# **ORGANOMETALLICS**

## Preparation and Reactivity Study of Chromium(III), Iron(II), and Cobalt(II) Complexes of 1,3-Bis(imino)benzimidazol-2-ylidene and 1,3-Bis(imino)pyrimidin-2-ylidene

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**Supporting Information** 



**ABSTRACT:** Chromium(III), iron(II), and cobalt(II) complexes of bis(imino)benzimidazol-2-ylidene and bis(imino)pyrimidin-2-ylidene were successfully prepared by reaction of either the benzimidazolium or pyrimidinium salts or the corresponding copper complexes with the respective metal halide. X-ray diffraction analysis of the Cr(III) complex of the pyrimidin-2-ylidene ligand demonstrated, for the first time, the ability of bis(imino)carbene-type ligands to coordinate to metal centers in a tridentate fashion. The coordination mode of these ligands was surprisingly highly dependent on the nature of both the metal and the ligand itself. The activity of these complexes in ethylene polymerization was assessed under ambient conditions (room temperature and 1 atm of  $C_2H_4$ ) using methylaluminoxane as cocatalyst. In contrast to the iron and cobalt complexes, both chromium complexes were active in ethylene polymerization.

#### **INTRODUCTION**

Iron, cobalt, and chromium complexes of tridentate 2,6bis(imino)pyridine ligands (A) exhibit excellent activities for the polymerization of ethylene, attaining those observed for group 4 metallocene catalysts.<sup>1–5</sup> The modular nature of ligand A allows for easy variations of the steric and electronic properties of these post-metallocene catalytic systems. This has led to several important structure-property relationships.<sup>1,5,6</sup> Despite the excellent activities in ethylene polymerization, complexes of A exhibit poor thermal stability, which results in short lifetimes at elevated temperatures.<sup>2,5,7,8</sup> Although mitigated by the choice of the right ligand substitution pattern, the ability of these bis(imino)pyridine complexes to either homopolymerize or copolymerize  $\alpha$ -olefins remains extremely poor and unacceptable for commercial applications.<sup>5,8,10</sup> Early to middle transition-metal complexes of the related 2,6-bis(Nheterocyclic carbene)pyridine ligand (B) have also been reported.<sup>11-13</sup> Although less active than complexes of A, they are excellent catalysts for the oligomerization of ethylene, with the best performance realized with chromium.

In light of those results and considering that transition-metal complexes of N-heterocyclic carbenes (NHC) have shown excellent thermal stability and enhanced performance over their



phosphine counterparts,<sup>14</sup> our group has recently prepared transition-metal complexes of ligand C and reported their activity in ethylene polymerization.<sup>15,16</sup> The ligand features a five-membered imidazol-2-ylidene ring, with angles that afford a coordination sphere notably more opened than that of the related six-membered pyridine ring of A and B, possibly

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facilitating coordination and insertion of  $\alpha$ -olefins. Furthermore, the imine fragments impart  $\pi$ -acidic character to the ligand, resulting in metal complexes that are more electropositive, and thus presumably more active, than complexes of **B**.

We have recently reported the isolation and the catalytic ethylene polymerization activity of chromium(III), iron(II), and cobalt(II) complexes of acyclic 1,3-bis[1-(2,6-dimethylphenylimino)ethyl and benzyl]imidazol-2-ylidene (C; R = Me, Ph).<sup>16</sup> In all complexes prepared, ligand C exclusively coordinated to the metal in a bidentate fashion, through the carbenoid carbon and through one of the imine substituents, as confirmed by their solid-state structures. Upon activation with methylaluminoxane, only chromium complexes gave polyethylene at moderate activities, with the electron-poor phenyl derivative (C; R = Ph) found to enhance the activity of the complex over that observed for the related methyl analogue (C; R = Me).<sup>16</sup> This suggests that a decrease in the electron-donating or an increase in the *π*-accepting capability of the ligand may produce more active olefin polymerization catalysts.

We therefore became interested in preparing Cr, Fe, and Co complexes of the less  $\sigma$ -electron donating benzimidazol-2ylidene ligand **D**,<sup>17</sup> which would result in more electropositive metal center. The increased steric bulk of the fused benzene ring may also facilitate coordination of the second imine fragment, leading to complexes that closely resemble those of **A**. This could also possibly be achieved by substituting the fivemembered imidazol-2-ylidene by a six-membered pyrimidin-2ylidene ring. We herein report the synthesis of the benzimidazolium and pyrimidinium salts, both precursors to carbenes **D** and **E**, respectively. The corresponding complexes of chromium, iron, and cobalt (and copper as transmetalating agent) were prepared and their catalytic activities assessed.

#### RESULTS AND DISCUSSION

Complexes of 1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazol-2-ylidene. Reaction of N-(2,6dimethylphenyl)acetimidoyl chloride with (1-(2,6dimethylphenylimino)ethyl)benzimidazole (1a) in toluene afforded the desired product 2a as a white solid (Scheme 1),

Scheme 1. Synthesis of 1,3-Bis[1-(2,6dimethylphenylimino)ethyl]benzimidazolium Chloride (2a)



with a  $\nu_{C=N}$  stretching frequency of 1690 cm<sup>-1</sup>. The <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum of **2a** revealed the presence of both the *E*,*Z* and *E*,*E* isomers. The central benzimidazolium proton (-NCHN-) of the symmetric *E*,*E* isomer resonates at a characteristic downfield chemical shift of 12.27 ppm. The benzimidazol-2-ylidene protons were observed at 9.02 (-NCCHCH-) and 7.75 ppm (-NCCHCH-), with the corresponding carbon resonances at 118.9 (-NCCHCH-) and 129.2 ppm (-NCCHCH-). The central azolium and iminic carbon nuclei resonate at 126.1 and 153.2 ppm, respectively.

Copper complex 3a was prepared by adding a THF solution of sodium hexamethyldisilazide (NaHMDS) and CuI to a

suspension of the benzimidazolium salt 2a at low temperature (Scheme 2). The desired copper adduct 3a was isolated in 28% yield as an orange solid. The presence of two vibrational stretching frequency bands at 1668 and 1653 cm<sup>-1</sup> in the FTIR spectrum of 3a suggests a bimetallic structure with the ligand coordinated to each metal center in a bidentate fashion with bridging iodides, as observed in a copper complex of C.<sup>15</sup> Upon coordination, the characteristic downfield <sup>1</sup>H NMR resonance for the central imidazolium proton disappeared. The benzimidazol-2-ylidene proton resonances shifted to lower frequencies at 8.44 (-NCCHCH-) and 7.41 ppm (-NCCHCH-). The corresponding <sup>13</sup>C NMR resonances shifted upfield to 116.3 and 125.3 ppm, respectively. The iminic carbon resonance shifted to a higher frequency by 3.4 ppm to 156.6 ppm, as was also observed in the related bis(imino)imidazol-2-ylidene copper(I) iodide complexes.<sup>15</sup> Due to poor solubility and long relaxation times, the resonance for the carbenoid carbon (-NCN-) in 3a was not observed.

The Cr(III) complex **4a** was prepared by the methodology we recently reported for the synthesis of chromium complexes of **C** (Scheme 2).<sup>16</sup> Copper carbene complexes have been found to be excellent transmetalating agents and have proven to be extremely valuable when more common methods to prepare carbene complexes are not successful (e.g., through the use of silver adducts as transmetalating agents) or simply not possible (e.g., isolation of the free carbene impossible due to competing deprotonation).<sup>16,18</sup>

Reaction of compound **3a** with  $CrCl_3$ ·3THF gave **4a** as a paramagnetic complex in 71% yield. A solution magnetic susceptibility of 3.75  $\mu_B$ , measured using the Evans method,<sup>19</sup> is consistent with the predicted value ( $\mu_{eff}(spin only) = 3.87 \mu_B$ ) for three unpaired electrons. The FTIR stretching frequency for the iminic group in **4a** showed two bands, at 1683 and 1622 cm<sup>-1</sup>, indicative of coordination of the ligand in a bidentate mode, with one iminic nitrogen remaining uncoordinated.

The corresponding iron (5a) and cobalt (6a) complexes were prepared using the synthetic methodology we previously reported for the synthesis of the corresponding imidazol-2ylidene complexes.<sup>16</sup> Addition of  $FeCl[N(SiMe_3)_2]$  or CoCl- $[N(SiMe_3)_2]$ , generated in situ by reaction of  $KN(SiMe_3)_2$  with MCl<sub>2</sub>, to a THF suspension of the benzimidazolium salt 2a at -37 °C afforded complexes 5a and 6a in good yield (Scheme 2). Complexes 5a and 6a are paramagnetic, high-spin species, as evidenced by their respective magnetic susceptibility of 5.86 and 4.27  $\mu_{\rm B}$  measured using the Evans method.<sup>19</sup> These values are in agreement with those reported for related complexes and are consistent with four and three unpaired electrons for the iron and cobalt complexes, respectively.<sup>2,16,20</sup> As previously observed for the iron and cobalt complexes of the related imidazol-2-ylidene ligand,<sup>16</sup> two C=N stretching bands were observed on the FTIR spectrum for both 5a (1683 and 1629 cm<sup>-1</sup>) and **6a** (1683 and 1607 cm<sup>-1</sup>), indicative of bidentate coordination of the ligand to the metal center. Repeated attempts to grow crystals of 4a-6a for X-ray diffraction studies proved unsuccessful.

**Complexes of 1,3-Bis**[1-(2,6-dimethylphenylimino)ethyl]pyrimidin-2-ylidene. Reaction of 1,4,5,6-tetrahydropyrimidine with N-(2,6-dimethylphenyl)acetimidoyl chloride in toluene afforded (1-(2,6-dimethylphenylimino)ethyl)pyrimidine (1b) as a light yellow oil in 87% yield (Scheme 3). The pyrimidinium salt 2b was synthesized in benzene by the reaction of 1b with another 1 equiv of N-(2,6-dimethylphenyl)acetimidoyl chloride in 57% yield. Only one band at 1628 cm<sup>-1</sup>



Scheme 3. Synthesis of 1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidinium Chloride (2b)



Scheme 4. Synthesis of Cu(I) (3b), Cr(III) (4b), Fe (5b), and Co(II) (6b) Complexes of 1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidin-2-ylidene



was identified in the FTIR spectrum for the iminic groups in **2b**. The central pyrimidinium proton (-NCHN-) resonance was observed in the <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum at 9.93 ppm. The backbone methylene protons resonate in a 2:1 ratio at 4.34  $(-NCH_2CH_2CH_2N-)$  and 2.47 ppm  $(-NCH_2CH_2CH_2N-)$ , with the corresponding carbon resonances at 42.2 and 18.7 ppm. The carbenoid carbon (-NCN-) and the iminic carbon (-C=N-) nuclei resonate at 154.1 and 153.7 ppm, respectively.

The chromium(III) (4b), iron(II) (5b), and cobalt(II) (6b) complexes of the pyrimidin-2-ylidene were prepared following the same procedure used for the synthesis of the benzimidazol-2-ylidene complexes (Scheme 4). The copper adduct 3b was prepared in good yield and used as transmetalating agent in the synthesis of compound 4b. In contrast to that observed for 3a, the FTIR spectrum of the pyrimidin-2-ylidene copper derivative 3b shows only one band for the imine group at 1635 cm<sup>-1</sup>. The stretching frequency, comparable to that of 2b, suggests that a linear copper iodide complex with two uncoordinated imine

nitrogen atoms was produced, similar to that observed in the synthesis of the copper complex of ligand C (R = Ph).<sup>15</sup>

Complex 4b was prepared in 86% yield via transmetalation using complex 3b and  $CrCl_3$ ·3THF (Scheme 4). The solution magnetic susceptibility of 4.14  $\mu_B$ , determined using the Evans method,<sup>19</sup> is similar to that of 4a and consistent with the predicted value for three unpaired electrons. The presence of only one band in the FTIR spectrum for the C=N bond at a frequency (1623 cm<sup>-1</sup>) lower than that observed in 3b, a result of  $\pi$ -back-donation from chromium to the C=N  $\pi^*$ antibonding orbitals, strongly suggests coordination of both iminic nitrogen atoms of the pyrimidin-2-ylidene ligand to the metal.

This was confirmed by X-ray diffraction studies (Figure 1). Suitable single crystals of **4b** were grown by slow evaporation of a saturated dichloromethane solution. The complex crystallized in the  $P2_1/n$  space group and adopts a distorted-octahedral geometry in the solid state, with C3 disordered over two positions. To our knowledge, complex **4b** is the first example of a bis(imino)carbene ligand unambiguously shown to coor-



**Figure 1.** ORTEP plot of **4b** (50% probability level). Hydrogen atoms and dichloromethane solvent molecule are omitted for clarity. Only the major component of the disordered structure at C3 is shown. Selected bond lengths (Å) and angles (deg): Cr1-C1 = 1.989(3), Cr1-N3 = 2.133(2), Cr1-N4 = 2.142(2), Cr1-Cl1 = 2.2945(8), Cr1-Cl2 = 2.3293(7), Cr1-Cl3 = 2.3479(8), C1-N1 = 1.335(4), C1-N2 = 1.329(4), C5-N3 = 1.286(4), C15-N4 = 1.289(4); N1-C1-N2 = 121.6(2), C1-N1-C5 = 114.0(2), C1-N2-C15 = 114.3(2), C1-Cr1-N3 = 75.65(10), C1-Cr1-N4 = 75.49(10), C1-Cr1-Cl1 = 96.90(8), C1-Cr1-Cl2 = 167.85(8), C1-Cr1-Cl3 = 76.91(8), C11-Cr1-Cl3 = 173.67(3), N3-Cr1-N4 = 150.59(9).

dinate to a metal in a tridentate fashion. The angles enforced by the six-membered ring of the pyrimidin-2-ylidene core likely play a dominant role in ligand E adopting such a coordination mode. As predicted, the C1–N1–C5 (114.0(2)°) and C1– N2–C15 (114.3(2)°) bond angles are significantly less obtuse than the related angles in the THF-solvated [1,3-bis((2,6dimethylphenylimino)benzyl)imidazol-2-ylidene]CrCl<sub>3</sub> (118.9(3), 119.6(3)°)<sup>16</sup> but comparable to those reported for [2,6-bis(1-(2,6-dimethylphenylimino)ethyl)pyridine]CrCl<sub>3</sub> (113.1(3), 113.7(3)°).<sup>4</sup> The N3–Cr1–N4 bond angle in **4b** is 150.59(9)°, slightly less obtuse than the corresponding angle in the 2,6-bis(1-(2,6-dimethylphenylimino)ethyl)pyridine (**A**) analogue.<sup>4</sup>

The Cr1–C1 bond (1.989(3) Å) is considerably shorter than the metal–carbene bonds in the CrCl<sub>3</sub> complexes of **B** (2.087(6) and 2.1206(6) Å) and **C** (2.048(3) Å).<sup>13,16</sup> While also considerably shorter than the Cr–N bond in the CrCl<sub>3</sub> complex of **B** (2.049(4) Å),<sup>13</sup> it is comparable to the Cr– N<sub>pyridine</sub> bond in the CrCl<sub>3</sub> complex of **A** (1.993(3) Å).<sup>4</sup> Both Cr–N<sub>imine</sub> bonds in 4b (2.133(2) and 2.142(2) Å) are shorter than the corresponding bond in the CrCl<sub>3</sub> complex of imidazol-2-ylidene **C** (R = Ph; 2.164(3) Å).<sup>16</sup> They are, however, surprisingly comparable to both Cr–N<sub>imine</sub> bonds in the CrCl<sub>3</sub> complex of **A** (2.123(3) and 2.140(3) Å)<sup>4</sup> and to the Cr– C<sub>carbene</sub> bonds in the complex of **B** (2.120(6) and 2.087(6) Å).<sup>13</sup>

As expected from the symmetry of the system, both iminic bond lengths are statistically equivalent (1.286(3) and 1.289(3) Å). Those values are close to those reported for the coordinated imine groups of THF-solvated [1,3-bis((2,6dimethylphenylimino)benzyl)imidazol-2-ylidene]CrCl<sub>3</sub> (1.294(4) Å)<sup>16</sup> and of [2,6-bis(1-(2,6-dimethylphenylimino)ethyl)pyridine]CrCl<sub>3</sub> (1.291(4) and 1.297(4) Å).<sup>4</sup> The C1– Cr1–N3 (75.65(10)°) and C1–Cr1–N4 (75.49(10)°) bite angles are smaller than that observed in the chromium trichloride complex of C  $(76.90(11)^{\circ})^{16}$  but are in line with those reported for the CrCl<sub>3</sub> complex of A (75.75(11) and  $77.24(11)^{\circ})^4$  and B (76.3(2) and  $75.68(9)^{\circ})$ .<sup>13</sup> Coordination of the new 1,3-bis(imino)pyrimidin-2-ylidene ligand (E) to Cr(III) thus generates a complex that structurally closely resembles those of the 2,6-bis(imino)pyridine (A) and of 2,6-bis(carbene)pyridine (B) ligands, while imparting very different electronic properties to the metal center.

The corresponding iron (5b) and cobalt (6b) complexes were synthesized in 81 and 74% yields, respectively, from the pyrimidinium salt **2b** (Scheme 4). Similar to the case for **5a** and 6a, the magnetic susceptibility of complexes 5b and 6b are 5.80 and 4.35  $\mu_{\rm B}$ , respectively, consistent with four and three unpaired electrons.<sup>19</sup> In both cases, two stretching frequency bands in the iminic region of the FTIR spectrum were observed (5b, 1617 and 1638 cm<sup>-1</sup>; 6b, 1612 and 1635 cm<sup>-1</sup>) with values strongly suggesting coordination of only one iminic nitrogen atom. Despite the favorable angles of the sixmembered central ring, the greater electron density of group 8 and 9 transition metals and their lower formal +2 oxidation state in comparison to Cr(III) seemingly preclude coordination of the second iminic nitrogen atom. Attempts to grow crystals of either complex to unambiguously determine the coordination mode of the ligand in 5b and 6b were not successful.

Polymerization Activity of Cr(III), Fe(II) and Co(II) Complexes 4–6. The catalytic activity of complexes 4a–6a and 4b–6b was evaluated in ethylene polymerization trials performed under 1 atm of  $C_2H_4$  and at room temperature over 10 min, with 1000 equiv of methylaluminoxane as cocatalyst. As reported for the first-generation imidazol-2-ylidene systems,<sup>16</sup> no ethylene uptake was observed with either iron or cobalt complexes, possibly due to the tendency of late-transition-metal complexes containing NHC ligands to undergo reductive elimination of an alkylimidazolium species.<sup>21</sup> In contrast, chromium complexes 4a,b both gave polyethylene in statistically equivalent rates with an average of 27 kg of PE (mol of  $(Cr)^{-1}$  bar<sup>-1</sup> h<sup>-1</sup>, a value that is surprisingly very close to that observed in the imidazol-2-ylidene chromium(III) series.<sup>16</sup> The observed rate is approximately 1 order of magnitude greater than literature values for chromium(III) complexes of related bidentate ligands<sup>22</sup> but more than 3 orders of magnitude lower than those reported for complexes of A and  $\mathbf{B}^{4,12,13}$ . The identical catalytic performances of both 4a and 4b are intriguing, considering the greater electron density about the metal center in 4b, a result of stronger  $\sigma$ -donating capability of the carbene<sup>17</sup> and of tridentate coordination of the ligand to chromium (vide supra). Polymerization trials with 4a,b were therefore repeated and performed over a 30 min period. A 1.5fold increase in polymer yield resulted (6.6 kg of PE (mol of Cr)<sup>-1</sup> over 30 min vs 4.5 kg of PE (mol of Cr)<sup>-1</sup> over 10 min), significantly less than the 3-fold increase expected for stable catalysts. These observations indicate a short catalyst lifetime, with rapid decomposition through reductive elimination of an alkylbenzimidazolium or alkylpyrimidinium salt and/or through cleavage of the carbene-imine bond, as we have observed in related titanium complexes.<sup>23</sup>

#### CONCLUSIONS

Chromium(III), iron(II), and cobalt(II) complexes of bis-(imino)benzimidazol-2-ylidene (D) and bis(imino)pyrimidin-2-ylidene (E) were successfully prepared, using either the benzimidazolium or pyrimidinium salts or the corresponding copper complex as transmetalating agent, further demonstrating the scope of application of this methodology. The pyrimidin-2ylidene ligand was unambiguously shown to coordinate to Cr(III) in a tridentate fashion, the first demonstration of such a binding capability for bis(imino)carbene ligands. The observed coordination mode is possibly due to appropriate bond angles imparted by the six-membered central ring and to a highly electropositive Cr(III) metal center. Interestingly, spectroscopic evidence points to coordination of the ligand to Fe(II) and Co(II) exclusively in a bidentate fashion. In contrast to the iron and cobalt complexes, both chromium complexes were active in ethylene polymerization, further corroborating our previous observations on the related imidazol-2-ylidene complexes. The synthesis of new derivatives of these ligands aimed at improving the performance of the corresponding transition-metal complexes in olefin polymerization is currently underway.

#### EXPERIMENTAL SECTION

General Comments. All experiments were performed under a dinitrogen atmosphere in a drybox or using standard Schlenk techniques. Solvents used in the preparation of air- and/or moisturesensitive compounds were dried by using an MBraun Solvent Purification System fitted with alumina columns and stored over molecular sieves under a positive pressure of dinitrogen (pentane, toluene, and THF) or dried by refluxing and then distilling from sodium (toluene) under a positive pressure of dinitrogen. Deuterated solvents were degassed using three freeze-pump-thaw cycles. C<sub>6</sub>D<sub>6</sub> was vacuum-distilled from sodium, and CDCl3 and CD3CN were vacuum-distilled from CaH2. NMR spectra were recorded on a Bruker AV 400 (1H at 400 MHz, 13C at 100 MHz) or Bruker AV 300 spectrometer (<sup>1</sup>H at 300 MHz, <sup>13</sup>C at 75.5 MHz) at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio solvent (<sup>1</sup>H) and solvent (<sup>13</sup>C) resonances, and chemical shifts were reported with respect to  $\delta$  0 for tetramethylsilane. Elemental composition was determined by Guelph Chemical

Laboratories Ltd. Solution magnetic susceptibilities were measured using the Evans method.  $^{19}\,$ 

Iron(II) chloride, cobalt(II) chloride, sodium and potassium hexamethyldisilazides, and 1,4,5,6-tetrahydropyrimidine were purchased from Sigma-Aldrich. Benzimidazole was purchased from Alfa-Aesar. Chromium(III) chloride was purchased from Strem Chemicals. N-(2,6-Dimethylphenyl)acetimidoyl chloride<sup>24</sup> and CrCl<sub>3</sub>·3THF<sup>25</sup> were synthesized using published procedures. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories. MAO was graciously donated by Albemarle Corp.

(1-(2,6-Dimethylphenylimino)ethyl)benzimidazole (1a). N-(2,6-Dimethylphenyl)acetimidoyl chloride (2.26 g, 12.5 mmol) was dissolved in dichloromethane (30 mL) and added to a dichloromethane solution (30 mL) of benzimidazole (2.94 g, 24.9 mmol) at room temperature. The reaction mixture was stirred for 18 h. Water was added to the mixture, and the organic product was extracted with dichloromethane. The combined dichloromethane layers were dried over Na2SO4 and subsequently filtered. The solvent was removed in vacuo to give the product as a light yellow solid (2.83 g, 10.8 mmol, 86%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.58 (dd, <sup>3</sup>J = 3.1 Hz, 1H, CNCCH), 8.41 (s, 1H, NCHN), 7.86 (dd, <sup>3</sup>J = 3.3 Hz, 1H, NCCH), 7.30–7.40 (m, 2H, CNCCHCH, NCCHCH), 7.10 (d,  ${}^{3}J$  = 7.5 Hz, 2H, m-CH<sub>(2,6-xylyl)</sub>), 6.98 (t,  ${}^{3}J$  = 7.2 Hz, 1H, p-CH<sub>(2,6-xylyl)</sub>), 2.33 (s, 3H,  $CH_{3(\text{imine})}$ ), 2.10 (s, 6H, o- $CH_{3(2,6\text{-xylyl})}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  150.6 (C=N), 145.5 ( $C_{\text{ipso}(2,6-xylyl)}$ ), 143.9 (NCCH), 141.3 (NCN), 132.4 (NCCH), 128.3 (*m*-CH<sub>(2,6-xylyl)</sub>), 126.7 (*o*-C<sub>(2,6-xylyl)</sub>), 125.2 (NCCHCH), 124.4 (NCCHCH), 123.7 (*p*-CH<sub>(2,6-xylyl)</sub>), 120.2 (CNCCH), 116.8 (NCCH), 18.4 (o-CH<sub>3(2,6-xylyl</sub>)). 16.7 (CH<sub>3(imine)</sub>).

1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazolium Chloride (2a). N-(2,6-Dimethylphenyl)acetimidoyl chloride (1.73 g, 9.55 mmol) was dissolved in 20 mL of toluene and added to a solution of 1-(2,6-dimethylphenylimino)benzimidazole (1a; 2.51 g, 9.55 mmol) in toluene (20 mL) at room temperature. The reaction mixture was stirred for 24 h to give an off-white precipitate. The white solid was washed with toluene and pentane and dried under vacuum (3.42 g, 7.70 mmol, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): major isomer (E,Z isomer)  $\delta$  9.41 (s, 1H, NCHN), 8.65 (dd, <sup>3</sup>J = 3.4 Hz, 1H, NCCHCH), 7.92 (dd,  ${}^{3}J$  = 3.4 Hz, 1H, NCCHCH), 7.46 (dd,  ${}^{3}J$  = 3.4 Hz, 2H, NCCHCH), 7.12 (d,  ${}^{3}J$  = 7.6 Hz, 2H, m-CH<sub>(2.6-xylyl)</sub>), ca. 7.05 (2H, *m*-CH<sub>(2,6-xylyl</sub>); obstructed by resonances from the minor isomer), ca. 6.98 (2H, p-CH<sub>(2,6-xylyl)</sub>; overlapping magnetically inequivalent nuclei), 2.63 (s, 3H,  $CH_{3(imine)}$ ), 2.43 (s, 3H,  $CH_{3(imine)}$ ), 2.11 (s, 6H, o-CH<sub>3(2,6-xylyl</sub>)), 2.08 (s, 6H, o-CH<sub>3(2,6-xylyl</sub>)); minor isomer (*E*,*E* isomer)  $\delta$  12.27 (s, 1H, NCHN), 9.02 (dd, <sup>3</sup>*J* = 3.2 Hz, 2H, NCCHCH), 7.75  $(dd, {}^{3}J = 3.2 Hz, 2H, NCCHCH), 7.14 (d, {}^{3}J = 7.6 Hz, 4H, m$  $CH_{(2,6\text{-xylyl})}$ ), ca. 7.05 (2H, p- $CH_{(2,6\text{-xylyl})}$ ; obstructed by resonances from the major isomer), 3.11 (s, 6H,  $CH_{3(\text{imine})}$ ), 2.16 (s, 12H, o- $CH_{3(2,6-xylyl)}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): major isomer (*E*,*Z*) isomer)  $\delta$  151.0, 145.8, 145.2, 145.0, 141.6, 131.8, 127.9, 126.6, 126.5, 125.9, 125.4, 125.1, 124.3, 123.9, 119.2, 117.2, 29.2, 18.3, 17.9, 17.0; minor isomer (E,E isomer):  $\delta$  153.2 (C=N), 144.1 (C<sub>ipso(2,6-xylyl)</sub>), 131.8 (NCCH), 129.2 (NCCHCH), 128.5 (m-CH<sub>(2,6-xylyl</sub>)), 128.3 (o-C<sub>(2,6-xylyl)</sub>), 126.1 (NCHN), 124.9 (*p*-CH<sub>(2,6-xylyl)</sub>), 118.9 (NCCHCH), 19.0 ( $CH_{3(\text{imine})}$ ), 18.5 (o- $CH_{3(2,6-\text{xylyl})}$ ). FTIR (neat):  $\nu_{C=N}$  1690 cm<sup>-1</sup>

[1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazol-2ylidene]copper(I) lodide (3a). Sodium hexamethyldisilazide (116 mg, 0.630 mmol) was dissolved in THF (4 mL) and added dropwise to a THF (5 mL) suspension of copper(I) iodide (119 mg, 0.622 mmol) at -37 °C. The reaction mixture was slowly warmed to room temperature and stirred for 1 h. It was then added dropwise to a THF (5 mL) suspension of 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazolium chloride (2a; 277 mg, 0.622 mmol) at -37 °C. The reaction mixture was slowly warmed to room temperature and stirred for an additional 20 h. The volatile was removed under vacuum to give an orange solid (105 mg, 0.175 mmol, 28%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.44 (dd, <sup>3</sup>J = 2.9 Hz, 2H, NCCHCH), 7.41 (dd, <sup>3</sup>J = 2.9 Hz, 2H, NCCHCH), 7.00 (d, <sup>3</sup>J = 7.5 Hz, 4H, *m*-CH<sub>(2,6-xylyl)</sub>), 6.84 (t, <sup>3</sup>J = 7.5 Hz, 2H, *p*-CH<sub>(2,6-xylyl)</sub>), 2.69 (s, 6H, CH<sub>3(imine</sub>)), 2.17 (s, 12H, *o*-CH<sub>3(2,6-xylyl)</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.6 (C=N), 145.3 (C<sub>ipso(2,6-xylyl)</sub>), 133.8 (NCCH), 128.3 (*m*-CH<sub>(2,6-xylyl)</sub>), 127.1 (*o*-*C*<sub>(2,6-xylyl</sub>)), 125.3 (NCCHCH), 123.9 (*p*-CH<sub>(2,6-xylyl</sub>)), 116.3 (NCCHCH), 19.5 (CH<sub>3(imine)</sub>), 19.1 (*o*-CH<sub>3(2,6-xylyl</sub>)). FTIR (neat)  $\nu_{C=N}$  1668, 1653 cm<sup>-1</sup>. Anal. Calcd for C<sub>27</sub>H<sub>28</sub>CuIN<sub>4</sub>: C, 54.14; H, 4.71; N, 9.35. Found: C, 53.97; H, 4.54; N, 9.08.

[1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazol-2ylidene]chromium(III) Chloride (4a). To a mixture of CrCl<sub>3</sub>·3THF (39.4 mg, 0.105 mmol) and 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazol-2-ylidene copper(I) iodide (3a; 62.9 mg, 0.105 mmol) was added 10 mL of dichloromethane at room temperature. The reaction mixture was stirred overnight and subsequently filtered. The solvent was removed in vacuo. The solid was then dissolved in toluene and filtered. The filtrate was collected, and the solvent was removed in vacuo to give a blue-green solid in 71% yield (42.5 mg, 0.0750 mmol). FTIR (neat):  $\nu_{C=N}$  1683, 1622 cm<sup>-1</sup>.  $\mu_{eff}$  = 3.75  $\mu_{B}$ . Anal. Calcd for C<sub>27</sub>H<sub>28</sub>CrCl<sub>3</sub>N<sub>4</sub>: C, 57.20; H, 4.98; N, 9.88. Found: C, 56.94; H, 4.98; N, 10.10.

[1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazol-2ylidene]iron(II) Chloride (5a). Potassium hexamethyldisilazide (65.6 mg, 0.329 mmol) was dissolved in THF (4 mL) and added dropwise to a THF (8 mL) suspension of iron(II) chloride (41.4 mg, 0.327 mmol) at -37 °C. The reaction mixture was slowly warmed to room temperature and stirred for 40 min, filtered, and added dropwise to a THF (5 mL) suspension of 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazolium chloride (2a; 144 mg, 0.323 mmol) at -37 °C. The reaction mixture was slowly warmed to room temperature and stirred for an additional 22 h. The reaction mixture was filtered, and the solution was concentrated to about 1 mL. Pentane was added to precipitate a yellow solid. The supernatant was removed, and the residual solid was dried to give the product in 71% yield (122 mg, 0.228 mmol). FTIR (neat):  $\nu_{C=N}$  1683, 1629 cm<sup>-1</sup>.  $\mu_{eff}$  = 5.86  $\mu_{B}$ . Anal. Calcd for C27H28FeCl2N4: C, 60.58; H, 5.27; N, 10.47. Found: C, 60.30; H, 5.02; N, 10.15.

[1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]benzimidazol-2ylidene]cobalt(II) Chloride (6a). Potassium hexamethyldisilazide (70.2 mg, 0.352 mmol) was dissolved in THF (4 mL) and added dropwise to a THF (8 mL) suspension of cobalt(II) chloride (45.5 mg, 0.350 mmol) at -37 °C. The reaction mixture was stirred for 40 min at room temperature. It was then filtered, and the filtrate was added dropwise to a THF (5 mL) suspension of 1,3-bis[1-(2,6dimethylphenylimino)ethyl]benzimidazolium chloride (2a; 153 mg, 0.344 mmol) at -37 °C. The reaction mixture was slowly warmed to room temperature and stirred for an additional 22 h. It was filtered, and the solution was concentrated to about 1 mL. Pentane was added to precipitate the product as a green solid in 62% yield (115 mg, 0.344 mmol). FTIR (neat):  $\nu_{C=N}$  1683, 1607 cm<sup>-1</sup>.  $\mu_{eff}$  = 4.27  $\mu_{B}$ . Anal. Calcd for C<sub>27</sub>H<sub>28</sub>CoCl<sub>2</sub>N<sub>4</sub>: C, 60.23; H, 5.24; N, 10.41. Found: C, 60.50; H, 5.02; N, 10.18.

(1-(2,6-Dimethylphenylimino)ethyl)-4,5,6-trihydropyrimidine (1b). *N*-(2,6-Dimethylphenyl)acetimidoyl chloride (100 mg, 0.554 mmol) was dissolved in toluene (3 mL) and added to a toluene solution (3 mL) of 1,4,5,6-tetrahydropyrimidine (90.6 mg, 1.10 mmol) at room temperature. The reaction mixture was stirred for 16 h. The mixture was filtered, and the solvent was removed in vacuo to give the product as a light yellow oil (111 mg, 87%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.89 (s, 1H, NCHN), 7.03 (d, <sup>3</sup>*J* = 7.4 Hz, 2H, *m*-CH<sub>(2,6-xylyl)</sub>), 6.88 (t, <sup>3</sup>*J* = 7.4 Hz, 1H, *p*-CH<sub>(2,6-xylyl)</sub>), 3.88 (t, <sup>3</sup>*J* = 6.0 Hz, 2H, CNCH<sub>2</sub>CH<sub>2</sub>), 3.49 (t, <sup>3</sup>*J* = 6.0 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 1.88 (s, 3H, CH<sub>3(imine)</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>): δ 152.4 (C=N), 146.7 (*C*<sub>ipso(2,6-xylyl)</sub>), 143.8 (NCN), 127.7 (*m*-CH<sub>(2,6-xylyl)</sub>), 127.2 (*o*-C<sub>(2,6-xylyl)</sub>), 122.3 (*p*-CH<sub>(2,6-xylyl)</sub>), 44.3 (CNCH<sub>2</sub>CH<sub>2</sub>), 41.0 (NCH<sub>2</sub>CH<sub>2</sub>), 20.9 (NCH<sub>2</sub>CH<sub>2</sub>), 18.0 (*o*-CH<sub>3(2,6-xylyl)</sub>), 14.2 (CH<sub>3(imine)</sub>).

**1,3-Bis**[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidinium Chloride (2b). *N*-(2,6-Dimethylphenyl)acetimidoyl chloride (462 mg, 2.54 mmol) was dissolved in 8 mL of benzene and added to a solution of (1-(2,6-dimethylphenylimino)ethyl)-4,5,6trihydropyrimidine (1b; 583 mg, 2.54 mmol) in benzene (10 mL) at room temperature. The reaction mixture was stirred for 20 h. The white solid was washed with toluene and pentane and dried in vacuo (594 mg, 1.45 mmol, 57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.93 (s, 1H, NCHN), 7.07 (d, <sup>3</sup>*J* = 7.5 Hz, 4H, *m*-CH<sub>(2,6-xylyl)</sub>), 6.98 (t, <sup>3</sup>*J* = 7.5 Hz, 2H, *p*-CH<sub>(2,6-xylyl)</sub>), 4.34 (t, <sup>3</sup>*J* = 5.7 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 2.59 (s, 6H, CH<sub>3(imine)</sub>), 2.47 (p, <sup>3</sup>*J* = 5.7 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 2.07 (s, 12H, o-CH<sub>3(2,6-xylyl)</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.1 (NCN), 153.7 (C=N), 144.5 ( $C_{ipso(2,6-xylyl)}$ ), 128.4 (*m*-CH<sub>(2,6-xylyl)</sub>), 126.5 (*o*-C<sub>(2,6-xylyl)</sub>), 124.5 (*p*-CH<sub>(2,6-xylyl)</sub>), 42.2 (NCH<sub>2</sub>CH<sub>2</sub>), 18.7 (NCH<sub>2</sub>CH<sub>2</sub>), 18.5 (*o*-CH<sub>3(2,6-xylyl)</sub>), 15.9 (CH<sub>3(imine)</sub>). FTIR (neat)  $\nu_{C=N}$  1628 cm<sup>-1</sup>.

[1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidin-2-ylidene]copper(I) lodide (3b). Sodium hexamethyldisilazide (50.7 mg, 0.276 mmol) was dissolved in THF (4 mL) and added dropwise to a THF (4 mL) suspension of copper iodide (52.1 mg, 0.274 mmol) at -37 °C. The reaction mixture was stirred for 30 min, and it was then added dropwise to a THF (5 mL) suspension of 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidinium chloride (2b; 112 mg, 0.273 mmol) at -37 °C. The reaction mixture was slowly warmed to room temperature and stirred for an additional 4 h. Pentane was added to precipitate a brown solid, and the supernatant was removed. The volatiles were removed in vacuo to give the product in 76% yield (118 mg, 0.208 mmol). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  7.09 (d, <sup>3</sup>J = 7.7 Hz, 4H, m-CH<sub>(2,6-xylyl)</sub>), 6.97 (t, <sup>3</sup>J = 7.7 Hz, 2H, p-CH<sub>(2,6-xylyl</sub>), 3.69 (t,  ${}^{3}J$  = 6.5 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 2.28 (s, 12H, o-CH<sub>3(2,6-xylyl</sub>)), 2.27 (m,  ${}^{3}J$  = 6.5 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 1.99 (s, 6H, CH<sub>3(imine)</sub>).  ${}^{13}$ C{<sup>1</sup>H} NMR (100 MHz, CD<sub>3</sub>CN):  $\delta$  162.3 (NCN), 146.1 (C=N), 130.3 (o- $C_{(2,6-xylyl)}$ ), 128.9 (m- $CH_{(2,6-xylyl)}$ ), 128.8  $(C_{ipso(2,6-xylyl)})$ , 125.2  $(p-CH_{(2,6-xylyl)})$ , 46.1  $(NCH_2CH_2)$ , 23.3  $(NCH_2CH_2)$ , 20.0  $(o-CH_{3(2,6-xylyl)})$ , 16.8  $(CH_{3(imine)})$ . FTIR (neat)  $\nu_{C=N}$  1635 cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>30</sub>CuIN<sub>4</sub>: C, 51.02; H, 5.35; N, 9.92. Found: C, 50.87; H, 5.16; N, 9.65.

[1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidin-2-ylidene]chromium(III) Chloride (4b). A dichloromethane solution of CrCl<sub>3</sub>·3THF (37.5 mg, 0.100 mmol) was added, at room temperature, to a dichloromethane suspension of 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidin-2-ylidene copper(I) iodide (3b; 56.7 mg, 0.100 mmol). The reaction mixture was stirred for 20 h and subsequently filtered. The filtrate was collected, and the solvent was removed in vacuo to give a light bluegreen solid. Yield: 45.9 mg, 0.0861 mmol, 86%. X-ray-quality crystals were grown from a concentrated dichloromethane solution of 4b by slow evaporation of the solvent. FTIR (neat):  $\nu_{C=N}$  1623 cm<sup>-1</sup>.  $\mu_{eff}$  = 4.14  $\mu_{\rm B}$ . Anal. Calcd for C<sub>24</sub>H<sub>30</sub>CrCl<sub>3</sub>N<sub>4</sub>: C, 54.09; H, 5.67; N, 10.51. Found: C, 54.57; H, 5.81; N, 9.96.

[1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidin-2-ylidene]iron(II) Chloride (5b). Potassium hexamethyldisilazide (51.6 mg, 0.259 mmol) was dissolved in THF (4 mL) and added dropwise to a THF (4 mL) suspension of iron(II) chloride (32.5 mg, 0.256 mmol) at -37 °C. The reaction mixture was kept at -37 °C for 3 h and agitated occasionally. It was then filtered, and the filtrate was added dropwise to a THF (4 mL) suspension of 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidinium chloride (2b; 101 mg, 0.245 mmol) at -37 °C. The reaction mixture was slowly warmed to room temperature and stirred for an additional 20 h. The mixture was then concentrated, and pentane was added to precipitate a reddish solid. The solid was dissolved in dichloromethane and then filtered. The volatiles were removed in vacuo to give the product in 81% yield (123 mg, 0.245 mmol). FTIR (neat):  $\nu_{C=N}$  1638, 1617 cm<sup>-1</sup>.  $\mu_{\text{eff}} = 5.80 \,\mu_{\text{B}}$ . Anal. Calcd for C<sub>24</sub>H<sub>30</sub>FeCl<sub>2</sub>N<sub>4</sub>: C, 57.50; H, 6.03; N, 11.18. Found: C, 57.21; H, 5.75; N, 10.89.

[1,3-Bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidin-2-ylidene]cobalt(II) Chloride (6b). Potassium hexamethyldisilazide (46.6 mg, 0.234 mmol) was dissolved in THF (4 mL) and added dropwise to a THF (4 mL) suspension of cobalt chloride (30.4 mg, 0.232 mmol) at -37 °C. The reaction mixture was kept at -37 °C for 3 h and agitated occasionally. It was then filtered, and the filtrate was added dropwise to a THF (4 mL) suspension of 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]-4,5,6-trihydropyrimidinium chloride (2b; 90.0 mg, 0.219 mmol) at -37 °C. The reaction mixture was slowly warmed to room temperature and stirred for an additional 20 h. The mixture was then concentrated, and pentane was added to precipitate a green solid. The solid was dissolved in dichloromethane and then filtered. The volatiles were removed under vacuum to give the product in 74% yield (81.8 mg, 0.162 mmol). FTIR (neat):  $\nu_{C=N}$  1635, 1612 cm<sup>-1</sup>.  $\mu_{eff}$  = 4.35  $\mu_{B}$ . Anal. Calcd for C<sub>24</sub>H<sub>30</sub>CoCl<sub>2</sub>N<sub>4</sub>: C, 57.15; H, 6.00; N, 11.11. Found: C, 56.88; H, 5.72; N, 10.94.

General Procedure for Ethylene Polymerization. Ethylene polymerization was performed at room temperature and at atmospheric pressure in a 500 mL Schlenk flask containing a magnetic stir bar. The flask was kept in an oven at 130 °C for at least 18 h prior to use. The hot flask was brought to room temperature under dynamic vacuum and back-filled with ethylene. Under an atmosphere of ethylene, the flask was charged with 20 mL of dry toluene and 1000 equiv of MAO with respect to the complex (7.6  $\mu$ mol). The solution was stirred for 10-15 min before a solution of the catalyst in either toluene or dichloromethane was introduced into the flask via a syringe. The reaction mixture was stirred for either 10 or 30 min after the addition of the catalyst and subsequently quenched with a 1:1 mixture of concentrated hydrochloric acid and methanol. The resulting mixture was filtered. Any solid collected was washed with distilled water and dried under vacuum at approximately 50 °C for 24 h. Complexes 4a,b each gave respectively 29 mg (3.8 kg of PE (mol of cat.)<sup>-1</sup>; 23 kg of PE  $(mol of cat.)^{-1} h^{-1}$  and 39 mg (5.1 kg of PE (mol of cat.)^{-1}; 31 kg of PE (mol of cat.)<sup>-1</sup>  $h^{-1}$ ) of polyethylene, as averages of three 10 min runs, with a standard deviation of 20%, common for batch polymerization experiments. In contrast, complexes 4a,b gave respectively 45 mg (5.9 kg of PE (mol of cat.)<sup>-1</sup>; 12 kg of PE (mol of cat.)<sup>-1</sup>  $\dot{h}^{-1}$ ) and 55 mg (7.3 kg of PE (mol of cat.)<sup>-1</sup>; 15 kg of PE (mol of cat.)<sup>-1</sup> h<sup>-1</sup>) of polyethylene, as averages of two 30 min runs, with a standard deviation of 20%.

X-ray Crystallographic Studies. X-ray crystallographic data for compound 4b were collected at the University of Toronto on a Bruker Kappa APEX-DUO diffractometer using a copper ImuS tube with multilayer optics and were measured using a combination of  $\phi$  scans and  $\omega$  scans. The data were processed using APEX2 and SAINT.<sup>26</sup> Absorption corrections were carried out using SADABS.<sup>26</sup> The structure was solved and refined using OLEX2 (v. 1.2)<sup>27</sup> with SHELXS-97<sup>28</sup> for full-matrix least-squares refinement that was based on  $F^2$ . All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with  $U_{\rm iso}$  tied to the carrier atom.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Tables and a CIF file giving crystallographic data for **4b** (CCDC reference number 900426), including tables of crystal data and structure refinement, bond lengths, angles, atomic coordinates and equivalent isotropic displacement parameters, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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