# Ketenimine Formation Catalyzed by a High-Valent Cobalt Carbene in Bulky Alkoxide Ligand Environment

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S Supporting Information

**ABSTRACT:** High-valent cobalt carbene  $Co(OR)_2(=CPh_2)$  (OR = OC<sup>t</sup>Bu<sub>2</sub>Ph) undergoes reaction with various isocyanides CNR' (CNR' = 2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide, 2-chloro-6methylphenyl isocyanide, adamantyl isocyanide) to yield the corresponding ketenimine. The reaction is accompanied by the formation of cobalt bis(alkoxide) bis(isocyanide) complexes Co(OR)<sub>2</sub>(CNR)<sub>2</sub>, which were independently synthesized and characterized. DFT calculations suggest the mechanism proceeds through isocyanide binding to Co, followed by intramolecular insertion into the Co-carbene bond to form the ketenimine. We have also conducted an investigation of the catalytic formation of ketenimines at room temperature using mixtures of diazoalkanes (diphenyldiazomethane, methyl diazo(phenyl)acetate, and ethyl diazoacetate) and isocyanides (2,6-dimethylphenyl isocyanide, 4-



methoxyphenyl isocyanide, adamantyl isocyanide, cyclohexyl isocyanide, and benzyl isocyanide). While no catalytic reactivity was observed for diphenyldiazomethane, ester-substituted diazoalkanes (diazoesters) demonstrate catalytic turnover. Relatively high yields are observed for the reactions involving bulkier aliphatic substrates adamantyl and cyclohexyl isocyanides. Mechanistic studies suggest that the lack of catalytic reactivity involving diphenyldiazomethane results from the inability of Co(OR)<sub>2</sub>(CNR)<sub>2</sub> to undergo carbene formation upon reaction with N<sub>2</sub>CPh<sub>2</sub>. In contrast, facile reaction is observed between  $Co(OR)_2(CNR)_2$  and diazoesters, which enables the overall catalytic reactivity.

# INTRODUCTION

Ketenimines  $R^{1}(R^{2})C = C = NR^{3}$  are reactive organic compounds isoelectronic with ketenes  $R^1(R^2)C=\check{C}=O$  and allenes  $R^{1}(R^{2})C = C = CR^{3}(R^{4})$ . Similar to ketenes, ketenimines exhibit dipolar reactivity featuring electrophilic behavior at the central carbon and nucleophilic behavior at the terminal carbon.<sup>1</sup> Ketenimines have been shown to undergo a multitude of transformations, including nucleophilic and radical additions,<sup>2</sup> electrocyclic ring closure reactions,<sup>3</sup> and cycloadditions.<sup>1,4</sup> Due to their reactive nature, ketenimines can serve as highly useful synthons in the production of nitrogencontaining molecules.<sup>5</sup> A variety of synthetic routes toward ketenimines were developed to enable their utilization, including Wittig reaction with isocyanates,<sup>6</sup> silylation of enolizable nitriles,7 aza-Claisen rearrangement of N-sulfonyl-N-allylynamides,<sup>8</sup> and others.<sup>1,9</sup> One of the earliest reported synthetic pathways toward ketenimines involved coupling of carbenes with isocyanides.<sup>1,10</sup> While this reaction is possible under thermal or photochemical conditions,<sup>1,10</sup> transition metal catalysis under ambient conditions generally enables higher yields and selectivity for the formation of the desired product. Transition-metal-mediated formation of ketenimines from isocyanides and metal-carbenes was also reported (see Figure 1 for selected examples);<sup>11,12</sup> however, a common problem in transition-metal-catalyzed formation of ketenimines

is product coordination to the metal that inhibits catalytic performance, especially at room temperature. For complexes of Fischer carbenes, the need to restore Fischer carbene functionality constitutes another obstacle to the catalytic performance.<sup>13</sup> Thus, catalytic formation of ketenimines via metal-catalyzed coupling of diazoalkane-derived carbenes with isocyanides is rare and mostly limited to *tert*-butyl isocyanide.<sup>12</sup> In this manuscript, we describe highly efficient formation of a variety of ketenimines, obtained by coupling of a well-defined cobalt-carbene functionality with isocyanides. We also demonstrate that the combination of several different isocyanides and diazoesters enables catalytic formation of ketenimines in the presence of a cobalt bis(alkoxide) complex.

We investigate group transfer reactivity of middle and late transition metal complexes in bulky alkoxide ligand environments.<sup>14</sup> Due to the weak-field nature of the alkoxide ligand, and low-coordination geometries enabled by their steric bulk, iron and chromium complexes were active in nitrene transfer catalysis to yield azoarenes and carbodiimides.<sup>15</sup> We have also reported synthesis, characterization, and initial reactivity of the first high-valent cobalt carbene complex  $Co(OR)_2$ (=CPh<sub>2</sub>) (2, Scheme 1).<sup>16</sup> While the combined spectroscopic and

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Ör(CO)₅



CMe(OMe) Me CNR R = Cyclohexyl

Ċr(CO)₅

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Figure 1. Examples of ketenimine-forming reactions between metalcarbenes and isocyanides.<sup>11c,d,e,1</sup>

Scheme 1. Synthesis of Ketenimines 6-9 and Isocyanide Complexes 3-5<sup>a</sup>



 $^{a}$ OR = OC<sup>t</sup>Bu<sub>2</sub>Ph.

theoretical study indicated significant radical character on the carbene functionality, only sluggish cyclopropanation reactivity with styrene was observed. We postulated that it is the steric hindrance around the metal-carbene which was responsible for the lack of coupling with styrene, and decided to pursue reactivity with a smaller  $(\eta^1)$  substrate, isocyanide. Herein we demonstrate that  $Co(OR)_2$  (=CPh<sub>2</sub>) undergoes efficient carbene transfer with a variety of isocyanides to form ketenimines in high yields. Theoretical investigations reveal

that the reaction proceeds via the initial coordination of isocyanide to the metal center, followed by intramolecular C-C coupling. We also show that for diphenyldiazomethane only one turnover is obtained while the use of ethyl diazoacetate and methyl diazo(phenyl)acetate leads to catalytic formation of ketenimines.

#### EXPERIMENTAL SECTION

General Methods and Characterization. All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox or by standard Schlenk line procedures. Cobalt chloride, ethyl diazoacetate (15% solution in toluene), 2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide, 2-chloro-6-methylphenyl isocyanide, benzyl isocyanide, cyclohexyl isocyanide, trimethoxybenzene, and hexamethylbenzene were purchased from Sigma-Aldrich. Adamantyl isocyanide was purchased from Alfa Aesar. The syntheses of complexes 1 and 2 were reported previously.<sup>14d,16</sup> Diphenyldiazo-methane<sup>17</sup> and methyl diazo(phenyl)acetate<sup>18</sup> were synthesized according to a reported literature procedure. All solvents were purchased from Fisher Scientific and of HPLC grade. The solvents were purified using an MBRAUN solvent purification system and stored over 3 Å molecular sieves. Deuterated benzene was purchased from Cambridge Laboratories, degassed under argon, and stored over 3 Å molecular sieves. Ethyl diazoacetate was degassed under argon before use. The complexes were characterized using NMR, IR, UV/vis spectroscopies, X-ray crystallography, elemental analysis, and solution magnetometry by the Evans method. NMR and GC-MS spectra were recorded at the Lumigen Instrument Center (Wayne State University). NMR was performed on a Varian Mercury or Agilent 400 MHz Spectrometer in C<sub>6</sub>D<sub>6</sub> at room temperature. Chemical shifts and coupling constants (J) were reported in parts per million ( $\delta$ ) and hertz (Hz), respectively. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. UV-visible spectra were obtained on a Shimadzu UV-1800 spectrometer. Elemental analyses were performed by Midwest Microlab LLC. Formation of the ketenimines and organic byproducts was confirmed by GC-MS using Agilent 6890N spectrometer, Thermo TG5MS 30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m column, 7683 series injector, and Agilent 5973 detector

Synthesis of Co(OR)<sub>2</sub>(CN(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>))<sub>2</sub> (3). A THF solution of 2,6-dimethylphenyl isocyanide (66 mg, 0.50 mmol) was added to a stirred blue THF solution of cobalt bis(alkoxide) 1 (80 mg, 0.13 mmol). There was an immediate color change of the solution to dark red. The reaction was stirred for 2 h, after which the volatiles were removed in vacuo. The resulting red residue was dissolved in diethyl ether (henceforth, ether), filtered, and placed in the freezer overnight at -35°C to afford X-ray quality crystals of 3 (84 mg, 88% yield). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  20.88 (2H,  $\Delta v_{1/2}$  38 Hz, OR-Ph), 19.02 (36H,  $\Delta v_{1/2}$  229 Hz, <sup>t</sup>Bu), 17.80 (4H,  $\Delta v_{1/2}$  22 Hz, OR-Ph), 10.34 (4H,  $\Delta v_{1/2}$  20 Hz, OR-Ph), 2.92 (6H,  $\Delta v_{1/2}$  20 Hz, CNR-Ph), -6.81 (12H,  $\Delta v_{1/2}$  40 Hz, Me). IR (cm<sup>-1</sup>): 2955 (w), 2878 (w), 2816 (s), 2160 (s), 1489 (w), 1381 (m), 1280 (w), 1088 (m), 165 (s), 1018 (m), 734 (w), 903 (w), 841 (w). 772 (s), 741 (s), 702 (s), 478 (m).  $\lambda_{\text{max}} (\varepsilon_{\text{M}})$  747 (661), 550 (612), 469 (417).  $\mu_{\text{eff}} = 3.9 \pm 0.4 \ \mu\text{B}$  (calcd 3.9). Anal. Calcd for C<sub>48</sub>H<sub>64</sub>N<sub>2</sub>O<sub>2</sub>Co: C, 75.9; H, 8.5; N, 3.7. Found: C, 75.5; H, 8.4; N, 3.8.

Synthesis of Co(OR)<sub>2</sub>(CN(4-MeOC<sub>6</sub>H<sub>4</sub>))<sub>2</sub> (4). A green THF solution of 4-methoxyphenyl isocyanide (56 mg, 0.42 mmol) was added to a stirred blue THF solution of cobalt bis(alkoxide) 1 (67 mg, 0.11 mmol). There was an immediate color change of the solution to dark red. The reaction was stirred for 2.5 h, upon which the volatiles were removed in vacuo. The resulting red residue was dissolved in ether, filtered, and placed in the freezer overnight at -35°C. The residue was washed several times with cold hexanes. The hexane washings were removed in vacuo, the ether decant added, and the solution put in the freezer overnight at  $-35^{\circ}$ C. This was repeated twice more before giving red X-ray quality crystals (64 mg, 78% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  19.96 (2H,  $\Delta \nu_{1/2}$  128 Hz, OR–Ph), 18.95 (36H,  $\Delta \nu_{1/2}$  288 Hz, <sup>1</sup>Bu), 16.93 (4H,  $\Delta \nu_{1/2}$  22 Hz, OR–Ph), 9.84 (4H,  $\Delta \nu_{1/2}$  19 Hz, OR–Ph), 2.72 (6H,  $\Delta \nu_{1/2}$  58 Hz, OMe), 1.58 (8H,  $\Delta \nu_{1/2}$  23 Hz, CNR–Ph). IR (cm<sup>-1</sup>): 2955 (w), 2901 (w), 2168 (s), 1605 (w), 1505 (s), 1381 (w), 1303 (w), 1258 (s), 1065 (s), 1018 (m), 857 (s), 748 (m), 718 (m), 687 (w).  $\lambda_{max}$  ( $\epsilon_{M}$ ) 731 (990), 550 (555).  $\mu_{eff}$  = 3.6 ± 0.4)  $\mu_{B}$  (calcd 3.9). Anal. Calcd for C<sub>46</sub>H<sub>60</sub>N<sub>2</sub>O<sub>4</sub>Co: C, 72.3; H, 7.9; N, 3.7. Found: C, 71.1; H, 7.5; N, 4.6.

Synthesis of Co(OR)<sub>2</sub>(CNAd)<sub>2</sub> (5). A THF solution of adamantyl isocyanide (74 mg, 0.46 mmol) was added to a stirred blue THF solution of cobalt bis(alkoxide) 1 (74 mg, 0.12 mmol). There was an immediate color change of the solution to dark red. The reaction was stirred for 2 h, upon which the volatiles were removed in vacuo. The resulting red residue was dissolved in ether, filtered, and placed in the freezer overnight at  $-35^{\circ}$ C to give a red powder (75 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  20.90 (2H,  $\Delta v_{1/2}$  39 Hz, OR–Ph), 19.26 (36H,  $\Delta v_{1/2}$  204 Hz, <sup>t</sup>Bu), 16.78 (4H,  $\Delta v_{1/2}$  16 Hz, OR–Ph), 10.02 (4H,  $\Delta v_{1/2}$  14 Hz, OR–Ph), 0.63 (2H,  $\Delta v_{1/2}$  33 Hz, Ad), -0.63 (6H,  $\Delta v_{1/2}$  23 Hz, Ad), -1.25 (6H,  $\Delta v_{1/2}$  20 Hz, Ad), -2.11 (6H,  $\Delta v_{1/2}$  3 Hz, Ad), -4.50 (10H,  $\Delta v_{1/2}$  83 Hz, Ad). IR (cm<sup>-1</sup>): 2956 (w), 2902 (w), 2855 (w), 2122 (s),1450 (m), 1350 (w), 1312 (w), 1072 (3), 887(w), 710 (w).  $\lambda_{max}$  ( $\varepsilon_{M}$ ) 751 (240), 550 (340), 464 (160).  $\mu_{\text{eff}} = 3.9 \pm 0.4 \mu_{\text{B}}$  (calcd 3.9). Anal. Calcd for  $C_{52}H_{76}N_2O_2Co$ : C, 76.2; H, 9.3; N, 3.4. Found: C, 75.9; H, 9.2; N, 3.4.

**Reaction of 3 and Diphenyldiazomethane.** A  $C_6D_6$  solution of diphenyldiazomethane (0.74 mL, 0.173 M) was added to a stirring dark red  $C_6D_6$  solution of **3** (49 mg, 0.064 mmol). The reaction was stirred at room temperature for 5 h; no color change was observed. <sup>1</sup>H NMR showed unreacted diphenyldiazomethane and peaks characteristic of **3**.

**Reaction of 5 and Ethyl Diazoacetate.** A toluene solution of ethyl diazoacetate (0.2 mL, 1.1 M) was added to a stirring dark red  $C_6D_6$  solution of **5** (90 mg, 0.11 mmol). A color change to dark brown with vigorous gas formation was observed. Reaction was stirred for 1 h at room temperature. NMR of the crude reaction mixture shows formation of ketenimine, although peaks were broadened. The reaction was filtered through a plug of silica. <sup>1</sup>H NMR of the filtered reaction mixture showed formation of ketenimine.

**Reaction of 1 and Methyl Diazo(phenyl)acetate.** A hexane solution of methyl diazo(phenyl)acetate (0.13 mL, 0.6 M) was added to a stirring blue hexane solution of **1** (50 mg, 0.078 mmol). The reaction turns teal immediately and dark brown within a minute. The reaction was stirred at room temperature for 1 h. Volatiles were removed in vacuo. NMR of the crude reaction mixture was taken in  $C_6D_6$  showing a hypothesized carbene (peaks assigned below) along with unreacted diazoester. Volatiles were removed in vacuo and the dark residue was dissolved in ether. Recrystallization at -35 °C gave colorless crystals of the respective olefin (13% yield). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  37.73 (3 H,  $\Delta v_{1/2}$  384 Hz, PhCCO<sub>2</sub>Me), 21.95 (6H,  $\Delta v_{1/2}$  180 Hz, *Ph*CCO<sub>2</sub>Me), 16.67 (2H,  $\Delta v_{1/2}$  28 Hz, Ph–OR), 12.77 (2H,  $\Delta v_{1/2}$  36 Hz, Ph–OR), 9.49 (36H,  $\Delta v_{1/2}$  220 Hz, <sup>1</sup>Bu–OR), 9.30 (4H, Ph–OR), 5.26 (2H,  $\Delta v_{1/2}$  36 Hz, Ph–OR).

General Procedure for Stoichiometric Formation of Ketenimines 6–9. A  $C_6D_6$  solution of the isocyanide (3 equiv) and TMB (1 equiv) was added to a stirring  $C_6D_6$  solution of 2 (1 equiv). A notable color change occurred to either dark red (2,6-dimethylphenyl isocyanide and adamantyl isocyanide) or dark brown (4-methoxyphenyl isocyanide and 2-chloro-6-methylphenyl isocyanide). NMR of the reaction mixture was taken after 1 h and yield was calculated with reference to 1,3,5-trimethoxybenzene (TMB). Products  $6^{19}$  and  $7^{20}$  have been previously reported. The formation of ketenimines was also confirmed by GC-MS in all cases.

Characterization of  $Ph_2C==C=N(2,6-Me_2C_6H_3)$  (6). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.36 (d, J = 4 Hz, 4H, o-Ph), 7.13 (t, J = 4 Hz, 4H, m-Ph), 7.01 (t, J = 4 Hz, 2H, p-Ph), 6.83 (bs, 3H, NC<sub>6</sub>H<sub>3</sub>), 2.22 (s, 6H, Me).

Characterization of  $Ph_2C=C=N(4-OMe-C_6H_4)$  (7). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.44 (d, J = 8 Hz, 4H, o-Ph), 7.28 (d, J = 8 Hz,

2H, o-NC<sub>6</sub>H<sub>4</sub>), 7.12 (t, J = 8 Hz, 4H, p-Ph), 7.02 (t, J = 8 Hz, 1H, m-NC<sub>6</sub>H<sub>3</sub>), 3.19 (s, 3H, Me).

Characterization of  $Ph_2C==C==N(2-Cf-Me-C_6H_3)$  (8). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.40 (d, J = 8 Hz, 4H, o-Ph), 7.13 (t, J = 8 Hz, 4H, m-C<sub>6</sub>H<sub>3</sub>), 7.01 (t, J = 8 Hz, 2H, p-Ph), 6.99 (d, J = 8 Hz, 1H, m-NC<sub>6</sub>H<sub>3</sub>Cl), 6.63 (d, 1H, m-NC<sub>6</sub>H<sub>3</sub>Me), 2.06 (s, 3H, Me).

Characterization of  $Ph_2C=C=NAd$  (9). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.50 (d, J = 4 Hz, 4H, o-Ph), 7.19 (t, J = 4 Hz, 4H, m- $C_6H_3$ ), 7.03 (t, J = 4 Hz, 2H, p-Ph), 1.89 (s, 6H), 1.83 (s, 3H), 1.41 (t, J = 12 Hz, 6H).

General Procedure for Catalytic Formation of Ketenimines in Table 1. A  $C_6D_6$  solution of the isocyanide (12 equiv), diazoalkane/diazoester (10 equiv), and TMB or hexamethylbenzene (HMB) (1 equiv) was added to a stirred  $C_6D_6$  solution of 2. A notable color change occurred to either dark red (2,6-dimethylphenyl isocyanide and adamantyl isocyanide) or dark brown (4-methoxyphenyl isocyanide, cyclohexyl isocyanide, and benzyl isocyanide) for methyl diazo(phenyl)acetate. A color change to orange occurred with ethyl diazoacetate and all isocyanides except 4-methoxyphenyl isocyanide and 2,6-dimethylphenyl isocyanide. Evolution of N2 was observed in most cases. NMR of the reaction mixture was taken after 24 h, and yield was calculated with reference to internal standard. Major byproducts were identified by NMR and GC-MS. All products were confirmed by GC-MS analysis of silica plugs of each reaction. Isolation of the ketenimines was done by removing all volatiles, dissolving in a minimal amount of hexane, and passing through a Pasteur pipet full of silica. HOR and standard were eluted via addition of 50 mL of hexane to solvent. Product was obtained by passing a 40 mL solution 5-10% ether/hexane solution through the pipet. Low isolated yields were obtained due to the high co-elution with HOR, standard, and byproducts.

Synthesis and characterization of ketenimines Ph<sub>2</sub>C=C=N(2,6- $Me_2C_6H_3$ ),  $Ph_2C=C=N(4-OMe-C_6H_4)$ , and  $Ph_2C=C=NCy$  have Cl-6-Me-C<sub>6</sub>H<sub>3</sub>), Ph<sub>2</sub>C=C=NAd, (Ph)(COOMe)C=C=NAd,  $(Ph)(COOMe)C=C=N(4-OMe-C_6H_4), (Ph)(COOMe)C=C=$ NCy, (Ph)(COOMe)C=C=NBn, (H)(COOEt)C=C=NAd, (H)(COOEt)C=C=NCy, and (H)(COOEt)C=C=NBn have not been previously reported. All ketenimines reported in this work were identified by <sup>1</sup>H NMR and GC-MS. The ketenimines which were obtained in high yields in catalytic reactions (Ph)(COOMe)C= C=NCy and (H)(COOEt)C=C=NAd were further purified, isolated as yellow oils, and characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR. NMR signals for the observed ketenimines in entries 1 and 2 are reported above (for the stoichiometric reactions); they were also observed in the catalytic NMR reactions. However, some of the peaks were found to be hidden under starting material, due to the poor catalytic performance with 2,6-dimethylphenyl isocyanide. For entry 3, Ph<sub>2</sub>C=C=NCy, the shifts were confirmed by comparing to literature reports:<sup>21'1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.46 (d, 4H, o-Ph), 7.18 (t, 4H, m-Ph), 7.08 (t, 2H, p-Ph), 3.29 (m, 1H, N-αCy), 1.87 (m, 2H, equatorial NCy), 1.51 (m, 2H, NCy), 1.3 (m, 3H, N-Cy), 0.96 (m, 3H, NCy).

Characterization of (*Ph*)(COOMe)C==C==N(4-OMe-C<sub>6</sub>H<sub>4</sub>) (entry 5). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.91 (d, J = 8 Hz, 2H, o-Ph), 7.19 (t, J = 8 Hz, 2H, *m*-Ph), 7.07 (d, J = 8 Hz, 2H, *p*-Ph-CNR), 7.03 (t, J = 8 Hz, 1H, *p*-Ph), 6.51 (d, J = 8 Hz, 2H, *m*-Ph-CNR), 3.44 (3H, s, CO<sub>2</sub>Me), 3.13 (s, 3H, Ar-OMe).

Characterization of (Ph)(COOMe)C=C=NAd (entry 6). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.95 (d, J = 8 Hz, 2H, o-Ph), 7.27 (t, J = 8 Hz, 2H, m-Ph), 7.02 (t, J = 8 Hz, 1H, p-Ph), 3.52 (s, 3H, Me), 1.84 (s, 6H, Ad), 1.77 (s, 3H, Ad), 1.35 (s, 6H, Ad).

Characterization of (Ph)(COOMe)C=C=NCy (entry 7). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.91 (d, J = 8 Hz, 2H, o-Ph), 7.24 (t, J = 8 Hz, 2H, m-Ph), 7.02 (t, J = 8 Hz, 1H, p-Ph), 3.33 (sept, J = 4 Hz, 1H, CNH), 1.69 (m, 2H, Cy), 1.43 (m, 2H, Cy), 1.32 (m, 3H), 1.19 (m, 1H), 0.92 (m, 3H). <sup>13</sup>C NMR (100 MHz,  $C_6D_6$ )  $\delta$  172.13 (-C=C=N-), 168.92 (COOMe), 132.65 (*ipso*-Ph), 129.20 (o-Ph), 127.5 (m-Ph), 126.2 (p-Ph), 61.40 (COOMe), 51.36 (Cy), 34.05 (Cy), 25.58 (Cy), 24.55 (Cy).

Characterization of (Ph)(COOMe)C=C=NBn (entry 8). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  7.68 (d, J = 8 Hz, 2H, *o*-Ph), 7.16 (t, J = 8 Hz, 2H, *m*-Ph), 7.02 (m, 5H, Ph–Bn), 6.98 (t, J = 8 Hz, 1H, *p*-Ph), 3.44 (s, 3H, OMe).

Characterization of (H)(COOEt)C=C=NAd (entry 11). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  4.28 (s, 1H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.07 (q, *J* = 8 Hz, 2H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.78 (s, 3H, Ad), 1.76 (s, 6H, Ad), 1.36 (s, 6H, Ad), 1.01 (q, *J* = 8 Hz, 3H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz,  $C_6D_6$ )  $\delta$  171.87 (-C=C=N-), 169.11 (COOEt), 61.64 (Ad), 60.21 (OCH<sub>2</sub>CH<sub>3</sub>), 51.82 (-C=C=N-), 44.06 (Ad), 36.24 (Ad), 30.32 (Ad), 14.93 (OCH<sub>2</sub>CH<sub>3</sub>).

Characterization of (H)(COOEt)C==C=NCy (entry 12). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ )  $\delta$  4.22 (s, 1H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.06 (q, *J* = 8 Hz, 2H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.17 (sept, *J* = 4 Hz, 1H, CNH), 1.58 (m, 2H, Cy), 1.41 (m, 2H, Cy), 1.25 (m, 3H), 1.16 (m, 1H), 0.98 (q, *J* = 8 Hz, 3H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.91 (t, *J* = 8 Hz, 3H).

Characterization of (H)(COOEt)C=C=NBn (entry 13). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.14 (s, 2H, Bn), 4.10(s, 1H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.00 (q, *J* = 8 Hz, 2H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.94 (q, *J* = 8 Hz, 3H, HCO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Computational Details.** Density functional theory calculations were performed using Gaussian  $09^{22}$  with default grids and density fitting. Geometry optimizations at the OPBE/6-31G(d) level of theory<sup>23</sup> were followed by stability calculations to ensure the reliability of the wave function.<sup>24</sup> Frequency calculations at the same level of theory were used to verify stationary points as minima or first-order saddle points based on the harmonic frequencies<sup>25</sup> and to derive thermodynamic corrections using standard approximations to estimate enthalpies, entropies, and Gibbs free energies.<sup>26</sup> Follow-up single point calculations using the much more flexible def2-TZVP basis set<sup>27</sup> included dispersion corrections based on the APFD functional<sup>28</sup> and implicit solvation effects (benzene) based on the SMD model.<sup>37</sup> Triple-zeta free energies were estimated as  $G_{TZ} = G_{DZ} - E_{DZ} + E_{TZ}$ . Cartesian coordinates for all optimized structures, as well as a summary of all thermodynamic values, may be found in the Supporting Information.

#### RESULTS AND DISCUSSION

Stoichiometric Reactivity of Co(OR)<sub>2</sub>(=CPh<sub>2</sub>) with Isocyanides. Carbene complex 2 was obtained by the treatment of cobalt bis(alkoxide) complex 1 with diphenyldiazomethane (Scheme 1), as previously described.<sup>16</sup> Treatment of 2 with 1 equiv of 2,6-dimethylphenyl isocyanide (CN(2,6- $Me_2Ph$ ) led to the formation of ketenimine 6 in approximately 30% yield by <sup>1</sup>H NMR. The formation of ketenimine 6 was also confirmed by GC-MS. Notably, formation of free ketenimine 6 did not require heating or photolysis, as in previously reported cases. We hypothesized that the low yield of 6 could be due to the isocyanide coordination to the  $[Co(OR)_2]$  fragment. To test this hypothesis, complex 2 was treated with excess isocyanide (3 equiv). The reaction with excess isocyanide led to the formation of 6 in 85% yield (Figure 2). In addition to ketenimine 6, formation of the paramagnetic complex  $Co(OR)_2(CN(2,6-Me_2Ph))_2$  (3) was also observed in the reaction mixture by <sup>1</sup>H NMR. Pure 3 was independently synthesized by treatment of 1 with excess isocyanide, and isolated in 88% yield (Scheme 1).

Clean formation of ketenimine **3** prompted us to investigate the reaction of **2** with other isocyanides. Reaction of **2** with excess 4-methoxyphenyl isocyanide formed ketenimine **7** in 97% yield. Similarly, treatment of **2** with 2-chloro-6methylphenyl isocyanide afforded ketenimine **8** in 66% yield. The reaction of **2** with alkyl (adamantyl) isocyanide produced ketenimine **9** in 86% yield. As for ketenimine **6**, the formation of **7-9** was quantified by <sup>1</sup>H NMR spectroscopy and supported by GC-MS. In all cases, <sup>1</sup>H NMR spectra of the reaction



**Figure 2.** NMR spectra demonstrating clean formation of ketenimine product (spectrum in blue) from 2,6-dimethylphenylisocyanide (spectrum in green). The reaction was conducted in the presence of an internal standard 1,3,5-trimethoxybenzene (TMB).

mixtures contained peaks attributable to the isocyanide complexes, whose formation was confirmed by their independent syntheses (Scheme 1).

Synthesis and Characterization of Co(OR)<sub>2</sub>(CNR')<sub>2</sub> Complexes. Treatment of blue THF solutions of Co- $(OR)_2(THF)_2$  (1) with excess 2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide, and adamantyl isocyanide immediately led to the formation of red solutions from which isocyanide complexes  $Co(OR)_2(CNR')_2$  3 (R' = 2,6-Me<sub>2</sub>Ph), 4 (R' = 4-MeOPh), and 5 (R' = Ad) were isolated in good yields by recrystallization from ether (Scheme 1). While a similar color change was observed for 2-chloro-6-methylphenyl isocyanide, we were not able to isolate pure  $Co(OR)_2(CN(2 Cl-6-MePh)_2$  in a crystalline state. Cobalt-isocyanide complexes were characterized by <sup>1</sup>H NMR spectroscopy, Xray crystallography (3 and 4), solution magnetic moment determination (by Evans method), IR/UV-vis spectroscopy, and elemental analysis. All complexes exhibited well-resolved paramagnetic NMR spectra spread over approximately 30 ppm allowing full assignment of the resonances. Thus, alkoxide tertbutyl (OC<sup>t</sup>Bu<sub>2</sub>Ph) resonances appears at 19.02, 18.95, and 19.26 ppm for 3, 4, and 5, respectively, whereas the alkoxide phenyl (OC<sup>t</sup>Bu<sub>2</sub>Ph) group gives rise to three distinct resonances at 20.88/19.96/20.90 ppm, 17.80/16.93/16.78 ppm, and 10.34/9.84/10.02 ppm for 3/4/5, respectively. As noted above, these well-resolved spectra allow identification of bis(isocyanide) complexes as byproducts in ketenimine formation. The IR spectra of compounds 3 and 4 contain  $C \equiv N$  signals at 2160 and 2168 cm<sup>-1</sup>, respectively. These values are close to those previously reported for cobalt(II) aryl isocyanide complexes.<sup>29\*</sup> Adamantyl isocyanide complex 5 demonstrates a lower-energy C $\equiv$ N stretch at 2122 cm<sup>-1</sup>. Assuming  $C_{2\nu}$  symmetry, two signals for the CN stretch should be expected. However, only one is observed for all the compounds, albeit somewhat broadened. It is possible that the peaks appear very close to each other, as was observed for the iron analogue of 3.

The structures of the isocyanide complexes 3 and 4 are presented in Figure 3 below. Both complexes crystallize in the  $C_2/c$  space group. The cobalt center occupies a special position in both structures, resulting in the crystallographic  $C_2$  symmetry. The geometry around the metal for both 3 and 4



Figure 3. X-ray structures of complexes 3 and 4, 50% probability ellipsoids. H atoms were omitted for clarity. Selected bond distances (Å) and angles (deg) for 3/4: Co-O1 1.850(1)/1.848(1), Co-C1 2.039(2)/2.023(2), C1-N1 1.151(2)/1.157(2), O1-Co-O1' 118.4(1)/118.8(1), C1-Co-C1' 103.4(1)/97.5(1).

is distorted tetrahedral, with slightly wider O–Co–O angles and slightly narrower C–Co–C angles as compared with tetrahedral values of 109.5°. Nearly identical Co–O bonds and O–Co–O angles are observed (see Figure 3). In contrast, the structures exhibit differences in Co–C bonds (2.039(2) Å for 3 vs 2.023(2) Å for 4 and C–Co–C angles (103.4(1) ° for 3 and 97.5(1) ° for 4), presumably due to the steric bulk imposed by 2,6-dimethylphenyl isocyanide.

Magnetic properties of complexes 3-5 in solution were investigated by Evans method. Spin states of Co- $(OR)_2(CNR')_2$  complexes are of interest due to the combination of weak-field (alkoxide) and strong-field (isocyanide) ligands. We note that all other previously reported complexes featuring OC<sup>t</sup>Bu<sub>2</sub>Ph ligation were high-spin with the notable exception of the low-spin trigonal planar  $Co(OR)_2$  (=CPh)<sub>2</sub> (S = 1/2).<sup>16</sup> In contrast, tetra-coordinate cobalt complexes featuring predominantly isocyanide ligation have been shown to be low-spin.<sup>30</sup> All complexes exhibit magnetic moments of  $3.9 \pm 0.4 \mu_{\rm B} (C_6 D_{60} \text{ room temperature})$ , consistent with high-spin d<sup>7</sup> Co(II) complexes. To understand this finding, we probed the doublet and quartet states using density functional theory. Spin state splitting is a well-known challenge for DFT,<sup>31</sup> so we opted to use the OPBE functional that has shown excellent performance for predicting spin states.<sup>23</sup> These were performed on a model of 3 and 4 with phenyl isocyanide instead of the substituted isocyanides, and both mono- (10) and bis-isocyanide (11) complexes were calculated. At the OPBE-APFD-SMD(benzene)/def2-TZVP// OPBE/6-31G(d) level of theory<sup>23,27,28,37</sup> 10 is predicted to favor the low-spin doublet by 3.9 kcal/mol, whereas 11 favors the high-spin quartet by 3.0 kcal/mol. The finding that more strong-field isocyanide ligands induced a low- to high-spin switch was surprising. To understand this, we compared the frontier orbitals of the doublet species of both 10 and 11 as shown in Figure 4. The most important change in the electronic structure between these two is the 0.8 eV increase in the HOMO of 10 due to the nonbonding to antibonding character induced by binding of the second isocyanide. This causes this orbital to become the SOMO in the doublet of 11. Importantly, this compresses the energy gap of these three d orbitals from 1.7 eV in 10 to 1.1 eV in 11 that enables the high-spin configuration.

Computational Studies on the Mechanism of Carbene Transfer. Previous DFT studies on the mechanism of ketenimine formation by Fernández and co-workers



Figure 4. Frontier orbital diagram for doublet species of 10 (left) and 11 (right). Orbital energies are based on alpha orbital energies only, and isosurface plots use isocontour value of 0.05 a.u.

demonstrated that isocyanide inserts directly into the metalcarbene bond for Cr, Fe, and W-based Fischer-type carbenes, followed by a series of isomerizations to afford the N-bound ketenimine complex.<sup>13</sup> The complexes they studied were coordinately saturated based on 18-electron arguments, so isocyanide binding to the metal prior to insertion was not likely. Due to the low-coordination environment of 2, one can envision two mechanisms: (i) direct insertion of phenyl isocyanide into the metal-carbene bond to afford ketenimine bound to Co through the C=C bond (12) or (ii) phenyl isocyanide binding to Co to afford an isocyanide/carbene complex (13) that then undergoes intramolecular insertion to afford 12. Once the ketenimine is formed it can bind through the C=C bond, the C=N bond (14) or the N lone pair (15)(Figure 5). Because we anticipate multiple spin states may be relevant based on our calculations for 10 and 11, doublets and guartets were calculated and will be denoted with subscript D and Q. The full model of 2 is used (i.e., no ligand simplifications), and phenyl isocyanide was used as the isocyanide in all calculations.

 $2_D$  is predicted to be lower in energy than  $2_Q$  by 3.9 kcal/ mol, consistent with our earlier experimental and computational studies.<sup>16</sup> Binding of isocyanide to this carbene to afford  $13_{\rm D}$  is calculated to be exergonic by 0.3 kcal/mol. No stable minimum corresponding to  $13_{Q}$  was located on the potential energy surface. This is reasonable because more  $\sigma$ -antibonding orbitals are occupied in the high-spin state, leading to a less favorable enthalpy for isocyanide binding. The barrier for formation of  $13_{D}$  (2–13–TS<sub>D</sub>) is 17.9 kcal/mol relative to  $2_{D}$ and isocyanide. From intermediate 13<sub>D</sub>, insertion into the metal-carbene bond is relatively facile with a barrier (13-12- $TS_{D}$ ) of 7.2 kcal/mol, leading to  $12_{D}$  that is lower in free energy by 9.3 kcal/mol. However, 12 prefers the quartet state over the doublet state by 6.9 kcal/mol. On the quartet surface, the direct insertion barrier  $(2-12-TS_0)$  is 32.4 kcal/mol, inconsistent with the mild experimental conditions and much higher in energy than the two-step pathway found on the doublet surface. We were unsuccessful in locating a direct insertion transition state on the doublet surface; all attempts

Article



**Figure 5.** Potential energy surface for the formation of various isomers of the Co ketenimine complex from **2** and phenyl isocyanide. Gibbs free energies in kcal/mol where black indicates doublet energies and red indicates quartet energies. Transition states that were not explicitly located are denoted with \*.



Figure 6. Potential energy surface for the formation of isocyanide (right) and diazoalkane (left) adducts from 160. Gibbs free energies in kcal/mol.

collapsed to  $13-12-TS_D$ . A spin-state crossing must occur along the reaction path from  $2_D$  to  $12_Q$ . In principle, one should locate this minimum energy crossing point (MECP) to make sure it is not rate-limiting.<sup>32</sup> However, single point calculations show that the quartet is higher in energy than the doublet at the stationary points prior to  $12 (2-13-TS_D, 13_D)$ , and  $13-12-TS_D$  implying that the MECP occurs after both barriers on the doublet surface, so we did not explicitly locate this point. Once the C=C bound isomer is formed, isomerization to C=N bound isomer 14 is exergonic by 8.6 kcal/mol and that to N-bound isomer 15 is exergonic by 13.6 kcal/mol. Barriers for these isomerizations were not located but both should be accessible through ketenimine dissociation (*vide infra*). A summary of these free energies are shown in Figure 5.

 $2_{\rm D}$  has Mulliken spins of 1.3 on the Co and -0.4 on the carbene C, consistent with a formulation between low-spin Co(IV) and intermediate-spin Co(III).<sup>16</sup> The Mulliken spins in  $13_{\rm D}$  are similar at 1.1 and -0.3, suggesting no qualitative change in the electronic structure upon isocyanide binding. After the C–C bond forms in  $12_{\rm Q}$  the spin on Co is 2.3 (and 2.9 if you include spins on the alkoxide ligands) and negligible on the ketenimine. This agrees with the expected value for a high-spin, S = 3/2 Co(II) ion and suggests that reductive elimination is concurrent with insertion.

Next, we probed how this ketenimine adduct accesses the bis(isocyanide) complex (11) or reforms 2 enabling catalysis. Loss of ketenimine from  $12_Q$  to form  $Co(OR)_2$  (16) is exergonic by 12.6 kcal/mol. The barrier for this reaction, 12- $16-TS_{Q'}$  is only 5.8 kcal/mol. Ketenimine loss from intermediate  $\mathbf{12}_{\mathbf{Q}}$  is therefore predicted to be kinetically more facile than the various isomerizations. Once  $16_0$  forms, it can bind either phenyl isocyanide to form 10 or diphenyldiazomethane to form a monodiazoalkane complex coordinated through the terminal nitrogen lone pair that we denote as 17. We were unable to locate stationary points corresponding to an associative mechanism with either of these ligands and species  $12_Q$ .  $10_D$  is exothermic relative to  $16_Q$  and free isocyanide by 19.9 kcal/mol, and the barrier for binding on the quartet surface, **10–16–TS**<sub>Q</sub>, is 6.5 kcal/mol. Bis(isocyanide) complex 110 is calculated to be slightly exergonic relative to  $10_D$  by 0.3 kcal/mol. Both doublet and quartet states were probed for 17, and the quartet was found to be favored over the doublet by 2.1 kcal/mol. The formation of this adduct from  $16_0$  is only exergonic by 4.9 kcal/mol with a small barrier of 3.9 kcal/mol. Alternative isomers of the monodiazoalkane complex were calculated to be endergonic (see Supporting Information).<sup>33</sup> Figure 6 summarizes these thermodynamics, though it should be noted that it is possible that other pathways could connect these intermediates. In light of the

#### Table 1. Formation of Ketenimines via Carbene Group Transfer to Isocyanides

R <sup>1</sup>		10-20 mol% Co(OR) <sub>2</sub>	(THF) <sub>2</sub>	$R^1$ $R^3$ $R^1$ $R^1$	$R^2$	R <sup>1</sup> R	2
$\mathbb{R}^2$	$C = N_2 + xs. CNR^3$	C <sub>6</sub> D <sub>6</sub> , RT, 24 hrs	→ }	$R^2 \xrightarrow{C=C=N} + \xrightarrow{R^2}$	+ >	- +	
		- N <sub>2</sub>		R* R*	K.		$\mathbb{R}^2$
Entry	Diazoalkane	Isocvanide	Mol%	Ketenimine	Yield	 Conver	Bv-products
		·····	cat		(%)	-sion <sup>a</sup>	( /  /   ) (%)
1	Ph	$\rightarrow$	10	Ph	6	24	<i>—/—/6</i>
	Ph	CN		Ph			
2			10		9	53	<i>—/—/</i> 10
				Ph T			
3			10	Ph	5	16	<i>—/—/5</i>
4	Ph		10	Ph,	NR	—	<i>//</i> 5
	MeO <sub>2</sub> C						
5			10	Ph	28	50	5/15/5
				C=C=N-OMe MeO <sub>2</sub> C			
6			10	Ph	35	30	/2/
			10	c=c=n			
				MeO <sub>2</sub> C			
7a			10	Ph	42	90	16/—/17
7b			20		84	100	5/5/5
8		CN	10	Ph	19	78	_/_/
		Ph		MeO <sub>2</sub> C Ph			
9	H	$\searrow$	10	н, >	NR	-	<i>//</i>
	EtO <sub>2</sub> C	CN-		EtO <sub>2</sub> C			
10			10	/	NR		
			10				//
11			10		100	100	//
							, ,
122			10	EtO <sub>2</sub> C	48	48	//
120		cn—〈 〉	20	c=c=n-		74	
120			20	EtO <sub>2</sub> C´	/1	/1	//
13		CN-	10	Ph	28	38	_/_/_
		Ph		EtO <sub>2</sub> C Ph			

<sup>a</sup>Percent conversion of diazoalkane.

calculated thermal accessibility of the diazoalkane complex relative to the bis(isocyanide) complex (+15 kcal/mol) that we worried might be a thermodynamic sink, we explored the catalytic potential of these species.

**Catalytic Reactivity in Carbene Transfer.** As the stoichiometric formation of ketenimines proved high-yielding for all substrates studied and based on the insight from our DFT calculations, we probed next the catalytic potential of this reaction. The reactions were conducted by combining isocyanides, diazoalkanes, and 10–20 mol % of complex 1 in  $C_6D_6$ , in the presence of an internal standard. Three different diazoalkanes were evaluated, diphenyldiazomethane, methyl diazo(phenyl)acetate, and ethyl diazoacetate. Several different

isocyanides were also tested, specifically two aryl isocyanides (2,6-dimethylphenyl isocyanide and 4-methoxyphenyl isocyanide) and three alkyl isocyanides differing by a steric bulk of the attached R group, including tertiary adamantyl isocyanide, secondary cyclohexyl isocyanide, and primary benzyl isocyanide. The results are summarized in Table 1.

Combination of diphenyldiazomethane with 2,6-dimethylphenyl isocyanide, 4-methoxyphenyl isocyanide, or cyclohexyl isocyanide (Table 1, entries 1–3) shows only stoichiometric or substoichiometric formation of the corresponding ketenimines. In contrast, combining methyl diazo(phenyl)acetate with alkyl isocyanides (Table 1, entries 6–8) in the presence of 10 mol % of Co(OR)<sub>2</sub>(THF)<sub>2</sub> for 24 h at room temperature led to

catalytic reactivity. The number of turnovers differs slightly for different alkyl isocyanides. For adamantyl and cyclohexyl isocyanides, approximately 3-4 turnovers were observed (yields of 35 and 42%, respectively). Increasing catalyst loading for a selected isocyanide (cyclohexyl) to 20 mol % increases the yield of the product for cyclohexyl isocyanide to 84%, suggesting a similar number of turnovers. Two turnovers are observed for the less bulky benzyl isocyanide. Electronic factors may explain the improved reactivity of alkyl versus aryl isocyanides: the strongly donating alkyl isocyanides will give less stable bis(isocyanide) complex 11, thus generating the carbene complex and improving catalysis. Interestingly, aryl isocyanides demonstrate divergent reactivity with methyl diazo(phenyl)acetate: Whereas no ketenimine formation was observed with 2,6-dimethylphenyl isocyanide (entry 4), 4methoxyphenyl isocyanide demonstrated approximately three turnovers (entry 5). We note that the control experiments combining methyl diazo(phenyl)acetate and adamantyl or cyclohexyl isocyanide in the absence of complex 1 demonstrated no formation of ketenimine and/or conversion of the diazoalkane under the identical reaction conditions (RT,  $C_6D_{60}$ 24 h).

Next, the reactivity of commercially available ethyl diazoacetate was studied. Adamantyl isocyanide forms the corresponding product in quantitative yield (10 turnovers, entry 11). Cyclohexyl isocyanide led to the formation of the corresponding ketenimine in 48% yield (Table 1, entry 12a); increasing catalyst concentration to 20 mol % (entry 12b) results in 71% yield of the ketenimine product. The reaction of ethyl diazoacetate with benzyl isocyanide demonstrates approximately 3 turnovers (28% yield of the product). Similar to methyl diazo(phenyl)acetate, no ketenimine product formation was observed for the mixture of ethyl diazoacetate and 2,6-dimethylphenyl isocyanide (Table 1, entry 9). As for methyl diazo(phenyl)acetate, control experiments for ethyl diazoacetate indicate no reactivity in the absence of  $Co-(OR)_2(THF)_2$ .

Interrogation of the NMR spectra and GC-MS traces of the reaction mixtures allowed us to shed light on the nature of some of the byproducts in these transformations. Reactions involving diphenyldiazomethane led primarily to the formation of benzophenone azine as a byproduct. Little or no byproducts were observed for ethyl diazoacetate, with reaction mixtures comprising of starting materials and/or ketenimine products. In contrast, significant amounts of byproducts were observed for methyl diazo(phenyl)acetate, which included trans-olefin (dimethyl 2,3-diphenylfumarate), cis-olefin (dimethyl 2,3diphenylmaleate), and the corresponding azine (dimethyl 2,2'-(hydrazine-1,2-diylidene)bis(2-phenylacetate)). Formation of both olefins and azine as carbene homocoupling byproducts was previously reported for methyl diazo(phenyl)acetate.<sup>34</sup> The formation of *trans*-olefin was also confirmed by the X-ray structure determination (see below). The reactions involving cyclohexyl and 4-methoxyphenyl isocyanide resulted in the most significant yields of these byproducts. For the reaction of cyclohexyl isocyanide using 10 mol % of 1 (entry 7a), approximately 90% of the diazoester is converted, with formation of cis-olefin and azine in 16% and 17% yield, respectively. Increasing the catalyst loading to 20 mol % (entry 7b) not only increased the yield of the ketenimine but also diminished formation of these byproducts, giving each in  $\sim 5\%$ yield. With 4-methoxyphenyl isocyanide, 50% of the diazoester is converted with formation of the trans-olefin, cis-olefin, and

azine in 5, 15, and 5%, respectively. Only a small amount of *trans*-olefin is formed with adamantyl isocyanide (<2%), and no byproducts are observed in the NMR with benzyl isocyanide. The lack of observed olefin/azine byproducts for benzyl isocyanide/methyl diazo(phenyl)acetate reaction is puzzling, particularly due to the discrepancy between the high conversion rate and relatively low ketenimine yield. This discrepancy likely implies formation of additional byproducts (for example, resulting from further reactions of unstable ketenimine) which we were not able to identify. In most of the cases, formation of ROH was also observed by NMR and GC-MS.

Mechanistic experiments were conducted next, aiming at (1)understanding the origins of the diverging reactivity between diphenyldiazomethane and diazoesters and (2) attempting to shed light on the reaction intermediates. As  $Co(OR)_2(CNR')_2$ was previously observed in all of the reactions involving  $[Co(OR)_2]$  complexes and isocyanides, we hypothesized that  $Co(OR)_2(CNR')_2$  constitutes a key species in the reaction mechanism, and that it may exhibit different reactivity with different diazoalkanes. Mixing 3 with diphenyldiazomethane in THF or C<sub>6</sub>D<sub>6</sub> retained the red color of isocyanide complexes and failed to produce black-brown color indicative of 2. Furthermore, NMR spectra of the reaction mixtures contained peaks indicative of unreacted 3 and diphenyldiazomethane, further supporting the lack of reactivity of  $Co(OR)_2(CNR')_2$ with N<sub>2</sub>CPh<sub>2</sub>. In contrast, treatment of  $Co(OR)_2(CNAd)_2$  (5) with ethyl diazoacetate enabled turnover. The NMR monitoring of the reaction indicated formation of the ketenimine product, and disappearance of the starting complex (see the Supporting Information for details).

We also attempted to shed light on the nature of the corresponding carbene intermediates. Postulating that methyl diazo(phenyl)acetate will lead to the more stable carbene (as compared with ethyl diazoacetate), we interrogated its stoichiometric reactivity with 1. Adding methyl diazo(phenyl)-acetate to a stirring solution of 1 in  $C_6D_6$  showed an immediate color change to dark brown; the color change was accompanied by the evolution of N<sub>2</sub>. NMR characterization of the crude reaction mixture suggests formation of the major paramagnetic product, postulated  $[Co(OR)_2(=C(CO_2Me)-Ph]$  (18, Figure 7), along with unreacted diazoalkane (see the Supporting Information for details). The UV–vis spectrum contains a single peak around 560 nm. We note the overall similarity between the UV–vis of 18 and that of 2, which also contained a single peak in the visible, albeit significantly



Figure 7. Proposed formation and decomposition of 18 to give 19.

bathochromically shifted, is observed for the UV–vis of **18**. Monitoring this reaction over 50 min showed gradual disappearance of the peak at 560 nm and growth of a peak at 648 nm. Attempted crystallization of "Co(OR)<sub>2</sub>(=  $C(CO_2Me)Ph$ " yielded instead crystals of *trans*-olefin **19**, whose characterization was previously reported.<sup>35</sup> The structure of **19** is also given in Figure 7. Somewhat different structures of dimethyl 2,3-diphenylfumarate were previously reported;<sup>36</sup> the structure of *cis*-olefin was also described.<sup>34b</sup> Since olefin is a known product of a transient carbene, particularly in the absence of other substrates, olefin formation further supports the existence of the transient carbene in our system.

On the basis of the considerations presented above, a simple reaction mechanism is proposed (Scheme 2). A carbene

Scheme 2. Proposed Catalytic Mechanism for the Formation of Ketenimines with  $[Co(OR)_2]$  System



complex, initially formed from 1 and diazoalkane, undergoes an intramolecular reaction with an isocyanide to form ketenimine product. In the presence of excess isocyanide, isocyanides replace ketenimine to give  $Co(OR)_2(CNR')_2$ .  $Co(OR)_2(CNR')_2$  next reacts with diazoesters to restore carbene functionality, releasing two equivalents of isocyanide and dinitrogen molecule.

### SUMMARY AND CONCLUSIONS

In summary, we demonstrated that our high-valent cobaltcarbene complex  $Co(OR)_2$  (=CPh<sub>2</sub>) forms ketenimines upon reaction with different isocyanides. NMR monitoring of the reaction reveals that ketenimine formation is accompanied by the formation of the cobalt isocyanide complexes Co- $(OR)_2(CNR')_2$ , which were independently synthesized and characterized. Density functional theory calculations shed light on the mechanism of ketenimine formation, suggesting that isocyanide coordinates to the carbene complex prior to C-C bond formation. This intramolecular insertion is concurrent with reductive elimination, resulting in a ketenimine adduct that is calculated to lose this new ligand in a facile manner. Catalytic formation of a variety of ketenimines was observed for mixtures of diazoalkanes and isocyanides, with Co- $(OR)_2(THF)_2$  as a precatalyst. The reactivity depends on both substrates. While mixtures of diphenyldiazomethane with both alkyl and aryl isocyanides form ketenimines in stoichiometric amounts only, both methyl diazo(phenyl)acetate and ethyl diazoacetate enable several turnovers. The highest number of turnovers was observed for tertiary and secondary alkyl isocyanide (adamantyl and cyclohexyl). In contrast, low to moderate reactivity was observed for the less

bulky alkyl (benzyl) or aryl (*p*-methoxy) isocyanides. Significant amounts of byproducts (*cis-* and *trans-*olefin and azine) were observed in the catalytic reactions, particularly for methyl diazo(phenyl)ester. Our future studies will focus on the design of more efficient ketenimine formation catalysts. We anticipate that varying the nature of the carbene precursor will help to suppress the formation of byproducts and may lead to higher yields of ketenimines. The nature of the alkoxide ligand and the metal in  $M(OR)_2(=CR'R'')$  reactive intermediates will be also varied, targeting more efficient carbene transfer catalysts.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00911.

Details on the X-ray data collection, solution and refinement, details on Evans measurements, NMR spectra, GC-MS traces, and computational details (PDF)

Cartesian coordinates (XYZ)

### Accession Codes

CCDC 1884461–1884463 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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