforded hydrazine in 17% yield,<sup>20</sup> and, in our hands, the reactions of Yamamophosphine-cobalt(-1)-N<sub>2</sub> to's complex  $[(Ph_3P)_3Co(N_2)Li(OEt_2)_3]^{4c}$  with HCl and triflic acid in diethyl ether gave hydrazine 18% and 3% yields, respectively (Table 2). The high yields of hydrazine obtained in the current study might be related to strong N2 activation of these NHC-cobalt(-1)- $N_2$  complexes as revealed by their spectroscopic data and calculation study. In contrast, the protonation reactions of the NHC-cobalt(0)-N<sub>2</sub> complex  $[(ICy)_3Co(N_2)]$  (1) under similar conditions merely gave hydrazine in trace amounts (Table 2), which signifies the effect of the oxidation-state of cobalt center for the degree of N<sub>2</sub> activation of the bound ligand. Notably, in all these reactions, only trace amount of ammonia was detected, which is different from the protonation reactions of molybdenum-, and tungsten-N2 complexes that have ammonia as the major N-containing products.<sup>21</sup> The attempts to apply these cobalt-N<sub>2</sub> complexes as catalysts for the reduction of N<sub>2</sub> into hydrazine or ammonia with  $[H(Et_2O)_2][BAr_4^F]$  or [Ph<sub>2</sub>NH<sub>2</sub>][OTf] as the proton source and KC<sub>8</sub> as the electron source were unsuccessful. Among which, only trace amount of  $NH_3$  (less than 0.7 equiv. relative to the amount of catalyst) was formed. The poor catalytic performance might be due to the sensitivity of these cobalt-NHC ligand toward acid.

Scheme 2. Silylation of  $N_2$  Mediated by the Cobalt-NHC Species and the Probable Stoichiometry for the Formation of the Diazene Complex



The production of hydrazine hints at the involvement of diazenido or diazene complexes as the probable intermediates in these protonation reactions. While our efforts to isolate the intermediates via the reactions of the bis(dinitrogen)cobalt(-1) complexes with one or two equiv. of acids, e.g.  $[H(OEt_2)_2][BAr^{F_4}]$ , HCl, and  $[HNMe_2Ph][BAr^{F_4}]$ , were futile, the reactions of 2a with one equiv. of Me<sub>3</sub>SiCl and Et<sub>3</sub>SiCl, in toluene gave green suspensions, from which the cobalt diazene complexes  $[(ICy)_2Co(\eta^2 - R_3SiNNSiR_3)]$  (R = Me, **6a**; Et, **6b**) were isolated as green crystals in 36% and 19% yields (based on cobalt), respectively, (Scheme 2). A balanced equation for the production of the diazene complexes points out the involvement of other cobalt species as the byproduct. hile the attempts to isolate it were unsuccesful, the observation of the relative higher isolated yield of 6a in the equimolar reaction of  $K[(ICy)_2Co(N_2)_2]$  with Me<sub>3</sub>SiCl over other stoichiometies is in line with the equation with  $(ICy)_2Co(N_2)_2$  as the byproduct (eq. 1 in Scheme 2). The attempts to prepare it *via* the reaction of **2a** with  $[Cp_2Fe][BF_4]$  merely led to the isoaltion of [(ICy)<sub>3</sub>Co(N<sub>2</sub>)] (1) in low yields. On the other hand, the attemps to improve the yield of **2a** by adding one equivalent of KC<sub>8</sub> to the reaction mixture of **1** with two equiv. of Me<sub>3</sub>SiCl did not improve the yield. As a comparison to the silylation reaction, the interaction of the cobalt(0)-N<sub>2</sub> complex [(ICy)<sub>3</sub>Co(N<sub>2</sub>)] (1) with Me<sub>3</sub>SiCl led to fast evolution of N<sub>2</sub> and the cobalt(I) complex [(ICy)<sub>3</sub>CoCl] was identified by <sup>1</sup>H NMR spectroscopy as the major product. This outcome is different from the formation of the diazenido complex [(PhB(CH<sub>2</sub>PPr<sup>*i*</sup><sub>2</sub>)<sub>3</sub>)Co(NNSiMe<sub>3</sub>)] in the reaction of the cobalt(0) complex [(PhB(CH<sub>2</sub>PPr<sup>*i*</sup><sub>2</sub>)<sub>3</sub>)Co(N2)]<sub>2</sub>Mg(THF)<sub>4</sub> with Me<sub>3</sub>SiCl reported by Peters.<sup>3f</sup> Steric hindrance exerted by the three cyclo-hexyl groups surrounding the N<sub>2</sub> moiety in **1** might account for the failure of silylation of the N<sub>2</sub> moiety in **1**.

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Figure 7. Molecular structure of  $[(ICy)_2Co(\eta^2-Et_3SiNNSiEt_3)]$  (**6b**, left) showing 30% probability ellipsoids and the partial atom numbering scheme, and the EPR spectrum of **6b** measured at 40 K in a toluene glass (right). Selected distances (Å) and angles (deg): Co1-C1 1.9359(17), Co1-C1A 1.9358(17), Co1-N1 1.8672(15), Co1-N1A 1.8672(15), N1-N1A 1.457(3), C1-Co1-N1 109.21(7), N1A-Co1-N1 45.93(9), C1A-Co1-C1 95.89(10). Instrumental parameters for EPR measurement: v = 9.387 GHz, modulation frequency = 100 kHz, modulation amplitude = 2 G, microwave power = 2 mW, time constant = 81.92 ms, sweep time = 240 s. Simulation parameters for the EPR spectrum: S = 1/2,  $g_1$ = 3.39,  $g_2 = 2.22$ ,  $g_3 = 1.87$ ;  $A_{-}Co_1 = 580$  MHz,  $A_{-}Co_2 = 166$ MHz,  $A_{-}Co_3 = 49$  MHz; line width lw = 85 G.



Mayer bond order: N-N 0.86; Co-N 0.70; Co-C 0.93

Figure 8. Mulliken atomic spin density distribution of  $(ICy)_2Co(Me_3SiNNSiMe_3)$  at its S = 1/2 state.

Complexes **6a** and **6b** have the solution magnetic moments around 3.0  $\mu_B$  that is consistent with those of the reported lowspin cobalt(II)-NHC complexes.<sup>22</sup> As the representative, the X-band EPR spectrum of **6b** in its toluene glass at 40 K was measured that exhibits signals typical for low-spin square pla-

nar cobalt(II) species (Figure 7).<sup>23</sup> The spectrum is simulated nicely as an S = 1/2 system with g values of  $g_1 = 3.39$ ,  $g_2 =$ 2.22, and  $g_3 = 1.87$ , and <sup>59</sup>Co nuclear hyperfine splitting of  $A_1$ = 580 MHz,  $A_2$  = 166 MHz, and  $A_3$  = 49 MHz. X-ray diffraction studies revealed that **6a** and **6b** are  $\eta^2$ -diazene cobalt complexes bearing two ICy ligands, being distinct from the reported diazenido and hydrazido complexes,  $L_n M(\eta^1-NNR)$ and  $L_n M(\eta^1 - NNR_2)$  (R = H, alkyl, silyl), respectively, isolated from N<sub>2</sub>-functionalization reactions.<sup>24</sup> Figure 7 depicts the structure of 6b, and that of 6a is shown in Figure S7. The diazene ligands  $\eta^2$ -R<sub>3</sub>SiNNSiR<sub>3</sub> in **6a** and **6b** have the two N atoms exhibiting pyramidal geometry and being coplanar with the cobalt center and the C(carbene) atoms, and the two silvl moieties being a transoid-alignment. The N-N distances (1.450(4) and 1.457(3) Å, for those in 6a and 6b, respectively)fall in the range of N-N single bonds. They are comparable to those of N<sub>2</sub>H<sub>4</sub> (1.460 Å),<sup>25</sup> [Cp<sub>2</sub>Zr( $\eta^2$ -PhNNPh)(py)] (1.434(4) Å),<sup>26</sup> and [(dmpe)<sub>2</sub>Fe( $\eta^2$ -HNNH)] (1.427(7) Å),<sup>7e</sup> and are significantly longer than those of Me<sub>3</sub>SiNNSiMe<sub>3</sub> (1.226(2) Å),<sup>2</sup> [CpCo(PMe<sub>3</sub>)( $\eta^2$ -PhNNPh)] (1.367(9) Å), <sup>28</sup> [(nacnac)Fe( $\eta^2$ -PhNNPh)] (1.398(2) Å), <sup>29</sup> [(nacnac)Cu( $\eta^2$ -(ArNNAr)] (1.352(2) Å, Ar = C<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub>), <sup>30</sup> and [(Bu<sup>4</sup>NC)<sub>2</sub>Ni( $\eta^2$ -PhNNPh)] (1.385(5) Å).<sup>31</sup> The N-N bonds of the latter compounds are double bond in nature. Consistent with the characterization data, geometry optimization on  $(ICy)_2Co(\eta^2 -$ Me<sub>3</sub>SiNNSiMe<sub>3</sub>) at an S = 1/2 state well reproduced the molecular structure of 6a obtained from X-ray diffraction study (Table S3). Analyzing the composition of the frontier molecular orbitals revealed an electronic configuration of  $(\pi_{xy})^2 (d_z^2)^2 (d_x^2 - y^2)^2 (d_{yz})^2 (d_{xz})^1 (\pi_{xy}^*)^0$  for the cobalt complex (Figure S51) that has the unpaired spin locating essentially on the cobalt center (Figure 8) and the Mayer bond order of 0.86 of the N-N bond. The calculation results, in addition with the characterization data, thus, collectively pointed out the identity of 6a and 6b as low-spin cobalt(II) complexes bearing dianionic ligands  $[\eta^2 - R_3 SiNNSiR_3]^2$ .



Figure 9. Space-filling models of  $[(ICy)_2Co(N_2)_2]^-$ ,  $[(^{Mes}CNC)Fe(N_2)_2]$ , <sup>16b</sup> and  $[(Et_2PCH_2N(C_6H_3-2,6-F_2)CH_2PEt_2)_2Cr(N_2)_2]^{-16c}$  based on their structures from X-ray diffraction studies.

As mentioned earlier, diazene complexes were proposed as the key intermediates in the alternating  $N_2$  reduction pathway by nitrogenase and certain iron complexes,<sup>7</sup> as well as the  $N_2$ dissociation and hydrogenation reaction on silica-supported isolated tantalum atom.<sup>32</sup> While the transformations from the side-on  $N_2$ -complexes to diazene complexes are known for

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lanthanides and early transition-metals, the reported N<sub>2</sub>functionalization reactions of late transition-metal N<sub>2</sub> complexes usually gave the  $\eta^{1}$ -type species  $L_n M(\eta^{1}-NNR)$  and  $L_n M(\eta^1$ -NNR<sub>2</sub>), and pertinent transformation to late transitionmetal diazene complex remained elusive.<sup>1</sup> It should also be mentioned that there are a plenty of late transition-metal diazene complexes scattering in literature, however, all of them are prepared from hydrazines or organodiazo compounds, rather than from N<sub>2</sub> complexes.<sup>33</sup> Thus, the conversion of **2a** to 6a and 6b is the first example of the type for late transitionmetal complexes, which gives support to the proposed alter-10 nating N<sub>2</sub> reduction pathways. While the causes leading to the 11 production of the  $\eta^2$ -diazene complexes, instead of  $\eta^1$ diazenido and  $\eta^1$ -hydrazido complexes, in the current system 12 are not clear yet, it seems that the low-coordinate nature of the 13 NHC-cobalt fragment (ICy)<sub>2</sub>Co seems to play an important 14 role. Comparing the space-filling models of the bis(dinitrogen) 15 complexes, the anion  $[(^{Mes}CNC)Fe(N_2)_2]$ ,<sup>17b</sup>  $[(ICy)_2Co(N_2)_2]$ in 2a, 16 and [(Et<sub>2</sub>PCH<sub>2</sub>N(C<sub>6</sub>H<sub>3</sub>-2,6-17  $F_2$ )CH<sub>2</sub>PEt<sub>2</sub>)<sub>2</sub>Cr(N<sub>2</sub>)<sub>2</sub>],<sup>17c</sup> clearly indicates the stepwisely 18 increasing of steric shielding on the N<sub>2</sub> ligands as the 19 coordination numbers of the metal center increasing from 4 to 20 5 to 6 in the series of *cis*-type bis(dinitrogen)metal complexes 21 (Figure 9). Therefore, we reasoned that the open-coordination 22 sites on the low-coordinate fragement (ICy)<sub>2</sub>Co might enable the alternating functionalization of both N atoms of a bound 23 N<sub>2</sub> ligand and also the coordination of the reduced N<sub>2</sub> species 24 in an  $\eta^2$ -fashion over an  $\eta^1$ -fashion. As the evidence 25 supporting this assertion, the single point energies of the  $\eta^2$ -26 diazene complex (ICy)<sub>2</sub>Co( $\eta^2$ -Me<sub>3</sub>SiNNSiMe<sub>3</sub>) at its ground 27 spin-state (S = 1/2) are lower than its isomer (ICy)<sub>2</sub>Co( $\eta^{-1}$ -28 NN(SiMe<sub>3</sub>)<sub>2</sub>) by 6.9 and 11.4 kcal/mol at the BP and B3LYP 29 level of theory, respectively. 30

Scheme 3. Possible Routes for the Production of N<sub>2</sub>-**Functionalization Products from 2a** 



The mechanisms leading to the production of hydrazine and the diazene complexes from 2a are not clear at this stage. As a probable route, we propose that both reactions might go via similar route involving diazenido and diazene species,  $(ICy)_2Co(NNE)$  (A, E = H, SiR<sub>3</sub>) and  $(ICy)_2Co(ENNE)$  (B, E = H, SiR<sub>3</sub>), respectively, as the key intermediates (Scheme 3). The interaction of 2a with a proton or R<sub>3</sub>SiCl could initially give diazenido intermediates A. This process is well-known

for transition-metal-N<sub>2</sub> complexes.<sup>1</sup> The diazenido species could then further interact with proton or R<sub>3</sub>SiCl, in addition with one reducing equivalent, presumably  $[(ICy)_2Co(N_2)_2K]$ , to produce the diazene species **B**. In the silvlation reaction, **B** in the side-on form represents the products 6a and 6b. In the case of the reaction with acides, further protonation of A could give hydrazine and cobalt(II) species. It should be stated that this proposed route is far from conclusive. Important questions, as to whether the isomers of the diazenido and diazene intermediates (side-on or end-on form) can interconvert with each other or not, and whether the N-E (E = H, or SiR<sub>3</sub>) bondforming steps go via nucleophilic attack toward the electrophiles,<sup>2c, 7a</sup> radical rebound with  $E \cdot$ , <sup>3g, 24d</sup> or proton-coupled electron-transfer <sup>34</sup> for the protonation reaction, need further study.

Catalytic Silvlation of N<sub>2</sub> Using the NHC-Cobalt Complexes as Catalysts. In addition to the stoichiometric N<sub>2</sub>functionalization reactions, the NHC-cobalt-N2 complexes also proved effective in catalyzing the silvlation of N<sub>2</sub>. As shown in Table 3, using excess amounts of KC<sub>8</sub> and Me<sub>3</sub>SiCl (2000 equiv. relative to the molar of cobalt) and N<sub>2</sub> (1 atm.), the catalytic reaction with  $[(ICy)_3Co(N_2)]$  (1) as catalyst at room temperature in 24 hours can produce N(SiMe<sub>3</sub>)<sub>3</sub> in 19% vield (relative to Me<sub>3</sub>SiCl), which equals to a TON of 125(6) (entry 1). Under similar conditions, the reactions employing the bis(dinitrogen)cobalt(-1) complexes 2a-2c, and 4 yielded N(SiMe<sub>3</sub>)<sub>3</sub> with comparable yields (15-18%) and TONs (103-120) (entries 2-5). In addition to the dinitrogen complexes, the NHC-cobalt(II) complexes  $[(ICy)_2Co(\eta^2-R_3SiNNSiR_3)]$  (6a and **6b**) and (ICy)<sub>2</sub>CoCl<sub>2</sub> also promote the N<sub>2</sub> silvlation reactions with similar yields and TONs as the cobalt-N<sub>2</sub> catalysts (entries 6-8). In these reactions, Me<sub>3</sub>SiCl was detected at the major remaining silicon-containing species and the disliane Me<sub>3</sub>SiSiMe<sub>3</sub> as a minor side product (Figure S55). In according with Lu's observation,<sup>3g</sup> CoCl<sub>2</sub> in the absence of other ancillary ligands proved a poor catalyst for the N<sub>2</sub> silvlation reaction under our reaction conditions (entry 9).

Table 3. Catalytic performance of the NHC-cobalt complexes in catalytic silvlation of N<sub>2</sub>.<sup>a</sup>

N			Cat.		
(1 atm.)	(2000 equiv./cat.) (20	100 equiv./cat.)	Et <sub>2</sub> O (10 mL) r.t., 24 h	N(SIIVIe <sub>3</sub> ) <sub>3</sub>	
entry	Cat.	TON <sup>b</sup>	Yield N(SiMe <sub>3</sub> ) <sub>3</sub>	of (%) <sup>c</sup>	
1	1	125(6)	19(1)		
2	2a	107(16)	16(3)		
3	2b	120 (5)	18(1)		
4	2c	103(18)	15(3)		
5	4	118(16)	18(3)		
6	6a	109(7)	16(1)		
7	6b	121(16)	18(3)		
8 <sup>d</sup>	(ICy) <sub>2</sub> CoCl <sub>2</sub>	115(14)	17(2)		
9 <sup>d</sup>	CoCl <sub>2</sub>	15(5)	3(1)		

<sup>a</sup> The reactions were run using 0.005 mmol of the catalyst in 10 ml Et<sub>2</sub>O with the addition of the reducing reagent prior to catalyst. TONs and yields were the averaged data of three runs.<sup>b</sup> Turnover numbers were calculated as the molar ratio of N(SiMe<sub>3</sub>)<sub>3</sub> to cobalt. <sup>c</sup> Yields of N(SiMe<sub>3</sub>)<sub>3</sub> were based on Me<sub>3</sub>SiCl and determined by GC with cyclododecane as the internal standard.  $^{d}$  0.010 mmol in 20 ml Et<sub>2</sub>O.

The reductive silvlation of N<sub>2</sub> to give silvlamine is among the rare methods of catalytic N<sub>2</sub>-functionalization reactions. While the seminal report by Shiina's in 1972 showed that simple metal salts could serve as precatalyst to give N(SiMe<sub>3</sub>)<sub>3</sub> with TONs less than 10,<sup>3f</sup> recent endeavors have resulted in the discovery of new catalysts with improved TONs, e.g. Nishibayashi's molybdenum catalyst supported by ferrocenebridged bis(phosphine) ligand  $trans-[(depf)_2Mo(N_2)_2]$  (226) equiv. per Mo, or 75 equiv. per metal atom when the two ferrocene-based ligands are also considered),<sup>24d</sup> Lu's dicobalt complexes with (triamido-triphosphine) ligation (98 equiv. per Co),<sup>3g</sup> the cobalt-phosphine catalyst  $CoCl_2/PPr_2^i$  Me (94 equiv. per Co), <sup>3g</sup> Nishibayashi's Co<sub>2</sub>(CO)<sub>8</sub>/bipyridine (49 equiv. per Co), <sup>3h</sup> Peters' iron(0) complex [(Et<sub>2</sub>-cAAC)<sub>2</sub>Fe] (24 equiv. per Mézailles' molybdenum catalyst Fe),  $[(P(CH_2CH_2PCy_2)_3)Mo(NN(SiMe_3)_2)]$  (15 equiv. per Mo),<sup>2</sup> and Ohki's  $[Fe_4(\mu-H)_4(\mu_3-H)_2(N(SiMe_3)_2)_2(PEt_3)_4]$  (40 equiv. per Fe).<sup>35</sup> Significantly, the turnover numbers of these NHCcobalt catalysts outperform the majority of the reported catalysts, and are exceeded solely by trans-[(depf)<sub>2</sub>Mo(N<sub>2</sub>)<sub>2</sub>].<sup>24d</sup> The fine catalytic performance of the NHC-cobalt complexes should benefit from the use of NHC ligands, with which, the aforementioned study has shown the bis(dinitrogen)cobalt(-1) complexes are accessible and can be transferred to side-on diazene complexes.

The achievment of the catalytic silvlation reaction raised intersting question as to the relevance of the diazene complex  $(ICy)_2Co(Me_3SiNNSiMe_3)$  (6a) to the catalytic production of  $N(SiMe_3)_3$ . In order to throw light on this, the reactions of **6a** with reducing reagents and Me<sub>3</sub>SiCl were examined. Complex **6a** proved unreactive toward  $KC_8$  in THF at room temperature, and it does not react with Me<sub>3</sub>SiCl at room temperature either. However, the reaction of 6a with an excess amount of Me<sub>3</sub>SiCl and KC<sub>8</sub> in diethyl ether under an argon atmosphere can produce N(SiMe<sub>3</sub>)<sub>3</sub> in 85% GC yield (Scheme 2 and Figure S56). These results, in combination with the comparable catalytic efficiency of 6a as those of (ICy)<sub>2</sub>CoCl<sub>2</sub> and  $[(ICy)_2Co(N_2)_2M]_n$  in the catalytic silvlation reaction, point out that the diazene complex 6a is a possible intermediate for the cobalt-catalyzed silvlation reaction of N2. Mechanistic questions as to the nature of the genuine catalytic species and the detailed mechanisms of the cobalt complex-promoted N-Si bond formation and N-N bond scission reactions are under investigation.

#### Conclusion

In this study, the synthesis, structure, reactivity, and catalytic application in  $N_2$  silylation of NHC-cobalt- $N_2$  complexes have been investigated. The principle findings are listed as following.

Upon the reduction of the cobalt(I) complex [(ICy)<sub>3</sub>CoCl] with one equiv. of KC<sub>8</sub> in a dinitrogen atmosphere, the 17e cobalt(0)-N<sub>2</sub> complex [(ICy)<sub>3</sub>Co(N<sub>2</sub>)] has been synthesized. The further reduction of the cobalt(0)-N<sub>2</sub> complex by different alkaline metals under N<sub>2</sub> led to the formation of novel 18e bis(dinitrogen)cobalt(-1) complexes [(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>M]<sub>n</sub> (M = K, Rb, Cs). The bis(dinitrogen)cobalt(-1) complexes are among the rare examples of bis(dinitrogen) metal complexes of the late transition-metals, and have been fully characterized by various spectroscopic methods. The long N-N separation (*ca.* 1.16 Å) and low N-N stretching frequencies suggest strong activation of their end-on  $N_2$  ligands.

Reactivity study revealed the bound N<sub>2</sub> ligands in the NHCcobalt(-1) complexes can be converted to other reduced N<sub>2</sub> species, which add new rare examples of N<sub>2</sub>-functionalization by late transition-metal complexes beyond the iron group. The protonation reactions of the bis(dinitrogen)cobalt(-1) complexes with triflic acid and anhydrous HCl in ether at low temperature produce hydrazine, and the reactions of the bis(dinitrogen)cobalt(-1) complexes with R<sub>3</sub>SiCl (R = Me, Et) result in the formation of diazene complexes [(ICy)<sub>2</sub>Co( $\eta^2$ -R<sub>3</sub>SiNNSiR<sub>3</sub>)] that represent the first diazene complexes of late transition-metals prepared from N<sub>2</sub>-functionalization reactions. The low-coordinate low-valent nature of the NHCcobalt fragment (ICy)<sub>2</sub>Co is thought the key factor inducing the production of the novel  $\eta^2$ -diazene complexes.

Investigation on the catalytic performance of the NHCcobalt complexes revealed the capability of the cobalt(0)- $N_2$ , cobalt(-1)- $N_2$  and the cobalt(II) complex (ICy)<sub>2</sub>CoCl<sub>2</sub> in promoting the reaction of  $N_2$  with R<sub>3</sub>SiCl and KC<sub>8</sub> to afford N(SiMe<sub>3</sub>)<sub>3</sub>. Despite of their structure difference, these NHCcobalt catalysts exhibit comparable TONs (*ca.* 120 equiv. N(SiMe<sub>3</sub>)<sub>3</sub> per Co) that exceed the known 3d metal-based catalysts. The comparable catalytic performance of these NHCcobalt complexes hints at the involvement of common lowvalent cobalt- $N_2$  complexes in the catalytic cycle. The unique performance of the NHC-cobalt complexes in mediating the stoichiometric and catalytic  $N_2$  functionalization reactions points out that the design of new late transition-metal catalysts for N<sub>2</sub>-functionalization could embrace ligand sets that could stabilize low-valent low-coordinate metal species.

#### **Experimental Section**

General Considerations. All experiments were performed under an atmosphere of dry N2 with the rigid exclusion of air and moisture using standard Schlenk techniques, or in a glovebox. All organic solvents were dried with a solvent purification system (Innovative Technology) and bubbled with dry N2 gas prior to use. 1,3-Dicyclohexylimidazol-2-ylidene (ICy)<sup>36</sup> and potassium graphite  $(KC_8)^{37}$  were synthesized according to the literature procedures. All other chemicals were purchased from chemical vendors and used as received unless otherwise noted. <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra were recorded on an Agilent 400, Bruker DRX400, or Mercury 300 MHz spectrometer. All chemical shifts were reported in units of ppm with references to the residual protons of the deuterated solvents for proton chemical shifts, the <sup>13</sup>C of deuterated solvents for carbon chemical shifts, the <sup>15</sup>N of CH<sub>3</sub>NO<sub>2</sub> (external standard) for nitrogen chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Magnetic moments were measured 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>38</sup> IR spectra of solid samples were recorded with a NICOLET AVATAR 330 FT-IR spectrophotometer on KBr pallets, and IR spectra of samples in solution were recorded with METTLER TOLEDO ReactIR 45m. Absorption spectra were recorded with a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. Cyclic voltammetry measurement was made with a CHI 600D potentiostat in THF solution using a sweep rate of 100 mV/s, a

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glassy-carbon working electrode, 0.1 M  $[Bu^n_4N][PF_6]$  supporting electrolyte, and a saturated calomel electrode as reference electrode. Under these conditions,  $E_{1/2} = 0.55$  V for the  $[Cp_2Fe]^{0/+}$  couple. The X-band CW-EPR experiments were performed on a JEOL spectrometer JES-FA2000 equipped with a with a liquid nitrogen cryostat system (for 1) and a Bruker EMX plus spectrometer equipped with a He temperature control cryostat system (for **6b**).

Preparation of [(ICy)<sub>3</sub>CoCl]. To a colorless solution of ICy (17.8 g, 76.7 mmol) in THF (100 mL) was added CoCl<sub>2</sub> (3.30 g, 25.6 mmol) at room temperature. The color of the mixture changed to clear blue after stirring for 2 hours. Then, sodium amalgam (25.6 mmol of sodium dissolved in 58.9 g of mercury) was added to the mixture and the resulting mixture was further stirred at room temperature for 24 hours. After which, the color of the mixture changed to brown. The mixture was then filtered through diatomaceous earth. The filtrate was concentrated under vacuum to afford a brown residue that was washed with n-hexane (50 mL) and dried under vacuum to give (ICy)<sub>3</sub>CoCl as a red solid (12.2 g, 61%). The crystals suitable for single-crystal X-ray diffraction study were obtained by diffusing *n*-hexane into its toluene solution at room temperature. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 20 °C):  $\delta$  (ppm) 53.72 (very br), 19.67 (very br), 16.21 (very br), 5.07 (very br), 0.93 (very br), -3.76 (very br), -18.13 (very br). Magnetic susceptibility (C<sub>6</sub>D<sub>6</sub>, 294 K):  $\mu_{eff} = 3.4(1) \mu B$ . Absorption spectrum (THF):  $\lambda_{\text{max}}$ , nm ( $\varepsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 257 (7750), 331 (6840), 432 (5890), 781 (245), 1114 (200), 1338 (200). Anal. Calcd for C<sub>45</sub>H<sub>72</sub>ClCoN<sub>6</sub>: C, 68.29; H, 9.17; N, 10.62; Found: C, 67.81; H, 9.03; N, 10.95%.

28 Preparation of [(ICy)<sub>3</sub>Co(N<sub>2</sub>)] (1). To a red solution of (ICy)<sub>3</sub>CoCl (606 mg, 0.77 mmol) in THF (10 mL) was added 29 KC<sub>8</sub> (124 mg, 0.92 mmol) at -78 °C under a dinitrogen atomo-30 sphere. The mixture was allowed to warm to room temperature 31 and stirring for 7 hours. During the course, the color of the 32 solution changed to dark red. The mixture was then filtered 33 through diatomaceous earth, and the filtrate was concentrated 34 under vacuum to remove all the volatiles to afford 1 as a dark 35 red solid (523 mg, 87%). The crystals of 1 suitable for single-36 crystal X-ray diffraction study were obtained by standing its 37 saturated diethyl ether solution at room temperature overnight. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  (ppm) 20.37 (very br), 38 8.76 (very br), 2.95 (very br), 1.76 ( $v_{1/2}$  = 22 Hz), 0.99 ( $v_{1/2}$  = 39 48 Hz). Magnetic susceptibility (C<sub>6</sub>D<sub>6</sub>, 294 K):  $\mu_{eff} = 2.6(1) \mu B$ . 40 Absorption spectrum (THF):  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 269 41 (6185), 331 (5155), 439 (3135), 662 (904), 1275 (230). IR:  $v_{\rm NN}$ 42  $(KBr) = 1917 \text{ cm}^{-1}$ ,  $v_{NN}$  (THF) = 1921 cm<sup>-1</sup>. Anal. Calcd for 43 C<sub>45</sub>H<sub>72</sub>CoN<sub>8</sub>: C, 68.94; H, 9.26; N, 14.29; Found: C, 68.71; H, 44 9.39; N, 13.70%. The complex [(ICy)<sub>3</sub>Co(N<sub>2</sub>)] shows decom-45 position when standing its  $C_6D_6$  solution in glove-box at 30 °C 46 as indicated by apparent color change from red to green.

**Preparation of**  $[(ICy)_2Co(N_2)_2K]_n$  (2a). To a dark red solution of  $[(ICy)_3Co(N_2)]$  (1.20 g, 1.48 mmol) in THF (10 mL) was added potassium metal (69 mg, 1.78 mmol). The color of the mixture changed from dark red to brownish red after stirring at room temperature for 8 hours. The mixture was filtered through diatomaceous earth, and the filtrate was concentrated under vacuum to afford a brownish red residue that was washed with *n*-pentane and dried under vacuum to give 2a as a red solid (340 mg, 37%). The crystals of 2a·0.5 toluene suitable for single-crystal X-ray diffraction study were obtained by diffusing *n*-hexane into its toluene solution at room tempera-

ture. <sup>1</sup>H NMR (400 MHz,  $d_8$ -THF, 21 °C):  $\delta$  (ppm) 6.76 (br, 4H), 4.95 (br, 4H), 1.99 (br, 8H), 1.69-1.53 (br, 23H, overlap with residual solvent peaks), 1.35-1.16 (br, 14H, overlap with residual solvent peaks). <sup>13</sup>C NMR (101 MHz,  $d_8$ -THF, 21 °C):  $\delta$  (ppm) 211.1, 113.6, 56.25, 34.00, 25.94, 25.87. <sup>15</sup>N NMR (40.56 MHz, C<sub>6</sub>D<sub>6</sub>/THF (1/1, v/v), 27 °C):  $\delta$  (ppm) -33.23, -55.54. Absorption spectrum (THF):  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 269 (9566), 316 (7294), 595 (1267), 656 (1014). IR:  $v_{NN}$  (KBr) = 1807 and 1881 cm<sup>-1</sup>,  $v_{NN}$  (THF) = 1817 and 1890 cm<sup>-1</sup>. Despite of several attempts, satisfied elemental analysis on the C, H and N content of the complex has not been obtained. The complex shows decomposition when standing its C<sub>6</sub>D<sub>6</sub> solution in glove-box at room temperature overnight as indicated by apparent color change from red to brown.

**Preparation of**  $[(ICy)_2Co(N_2)_2Rb]_n$  (2b). To a dark red solution of [(ICy)<sub>3</sub>Co(N<sub>2</sub>)] (1.10 g, 1.40 mmol) in THF (10 mL) was added Rb (146 mg, 1.70 mmol). The color of the mixture changed from dark red to brownish red after stirring at room temperature for 8 hours. The mixture was then filtered through diatomaceous earth, and the filtrate was concentrated under vacuum to afford a brownish red residue that was washed with *n*-pentane and dried under vacuum to give 2b as a red solid (390 mg, 42%). The crystals of 2b.0.5 toluene suitable for single-crystal X-ray diffraction study were obtained by diffusing *n*-hexane into its toluene solution at room temperature.  ${}^{1}H$ NMR (400 MHz,  $d_8$ -THF, 21 °C):  $\delta$  (ppm) 6.75 (br, 4H), 4.96 (br, 4H), 1.99 (br, 8H), 1.54 (br, 27H, overlap with residual solvent peaks), 1.35-1.17 (br, 16H, overlap with residual solvent peaks). <sup>13</sup>C NMR (101 MHz,  $d_{\delta}$ -THF, 21 °C):  $\delta$  (ppm) 214.8, 117.2, 59.93, 37.70, 29.55 (two overlapping peaks). Absorption spectrum (THF):  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 260 (8539), 324 (7427), 479 (3397), 681 (1224). IR:  $v_{\rm NN}$  (KBr) = 1804 and 1888 cm<sup>-1</sup>,  $v_{\rm NN}$  (THF) = 1816 and 1891 cm<sup>-1</sup>. Anal. Calcd for  $C_{67}H_{104}Co_2N_{16}Rb_2$  ([(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>Rb]<sub>2</sub>+toluene): C, 56.57; H, 7.37; N, 15.75; Found: C, 56.35; H, 7.42; N, 15.95%.

**Preparation of**  $[(ICy)_2Co(N_2)_2Cs]_n$  (2c). To a dark red solution of [(ICy)<sub>3</sub>Co(N<sub>2</sub>)] (1.0 g, 1.30 mmol) in THF (10 mL) was added Cs (223 mg, 1.70 mmol). The color of the mixture changed from dark red to brownish red after stirring at room temperature for 8 hours. The mixture was then filtered through diatomaceous earth, and the filtrate was concentrated under vacuum to afford a brownish red residue that was washed with *n*-pentane and dried under vacuum to give 2c as a red solid (591 mg, 64%). The crystals of 2c.0.5 Et<sub>2</sub>O suitable for single-crystal X-ray diffraction study were obtained by diffusing diethyl ether into its THF solution at room temperature. <sup>1</sup>H NMR (400 MHz,  $d_8$ -THF, 21 °C):  $\delta$  (ppm) 6.78 (br, 4H), 4.94 (br, 4H), 1.97 (br, 8H), 1.54 (br, 27H, overlap with residual solvent peaks), 1.35-1.16 (br, 15H, overlap with residual solvent peaks). <sup>13</sup>C NMR (101 MHz,  $d_8$ -THF, 21 °C):  $\delta$  (ppm) 214.6, 117.5, 59.99, 37.73, 29.58, 29.51. <sup>15</sup>N NMR (40.56 MHz, C<sub>6</sub>D<sub>6</sub>/THF (1/1, v/v), 27 °C): δ (ppm) -31.96, -56.23. Absorption spectrum (THF):  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 266 (8510), 314 (7639), 496 (2761), 691 (1408). IR:  $v_{\rm NN}$  (KBr) = 1811 and 1882 cm<sup>-1</sup>,  $v_{\rm NN}$  (THF) = 1817 and 1894 cm<sup>-1</sup>. Anal. Calcd for  $C_{64}H_{106}Co_2Cs_2N_{16}O$  ([ICy<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>Cs]<sub>2</sub>+Et<sub>2</sub>O): C, 51.27; H, 7.13; N, 14.95; Found: C, 51.25; H, 6.67; N, 14.42%.

**Preparation of [(ICy)<sub>3</sub>Co][BF<sub>4</sub>] (3).** *Method A.* To a dark red solution of  $[(ICy)_3Co(N_2)]$  (425 mg, 0.54 mmol) in THF (10 mL) was added  $[Cp_2Fe][BF_4]$  (148 mg, 0.54 mmol). The color of the mixture turned into deep red after stirring at room temperature for 4 hours. The mixture was then concentrated

under vacuum to afford a red residue which was washed with *n*-hexane (10 mL) and Et<sub>2</sub>O (10 mL) to give **3** as a red solid (370 mg, 81%). <sup>1</sup>H NMR (400 MHz,  $d_8$ -THF, 19 °C):  $\delta$  (ppm) 42.44 ( $v_{1/2} = 16$  Hz), -1.91 (very br), -2.79 ( $v_{1/2} = 34$  Hz), -3.14 (very br), -3.16 (very br), -4.31 (very br), -10.79 (very br), -54.66 ( $v_{1/2}$  = 188 Hz). Magnetic susceptibility (C<sub>6</sub>D<sub>6</sub>, 294 K):  $\mu_{\text{eff}} = 3.6(1) \ \mu\text{B}$ . Absorption spectrum (THF):  $\lambda_{\text{max}}$ , nm ( $\varepsilon$ , M  $^{1}$  cm<sup>-1</sup>) = 265 (9290), 292 (7590), 353 (5470), 494 (1990), 785 (164), 1093 (74), 1872 (204). The IR spectra of  $[(ICy)_3Co][BF_4]$  in solid (KBr) did not show obvious peak in the range between 2300 and 1700 cm<sup>-1</sup>. Anal. Calcd for C<sub>45</sub>H<sub>72</sub>BF<sub>4</sub>CoN<sub>6</sub>: C, 64.13; H, 8.61; N, 9.97; Found: C, 63.92; H, 8.54; N, 9.87%. Method B. To a red solution of [(ICy)<sub>3</sub>CoCl] (330 mg, 0.42 mmol) in THF (10 ml) was added  $NaBF_4$  (68 mg, 0.50 mmol). The mixture was stirred at room temperature for 12 hours, and then filtered through diatomaceous earth. The solution was concentrated under vacuum to afford a red residue that was dissolved in THF (5 mL). Diffusion of diethyl ether into the THF solution led to the precipitation of **3** as a red crystalline solid (269 mg, 69%). The <sup>1</sup>H NMR spectrum of the sample prepared in this way is identical to that prepared via Method A.

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Preparation of  $[(ICy)_2Co(N_2)_2K(18-C-6)]$  (4). To a red solution of [(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>K]<sub>n</sub> (152 mg, 0.25 mmol) in THF (10 mL) was added 18-crown-6 (78 mg, 0.30 mmol). The mixture was stirred at room temperature for 4 hours and then concentrated under vacuum to afford a red residue. The residue was washed with *n*-hexane (10 mL), and dried under vacuum to give 4 as a red solid (154 mg, 71%). The crystals of 4 suitable for single-crystal X-ray diffraction study were obtained by diffusing *n*-hexane into its toluene solution at room temperature. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 29 °C):  $\delta$  (ppm) 6.87 (s, 4H), 5.40 (t, J = 11.2 Hz, 4H), 3.33 (s, 24H), 2.43 (d, J = 10.5, 8H), 1.75 (m, 22H, overlap with solvent peaks), 1.48 (m, 9H, overlap with solvent peaks), 1.23 (m, 5H, overlap with solvent peaks); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 29 °C):  $\delta$  (ppm) 213.2, 114.4, 69.83, 56.80, 34.77, 26.67, 26.56. Absorption spectrum (THF):  $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 262 (8115), 326 (6074), 505 (1912), 690 (1116). IR:  $v_{\rm NN}$  (KBr) = 1812 and 1892 cm<sup>-1</sup>,  $v_{\rm NN}$  (THF) = 1828 and 1906 cm<sup>-1</sup>. Anal. Calcd for C<sub>42</sub>H<sub>72</sub>CoKN<sub>8</sub>O<sub>6</sub>: C, 57.12; H, 8.22; N, 12.69; Found: C, 57.59; H, 8.23; N, 12.33%.

Preparation of [(ICy)<sub>2</sub>Co(Me<sub>3</sub>SiNNSiMe<sub>3</sub>)] (6a). To a red solution of [(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>K]<sub>n</sub> (500 mg, 0.81 mmol) in toluene (10 mL) was added Me<sub>3</sub>SiCl (105 mg, 0.97 mmol) at -78 °C. The mixture was allowed to warm to room temperature and stirred for overnight. During the course, the color of the mixture changed from red to light green. The mixture was then filtered through diatomaceous earth and the filtrate was concentrated under vacuum to afford a green residue that was washed with *n*-hexane and dried under vacuum to give **6a** as a green solid (205 mg, 36%). The crystals of 6a suitable for single-crystal X-ray diffraction study were obtained by diffusing *n*-hexane into its toluene solution at room temperature.  ${}^{1}H$ NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 21 °C): δ (ppm) 35.79 (very br), 30.60  $(v_{1/2} = 56 \text{ Hz}), 16.03 (v_{1/2} = 34 \text{ Hz}), 14.16 (v_{1/2} = 35 \text{ Hz}), 4.65$  $(v_{1/2} = 53 \text{ Hz})$ , 3.83 (very br), 3.72 (very br), 1.88  $(v_{1/2} = 33 \text{ Hz})$ Hz), -0.10 ( $v_{1/2}$  = 24 Hz), -0.38 (very br), -1.26 ( $v_{1/2}$  = 28 Hz), -1.87 ( $v_{1/2}$  = 56 Hz), -4.13 ( $v_{1/2}$  = 46 Hz), -4.62 ( $v_{1/2}$  = 40 Hz), -4.86 ( $v_{1/2}$  = 36 Hz), -6.40 ( $v_{1/2}$  = 44 Hz), -7.73 ( $v_{1/2}$  = 47 Hz), -8.11 ( $v_{1/2}$  = 36 Hz), -8.55 ( $v_{1/2}$  = 51 Hz), -10.08 ( $v_{1/2}$  = 39 Hz), -13.65 ( $v_{1/2}$  = 49 Hz), -15.28 ( $v_{1/2}$  = 51 Hz), -24.32 ( $v_{1/2}$  = 58 Hz), -89.12 ( $v_{1/2}$  = 181 Hz). Magnetic susceptibility (C<sub>6</sub>D<sub>6</sub>, 294

K):  $\mu_{eff} = 3.0(2) \,\mu$ B. Absorption spectrum (hexane):  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 269 (6631), 326 (2921), 450 (1384), 574 (1092), 679 (984). Anal. Calcd for C<sub>36</sub>H<sub>66</sub>CoN<sub>6</sub>Si<sub>2</sub>: C, 61.94; H, 9.53; N, 12.04; Found: C, 61.62; H, 9.48; N, 11.36%.

Preparation of [(ICy)<sub>2</sub>Co(Et<sub>3</sub>SiNNSiEt<sub>3</sub>)] (6b). To a red solution of [(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>K]<sub>n</sub> (300 mg, 0.49 mmol) in toluene (10 mL) was added Et<sub>3</sub>SiCl (80 mg, 0.53 mmol) at -78 °C. The mixture was allowed to warm to room temperature and stirred for overnight. During the course, the color of the mixture changed from red to light green. The mixture was then filtered through diatomaceous earth and the filtrate was concentrated under vacuum to afford a green residue. Redissolving the residue in n-hexane (2 mL) gavea green solution that was standing at -29 °C for days to give 6b as a green crystalline solid (75 mg, 19%). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 21 °C):  $\delta$  (ppm) 40.02 (very br), 31.41 ( $v_{1/2}$  = 54 Hz), 17.21 ( $v_{1/2}$  = 12 Hz), 14.21 ( $v_{1/2}$  = 32 Hz), 7.59 (br), 7.57 (br), 6.00 ( $v_{1/2}$  = 18 Hz), 4.47 ( $v_{1/2} = 11$  Hz), 4.01 ( $v_{1/2} = 34$  Hz), 3.11 ( $v_{1/2} = 28$  Hz), 2.53 (br), 2.50 (br), 1.35 (very br), -0.02 ( $v_{1/2} = 23$  Hz), -2.45  $(v_{1/2} = 37 \text{ Hz}), -3.52 \text{ (br)}, -3.55 \text{ (br)}, -4.11 \text{ (}v_{1/2} = 28 \text{ Hz}), -5.28 \text{ Hz})$  $(v_{1/2} = 37 \text{ Hz}), -5.61 (v_{1/2} = 52 \text{ Hz}), -6.23 (v_{1/2} = 23 \text{ Hz}), -6.70$  $(v_{1/2} = 35 \text{ Hz})$ , -8.81  $(v_{1/2} = 31 \text{ Hz})$ , -9.47  $(v_{1/2} = 31 \text{ Hz})$ , -10.44  $(v_{1/2} = 43 \text{ Hz})$ , -16.35  $(v_{1/2} = 37 \text{ Hz})$ , -18.17  $(v_{1/2} = 53 \text{ Hz})$ , -72.58 (very br). Magnetic susceptibility (C<sub>6</sub>D<sub>6</sub>, 294 K):  $\mu_{eff}$  = 2.9(1)  $\mu$ B. Absorption spectrum (hexane):  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup>cm<sup>-1</sup>) = 239 (10940), 284 (7269), 327 (4710), 446 (2110), 571 (533), 674 (944). Anal. Calcd for C42H78CoN6Si2: C, 64.49; H, 10.05; N, 10.74; Found: C, 64.88; H, 10.37; N, 10.83%.

Procedure for the  ${}^{14}N_2 {}^{-15}N_2$  Exchange Experiments of Solid Sample. The crystalline solid of the N<sub>2</sub> complex (1, *ca.* 10 mg) was ground up into a fine powder, and added to 10 mL Schlenk flask. The sample was subjected to vacuum for one minute and then a  ${}^{15}N_2$  atmosphere (2.4 atm.) was introduced. The sample was further kept under the  ${}^{15}N_2$  at room temperature for 14 hours. Their IR spectra indicated the occurrence of  ${}^{14}N_2 {}^{-15}N_2$  exchange (Figures S20).

General Procedures for the  ${}^{14}N_2 {}^{-15}N_2$  Exchange Experiments of Solution Samples. The crystalline solid of (2a-2c, or 4, *ca.* 30 mg) was ground up into a fine powder, and added to 10 mL Schlenk flask. THF (3 ml) was then added to dissolve the sample. The mixture was subjected to a flash vacuum and then a  ${}^{15}N_2$  atmosphere (2.4 atm.) was introduced. The solution was standing under the  ${}^{15}N_2$  at room temperature for 14 hours, and the IR spectrum of the solution indicated the occurrence of  ${}^{14}N_2 {}^{-15}N_2$  exchange (Figures S23, S26, S29 and S32).

General Procedures for the Protonation Reaction of the Cobalt-N<sub>2</sub> Complexes. To a solution of a cobalt-N<sub>2</sub> complex (0.08 mmol) in Et<sub>2</sub>O (2 mL) at -78 °C were added acid (HCl in diethyl ether or TfOH, 1.28 mmol) or room temperature. The mixture was stirred for 2 hours and then extracted with water trice (3 x 3 mL). The content of NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> of the colorless aqueous solution was analyzed by colorimetric methods,<sup>39, 40</sup> and the results are compiled in Table 2.

General Procedures for the Catalytic Reductive Silylation of N<sub>2</sub> Using NHC-Cobalt Complexes as Catalysts. A 50 mL flask was charged with KC<sub>8</sub> (1.35 g, 10 mmol), NHCcobalt complexes (0.005 mmol) and Me<sub>3</sub>SiCl (1.08 g, 10 mmol). Et<sub>2</sub>O (10 mL) was then added. The reaction mixture was stirred at room temperature for 24 hours under 1 atm of N<sub>2</sub> and then filtered through diatomaceous earth. The filtrate was concentrated under vacuum to *ca.* 5 mL and cyclododecane (68 mg, 0.40 mmol) was added as an internal standard.

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The mixture was then subjected to GC analysis to qualify the yield of  $N(SiMe_3)_3$ . The yields are compiled in Table 3.

**Reaction of**  $[(ICy)_2Co(Me_3SiNNSiMe_3)]$  (6a) with Me<sub>3</sub>SiCl and KC<sub>8</sub> under an Argon Atmosphere. A 50 mL flask was charged with  $[(ICy)_2Co(Me_3SiNNSiMe_3)]$  (6a) (75 mg, 0.11 mmol), Me<sub>3</sub>SiCl (5.8 g, 53 mmol), KC<sub>8</sub> (7.1 g, 53 mmol), and Et<sub>2</sub>O (10 mL) under an argon atmosphere. The brownish yellow suspension was kept stirring at room temperature for 24 hours and then filtered through diatomaceous earth. The brown filtrate was concentrated under vacuum to *ca*. 5 mL and cyclododecane (12 mg, 0.07 mmol) was added as the internal standard. The mixture was then subjected to GC analysis to qualify the yield of N(SiMe<sub>3</sub>)<sub>3</sub>. Figure S56 shows the GC graph. The GC yield of N(SiMe<sub>3</sub>)<sub>3</sub> was 85% (relative to nitrogen).

X-Ray Structure Determination. The structures of nine [(ICy)<sub>3</sub>CoCl], complexes  $[(ICy)_3Co(N_2)]$ (1).  $[(ICy)_2Co(N_2)_2K]_n \cdot (0.5)$ (2a·0.5 toluene)<sub>n</sub> toluene), (2b·0.5  $[(ICy)_2Co(N_2)_2Rb]_n \cdot (0.5)$ toluene)<sub>n</sub> toluene),  $[(ICy)_2Co(N_2)_2Cs]_n \cdot (0.5 Et_2O)_n (2c \cdot 0.5 Et_2O), [(ICy)_3Co][BF_4]$ (3),  $[(ICy)_2Co(N_2)_2K(18-C-6)]$  (4),  $[(ICy)_2Co(Me_3SiNNSiMe_3)]$ (6a), and [(ICy)<sub>2</sub>Co(Et<sub>3</sub>SiNNSi Et<sub>3</sub>)] (6b) in Tables S1 and S2 were determined. Crystals were coated with Paratone-N oil and mounted on a Bruker APEX CCD based diffractometer equipped with an Oxford low-temperature apparatus. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentzpolarization and decay. Absorption corrections were applied using SADABS.<sup>41</sup> Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.<sup>42</sup> The metal and first coordination sphere atoms were located from direct-methods E maps. Non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement cycles and during the final cycles were refined anisotropically. Final crystal parameters and agreement factors are reported in Tables S1 and S2.

**Computational Details.** Density functional theory<sup>43</sup> studies have been performed with the ORCA 3.03 program<sup>44</sup> using the BP<sup>45</sup> and B3LYP<sup>46</sup> method. The SVP basis set<sup>47</sup> was used for the N, C and H atoms, and the TZVP basis set<sup>48</sup> was used for the Co and N atoms. The RIJCOSX approximation<sup>49</sup> with matching auxiliary basis sets<sup>47, 50</sup> was employed to accelerate the calculations. Geometry optimization on (ICy)<sub>3</sub>Co(N<sub>2</sub>), [(ICy)<sub>2</sub>Co(N<sub>2</sub>)<sub>2</sub>]<sup>1-</sup>, (ICy)<sub>2</sub>Co(Me<sub>3</sub>SiNNSiMe<sub>3</sub>), and (ICy)<sub>2</sub>Co(NN(SiMe<sub>3</sub>)<sub>2</sub>) were performed and TIGHTSCF was used for SCF calculations.<sup>44</sup> The qualitative MO schemes are shown in Figures S48, and S50-S52, and the single point energies of (ICy)<sub>2</sub>Co(Me<sub>3</sub>SiNNSiMe<sub>3</sub>) and (ICy)<sub>2</sub>Co(NN(SiMe<sub>3</sub>)<sub>2</sub>) are compile in Table S3. Coordinates of the calculated structure are included in the Supporting Information.

# ASSOCIATED CONTENT

**Supporting Information**. The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxx

53 Crystallographic data (CIF)

Table for crystal data, molecular structures, absorption spectra, IR
 spectra, NMR spectra, cyclic voltammogram, qualitative MO
 schemes, Mulliken spin populations, and Cartesian coordinates of
 the optimized structure (PDF)

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Notes

The authors declare no competing financial interests.

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### REFERENCES

- 1 For recent reviews on N<sub>2</sub> activation by metal species, please see: (a) Fryzuk, M. D.; Johnson, S. A. Coord. Chem. Rev. 2000, 200-202, 379-409. (b) Peters, J. C.; Mehn, M. P. In Activation of Small Molecules; Tolman, W. B., Ed.; Wiley: New York, 2006, p. 81-119. (c) Cory Macleod, K.; Holland, P. L. Nat. Chem. 2013, 5, 559-565. (d) Hellman, A.; Honkala, K.; Dahl, S. W.; Christensen, C. H.; Nørskov, J. K.. In Comprehensive Inorganic Chemistry II (Second Edition): From Elements to Applications; Reedijk, J.; Poeppelmeier, K., Eds.; Elsevier: Amsterdam, 2013, Vol. 7, p. 459-474. (e) Giddey, S.; Badwal, S. P. S.; Kulkarni, A. Int. J. Hydrogen Energy, 2013, 38, 14576-14594. (f) Jia, H.-P.; Quardrelli, E. A. Chem. Soc. Rev. 2014, 43, 547-564. (g) Hoffman, B. M.; Lukoyanov, D.; Yang, Z.-Y.; Dean, D. R.; Seefeldt, L. C. Chem. Rev. 2014, 114, 4041-4062. (h) Köthe, C.; Limberg, C. Z. Anorg. Allg. Chem. 2015, 641, 18-30. (i) Khoenkhoen, N.; de Bruin, B.; Reek, J. N. H.; Dzik, W. I. Eur. J. Inorg. Chem. 2015, 567-598. (j) Burford, R. J.; Fryzuk, M. D. Nat. Rev. Chem. 2017, 1, 1-13. (k) Medford, A. J.; Hatzell, M. C. ACS Catal. 2017, 7, 2624-2643. (1) Topics in Organometallic Chemistry-Nitrogen Fixation; Nishibayashi, Y., Ed.; Springer, 2017.
- For recent examples of N<sub>2</sub> activation by metal complexes, please see: (a) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. Nature 2004, 427, 527-530. (b) Knobloch, D. J.; Lobkovsky, E.; Chirik, P. J. Nat. Chem. 2010, 2, 30-35. (c) Anderson, J. S.; Rittle, J.; Peters, J. C. Nature 2013, 501, 84-88. (d) Creutz, S. E.; Peters, J. C. J. Am. Chem. Soc. 2015, 137, 7310-7313. (e) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. Science 2011, 334, 780-783. (f) Čorić, I.; Mercado, B. Q.; Bill, E.; Vinyard, D. J.; Holland, P. L. Nature 2015, 526, 96-99. (g) Shima, T.; Hu, S.-W.; Luo, G.; Kang, X.-H.; Luo, Y.; Hou, Z.-M. Science 2013, 340, 1549-1552. (h) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. Nat. Chem. 2011, 3, 120-125. (i) Lee, Y.; Sloane, F. T.; Blondin, G.; Abboud, K. A.; Serres-García, R.; Murray, L. J. Angew. Chem., Int. Ed. 2015, 54, 1499-1503. (J) Hill, P. J.; Doyle, L. R.; Crawford, A. D.; Myers, W. K.; Ashley, A. E. J. Am. Chem. Soc. 2016, 138, 13521-13524. (k) Klopsch, I.; Kinauer, M.; Finger, M.; Würtele, C.; Schneider, S. Angew. Chem., Int. Ed. 2016, 55, 4786-4789. (1) Duman, L. M.; Farrell, W. S.; Zavalij, P. Y.; Sita, L. R. J. Am. Chem. Soc. 2016, 138, 14856-14859. (m) McSkimming, A.; Harman, W. H. J. Am. Chem. Soc. 2015, 137, 8940-8943. (n) Geri, J. B.; Shanahan, J. P.; Szymczak, N. K. J. Am. Chem. Soc. 2017, 139, 5952-5956.
- For catalytic N<sub>2</sub> fixation reactions catalyzed by cobalt-based catalysts, please see: (a) Hagen, S.; Barfod, R.; Fehrmann, R.; Jacobsen, C. J. H.; Teunissen, H. T.; Ståhl, K.; Chorkendorff, I. *Chem. Commun.* 2002, 1206-1207. (b) Hagen, S.; Barfod, R.; Fehrmann, R.; Jacobsen, C. J. H.; Teunissen, H. T.; Chorkendorff, I. J. Catal. 2003, 214, 327-335. (c) Raróg-Pilecka, W.; Miśkiewicz, E.; Matyszek, M.; Kaszkur, Z.; Kępiński, L.; Kowalczyk, Z. J. Catal. 2006, 237, 207-210. (d) Karolewska, M.; Truszkiewicz, E.; Mierzwa, B.; Kępiński, L.; Raróg-Pilecka, W. Appl.

Catal. A 2012, 445, 280-286. (e) Zybert, M.; Karasińska, M.; Truszkiewicz, E.; Mierzwa, B.; Raróg-Pilecka, W. Pol. J. Chem. Tech. 2015, 17, 138-143. (f) Shiina, K. J. Am. Chem. Soc. 1972, 94, 9266-9267. (g) Siedschlag, R. B.; Bernales, V.; Vogiatzis, K. D.; Planas, N.; Clouston, L. J.; Bill, E.; Gagliardi, L.; Lu, C. C. J. Am. Chem. Soc. 2015, 137, 4638-4641. (h) Imayoshi, R.; Tanaka, H.; Matsuo, Y.; Yuki, M.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Chem. Eur. J. 2015, 21, 8905-8909. (i) Del Castillo, T. J.; Thompson, N. B.; Suess, D. L. M.; Ung, G.; Peters, J. C. Inorg. Chem. 2015, 54, 9256-9262. (j) Kuriyama, S.; Arashiba, K.; Tanaka, H.; Matsuo, Y.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Angew. Chem., Int. Ed. 2016, 55, 14291-14295.

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- For examples of cobalt N<sub>2</sub> complexes, please see refs. 3g-3j, and 4. (a) Yamamoto, A.; Kitazume, S.; Pu, L. S.; Ikeda, S. Chem. Commun. 1967, 79-80. (b) Enemark, J. H.; Davis, B. R.; McGinnety, J. A.; Ibers, J. A. Chem. Commun. 1968, 96-97. (c) Yamamoto, A.; Miura, Y.; Ito, T.; Chen, H.-L.; Iri, K.; Ozawa, F. Organometallics 1983, 2, 1429-1436. (d) Klein, H.-F.; König, H.; Koppert, S.; Ellrich, K.; Riede, J. Organometallics 1987, 6, 1341-1345. (e) Hammer, R.; Klein, H.-F.; Friedrich, P.; Huttner, G. Angew. Chem., Int. Ed. 1977, 16, 485-486. (f) Betley, T. A.; Peters, J. C. J. Am. Chem. Soc. 2003, 125, 10782-10783. (g) Whited, M. T.; Mankad, N. P.; Lee, Y.; Oblad, P. F.; Peters, J. C. Inorg. Chem. 2009, 48, 2507-2517. (h) Suess, D. L. M.; Tsay, C.; Peters, J. C. J. Am. Chem. Soc. 2012, 134, 14158-14164. (i) Fout, A. R.; Basuli, F.; Fan, H.-J.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. Angew. Chem., Int. Ed. 2006, 45, 3291-3295. (j) Ding, K.-Y.; Pierpont, A. W.; Brennessel, W. W.; Lukat-Rodgers, G.; Rodgers, K. R.; Cundari, T. R.; Bill, E.; Holland, P. L. J. Am. Chem. Soc. 2009, 131, 9471-9472. (k) Greenwood, B. P.; Forman, S. I.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. Inorg. Chem. 2009, 48, 6251-6260. (1) Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. J. Am. Chem. Soc. 2010, 132, 44-45. (m) Napoline, J. W.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Chem. Commun. 2013, 49, 4388-4390. (n) Wu, B.; Gramigna, M. K.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Inorg. Chem. 2015, 54, 10909-10917. (o) Alex Rudd, P.; Liu, S.-S.; Gagliardi, L.; Young, V. G.; Jr.; Lu, C. C. J. Am. Chem. Soc. 2011, 133, 20724-20727. (p) Alex Rudd, P.; Planas, N.; Bill, E.; Gagliardi, L.; Lu, C. C. Eur. J. Inorg. Chem. 2013, 3898-3906. (q) Clouston, L. J.; Bernales, V.; Carlson, R. K.; Gagliardi, L.; Lu, C. C. Inorg. Chem. 2015, 54, 9263-9270. (r) Bowman, A. C.; Milsmann, C.; Atienza, C. C. H.; Lobkovsky, E.; Wieghardt, K.; Chirik, P. J. J. Am. Chem. Soc. 2010, 132, 1676-1684. (s) Mo, Z.-B.; Chen, D.-K.; Leng, X.-B.; Deng, L. Organometallics 2012, 31, 7040-7043. (t) Carpenter, A. E.; Margulieux, G. W.; Millard, M. D.; Moore, C. E.; Weidemann, N.; Rheingold, A. L.; Figueroa, J. S. Angew. Chem., Int. Ed. 2012, 51, 9412-9416. (u) Rozenel, S. S.; Padilla, R.; Arnold, J. Inorg. Chem. 2013, 52, 11544-11550. (v) Simler, T.; Braunstein, P.; Danopoulos, A. A. Chem. Commun. 2016, 52, 2717-2720. (w) Ibrahim, A. D.; Tokmic, K.; Brennan, M. R.; Kim, D.-Y.; Matson, E. M.; Nilges, M. J.; Bertke, J. A.; Fout, A. R. Dalton Trans. 2016, 45, 9805-9811.
  - Recently, Peters *et. al.* reported N<sub>2</sub>-functionalization reactions by Ru- and Os-complexes, for reference, please see: Fajardo, Jr, J.; Peters, J. C. J. Am. Chem. Soc. **2017**, *139*, 16105-16108.
    - (a) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* 2000, 100, 39-91. (b) Glorius, F., *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Topics in Organometallic Chemistry, Vol. 21, Springer: Berlin, 2007. (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* 2008, 47, 3122-3172.
  - For references on the alternating pathway, please see: 1f, 1g, 1i, and (a) Chatt, J.; Heath, G. A.; Richards, R. L. J. Chem. Soc., Dalton Trans. 1974, 2074-2082. (b) Dilworth, M. J.; Eady, R. R. Biochem. J. 1991, 277, 465-468. (c) Sellmann, D.; Fürsattel, A. Angew. Chem., Int. Ed. 1999, 38, 2023-2026. (d) Barney, B. M.; McClead, J.; Lukoyanov, D.; Laryukhin, M.; Yang, T.-C.; Dean, D. R.; Hoffman, B. M.; Seefeldt, L. C. Biochemistry 2007, 46, 6784-6794. (e) Field, L. D.; Li, H. L.; Dalgarno, S. T.; Turner, P. Chem. Commun. 2008, 1680-1682. (f) Field, L. D.; Li, H. L.;

Magill, A. M. Inorg. Chem. 2009, 48, 5-7. (g) Yelle, R. B.;
Crossland, J. L.; Szymczak, N. K.; Tyler, D. R. Inorg. Chem.
2009, 48, 861-871. (h) Li, Y.; Li, Y.; Wang, B.-M.; Luo, Y.; Yang, D.-W.; Tong, P.; Zhao, J.-F.; Luo, J.; Zhou, Y.-H.; Chen, S.;
Cheng, F.; Qu, J.-P. Nat. Chem. 2013, 5, 320-326. (i) Luo, Y.; Li,
Y.; Yu, H.; Zhao, J.-F.; Chen, Y.-H.; Hou, Z.-M.; Qu, J.-P. Organometallics 2012, 31, 335-344. (j) Djurdjevic, I.; Einsle, O.;
Decamps, L. Chem. Asian J. 2017, 12, 1447-1455.

- Ouyang, Z.-W.; Cheng, J.; Li, L.-L.; Bao, X.-L.; Deng, L. Chem. Eur. J. 2016, 22, 14162–14165.
- Large magnetic moments were also observed on NHC-Co(0)olefin complexes, see: Sun, J.; Gao, Y.-F.; Deng, L. *Inorg. Chem.* 2017, 56, 10775-10784.
- Pilloni, G.; Toffoletti, A.; Bandoli, G.; Longato, B. *Inorg. Chem.* 2006, 45, 10321-10328.
- Deblon, S.; Liesum, L.; Harmer, J.; Schönberg, H.; Schweiger, A.; Grützmacher, H. Chem. Eur. J. 2002, 8, 601-611.
- (a) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. *J. Am. Chem. Soc.* **2006**, *128*, 756-769. (b) McWilliams, S. F.; Rodgers, K. R.; Lukat-Rodgers, G.; Mercado, B. Q.; Grubel, K.; Holland, P. L. *Inorg. Chem.* **2016**, *55*, 2960-2968.
- Pfirrmann, S.; Limberg, C.; Herwig, C.; Stöβer, R.; Ziemer, B. Angew. Chem., Int. Ed. 2009, 48, 3357-3361.
- 14. Ung, G.; Peters, J. C. Angew. Chem., Int. Ed. 2015, 54, 532-535.
- Hanna, T. E.; Lobkovsky, E.; Chirik, P. J. J. Am. Chem. Soc. 2004, 126, 14688-14689.
- 16. Holland, P. L. Dalton Trans. 2010, 39, 5415-5425.
- For examples, see ref. 14, and (a) Rehder, D.; Woitha, C.; Priebsch, W.; Gailus, H. J. Chem. Soc., Chem. Commun. 1992, 364-365. (b) Yu, R. P.; Darmon, J. M.; Hoyt, J. M.; Margulieux, G. W.; Turner, Z. R.; Chirik, P. J. ACS Catal. 2012, 2, 1760-1764. (c) Egbert, J. D.; O'Hagan, M.; Wiedner, E. S.; Bullock, R. M.; Piro, N. A.; Kassel, W. S.; Mock, M. T. Chem. Commun. 2016, 52, 9343-9346. (d) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Miani, F.; Pelizzi, G. Inorg. Chem. 2000, 39, 3283-3293. (e) Grubel, K.; Brennessel, W. W.; Mercado, B. Q.; Holland, P. L. J. Am. Chem. Soc. 2014, 136, 16807-16816.
- Tang, C. Y.; Thompson, A. L.; Aldridge, S. J. Am. Chem. Soc. 2010, 132, 10578-10591.
- George, T. A.; Rose, D. J.; Chang, Y.-D.; Chen, Q.; Zubieta, J. Inorg. Chem. 1995, 34, 1295-1298.
- 20. Lee, Y.; Mankad, N. P.; Peters, J. C. Nat. Chem. 2010, 2, 558-565.
- 21. Yuki, M.; Miyake, Y.; Nishibayashi, Y. Organometallics 2008, 27, 3947-3953.
- (a) Sun, J.; Luo, L.; Luo, Y.; Deng, L. Angew. Chem., Int. Ed.
   2017, 56, 2720–2724. (b) Mo, Z.-B.; Liu, Y.; Deng, L. Angew. Chem., Int. Ed. 2013, 52, 10845-10849. (c) Mo, Z.-B.; Li, Y.-X.; Lee, H.-K.; Deng, L. Organometallics 2011, 30, 4687-4694.
- (a) Pezeshk, A.; Greenaway, F. T.; Vincow, G. Inorg. Chem. 1978, 17, 3421-3425. (b) Cibian, M.; Hanan, G. S. Chem. Eur. J. 2015, 21, 9474-9481.
- For examples, please see refs. 3a, 3h-3j, 3l, 4f, 13, and: (a) Chatt, J.; Leigh, G. J. J. Organomet. Chem. 1975, 84, C11-C12. (b) Chatt, J.; Diamantis, A. A.; Heath, G. A.; Hooper, N. E.; Leigh, G. J.; J. Chem. Soc., Dalton Trans. 1977, 688-697. (c) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. J. Am. Chem. Soc. 2005, 127, 7901-7911. (d) Tanaka, H.; Sasada, A.; Kouno, T.; Yuki, M.; Miyake, Y.; Nakanishi, H.; Nishibayashi, Y.; Yoshizawa, K. J. Am. Chem. Soc. 2011, 133, 3498-3506. (e) Liao, Q.; Saffon-Merceron, N.; Mézailles, N. Angew. Chem., Int. Ed. 2014, 53, 14206–14210. (f) Rittle, J.; Peters, J. C. J. Am. Chem. Soc. 2016, 138, 4243-4248. (g) Bhattacharya, P.; Prokopchuk, D. E.; Mock, M. T. Coord. Chem. Rev. 2017, 334, 67-83.
- 25. Collin, R. L.; Lipscomb, W. N. Acta Crystallogr. 1951, 4, 10-14.
- Walsh, P. J.; Hollander, F. J.; Bergman, R. G. J. Am. Chem. Soc. 1990, 112, 894-896.
- 27. Baumann, W.; Michalik, D.; Reiβ, F.; Schulz, A.; Villinger, A.

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Angew. Chem., Int. Ed. 2014, 53, 3250-3253.

- Klein, H.-F.; Helwig, M.; Koch, U.; Flörke, U.; Haupt, H.-J. Z. Naturforsch. 1993, 48b, 778-784.
- Sadique, A. R.; Gregory, E. A.; Brennessel, W. W.; Holland, P. L. J. Am. Chem. Soc. 2007, 129, 8112-8121.
- Tomson, N. C.; Williams, K. D.; Dai, X.-L.; Sproules, S.; De-Beer, S.; Warren, T. H.; Wieghardt, K. *Chem. Sci.* 2015, *6*, 2474-2478.
- 31. Dickson, R. S.; Ibers, J. A. J. Am. Chem. Soc. 1972, 94, 2988-2993.
- Avenier, P.; Taoufik, M.; Lesage, A.; Solans-Monfort, X.; Baudouin, A.; de Mallmann, A.; Veyre, L.; Basset, J. M.; Eisenstein, O.; Emsley, L.; Quadrelli, E. A. *Science* 2007, *317*, 1056-1060.
- For reviews on transition-metal diazene complexes, please see:
   (a) Sutton, D. *Chem. Rev.* 1993, *93*, 995-1022. (b) Dilworth, J. R. *Coord. Chem. Rev.* 2017, *330*, 53-94.
- (a) Pappas, I.; Chirik, P. J. J. Am. Chem. Soc. 2016, 138, 13379-13389. (b) Chalkley, M. J.; Del Castillo, T. J.; Matson, B. D.; Roddy, J; P.; Peters, J. C. ACS Cent. Sci. 2017, 3, 217-223.
- 35. Araake, R.; Sakadani, K.; Tada, M.; Sakai, Y.; Ohki, Y. J. Am. Chem. Soc. 2017, 139, 5596-5606.
- Ortega, N.; Richter, C.; Glorius, F. Org. Lett. 2013, 15, 1776-1779.
- Schwindt, M. A.; Lejon, T.; Hegedus, L. S. Organometallics 1990, 9, 2814-2819.
- (a) Evans, D. F. J. Chem. Soc. 1959, 2003-2005. (b) Sur, S. K. J. Magn. Reson. 1989, 82, 169-173.
- 39. Weatherburu, M. W. Anal. Chem. 1967, 39, 971-974.

- 40. Watt, G. W.; Chrisp, J. D. Anal. Chem. 1952, 24, 2006-2008.
- Sheldrick, G. M. SADABS: Program for empirical absorption correction of area detector data; University of Göttingen: Germany, 1996.
- Sheldrick, G. M. SHELXTL 5.10 for Windows NT: Structure determination software programs; Bruker Analytical X-ray systems, Inc.: Madison, Wisconsin, USA, 1997.
- 43. (a) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864-B871.
  (b) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133-A1138.
- Neese, F., ORCA-an ab initio, Density Functional and Semiempirical Program Package (v. 3.0.3), Max-Planck Institute for Bioinorganic Chemistry: Mülheim an der Ruhr, Germany, 2015.
- 45. (a) Vosko, S. H.; Wilk, L.; Nusair, M. Can. J. Phys. 1980, 58, 1200-1211. (b) Becke, A. D. Phys. Rev. A 1988, 38, 3098-3100.
  (c) Perdew, J. Phys. Rev. B: Condens. Matter 1986, 33, 8822-8824.
- (a) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785-789.
- 47. Schäfer, A.; Horn, H.; Ahlrichs, R. J. Chem. Phys. 1992, 97, 2571-2577.
- Schäfer, A.; Huber, C.; Ahlrichs, R. J. Chem. Phys. 1994, 100, 5829-5835.
- Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Chem. Phys. 2009, 356, 98-109.
- 50. Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.

