# Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

## Hydroboration of Terminal Olefins with Pinacolborane Catalyzed by New Mono(2-Iminopyrrolyl) Cobalt(II) Complexes

Tiago F. C. Cruz,<sup>†</sup> Patrícia S. Lopes,<sup>†</sup> Laura C. J. Pereira,<sup>‡</sup> Luís F. Veiros,<sup>†</sup><sup>©</sup> and Pedro T. Gomes<sup>\*,†</sup><sup>©</sup>

<sup>†</sup>Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

<sup>‡</sup>C<sup>2</sup>TN-Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, 2695-066 Bobadela LRS, Portugal

Supporting Information

ABSTRACT: The 5-substituted 2-aryliminopyrrolyl ligand precursors of the type 5-R-2-[N-(2,6-diisopropylphenyl) formimino]-1*H*-pyrrole (R = 2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub> (1a), 2,4,6-<sup>i</sup>Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub> (1b), 2,4,6- $Ph_3-C_6H_3$  (1c; reported in this work), anthracen-9-yl (1d),  $CPh_3$ (1e; reported in this work)) were treated with  $K[N(SiMe_3)_2]$  in toluene to yield the respective 5-R-2-[N-(2,6-diisopropylphenyl)formimino]pyrrolyl potassium salts 2a-e in high yields. The paramagnetic 15-electron Co(II) complexes of the type [Co- $\{\kappa^2 N_1 N' - 5 - R - NC_4 H_2 - 2 - C(H) = N(2_1 6^{-i} Pr_2 - C_6 H_3)\}(Py)Cl]$  (3ae; Py = pyridine) were prepared by salt metathesis of  $CoCl_2(Py)_4$ with the respective potassium salts 2a-e in moderate to good yields. When the CoCl<sub>2</sub>(THF)<sub>1.5</sub> precursor was combined with



the in situ prepared sodium salt of ligand precursor 1b, the trinuclear complex  $[Co{\kappa^2N_1N'-5-(2,4,6-Pr_3-C_6H_2)-NC_4H_2-2-K_6H_2)-NC_4H_2-2-K_6H_2-K_6H$  $C(H) = N(2,6-iPr_2-C_6H_3)\{(\mu-Cl)\}_2[(\mu-Cl)]_2Co(THF)_2]$  (4) was obtained in high yields. Complexes 3a-e have high-spin electronic configurations both in solution and in the solid state. X-ray diffraction studies of complexes 3a,e confirmed distorted tetrahedral coordination geometries. Complex 4, on the other hand, is a linear trinuclear Co(II)-Co(II)-Co(II) complex with two terminal distorted tetrahedral four-coordinate sites and a central octahedral six-coordinate site, all in the high-spin state, S =3/2, as confirmed by the magnetization measurements and DFT calculations. Solid-state magnetic measurements in both complexes 3a and 4 point to paramagnetic behavior with a significant contribution of spin-orbit coupling. Additionally, intramolecular antiferromagnetic coupling of the adjacent cobalt atoms is observed in 4. The Co(II) family 3a-d, on activation with K(HBEt<sub>3</sub>), catalyzed the hydroboration of several  $\alpha$ -olefins with pinacolborane, in good to high yields (50-80%). This system almost exclusively yielded the anti-Markovnikov (a-Mk) addition product, except when styrene was used, where the selectivity in the Markovnikov (Mk) product increased with increasing steric bulkiness of the 5-R-2-iminopyrrolyl substituent, with the a-Mk:Mk molar ratio varying from 2.33:1 (3a,  $R = 2,6-Me_2-C_6H_3$ ) to 0.75:1 (3c,  $R = 2,4,6-Ph_3-C_6H_3$ ). Preliminary mechanistic studies indicate that the activation by  $K(HBEt_3)$  gave rise to a Co(I) species, the catalyst system likely following an oxidative addition pathway.

#### INTRODUCTION

The hydroboration of olefins consists of the formal addition of a H-B fragment to the unsaturated bond and is a viable source of organoboron reagents that are often used in cross-coupling, oxidation, or other important organic chemistry reactions. Hydroboration has been typically catalyzed by the expensive platinum-group elements, more specifically by rhodium and iridium.<sup>2</sup> The development of metal-catalyzed hydroboration has allowed more selective reactions by enabling the use of previously unreactive boranes, such as pinacolborane (HBPin). When this is taken into account, it is important to develop alternative cheap and abundant mediators that can perform selective and versatile transformations.<sup>3</sup> Recently, iron and cobalt have been increasingly used in catalytic systems for the hydroboration of alkenes<sup>4</sup> and alkynes.<sup>5</sup>

Specifically considering cobalt catalyzed hydroboration of alkenes, Chirik et al. have developed groundbreaking work in the hydroboration of alkenes by using tridentate (bis(imino)pyridine)CoMe precatalysts (Chart 1, A), achieving the respective organoboranes under neat, mild conditions.<sup>4b</sup> In an example with neutral tridentate 6-phosphino-2,2'-bipyridine ligands, Huang et al. reported that PNN pincer complexes (6phosphino-2,2'-bipyridine)CoCl<sub>2</sub> (Chart 1, B) catalyzed the hydroboration of alkenes with very high activities, when activated by K(HBEt<sub>3</sub>).<sup>4k</sup> The cases of catalyst precursors containing anionic ligands are scarce, and one can consider the work of Turculet et al. using a P,N-bidentate (Nphosphinoamidinate) $Co(N(SiMe_3)_2)$  complex (Chart 1, C)

Received: March 5, 2018





Scheme 1. Preparation of the 5-Substituted 2-Iminopyrrolyl Ligand Precursors 1a-e Used in This Work



to catalyze hydroboration reactions in neat and mild conditions.<sup>4f,g</sup> In all of the reports mentioned above, the reactions were directed toward the anti-Markovnikov addition products. However, Thomas and co-workers reported the uncommon Markovnikov-selective hydroboration of alkenes with a bipyridyl–oxazoline cobalt(II) complex (Chart 1, **D**), activated with NaO<sup>t</sup>Bu.<sup>4n</sup>

The chemistry of Co bearing one anionic bidentate N,N ligand is limited. A chloride complex containing the N,N  $\beta$ -diketiminate framework, LCoCl (L = [{2,6-diisopropylphenyl-NC(<sup>t</sup>Bu)}<sub>2</sub>CH]<sup>-</sup>) (Chart 1, E), has been reported by Holland et al.<sup>6</sup> In fact, arene Co complexes of  $\beta$ -diketiminate ligands have been reported as active mediators of hydrosilylation reactions of terminal alkenes, but not yet in hydroboration.<sup>7</sup> In a different work, the amidinato/guanidinato scaffold has been used to stabilize Co complexes of the type [LCoCl]<sub>2</sub> (with L = [(2,6-diisopropylphenyl-N)<sub>2</sub>CR]<sup>-</sup>, with R being <sup>t</sup>Bu, N<sup>i</sup>Pr<sub>2</sub>, or NCy<sub>2</sub>) (Chart 1, F).<sup>8</sup> On a similar note, Betley and co-workers reported a tetracoordinated Co(II) complex containing a dipyrromethene bidentate framework (Chart 1, G).<sup>9</sup>

We have been interested in the coordination/organometallic chemistry of complexes bearing 2-iminopyrrolyl ligands, having prepared complexes of the late transition metals Fe, Ni, and Cu<sup>10,11</sup> and Zn,<sup>12</sup> as well as of the main-group elements Na<sup>13</sup> and B.<sup>14</sup> Our group also reported some homoleptic bis(2-iminopyrrolyl) complexes of Co with different steric environments.<sup>11,15</sup> Thus far, the only case of a mono-chelated 2-iminopyrrolyl cobalt(II) complex,  $[LCoCl_2][Li(THF)_4]$  (Chart 1, H), with the bis(arylimino)pyrrolyl ligand L<sup>-</sup> = 2,5-([CH = N(2,6-<sup>i</sup>Pr\_2-C\_6H\_3)\_2]C\_4H\_2N<sup>-</sup>, was that reported by Bochmann et al.<sup>16</sup> Taking into account that we have previously described the preparation of bulky 5-substituted 2-iminopyr-

role ligand precursors,<sup>15d</sup> from their corresponding 5substituted-2-formylpyrroles,<sup>17</sup> we report herein the synthesis and complete characterization of new mono(5-substituted 2iminopyrrolyl) Co(II) complexes encompassing varying degrees of steric bulkiness. These Co(II) complexes were tested as catalysts for the hydroboration of terminal  $\alpha$ -olefins upon activation by K(HBEt<sub>3</sub>), enabling the establishment of a structure/reactivity relationship.

#### RESULTS AND DISCUSSION

Synthesis and Characterization of Unsolvated Ligand Potassium Salts. The 5-substituted 2-iminopyrrole ligand precursors 1a-e used in this work were prepared by a multistep strategy (Scheme 1) reported by our group for the synthesis of 1a.<sup>15d</sup> The syntheses of the ligand precursors 1b-eare reported in the present work. These ligand precursors were characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and elemental analysis and for two of them (1c,e) by single-crystal X-ray diffraction.

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **1b**–e (Figures S4– S11 in the Supporting Information) show the expected resonances for the respective moieties, with the NH protons being present as broad resonances at 8.59-9.21 ppm and the iminic protons appearing at 7.66-8.04 ppm. The pyrrolyl protons at positions 3 and 4 appear at 6.31 and 5.67 ppm, respectively, for **1c**, whereas **1b**,d,e display those resonances at 6.54-6.97 and 6.12-6.66 ppm. The shift of the 4-pyrrolyl proton of **1c** to higher field is an indication of ring current anisotropy effects induced by the phenyl groups in the ortho positions of the 5-(2,4,6-triphenylphenyl) substituent, in contrast with previously prepared 5-aryl-2-iminopyrrolyl ligand precursors.<sup>15d</sup> The molecular structures of ligand precursors

**1c**,**e** obtained from single-crystal X-ray diffraction are presented in Figure S27 of the Supporting Information.

In order to obtain unsolvated 5-substituted 2-iminopyrrolyl alkali-metal salts as precursors of this ligand system, the 5-substituted 2-iminopyrroles 1a-e were deprotonated with  $K[N(SiMe_3)_2]$  in toluene to form the respective 5-substituted 2-iminopyrrolyl potassium salts 2a-e (Scheme 2). The

Scheme 2. Synthesis of the 5-Substituted 2-Iminopyrrolyl Potassium Salts 2a-e



potassium salts 2a-c,e gradually precipitated from toluene and were isolated by filtering off the respective supernatants. In the case of 2d, which was very soluble in toluene, evaporation of the solvent was necessary for its isolation. Compounds 2a-e were characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. The NMR spectra of the potassium salts 2a-e are presented in Figures S12–S21 of the Supporting Information.

In THF- $d_8$ , the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of compounds  $2\mathbf{a}-\mathbf{e}$  show the expected resonances for their respective moieties; in general, the isopropyl protons are equivalent and the iminic protons appear in the range 7.52–7.71 ppm. The protons of the pyrrolyl moiety in positions 3 and 4 appear in the ranges 6.45–6.55 and 5.85–5.92 ppm, respectively, for  $2\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{e}$ . In a different observation, the same pyrrole 3- and 4-proton resonances are shifted to higher fields at 6.25 and 5.48 ppm for  $2\mathbf{c}$  and to lower fields, at 6.79 and 6.38 ppm, in 2d. As in the case of the parent 2-iminopyrrole 1c, the shift of the pyrrolyl 4-proton of  $2\mathbf{c}$  to higher field is an indication of ring current anisotropy induced by the 5-(2,4,6-triphenylphenyl) substituent.

Compound **2d** was also characterized by X-ray diffraction, crystallizing in the monoclinic system, in the I2/a space group. The asymmetric unit is composed of two independent 5-anthracen-9-yl-2-iminopyrrolyl ligands and two potassium atoms, cocrystallized with one toluene molecule. The ORTEP-3 diagrams relevant to the molecular structure of **2d** are shown in Figure 1, a selection of bond lengths and angles being shown in Table S2 of the Supporting Information. In this structure, the potassium atom is coordinated to one 5-(anthracen-9-yl)-2-iminopyrrolyl ligand through the iminic and pyrrolyl nitrogen atoms and to the pyrrolyl ring of the next fragment in an  $\eta^5$  coordination mode. The structure self-



**Figure 1.** ORTEP-3 diagrams of compound **2d**: (a) representation of a repeating unit of **2d**; (b) representation of the asymmetric unit of **2d**; (c) representation of an octamer of **2d**, with the anthracen-9-yl and the 2,6-<sup>i</sup>Pr<sub>2</sub> groups omitted for clarity (bottom). All diagrams were drawn showing 20% probability ellipsoids, the hydrogen atoms and the cocrystallized toluene molecule being omitted for clarity.

assembles in a 1D-coordination polymer, with the 5-(anthracen-9-yl)-2-iminopyrrolyl moieties and the potassium atoms being sequentially arranged in a zigzag conformation.

The K-N<sub>pyrrolyl</sub> and K-N<sub>imine</sub> bond distances of both fragments in the asymmetric unit are in the ranges of 2.641-2.656 and 2.822-2.874 Å, respectively, with a bite angle in the range of 61.89-63.42°. This observation is related to the higher  $\sigma$ -donor character of the K-N<sub>pyrrolyl</sub> bond. The potassium distance to the centroid of the  $\eta^5$ -coordinated pyrrolyl rings is in the range of 2.836-3.048 Å. This observation is comparable to those of the 2-iminopyrrolyl sodium salt features reported by our group,<sup>13</sup> as well as other compounds containing a potassium  $\eta^5$ -coordinated to pyrrolyl anions.<sup>18</sup> The torsion of the 2,6-diisopropylphenyl ring relative to the 2-iminopyrrolyl moiety is in the range of 74.58-89.12°. In the K1 center, the five-membered chelate is relatively close to planarity (the angle between the planes N1-K1-N2 and N1-C2-C6-N2 is  $10.90^{\circ}$ ), giving rise to a relatively orthogonal anthracen-9-yl group, with a torsion of 64.57°. In the K1A center, the five-membered chelate is well away from planarity, with a severe pyramidalization of the N<sub>pyrrolvl</sub> atom, the angle between the planes N1A-K1A-N2A and N1A-C2A-C6A-N2A being 21.77°.

Synthesis and Characterization of the Pyridine Chloride Co(II) Complexes. The metathetical exchange reaction of the  $CoCl_2(Py)_4$  (Py = pyridine) starting material with the respective potassium salts  $2\mathbf{a}-\mathbf{e}$ , in toluene at 80 °C, afforded after standard workup procedures the corresponding pyridine chloride Co(II) complexes [ $Co\{\kappa^2N,N'-5\text{-R-NC}_4H_2-2\text{-C}(H)=N(2,6\text{-}^{1}Pr_2\text{-}C_6H_3)\}(Py)Cl]$  ( $3\mathbf{a}-\mathbf{e}$ ) (Scheme 3) in moderate to good yields as dark blue-violet microcrystalline solids, which precipitated from concentrated toluene/*n*-hexane solutions.



Complexes 3a-e are paramagnetic, and their solutions are sensitive to air and moisture, being formally unsaturated 15electron compounds. These complexes are partially soluble in *n*-hexane and Et<sub>2</sub>O and soluble in toluene. Complexes 3a-eshow paramagnetically shifted and broad <sup>1</sup>H NMR spectra (presented in Figures S22–S26 of the Supporting Information). Although the resonances corresponding to 5-substituted 2-iminopyrrolyl and pyridine ligand moieties are present, no accurate attributions can be made. In toluene- $d_8$  solutions, complexes 3a-e show effective magnetic moments in the range of  $3.7-4.8 \mu_B$  (Table 1), a typical observation for d<sup>7</sup> electronic distributions in the high-spin state (S = 3/2;

Table 1. Effective Magnetic Moments  $\mu_{\text{eff}}(\mu_{\text{B}})$  for the Co(II) Complexes 3a–e, Measured in Toluene- $d_8$  Solution (Evans Method), at Room Temperature

$\mu_{ m eff}~(\mu_{ m B})$
4.1
4.5
4.5
3.7
4.8

 $\mu_{\rm eff}({\rm spin only}) = 3.88 \ \mu_{\rm B})$ , with spin-orbit coupling effects.<sup>19</sup> Complex 3a was additionally characterized in the solid state by SQUID variable-temperature magnetometry (see Figure S36 of the Supporting Information) At room temperature,  $\chi T$  is 2.58 emu K mol<sup>-1</sup> and corresponds to an effective moment,  $\mu_{\rm eff}$ , of 4.55  $\mu_{\rm B}/{\rm Co}$  and g = 2.35. This value is higher than the spin-only value of Co(II) in the high-spin configuration (S = 3/2;  $\mu_{\rm eff} = 3.88 \ \mu_{\rm B}$ ; g = 2), suggesting a significant contribution of the unquenched orbital angular momentum due to the spin-orbit coupling, typical of Co(II),<sup>19</sup> and agrees well with the magnetic moments determined by the Evans method (Table 1).

The Co(II) complexes **3a,c** were characterized by X-ray diffraction, having crystallized in the monoclinic system in the  $P2_1$  and  $P2_1/c$  space groups, respectively. The ORTEP-3 drawings of complexes **3a,c** are presented in Figure 2, a selection of bond distances and angles being given in Table S3 of the Supporting Information. In both structures, it is possible to observe that a single 5-R-2-iminopyrrolyl ligand is coordinated to the Co atom in a bidentate fashion through the pyrrolyl and iminic nitrogen atoms.

The tetracoordinated Co centers are further bonded to a chlorine atom and a pyridine ligand. The Co-N bond distances are in the range of 1.982-2.064 Å, in the order  $Co-N_{pyrrolyl}$  <  $Co-N_{pyridine}$  <  $Co-N_{imine}$  in both complexes, very likely associated with the decreasing degree of the  $\sigma$ -donor character of the respective bonds. The Co-Cl bond distances are in the range of 2.211–2.227 Å. Considering the  $\tau_4$ parameters of 3a (0.78) and 3c (0.75),<sup>20</sup> the coordination geometries are best described as distorted tetrahedral and trigonal pyramidal, respectively. In both complexes, the torsion angles of the aryl rings bonded to the iminic nitrogen are 86.83 and 87.60°, respectively, making them nearly perpendicular to the iminopyrrolyl moiety. On the other hand, the dihedral angle between the 5-aryl group relative to the iminopyrrolyl moiety presents a significant deviation in both complexes. In complex 3a, the torsion of the  $5-(2,6-Me_2-C_6H_3)$  ring is 64.51°. In the case of 3c, two different dihedral angles can be defined since a slight dearomatization of the C5 atom of the pyrrolyl ring is observed. In fact, this carbon deviates 9.27-11.17° from planarity (considering the C3-C4-C5-C1 and C2-N1-C5-C1 dihedrals). This gives rise to a torsion of the  $5-(2_14_16-Ph_3-C_6H_2)$  substituent of  $55.00-60.01^\circ$  relative to the 2-iminopyrrolyl moiety. The less pronounced torsion of the 5- $(2,4,6-Ph_3-C_6H_2)$  group in comparison to that of  $5-(2,6-Me_2-$ C<sub>6</sub>H<sub>3</sub>) leads to a slight pyramidalization of the pyrrolyl nitrogen. The latter observation is quantified by an angle between the plane defined by N1-Co1-N2 and the 2iminopyrrolyl plane (defined by N1-C2-C6-N2) of 11.23° (in comparison to the near-planar chelate in **3a**).

The structures of complexes 3a-e were also studied by DFT calculations, the bond parameters determined by X-ray



Figure 2. ORTEP-3 diagrams of the X-ray diffraction molecular structures of 3a (left) and 3c (right) showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.





diffraction for 3a,c being consistently reproduced (see pages \$29-\$33 of the Supporting Information).

Isolation of a Trinuclear Chloride Co(II) Complex in the Absence of the Pyridine Donor. The reaction between the respective sodium salts of the 5-substituted 2-iminopyrrole ligand precursors 1a-e prepared in situ (by reacting 1a-e with NaH in refluxing THF) with  $CoCl_2(Py)_4$  in THF solutions also afforded, after standard workup conditions, complexes 3a-e in comparable yields, albeit with more troublesome and somewhat irreproducible purification procedures. In preliminary attempts of the preparation of Co(II) complexes bearing a single 5-substituted 2-iminopyrrolyl ligand, the reaction of the in situ prepared sodium salt of 1b with an excess of  $CoCl_2(THF)_{1.5}$  was performed, in toluene at 80 °C. With this reaction, we sought the isolation of the THF chloride Co(II) complex  $[Co{\kappa^2N,N'-5-(2,4,6-iPr_3-C_6H_2)-NC_4H_2-2 <math>C(H)=N(2,6-iPr_2-C_6H_3){(THF)Cl]}$  (*N,N'CoCl*(THF)). Instead, after a workup procedure that did not involve the evaporation of volatile materials, the trinuclear complex  $[Co\{\kappa^2N,N'-5\cdot(2,4,6\cdot^{i}Pr_3\cdot C_6H_2)\cdot NC_4H_2\cdot 2\cdot C(H)=N(2,6\cdot^{i}Pr_2\cdot C_6H_3)\}(\mu-Cl)]_2[(\mu-Cl)_2Co(THF)_2]$  (4) was the only isolated product (Scheme 4). Reactions of the same components in THF, with evaporation of volatile materials to dryness, point to the formation of impure Co(II) entities containing the respective 2-iminopyrrolyl and chloride ligands, likely contaminated with NaCl(THF)\_x, considering the respective combustion analysis. The formation of these multinuclear species is a consequence of irreproducible workup conditions, the nonexistence of a strongly coordinating ligand in the reaction medium, and the sensitivity of some reaction intermediates to vacuum conditions.

The trinuclear complex 4 exhibits a total effective magnetic moment in solution of 8.3  $\mu_{\rm B}$ , which is higher than the value expected for a spin-only system of three uncoupled Co(II)

with  $S = 3/2 \ (\mu_{\text{eff}} = g \times [3 \times (3/2 \times (3/2 + 1))]^{1/2} \cong 6.71 \ \mu_{\text{B}}/$ fu, g = 2) but well within the expected experimental values corresponding to a ground state ( $S = 3 \times 3/2 = 9/2$ ), with some degree of spin-orbit coupling. Complex 4 was additionally characterized by variable-temperature SQUID magnetometry (see Figures S36 and S37 of the Supporting Information),  $\chi T$  exhibiting a continuous decrease as the temperature decreases, from 8.85 emu K mol<sup>-1</sup> at 300 K down to 6.2 emu K mol<sup>-1</sup> at 16.5 K. At room temperature, the value per Co(II) trimer corresponds to an effective moment  $\mu_{eff}$  = 8.42  $\mu_{\rm B}$ /fu with g = 2.51, in agreement with the value determined by the Evans method. According to the theoretical calculations for the electronic structure (see below), this reveals a significant orbital contribution, as frequently observed in other linear trinuclear cobalt(II) complexes.<sup>21</sup> Below 16 K and upon cooling,  $\chi T$  sharply increases to 8.94 emu K mol<sup>-1</sup> with the appearance of a narrow peak at 5.6 K, followed by a rapid decrease down to 7.92 emu K mol<sup>-1</sup> at 2 K. This maximum suggests that the appearance of magnetic exchange interactions between the Co(II) centers is expected to be antiferromagnetic (AFM). These results are still preliminary, and a complete interpretation of these data will be the subject of a new publication.

The molecular structure of complex 4 was determined by Xray diffraction (Figure 3), a selection of bond distances and



**Figure 3.** ORTEP-3 diagram of the X-ray diffraction structure of **4** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

angles being shown in Table S4 of the Supporting Information. Complex 4 crystallized in the monoclinic system, in the  $P2_1/c$  space group. This compound is an example of a linear trinuclear Co complex, the Co–Co–Co angle being 175.3144(6)°. Complex 4 is composed of two tetracoordinated 15-electron Co(II) centers (Co1 and Co3) and one hexacoordinated 19-electron Co(II) center (Co2). The tetracoordinated Co(II) centers have distorted tetrahedral coordination geometries and are bonded to a 5-(2,4,6-triisopropyl)-2-iminopyrrolyl moiety in the usual bidentate chelation mode and two bridging chlorides to the hexacoordinated to two THF molecules, displaying a nearly octahedral geometry. The Co–Co distances are in the range of 3.319–3.328 Å. The Co–N bond distances in the tetracoordinated sites are in the range of 1.968–2.070 Å, with the Co– $N_{\rm pyrrolyl}$  bonds being, on average, 0.09 Å shorter than the Co– $N_{\rm imine}$  bonds.

The Co–Cl bond distances are in the range of 2.274–2.285 Å for the tetracoordinated Co(II) centers and around 2.474–2.503 Å for the hexacoordinated Co(II) center. The significantly longer Co2–Cl bond distances in the latter case (0.21 Å longer, on average, in relation to those of Co1 and Co3) is attributed to the coordinative supersaturation of the central Co(II) atom. The observed long Co2–Cl bond distances fall in the 5% longest Co–Cl bonds crystalographically characterized in Co chloride complexes.<sup>22</sup> In fact, most of the compounds with a Co–Cl bond distance in this range correspond to bis chloride octahedral Co(II) complexes.<sup>23</sup>

In order to understand the spin-state distribution of the Co atoms of the trinuclear complex 4, geometry optimizations on two spin isomers were performed by DFT calculations. The spin isomers chosen were that corresponding to the three Co atoms in the high-spin state ( $S = 3 \times 3/2 = 9/2$ ),  $4_{9/2}$ , and that corresponding to two terminal high-spin Co atoms and one central low-spin Co atom ( $S = 2 \times 3/2 + 1/2 = 7/2$ ),  $4_{7/2}$ . The coordinates of the optimized structures are shown in pages S33–S36 of the Supporting Information. The energy balance between both structures indicates that isomer  $4_{9/2}$  is 24 kcal mol<sup>-1</sup> more stable than isomer  $4_{7/2}$ .

The spin density calculated for  $4_{9/2}$  (Figure 4) is essentially centered on the Co atoms, with small contributions from the



**Figure 4.** Total spin density plot of the optimized  $4_{9/2}$  spin isomer (*S* = 9/2) of the trinuclear complex 4.

coordinating nitrogen and oxygen atoms, being equally distributed by the three Co atoms, in accordance with the same high-spin nature for the three metal centers.

In summary, the DFT results corroborate the experimental data obtained by both the Evans method and SQUID magnetochemistry studies, in which the trinuclear complex 4 exhibits a global high-spin S = 9/2 electronic configuration.

Hydroboration of Terminal Alkenes Catalyzed by Complexes 3a-e Activated by K(HBEt<sub>3</sub>). Bearing in mind that the synthesized tetracoordinated Co(II) complexes 3a-eare coordinatively unsaturated (formally 15-electron species) and contain potentially labile or reactive ligands, we envisioned

their use as precatalysts for the hydroboration of  $\alpha$ -olefins with pinacolborane (HBPin). A preliminary hydroboration of styrene was attempted, using 1 mol % of **3a** with 3 mol % of K(HBEt<sub>3</sub>) as the catalytic system, under neat conditions, and it was possible to observe that, in 16 h, the mixture contained exclusively the respective addition products in a 2.33:1 anti-Markovnikov:Markovnikov molar ratio (a-Mk:Mk) in 63% yield (Table 3). Encouraged by this result, we decided to analyze the  $\alpha$ -olefin substrate scope with the catalyst system **3a**/K(HBEt<sub>3</sub>). These results are presented in Table 2, the <sup>1</sup>H NMR spectra of the alkylboronates being shown in Figures **S28–S32** of the Supporting Information. The system is inactive in the absence of activation by K(HBEt<sub>3</sub>).

Table 2. Substrate Scope of the Hydroboration of Terminal Alkenes Catalyzed by the System 3a/K(HBEt<sub>3</sub>)



<sup>*a*</sup>Conditions: 1 mol % of **3a**, 3 mol % of K(HBEt<sub>3</sub>), 2 mmol of substrate, 2.5 mmol of HBPin, reaction time 16 h, temperature 25 °C. <sup>*b*</sup>Yields determined by weighing the isolated reaction products. <sup>*c*</sup>Calculated by <sup>1</sup>H NMR. <sup>*d*</sup>Owing to the symmetry of cyclohexene, a single reaction product is obtained.

Under neat and mild conditions, this catalyst system leads to good yields (62–75%) in addition products of HBPin to the respective  $\alpha$ -olefins, being almost exclusively selective in the anti-Markovnikov (*a*-Mk) products, except for the case of styrene. The system **3a**/K(HBEt<sub>3</sub>) is also suitable for the hydroboration of cyclohexane, albeit in a more modest yield.

In this work, the organoboranes were produced in yields that are in the range of those obtained by some authors reporting cobalt-catalyzed hydroboration of a similar substrate scope.<sup>4c,d</sup> Although respectable, the yields obtained in the present work are lower than the best results reported to date. In fact, some authors have obtained yields higher than 90% for most of the substrates presently considered in less than 1 h, under similar reaction conditions.<sup>4b,f,k</sup> In our case (except for styrene) and in those reported by other authors, the reactions were exclusively selective in the anti-Markovnikov products.

Aside from the substrate scope, we evaluated the effect of the different precatalysts in the hydroboration of styrene, which was the substrate that revealed regioselectivity problems. The results for the hydroboration of styrene with HBPin using the different Co(II) precatalysts 3a-e activated by K(HBEt<sub>3</sub>) are shown in Table 3.

The Co(II) precatalysts activated by K(HBEt<sub>3</sub>) systematically yielded a mixture of products in moderate to good yields, Table 3. Structure/Selectivity Relationship for the Hydroboration of Styrene Catalyzed by the System  $3a-e/K(HBEt_3)$ 

$ \begin{array}{c} \sum_{i=1}^{n} \sum_{i=1}^{n} \\ D_{B} \\ H \end{array} $ HBPin	1 mol% of <b>3a-e</b> 3 mol% K(HBEt <sub>3</sub> ) 25 °C, neat	PinB Ph + a-Mk	BPin Ph Mk
complex <sup>a</sup>	yield (%) <sup>b</sup>	selectivity (a-Mk:1	Mk) <sup>c</sup>
3a	63	2.33:1	
3b	35	2.14:1	
3c	44	0.75:1	
3d	62	1:1	
3e	d	0.78:1 <sup>d</sup>	

<sup>*a*</sup>Conditions: 1 mol % of **3a–e**, 3 mol % of K(HBEt<sub>3</sub>), 2 mmol of styrene, 2.5 mmol of HBPin, reaction time 16 h, temperature 25 °C. <sup>*b*</sup>Isolated yields determined by weighing the isolated reaction products. <sup>*c*</sup>Calculated by <sup>1</sup>H NMR. <sup>*d*</sup>Complex **3e** was not completely selective in the hydroboration of styrene.

but it can be seen that precatalyst 3c, containing the highly encumbering 5-(2,4,6-triphenylphenyl) substituent, reverses the a-Mk:Mk molar ratio, favoring the Markovnikov addition product. A superimposition of the <sup>1</sup>H NMR spectra of the products obtained by  $3a-d/K(HBEt_3)$  in the region of the  $\alpha$ protons (relative to the boron atom) is shown in Figure S33 of the Supporting Information, revealing the increasing selectivity in the Markovnikov product in the order 3a < 3b < 3d < 3c. In fact, it can be observed that increasing the steric bulkiness of the ortho groups of the precatalyst 5-aryl substituent, going from methyl (3a) to isopropyl (3b) and phenyl (3c), the catalyst system becomes more selective in the Markovnikov product.

The use of the also bulky, although flat, 5-(anthracen-9-yl) substituent (precatalyst 3d) leads to an equimolar mixture of addition products. Complex 3e, the only 5-alkyl derivative in the series, exhibited a lower selectivity toward hydroboration, yielding a complex mixture of reaction products, the two desired addition products of hydroboration being obtained in a 0.78:1 a-MK:Mk molar ratio, an evidence of the also high steric bulkiness of the CPh<sub>3</sub> group.

Markovnikov-rich cobalt-catalyzed hydroboration of alkenes is not common and the present system showed moderate selectivity, by stereochemical tuning of the complexes used. Only very recently did some authors report nearly Markovnikov exclusive cobalt-based systems for these reactions, with ratios as high as 2:98 (a-Mk:Mk).<sup>4n-p</sup>

Preliminary stoichiometric reactions of some of the precatalysts with  $K(HBEt_3)$  were attempted. In particular, a NMR-scale reaction of complex **3b** with 3 equiv of  $K(HBEt_3)$  in  $C_6D_6$  was performed, giving rise to a sudden color change from dark blue-violet to dark red with concomitant effervescence. The <sup>1</sup>H NMR spectrum reveals an excess of  $K(HBEt_3)$  and a single paramagnetic species, whereas the <sup>11</sup>B{<sup>1</sup>H} spectrum also exhibits the excess of  $K(HBEt_3)$  and another species at 0.98 ppm that can be assigned to a Py–BEt<sub>3</sub> adduct<sup>24</sup> (the NMR spectra of this reaction are presented in Figures S34 and S35 of the Supporting Information). These observations point to the formation of a putative Co(II) hydride complex that readily undergoes reductive elimination of molecular dihydrogen to form a potential Co(I) species,

Taking the latter results into account, we propose that the activation by  $K(HBEt_3)$  very likely generates a low-oxidation-state "(NN')Co<sup>I</sup>" entity (Scheme 5, cycle A). Considering





mechanistic discussions proposed by other authors for cobaltcatalyzed hydroboration of alkenes,<sup>4d,h</sup> the "(**NN**')**Co**<sup>I</sup>" entity is prone to coordination of the olefin and subsequent oxidative addition of HBPin to that center, giving rise to (NN')- $Co^{III}(H)(BPin)(\eta^2-CH_2=CHR)$ . The resulting hydrideboryl species generates the intermediates (NN')- $Co^{III}(CH_2CHBPinR)(H)$  and/or  $(NN')Co^{III}[CH(R)-$ CH<sub>2</sub>BPin](H), possibly via a migratory insertion of the BPin boryl moiety. Alternatively, a migratory insertion of the hydride can occur, generating the intermediates (NN')-Co<sup>III</sup>(CH<sub>2</sub>CH<sub>2</sub>R)(BPin) and/or (NN')Co<sup>III</sup>[CH(R)CH<sub>3</sub>]-(BPin). Finally, a reductive elimination reaction yields the reaction products and regenerates the active "(NN')CoI" species. The enhanced Markovnikov selectivity in the case of styrene is very likely justified by a more favorable 2,1-insertion of the boryl or hydride ligands (as opposed to the nearquantitative 1,2-insertion in the remaining substrates), which might result from the preferential  $\eta^3$  stabilization of the resulting styryl group through  $\eta^3$ -benzylic coordination, thus increasing the amount of the (NN')Co<sup>III</sup>[CH(R)CH<sub>2</sub>BPin]-(H) or (NN')Co<sup>III</sup>[CH(R)CH<sub>3</sub>](BPin) intermediate species.

One cannot discard the possibility of a hydride route mechanism (Scheme 5, cycle B),<sup>4b</sup> in which the activation of the Co(II) complexes by  $K(HBEt_3)$  generates a putative

 $(NN')Co^{II}H$  hydride complex. In such a case, the coordination of the olefin to that hydride species and subsequent migratory insertion generates the intermediate complexes (NN')- $Co^{II}(CH_2CH_2R)$  and  $(NN')Co^{II}[CH(R)(CH_3)]$ . These intermediates then react with HBPin, possibly via a fourmembered concerted step, to yield the corresponding mixture of products, regenerating the hydride active species.

#### 

A family of new tetracoordinated Co(II) complexes bearing a single 5-substituted 2-iminopyrrolyl ligand and its catalytic application in the hydroboration of terminal alkenes was reported. First, the sterically demanding ligand precursors 1ae were treated with  $K[N(SiMe_3)_2]$  to afford the respective potassium salts 2a-e in high yields. The integrity of compounds 2a-e was probed in solution by NMR spectroscopy and, in the case of 2d, in the solid state by X-ray diffraction, revealing a 1D-coordination polymeric structure. Subsequently, by salt metathesis of 2a-e and  $CoCl_2(Py)_4$ , the pyridine chloride 5-substituted 2-iminopyrrolyl Co(II) complexes 3a-e were prepared in moderate to good yields. In solution, these compounds exhibit <sup>1</sup>H NMR spectra with paramagnetically shifted and broad resonances, displaying by the Evans method a high-spin configuration. Complexes 3a,e were also characterized by X-ray diffraction, demonstrating distorted tetrahedral geometries. It was also observed that, when traces of THF are present in the reaction media, adducts such as the linear trinuclear complex 4 can be formed and isolated, which exhibited high-spin behavior for all its Co(II) centers, as shown by the magnetic properties and confirmed by DFT calculations, and antiferromagnetic coupling between adjacent Co(II) atoms.

Complexes 3a-d served as efficient precatalysts for the hydroboration of  $\alpha$ -olefins with HBPin. On activation with K(HBEt<sub>3</sub>), complex 3a exclusively yielded the anti-Markovnikov and Markovnikov alkylboronate addition products, in 50-80% yields, except for the case of styrene. Specifically for this latter substrate, by using the different precatalysts 3a-d it was possible to observe that the selectivity in the Markovnikov addition product increased with the increase in steric bulkiness of the substituent at the position 5 of the 5-aryl-2iminopyrrolyl ligand, anti-Markovnikov:Markovnikov ratios of 2.33:1 (3a) to 0.75:1 (3c) being obtained. Considering these encouraging results, it is imperative to modify position 5 of the pyrrole, to favor the scarcer Markovnikov product or even turn the attention to less reactive substrates. Preliminary mechanistic studies indicate that activation by K(HBEt<sub>3</sub>) gave rise to a putative Co(I) species, meaning that the catalytic system likely followed an oxidative addition pathway. These studies are essential to the understanding of the system and will be reported in a timely fashion.

#### EXPERIMENTAL SECTION

**General Considerations.** All operations were performed under a dry dinitrogen atmosphere using standard glovebox and Schlenk techniques unless otherwise noted. Dinitrogen gas for all operations (purity <1 ppm of  $O_2$  and  $H_2O$ ) was supplied by Air Liquide and purified by passage through 4 Å molecular sieves. Solvents were predried with activated 4 Å molecular sieves and distilled by heating under dinitrogen over suitable drying agents (sodium/benzophenone for toluene, diethyl ether, and THF; CaH<sub>2</sub> for *n*-hexane). Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannulae, and mixtures were filtered in a similar

way using modified cannulae that could be fitted with glass fiber filter disks.

The ligand precursor  $1a^{15d}$  and starting materials  $CoCl_2(Py)_4^{25}$  and  $CoCl_2(THF)_{15}^{26}$  were prepared as described in the literature.

**General Procedure for the Synthesis of the Ligand Precursors 1b–e.** A mixture of the respective 5-R-2-formyl-1*H*pyrrole and 2,6-diisopropylaniline, with a catalytic amount of *p*toluenesulfonic acid, was dissolved in ca. 50 mL of toluene and refluxed in a flask equipped with a Soxhlet apparatus charged with activated molecular sieves and a CaCl<sub>2</sub> guard tube, until full consumption of the reagents (as indicated by <sup>1</sup>H NMR analysis). The mixture was filtered, and the resulting solution was evaporated to dryness. The crude product was purified by conventional solvent recrystallization or column chromatography.

 $5 \cdot (2,4,6-Triisopropylphenyl)-2 \cdot [N \cdot (2,6-diisopropylphenyl)-formimino]-1H-pyrrole (1b). The general procedure was followed using <math>5 \cdot (2,4,6-triisopropylphenyl)-2$ -formyl-1H-pyrrole<sup>17b</sup> (1.4 g, 4.8 mmol) and 2,6-diisopropylaniline (0.85 g, 4.5 mmol). The crude mixture was extracted with *n*-hexane, concentrated, and stored at -20 °C, precipitating as a brown powder. Yield: 1.60 g (77%).

Anal. Calcd for  $C_{32}H_{44}N_2$ , obtained (calculated): C, 84.14 (84.16); H, 9.30 (9.71); N, 6.00 (6.13). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.21 (br, 1H, NH), 7.96 (s, 1H, N=CH), 7.17–7.15 (m, 2H, 5-Ph-H<sub>meta</sub>), 7.11–7.07 (m, 3H, N-Ph-H<sub>meta</sub> and N-Ph-H<sub>para</sub>), 6.69 (br, 1H, H3), 6.23 (br, 1H, H4), 3.06 (h, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, 2H, N-Ph<sub>ortho</sub>-(CH(CH<sub>3</sub>)<sub>2</sub>)), 2.97 (h, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1H, 5-Ph<sub>para</sub>-(CH(CH<sub>3</sub>)<sub>2</sub>)), 2.83 (h, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, 2H, 5-Ph<sub>ortho</sub>(CH(CH<sub>3</sub>)<sub>2</sub>)), 1.33 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, 5-Ph<sub>para</sub>-(CH(CH<sub>3</sub>)<sub>2</sub>)), 1.22–1.18 (m, 24H, 5-Ph<sub>ortho</sub>-(CH(CH<sub>3</sub>)<sub>2</sub>) and N-Ph<sub>ortho</sub><sup>-</sup>(CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  151.3 (N=CH), 150.0 (5-Ph-C<sub>para</sub>), 149.3 (N-Ph-C<sub>ipso</sub> and 5-Ph-C<sub>ortho</sub>), 138.3 (N-Ph-C<sub>ortho</sub>), 134.6 (CS), 130.0 (C2), 127.8 (5-Ph-C<sub>ipso</sub>), 123.9 (N-Ph-C<sub>para</sub>), 123.1 (5-Ph-C<sub>meta</sub>), 121.0 (N-Ph-C<sub>meta</sub>), 115.6 (C3), 111.4 (C4), 34.6 (5-Ph<sub>para</sub><sup>-</sup>(CH(CH<sub>3</sub>)<sub>2</sub>), 30.94 (5-Ph<sub>ortho</sub><sup>-</sup>(CH(CH<sub>3</sub>)<sub>2</sub>), 28.1 (N-Ph<sub>ortho</sub><sup>-</sup>(CH(CH<sub>3</sub>)<sub>2</sub>), 24.7 (5-Ph<sub>ortho</sub>-(CH(CH<sub>3</sub>)<sub>2</sub>), 24.2 (5-Ph<sub>para</sub><sup>-</sup>(CH(CH<sub>3</sub>)<sub>2</sub>), 23.5 (N-Ph<sub>ortho</sub><sup>-</sup>(CH-(CH<sub>3</sub>)<sub>2</sub>).

5-(2,4,6-Triphenylphenyl)-2-[N-(2,6-diisopropylphenyl)-formimino]-1H-pyrrole (1c). The general procedure was followed using 5-(2,4,6-triphenylphenyl)-2-formyl-1H-pyrrole (2.0 g, 5.0 mmol) (synthesis described in the Supporting Information) and 2,6-diisopropylaniline (0.87 g, 4.9 mmol). The crude mixture was washed with*n*-hexane and recrystallized from a concentrated toluene/*n*-hexane solution (1/4 in volume), to yield the product as a pale yellow powder. Yield: 1.19 g (43%).



Anal. Calcd for  $C_{41}H_{38}N_2$ , obtained (calculated): C, 88.04 (88.13); H, 6.65 (6.86); N, 4.93 (5.01). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.59 (br, 1H, NH), 7.72 (m, 5H, H8 + H15 + N=CH). 7.48 (t, 2H, H13, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz), 7.39 (t, 1H, H17, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 7.38–7.30 (m, 10H, H11 + H12 + H16), 7.15–7.05 (m, 3H, N-Ph-H<sub>meta</sub> + N-Ph-H<sub>para</sub>), 6.32 (d, 1H, H3, <sup>3</sup>J<sub>HH</sub> = 3.3 Hz), 5.67 (d, 1H, H4, <sup>3</sup>J<sub>HH</sub> = 3.3 Hz), 2.78 (h, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz), 1.14 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz), NH resonance absent. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  151.3 (N=CH), 148.9 (N-Ph-C<sub>ipso</sub>), 142.9 (C6), 141.8 (C10), 140.9 (C9), 140.2 (C14), 138.4 (N-Ph-C<sub>ortho</sub>), 133.5 (C2), 129.8 (C5), 129.4 (C11), 129.0 (C16), 128.7 (C8), 128.2 (C12), 127.9 (C17), 127.3 (C15), 127.1 (C13), 123.9 (N-Ph-C<sub>para</sub>), 123.0 (N-Ph-C<sub>meta</sub>), 115.8 (C3), 113.9 (C4), 27.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.8 (CH(CH<sub>3</sub>)<sub>2</sub>), C7 resonance absent.

5-(Anthracen-9-yl)-2-[N-2,6-(diisopropylphenyl)formimino]-1Hpyrrole (1d). The general procedure was followed using 5-(anthracen-9-yl)-2-formyl-1H-pyrrole (1.9 g, 7.0 mmol) and 2,6-diisopropylaniline (1.2 g, 6.9 mmol). The crude mixture was washed with *n*-hexane, extracted with diethyl ether, and evaporated to dryness. A second washing with *n*-hexane gave the title compound as a golden yellow solid. Yield: 2.03 g (68%).



Anal. Calcd for  $C_{31}H_{30}N_2 \cdot 0.25C_4H_{10}O$ , obtained (calculated): C, 85.31 (85.58); H, 7.84 (7.29); N, 6.01 (6.24). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.56 (s, 1H, H13), 8.14–8.04 (m, 5H, CH=N + H8 + H11), 7.56–7.48 (m, 4H, H9 + H10), 7.23–7.17 (m, 3H, N-Ph-H<sub>meta</sub> + N-Ph-H<sub>para</sub>), 6.97 (br, 1H, H3), 6.66 (d, <sup>3</sup>J<sub>HH</sub> = 3.3 Hz, 1H, H4), 3.15 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), NH resonance absent. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  151.7 (CH=N), 131.5 (C12), 131.4 (C7), 128.7 (C8), 128.4 (C13), 126.4 (C9), 126.3 (C10), 125.5 (C11), 123.3 (N-Ph-C<sub>meta</sub> + N-Ph-C<sub>para</sub>), 116.2 (C3), 113.7 (C4) 28.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.8 (CH(CH<sub>3</sub>)<sub>2</sub>), N-Ph-C<sub>ipso</sub>, N-Ph-C<sub>ortho</sub>, C2, C5, and C6 resonances absent.

5-Triphenylmethyl-2-[N-(2,6-diisopropylphenyl)formimino]-1H-pyrrole (1e). The general procedure was followed using 5-triphenylmethyl-2-formyl-1H-pyrrole (1.4 g, 4.2 mmol) (synthesis described in the Supporting Information) and 2,6-diisopropylaniline (0.61 g, 4.0 mmol). The crude product was purified by column chromatography using as eluent *n*-hexane/ethyl acetate (4/1) to yield the product as a pale yellow powder. Yield: 1.02 g (51%).

Anal. Calcd for  $C_{36}H_{36}N_2$  obtained (calculated): C, 86.78 (87.05); H, 7.24 (7.31); N, 5.41 (5.64). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.95 (br, 1H, NH), 7.85 (s, 1H, N=CH), 7.33–7.24 (m, 9H, 5-CPh<sub>3</sub>-H<sub>ortho</sub> + CPh<sub>3</sub>-H<sub>para</sub>), 7.20–7.18 (m, 6H, C(Ph)<sub>3</sub>-H<sub>meta</sub>)), 7.11–7.04 (m, 3H, N-Ph-H<sub>meta</sub> + N-Ph-H<sub>para</sub>), 6.54 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 3.7 Hz, H3), 6.12 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 3.7 Hz, H4), 2.92 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.12 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  151.4 (N=CH), 148.8 (N-Ph-C<sub>ipso</sub>), 145.5 (CPh<sub>3</sub>-C<sub>ipso</sub>), 142.2 (C5), 138.4 (N-Ph-C<sub>ortho</sub>), 130.5 (CPh<sub>3</sub>-C<sub>ortho</sub>), 130.2 (C2), 127.9 (CPh<sub>3</sub>-C<sub>meta</sub>), 126.9 (CPh<sub>3</sub>-C<sub>para</sub>), 124.0 (N-Ph-C<sub>para</sub>), 123.2 (N-Ph-C<sub>meta</sub>), 115.3 (C3), 112.8 (C4), 60.96 (CPh<sub>3</sub>), 28.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.6 (CH(CH<sub>3</sub>)<sub>2</sub>).

General Procedure for the Synthesis of the 5-R-2-[N-(2,6diisopropylphenyl)formimino]pyrrolyl Potassium Salts 2a-e. Toluene solutions of K[N(SiMe<sub>3</sub>)<sub>2</sub>] (1.1 equiv) and the respective 5substituted 2-iminopyrrolyl ligand precursor (1a-e, one equivalent) were combined, giving rise to a thick suspension. The suspension was stirred for 2 h, the supernatant was filtered off, and the solid was washed three times with *n*-hexane. The pale yellow to off-white powders were dried under vacuum to yield the title salts.

Potassium 5-(2,6-Dimethylphenyl)-2-[N-(2,6-diisopropylphenyl)formimino]pyrrolyl (**2a**). The general procedure was followed, using 3.0 g (8.37 mmol) of ligand precursor **1a** and 1.83 g (9.20 mmol) of K[N(SiMe<sub>3</sub>)<sub>2</sub>], yielding an off-white powder. Yield: 2.69 g (81%).

<sup>1</sup>H NMR (300 MHz, THF-*d*<sub>8</sub>): δ δ 7.72 (s, 1H, N=CH), 7.06– 6.99 (m, 2H, 5-Ph-H<sub>para</sub> + N-Ph-H<sub>para</sub>), 6.97–6.84 (m, 4H, 5-Ph-H<sub>meta</sub> + N-Ph-H<sub>meta</sub>), 6.55 (br, 1H, H3), 5.92 (br, 1H, H4), 3.28 (br, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.23 (s, 6H, CH<sub>3</sub>), 1.15 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 4.2 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, THF-*d*<sub>8</sub>): δ 159.9 (N=CH), 154.1 (N-Ph-C<sub>ipso</sub>), 148.1 (C5), 143.9 (C2), 140.6 (5-Ph-C<sub>ipso</sub>), 139.6 (5-Ph-C<sub>ortho</sub>), 138.2 (N-Ph-C<sub>ortho</sub>), 127.5 (5-Ph-C<sub>meta</sub>), 125.7 (5-Ph-C<sub>para</sub>), 123.4 (N-Ph-C<sub>para</sub>), 122.9 (N-Ph-C<sub>meta</sub>), 121.9 (C3), 110.5 (C4), 28.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (CH(CH<sub>3</sub>)<sub>2</sub>).

Potassium  $5-(2,4,6-Triisopropylphenyl)-2-[N-(2,6-diisopropylphenyl)formimino]pyrrolyl (2b). The general procedure was followed, using 1.18 g (2.59 mmol) of ligand precursor 1b and 0.57 g (2.85 mmol) of K[N(SiMe_3)_2], yielding an off-white powder. Yield: 0.989 g (78%).$ 

<sup>1</sup>H NMR (300 MHz, THF- $d_8$ ):  $\delta$  7.70 (s, 1H, N=CH), 7.06–6.98 (d, 2H, N-Ph-H<sub>meta</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 6.95 (s, 2H, 5-Ph-H<sub>meta</sub>), 6.88 (t,

1H, N-Ph-H<sub>para</sub>,  ${}^{3}J_{HH} = 7.5 \text{ Hz}$ ), 6.53 (d, 1H, H3,  ${}^{3}J_{HH} = 3.0 \text{ Hz}$ ), 5.91 (d, 1H, H4,  ${}^{3}J_{HH} = 3.3 \text{ Hz}$ ), 3.27 (h, 2H, N-Ph-CH(CH<sub>3</sub>)<sub>2</sub>,  ${}^{3}J_{HH} = 6.9 \text{ Hz}$ ), 3.19 (h, 2H, 5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> artho,  ${}^{3}J_{HH} = 6.9 \text{ Hz}$ ), 2.87 (h, 1H, 5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> parar  ${}^{3}J_{HH} = 6.9 \text{ Hz}$ ), 1.27 (d, 6H, 5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> parar  ${}^{3}J_{HH} = 6.9 \text{ Hz}$ ), 1.27 (d, 6H, 5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> + 5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> ortho).  ${}^{13}C{}^{1}H{}^{1}$  NMR (75 MHz, THF-d<sub>8</sub>):  $\delta$  159.7 (N=CH), 154.1 (N-Ph-C<sub>ottoo</sub>), 149.2 (5-Ph-C<sub>ottoo</sub>), 147.9 (C5), 146.7 (5-Ph-C<sub>para</sub>), 140.5 (N-Ph-C<sub>ottoo</sub>), 139.9 (5-Ph-C<sub>ipso</sub>), 139.3 (C2), 123.4 (N-Ph-C<sub>meta</sub>), 122.8 (N-Ph-C<sub>para</sub>), 122.0 (C3), 120.3 (5-Ph-C<sub>meta</sub>), 111.5 (C4), 35.6 (5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> parar), 30.9 (5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> + 5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> ortho), 28.7 (N-Ph-CH(CH<sub>3</sub>)<sub>2</sub>), 25.3 (N-Ph-CH(CH<sub>3</sub>)<sub>2</sub> + 5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> ortho), 24.9 (5-Ph-CH(CH<sub>3</sub>)<sub>2</sub> parar). Potassium 5-(2,4,6-Triphenylphenyl)-2-[N-(2,6-Ph-CH)(2) + 2-[N-(2,6-Ph-CH)(2) + 2-[N-(2) +

Potassium  $5-(2,4,6-Triphenylphenyl)-2-[N-(2,6-disopropylphenyl)formimino]pyrrolyl (2c). The general procedure was followed, using 1.19 g (2.13 mmol) of ligand precursor 1c and 0.47 g (2.34 mmol) of K[N(SiMe_3)_2], yielding a pale yellow fluorescent powder. Yield: 0.813 g (64%).$ 



<sup>1</sup>H NMR (300 MHz, THF- $d_8$ ): δ 7.72 (d, 2H, H15, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 7.63 (s, 2H, H8), 7.52 (s, 1H, N=CH), 7.42 (t, 2H, H16, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 7.31–7.12 (m, 11H, H11 + H12 + H15 + H17), 6.99 (d, 2H, N-Ph-H<sub>meta</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 6.86 (t, 1H, N-Ph-H<sub>para</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 6.25 (br, 1H, H3), 5.48 (br, 1H, H4), 3.05 (h, 2H, CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz), 1.11 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, THF- $d_8$ ): δ 159.6 (N=CH), 153.3 (N-Ph-C<sub>ipso</sub>), 145.5 (C10), 145.4 (C2), 142.8 (C6), 142.3 (C14), 140.4 (C7), 139.4 (C5), 138.9 (N-Ph-C<sub>ortho</sub>), 130.6 (C11 + C15), 129.6 (C16), 129.0 (C8), 127.9 (N-Ph-C<sub>meta</sub>), 127.7 (C11 + C16), 127.6 (C13 + C17), 126.3 (N-Ph-C<sub>para</sub>), 123.2 (C3), 114.2 (C4), 28.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.7 (CH(CH<sub>3</sub>)<sub>2</sub>), C9 resonance absent.

Potassium 5-(Anthracen-9-yl)-2-[N-(2,6-diisopropylphenyl)formimino]pyrrolyl (2d). The general procedure was followed, using 1.51 g (3.50 mmol) of ligand precursor 1d and 0.77 g (3.85 mmol) of K[ $N(SiMe_3)_2$ ]. Since the reaction mixture was very soluble in toluene, all volatiles were removed under reduced pressure until an oil was formed. *n*-Hexane (ca. 30 mL) was added to the oil, immediately precipitating a dark brown powder that was further washed three times with *n*-hexane. Crystals suitable for X-ray diffraction were obtained from a concentrated toluene solution layered with 3-fold *n*-hexane at room temperature. Yield: 1.18 g (72%).



<sup>1</sup>H NMR (300 MHz, THF- $d_8$ ): δ 8.52 (d, 2H, H11, <sup>3</sup> $J_{\text{HH}}$  = 7.2 Hz), 8.29 (s, 1H, N=CH), 8.52 (m, 3H, H8 + H13), 7.48–7.02 (m, 6H,

H9 + H10 + N-Ph-H<sub>meta</sub>), 6.94 (t, 1H, N-Ph-H<sub>para</sub>)  ${}^{3}J_{HH} = 6.0$  Hz), 6.79 (br, 1H, H3), 6.38 (br, 1H, H4), 3.36 (br, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (br, 12H, CH(CH<sub>3</sub>)<sub>2</sub>).  ${}^{13}C{}^{1}H$  NMR (75 MHz, THF- $d_{8}$ ):  $\delta$  160.3 (N=CH), 153.9 (N-Ph-C<sub>ipso</sub>), 145.3 (C2), 140.9 (C6), 140.5 (C5), 133.4 (C12), 133.2 (C7), 130.6 (C11), 128.6 (C8), 125.5 (C9), 124.6 (C13), 124.4 (C10), 123.4 (N-Ph-C<sub>ortho</sub> + N-Ph-C<sub>meta</sub>), 123.1 (N-Ph-C<sub>para</sub>), 121.6 (C3), 114.4 (C4), 28.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>).

Potassium 5-(Triphenylmethyl)-2-[N-(2,6-diisopropylphenyl)-formimino]pyrrolyl (2e). The general procedure was followed, using 2.05 g (4.13 mmol) of ligand precursor 1e and 0.91 g (4.54 mmol) of K[N(SiMe<sub>3</sub>)<sub>2</sub>], yielding an off-white powder. Yield: 1.70 g (77%).

<sup>1</sup>H NMR (300 MHz, THF- $d_8$ ): δ 7.65 (s, 1H, N=CH), 7.35–7.24 (br, 6H, CPh<sub>3</sub>-H<sub>ortho</sub>), 7.22–7.11 (br, 9H, CPh<sub>3</sub>-H<sub>meta</sub> + CPh<sub>3</sub>-H<sub>para</sub>), 7.00 (d, 2H, N-Ph-H<sub>meta</sub> <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 6.86 (t, 1H, N-Ph-H<sub>para</sub>, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 6.45 (d, 1H, H3, <sup>3</sup>J<sub>HH</sub> = 2.7 Hz), 5.85 (d, 1H, H4, <sup>3</sup>J<sub>HH</sub> = 2.7 Hz), 3.18 (h, 2H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz), 1.11 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, THF- $d_8$ ): δ 156.4 (N=CH), 153.4 (CPh<sub>3</sub>) 140.4 (N-Ph-C<sub>ortho</sub>), 138.2 (CPh<sub>3</sub>-C<sub>ipso</sub>), 132.4 (CPh<sub>3</sub>-C<sub>ortho</sub>), 127.3 (CPh<sub>3</sub>-C<sub>meta</sub>), 125.9 (CPh<sub>3</sub>-C<sub>para</sub>), 123.3 (N-Ph-C<sub>ipso</sub> + N-Ph-C<sub>meta</sub>), 122.9 (N-Ph-C<sub>para</sub>), 121.0 (C3), 112.7 (C4), 28.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.5 (CH(CH<sub>3</sub>)<sub>2</sub>).

General Procedure for the Synthesis of  $[Co\{\kappa^2N,N'-5-R-NC_4H_2-2-C(H)]=N(2,6-Pr_2-C_6H_3)\}(Py)CI]$  (3a-e). Toluene was added to a solid mixture of  $CoCl_2(Py)_4$  (1 equiv) and the appropriate potassium salt (2a-e, 1 equiv). The mixture was stirred overnight at 80 °C, leaving a dark violet suspension. The dark violet solution was filtered, and all volatiles were evaporated to dryness, leaving a dark blue-violet residue. The residue was washed with *n*-hexane and extracted with toluene, the extracts being combined, concentrated, carefully layered with *n*-hexane (1/3), and stored at -20 °C. After a few days, the title complexes precipitated as dark blue-violet powders or crystals.

 $[Co\{\kappa^2 N, N'-5-(2,6-Me_2-C_6H_3)-NC_4H_2-2-C(H)=N(2,6-^iPr_2-C_6H_3)\}-(Py)CI]$  (**3a**). The general procedure was followed, using 0.32 g (0.8 mmol) of the potassium salt **2a** and 0.40 g (0.8 mmol) of CoCl<sub>2</sub>(Py)<sub>4</sub>, yielding a dark blue-violet crystalline solid. Yield: 0.322 g (76%).

Anal. Calcd for  $C_{30}H_{34}ClCoN_3$ , obtained (calculated): C, 67.77 (67.86); H, 6.53 (6.45); N, 7.69 (7.91).  $\mu_{eff}$  (toluene- $d_8$ ): 4.1  $\mu_B$ . <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  50.14, 5.31, 1.18, 0.83, 0.23, -2.30, -12.31, -22.68.

 $[Co\{\kappa^2 N, N'-5-(2,4,6^{-i}Pr_3-C_6H_2)-NC_4H_2-2-C(H)=N(2,6^{-i}Pr_2-C_6H_3)\}-(Py)CI]$  (**3b**). The general procedure was followed, using 0.39 g (0.8 mmol) of the potassium salt **2b** and 0.40 g (0.8 mmol) of CoCl<sub>2</sub>(Py)<sub>4</sub>, yielding a dark blue-violet powder. Yield: 0.259 g (52%).

Anal. Calcd for  $C_{37}H_{48}ClCoN_3$ , obtained (calculated): C, 69.87 (70.63); H, 7.79 (7.69); N, 6.66 (6.68).  $\mu_{eff}$  (toluene- $d_8$ ): 4.5  $\mu_B$ . <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  49.56, 6.56, 6.04, 2.66, 2.37, 1.59, 1.09, 0.88, 0.16, -11.51, -23.62.

 $[Co\{\kappa^2N,N'-5-(2,4,6-Ph_3-C_6H_2)-NC_4H_2-2-C(H)=N(2,6^{-l}Pr_2-C_6H_3)\}-(Py)Cl]$  (3c). The general procedure was followed, using 0.48 g (0.8 mmol) of the potassium salt 2c and 0.40 g (0.8 mmol) of CoCl<sub>2</sub>(Py)<sub>4</sub>, yielding a dark green-violet microcrystalline solid. Yield: 0.164 g (52%).

Anal. Calcd for  $C_{46}H_{42}$ ClCoN<sub>3</sub>·0.5C<sub>7</sub>H<sub>8</sub>, obtained (calculated): C, 76.45 (76.49); H, 6.65 (5.97); N, 5.02 (5.41).  $\mu_{eff}$  (toluene- $d_8$ ): 4.5  $\mu_{B}$ . <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 51.66, 11.84, 4.63, 4.34, 2.84, 1.22, 0.87, 0.74, -4.46, -8.98, -13.51, -23.14, -46.81.

 $[Co\{\kappa^2 N, N' - 5 - (anthracen - 9 - yl) - NC_4 H_2 - 2 - C(H) = N(2, 6^{-l}Pr_2 - C_6 H_3) - (Py)Cl]$  (3*d*). The general procedure was followed, using 0.47 g (1 mmol) of the potassium salt 2*d* and 0.49 g (1 mmol) of CoCl<sub>2</sub>(Py)<sub>4</sub>, yielding a dark green-brown crystalline solid. Yield: 0.448 g (75%).

Anal. Calcd for  $C_{36}H_{34}ClCoN_3$ , obtained (calculated): C, 71.95 (71.70); H, 5.73 (5.68); N, 6.72 (6.97).  $\mu_{eff}$  (toluene- $d_8$ ): 3.7  $\mu_B$ . <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ): 102.57, 50.80, 5.16, 1.94, 0.81, 0.23, -0.73, -0.86, -12.22, -22.36.

 $[Co\{\kappa^2 N, N'-5-(triphenylmethyl)-NC_4H_2-2-C(H)=N(2,6^{-l}Pr_2-C_6H_3)\}-(Py)Cl]$  (**3e**). The general procedure was followed, using 0.43 g (0.8

mmol) of the potassium salt **2e** and 0.40 g (0.8 mmol) of  $CoCl_2(Py)_{4}$ , yielding a dark blue-violet powder. Yield: 0.325 g (61%).

Anal. Calcd for C<sub>41</sub>H<sub>40</sub>ClCoN<sub>3</sub>, obtained (calculated): C, 73.79 (73.59); H, 6.33 (6.03); N, 5.92 (6.28).  $\mu_{\rm eff}$  (toluene- $d_8$ ): 4.8  $\mu_{\rm B}$ . <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 105.13, 52.45, 10.33, 5.11, 2.31, 1.13, 0.01, -2.04, -4.18, -9.99, -23.88, -92.32.

[Co{ $\kappa^2 N, N'$ -5-(2,4,6-<sup>i</sup>Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)-NC<sub>4</sub>H<sub>2</sub>-2-C(H)=N(2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)}(μ-Cl)]<sub>2</sub>[(μ-Cl)<sub>2</sub>Co(THF)<sub>2</sub>] (4). Ligand precursor 1b (0.46 g, 1 mmol) was added as a solid to a THF suspension of NaH (1.1 mmol, 0.026 g), and the mixture was refluxed for 3 h, after which the solution was filtered. All volatile materials were removed under reduced pressure to give a pale red waxy solid. The resulting solid was redissolved in toluene and added to a blue toluene suspension of CoCl<sub>2</sub>(THF)<sub>1.5</sub> (1.5 mmol, 0.36 g). The mixture was stirred overnight at 80 °C, forming a dark blue-violet suspension. The dark blue-violet toluene solution was filtered at room temperature, concentrated under reduced pressure, and stored at -20 °C, from which dark blue-violet crystals suitable for X-ray diffraction were obtained. Yield: 0.43 g (67%).

Anal. Calcd for  $C_{72}H_{102}Cl_4Co_3N_4O_2$ , obtained (calculated): C, 62.97 (62.93); H, 7.31 (7.48); N, 3.88 (4.08).  $\mu_{eff}$  (toluene- $d_8$ ): 8.3  $\mu_{B}$ .

General Procedure for Catalytic Hydroboration Experiments. A Schlenk flask was charged with the desired amount of complex 3a-e (1% mol) and K(HBEt<sub>3</sub>) (3% mol), after which a solution of the appropriate substrate (2 mmol) and pinacolborane (2.5 mmol) was added. The mixture was stirred at 25 °C for 16 h and quenched by adding ca. 15 mL of *n*-hexane and exposing the mixture to air. The solution was filtered through a plug of silica and the solvent evaporated to dryness. The resulting pale yellow oil was eluted with *n*-hexane through a Pasteur pipet with a plug of silica. The hydroboration products (already described in the literature<sup>4a</sup>) were isolated as nearly colorless oils. The selectivity of the products was determined by <sup>1</sup>H NMR spectroscopy (highlighted in the Supporting Information), and their yields were determined by weighing the isolated reaction products.

NMR-Scale Reaction of Complex 3b with K(HBEt<sub>3</sub>). Inside a glovebox,  $C_6D_6$  was carefully added to a solid mixture of complex 3b (0.026 g, 0.0413 mmol) and K(HBEt<sub>3</sub>) (0.0169 g, 0.123 mmol) inside a vial. An immediate color change to dark red was observed, accompanied by effervescence. The mixture was transferred to a J. Young tube and the NMR spectra acquired.

<sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  63.03, 18.67, 17.33, 13.72, 10.46, 8.15 (*Py*-BEt<sub>3</sub>), 7.89 (*Py*-BEt<sub>3</sub>), 6.02, 5.26, 4.69, 3.14, 2.38, 1.94, 1.26 (K(HBEt<sub>3</sub>)), 1.06 (K(HBEt<sub>3</sub>)), 0.50 to -0.20 (*Py*-BEt<sub>3</sub>), -4.82, -37.08. <sup>11</sup>B{<sup>1</sup>H} NMR (30 MHz,  $C_6D_6$ ):  $\delta$  0.98 (*Py*-BEt<sub>3</sub>), -13.26 (K(HBEt<sub>3</sub>)). The unassigned peaks correspond exclusively to the putative Co(I) species.

**NMR Measurements.** NMR spectra of complexes and polymers were recorded on a Bruker AVANCE III 300 MHz spectrometer at 299.995 MHz (<sup>1</sup>H) and 75.4296 MHz (<sup>13</sup>C), referenced to the solvent residual protio resonances (<sup>1</sup>H) and to the solvent carbon (<sup>13</sup>C) resonances. Solution samples were prepared in dried and degassed deuterated solvents at room temperature, using standard NMR tubes. For air-/moisture-sensitive compounds, the samples were prepared in a glovebox in J. Young NMR tubes. Magnetic susceptibility measurements in solution were performed on a Bruker AVANCE III 300 MHz spectrometer at 298 K using the Evans method,<sup>27</sup> the solution samples being prepared in toluene-*d*<sub>8</sub> with 3% of hexadimethylsiloxane. These solutions were prepared in a glovebox in J. Young NMR tubes filled with the same solvent mixture, in which hexamethyldisiloxane is the external reference.

Magnetic Measurements in the Solid State. Magnetic measurements by the dc extraction method were performed on polycrystalline samples (10-20 mg) of complexes 3a and 4 using a SQUID magnetometer, S700X (Cryogenic Ltd.). The temperature dependence of the magnetic susceptibility was measured under magnetic fields of 5 T in the temperature range 5–300 K. The isothermal magnetization measurements up to 5 T, taken at different

temperatures (1.7, 5, 10, and 30 K) were also performed. The diamagnetism correction for the experimental susceptibility data was estimated using the Pascal constants, corresponding to  $\chi_{\rm D} = -325.5 \times 10^{-6}$  emu mol<sup>-1</sup> and  $\chi_{\rm D} = -868.0 \times 10^{-6}$  emu mol<sup>-1</sup> for 3a and 4, respectively.

X-ray Diffraction. Crystallographic and experimental details of crystal structure determinations are given in Tables S5 and S6 of the Supporting Information. The crystals were selected under an inert atmosphere, covered with dry and degassed polyfluoroether oil, and mounted on a nylon loop. Crystallographic data were collected using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat, at 150 K. Cell parameters were retrieved using Bruker SMART<sup>28</sup> software and refined using Bruker SAINT<sup>29</sup> on all observed reflections. Absorption corrections were applied using SADABS.<sup>30</sup> Structure solution and refinement were performed using direct methods with the programs SIR2014<sup>3</sup> and SHELXL<sup>32</sup> included in the package of programs WINGX-Version 2014.1.33 All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were inserted in idealized positions and allowed to refine riding on the parent carbon atom. Graphic presentations were prepared with ORTEP-3.<sup>34</sup> Data were deposited with the CCDC under the deposit numbers 1827273 for 1c (shown in the Supporting Information), 1827274 for 1e (shown in the Supporting Information), 1827275 for 2d, 1827276 for 3a, 1827277 for 3c and 1827278 for 4.

**Computational Details.** Calculations were performed using the Gaussian 09 software package<sup>35</sup> and the OPBE functional without symmetry constraints. This functional combines Handy's OPTX modification of Becke's exchange functional<sup>36</sup> with the gradient-corrected correlation functional of Perdew, Burke, and Ernzerhof<sup>37</sup> and was shown to be accurate in the calculation of spin state energy splitting for first-transition-row species.<sup>38</sup> The geometry optimizations were accomplished without symmetry constraints using a standard 6-31G\*\* basis set<sup>40</sup> was used for the calculation of the spin isomers of 4 and a LanL2DZ<sup>41</sup> basis set for the calculations of the mononuclear complexes 3a-e, with an added f polarization function,<sup>42</sup> in both cases. The spin density plots were represented using Chemcraft.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00568.

Synthetic details, characterization data, NMR spectra, crystallographic data, preliminary mechanistic studies,

magnetic data, and details of the calculations (PDF)

#### **Accession Codes**

CCDC 1827273–1827278 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.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail for P.T.G.: pedro.t.gomes@tecnico.ulisboa.pt.

#### ORCID 🔍

Luís F. Veiros: 0000-0001-5841-3519 Pedro T. Gomes: 0000-0001-8406-8763

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We thank the Fundação para a Ciência e a Tecnologia for financial support (Projects UID/QUI/00100/2013 and UID/Multi/04349/2013) and fellowships to T.F.C.C., P.S.L., and P.T.G. (PD/BD/52372/201-CATSUS Ph.D. Program, SFRH/BD/88639/2012, and SFRH/BSAB/140115/2018, respectively).

#### REFERENCES

(1) Ananikov, V. P.; Tanaka, M. Hydrofunctionalization; Springer: 2013; Vol. 43.

(2) For example: (a) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. New Homogeneous Rhodium Catalysts for the Regioselective Hydroboration of Alkenes. J. Am. Chem. Soc. 1992, 114, 8863-8869. (b) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. Reactions of Catecholborane with Wilkinson's Catalyst: Implications for Transition Metal-Catalyzed Hydroborations of Alkenes. J. Am. Chem. Soc. 1992, 114, 9350-9359. (c) Westcott, S. A.; Marder, T. B.; Baker, R. T. Transition-Metal-Catalyzed Addition of Catecholborane to  $\alpha$ -Substituted Vinylarenes: Hydroboration vs Dehydrogenative Borylation. Organometallics 1993, 12, 975-979. (d) Vogels, C. M.; Westcott, S. A. Recent Advances in Organic Synthesis Using Transition Metal-Catalyzed Hydroborations. Curr. Org. Chem. 2005, 9, 687-699. (e) Burgess, K.; Ohlmeyer, M. J. Transition-metal promoted hydroborations of alkenes, emerging methodology for organic transformations. Chem. Rev. 1991, 91, 1179-1191. (f) Crudden, C. M.; Edwards, D. Catalytic Asymmetric Hydroboration: Recent Advances and Applications in Carbon-Carbon Bond-Forming Reactions. Eur. J. Org. Chem. 2003, 2003, 4695-4712. (g) Thomas, S. P.; Aggarwal, V. K. Asymmetric hydroboration of 1,1disubstituted alkenes. Angew. Chem., Int. Ed. 2009, 48, 1896-1898. (3) Bullock, R. M. Catalysis without Precious Metals; Wiley-VCH:

(3) Bullock, R. M. Catalysis without Precious Metals; Wiley-VCH Weinheim, Germany, 2010.

(4) For example: (a) Obligacion, J. V.; Chirik, P. J. Highly Selective Bis(imino)pyridine Iron-Catalyzed Alkene Hydroboration. Org. Lett. 2013, 15, 2680-2683. (b) Obligacion, J. V.; Chirik, P. J. Bis(imino)pyridine Cobalt-Catalyzed Alkene Isomerization-Hydroboration: A Strategy for Remote Hydrofunctionalization with Terminal Selectivity. J. Am. Chem. Soc. 2013, 135, 19107-19110. (c) Palmer, W. N.; Diao, T.; Pappas, I.; Chirik, P. J. High-Activity Cobalt Catalysts for Alkene Hydroboration with Electronically Responsive Terpyridine and  $\alpha$ -Diimine Ligands. ACS Catal. 2015, 5, 622-626. (d) Ibrahim, A. D.; Entsminger, S. W.; Fout, A. R. Insights into a Chemoselective Cobalt Catalyst for the Hydroboration of Alkenes and Nitriles. ACS Catal. 2017, 7, 3730-3734. (e) Scheuermann, M. L.; Johnson, E. J.; Chirik, P. J. Alkene Isomerization-Hydroboration Promoted by Phosphine-Ligated Cobalt Catalysts. Org. Lett. 2015, 17, 2716-2719. (f) Ruddy, A. J.; Sydora, O. L.; Small, B. L.; Stradiotto, M.; Turculet, L. (N-Phosphinoamidinate)cobalt-Catalyzed Hydroboration: Alkene Isomerization Affords Terminal Selectivity. Chem. - Eur. J. 2014, 20, 13918-13922. (g) Ogawa, T.; Ruddy, A. J.; Sydora, O. L.; Stradiotto, M.; Turculet, L. Cobalt- and Iron-Catalyzed Isomerization-Hydroboration of Branched Alkenes: Terminal Hydroboration with Pinacolborane and 1,3,2-Diazaborolanes. Organometallics 2017, 36, 417-423. (h) Zhang, H.; Lu, Z. Dual-Stereocontrol Asymmetric Cobalt-Catalyzed Hydroboration of Sterically Hindered Styrenes. ACS Catal. 2016, 6, 6596-6600. (i) MacNair, A. J.; Millet, C. R. P.; Nichol, G. S.; Ironmonger, A.; Thomas, S. P. Markovnikov-Selective, Activator-Free Iron-Catalyzed Vinylarene Hydroboration. ACS Catal. 2016, 6, 7217-7221. (j) Wu, J. Y.; Moreau, B.; Ritter, T. Iron-Catalyzed 1,4-Hydroboration of 1,3-Dienes. J. Am. Chem. Soc. 2009, 131, 12915-12917. (k) Zhang, L.; Zuo, Z.; Leng, X.; Huang, Z. A Cobalt-Catalyzed Alkene Hydroboration with Pinacolborane. Angew. Chem., Int. Ed. 2014, 53, 2696-2700. (1) Espinal-Viguri, M.; Woof, C. R.; Webster, R. L. Iron-Catalyzed Hydroboration: Unlocking Reactivity through Ligand Modulation. Chem. - Eur. J. 2016, 22,

11605–11608. (m) Tseng, K.-N. T.; Kampf, J. W.; Szymczak, N. K. Regulation of Iron-Catalyzed Olefin Hydroboration by Ligand Modifications at a Remote Site. ACS Catal. 2015, 5, 411–415. (n) Peng, J.; Docherty, J. H.; Dominey, A. P.; Thomas, S. P. Cobalt-catalysed Markovnikov selective hydroboration of vinylarenes. Chem. Commun. 2017, 53, 4726–4729. (o) Zuo, Z.; Yang, J.; Huang, Z. Cobalt-Catalyzed Alkyne Hydrosilylation and Sequential Vinylsilane Hydroboration with Markovnikov Selectivity. Angew. Chem., Int. Ed. 2016, 55, 10839–10843. (p) Zhang, G.; Wu, J.; Wang, M.; Zeng, H.; Cheng, J.; Neary, M. C.; Zheng, S. Cobalt-Catalyzed Regioselective Hydroboration of Terminal Alkenes. Eur. J. Org. Chem. 2017, 2017, 5814–5818.

(5) For example: (a) Nakajima, K.; Kato, T.; Nishibayashi, Y. Hydroboration of Alkynes Catalyzed by Pyrrolide-Based PNP Pincer-Iron Complexes. Org. Lett. 2017, 19, 4323-4326. (b) Greenhalgh, M. D.; Thomas, S. P. Chemo-, regio-, and stereoselective ironcatalysed hydroboration of alkenes and alkynes. Chem. Commun. 2013, 49, 11230-11232. (c) Krautwald, S.; Bezdek, M. J.; Chirik, P. J. Cobalt-Catalyzed 1,1-Diboration of Terminal Alkynes: Scope, Mechanism, and Synthetic Applications. J. Am. Chem. Soc. 2017, 139, 3868-3875. (d) Guo, J.; Cheng, B.; Shen, X.; Lu, Z. Cobalt-Catalyzed Asymmetric Sequential Hydroboration/Hydrogenation of Internal Alkynes. J. Am. Chem. Soc. 2017, 139, 15316-15319. (e) Ben-Daat, H.; Rock, C. L.; Flores, M.; Groy, T. L.; Bowman, A. C.; Trovitch, R. J. Hydroboration of alkynes and nitriles using an  $\alpha$ diimine cobalt hydride catalyst. Chem. Commun. 2017, 53, 7333-7336. (f) Zuo, Z.; Huang, Z. Synthesis of 1,1-diboronate esters by cobalt-catalyzed sequential hydroboration of terminal alkynes. Org. Chem. Front. 2016, 3, 434-438.

(6) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. Electronically Unsaturated Three-Coordinate Chloride and Methyl Complexes of Iron, Cobalt, and Nickel. *J. Am. Chem. Soc.* **2002**, *124*, 14416–14424.

(7) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. Rapid, Regioconvergent, Solvent-Free Alkene Hydrosilylation with a Cobalt Catalyst. *J. Am. Chem. Soc.* **2015**, *137*, 13244–13247.

(8) Jones, C.; Schulten, C.; Rose, R. P.; Stasch, A.; Aldridge, S.; Woodul, W. D.; Murray, K. S.; Moubaraki, B.; Brynda, M.; La Macchia, G.; Gagliardi, L. Amidinato- and Guanidinato-Cobalt(I) Complexes: Characterization of Exceptionally Short Co-Co Interactions. *Angew. Chem., Int. Ed.* **2009**, *48*, 7406-7410.

(9) King, E. R.; Sazama, G. T.; Betley, T. A. Co(III) Imidos Exhibiting Spin Crossover and C-H Bond Activation. J. Am. Chem. Soc. 2012, 134, 17858–17861.

(10) Bellabarba, R. M.; Gomes, P. T.; Pascu, S. I. Synthesis of allyland aryl-iminopyrrolyl complexes of nickel. *Dalton Trans.* 2003, 4431–4436.

(11) Gomes, C. S. B.; Duarte, M. T.; Gomes, P. T. Further iminopyrrolyl complexes of nickel, cobalt, iron and copper: synthesis and structural characterisation. *J. Organomet. Chem.* **2014**, *760*, 167–176.

(12) Gomes, C. S. B.; Gomes, P. T.; Duarte, M. T.; Di Paolo, R. E.; Maçanita, A. L.; Calhorda, M. J. Synthesis, Structure, and Photophysical Characterization of Blue-Green Luminescent Zinc Complexes Containing 2-Iminophenanthropyrrolyl Ligands. *Inorg. Chem.* **2009**, *48*, 11176–11186.

(13) Gomes, C. S. B.; Suresh, D.; Gomes, P. T.; Veiros, L. F.; Duarte, M. T.; Nunes, T. G.; Oliveira, M. C. Sodium complexes containing 2-iminopyrrolyl ligands: the influence of steric hindrance in the formation of coordination polymers. *Dalton Trans.* **2010**, *39*, 736–748.

(14) (a) Suresh, D.; Gomes, C. S. B.; Gomes, P. T.; Di Paolo, R. E.; Maçanita, A. L.; Calhorda, M. J.; Charas, A.; Morgado, J.; Duarte, M. T. Syntheses and photophysical properties of new iminopyrrolyl boron complexes and their application in efficient single-layer nondoped OLEDs prepared by spin coating. *Dalton Trans.* **2012**, *41*, 8502–8505. (b) Calhorda, M. J.; Suresh, D.; Gomes, P. T.; Di Paolo, R. E.; Maçanita, A. L. Photophysical properties of iminopyrrolyl boron

complexes: A DFT interpretation. Dalton Trans. 2012, 41, 13210-13217. (c) Gomes, P. T.; Suresh, D.; Gomes, C. S. B.; Lopes, P. S., Figueira, C. A. Mono- and Polynuclear Boron Iminopyrrolyl Complexes: Methods of Preparation and Use as Luminescent Materials. World Patent WO2013039413, 2013. (d) Suresh, D.; Lopes, P. S.; Ferreira, B.; Figueira, C. A.; Gomes, C. S. B.; Gomes, P. T.; Di Paolo, R. E.; Maçanita, A. L.; Duarte, M. T.; Charas, A.; Morgado, J.; Calhorda, M. J. Tunable Fluorophores based on 2-(N-Arylimino)pyrrolyl Chelates of Diphenylboron: Synthesis, Structure, Photophysical Characterization and Application in OLEDs. Chem. -Eur. J. 2014, 20, 4126-4140. (e) Suresh, D.; Gomes, P. T. Advances in Organometallic Chemistry and Catalysis; Wiley: 2013; Chapter 36. (f) Suresh, D.; Gomes, C. S. B.; Lopes, P. L.; Figueira, C. A.; Ferreira, B.; Gomes, P. T.; Di Paolo, R. E.; Maçanita, A. L.; Duarte, M. T.; Charas, A.; Morgado, J.; Vila-Viçosa, D.; Calhorda, M. J. Luminescent Di- and Trinuclear Boron Complexes Based on Aromatic Iminopyrrolyl Spacer Ligands: Synthesis, Characterization and Application in OLEDs. Chem. - Eur. J. 2015, 21, 9133-9149. (g) Suresh, D.; Ferreira, B.; Lopes, P. S.; Gomes, C. S. B.; Krishnamoorthy, P.; Charas, A.; Vila-Viçosa, D.; Morgado, J.; Calhorda, M. J.; Maçanita, A. L.; Gomes, P. T. Boron complexes of aromatic ring fused iminopyrrolyl ligands: synthesis, structure, and luminescence properties. Dalton Trans. 2016, 45, 15603-15620.

(15) (a) Carabineiro, S. A.; Silva, L. C.; Gomes, P. T.; Pereira, L. C. J.; Veiros, L. F.; Pascu, S. I.; Duarte, M. T.; Namorado, S.; Henriques, R. T. Synthesis and Characterization of Tetrahedral and Square Planar Bis(iminopyrrolyl) Complexes of Cobalt(II). *Inorg. Chem.* 2007, 46, 6880–6890. (b) Carabineiro, S. A.; Bellabarba, R. M.; Gomes, P. T.; Pascu, S. I.; Veiros, L. F.; Freire, C.; Pereira, L. C. J.; Henriques, R. T.; Oliveira, M. C.; Warren, J. E. Synthesis, Structure and Magnetic Behavior of Five-Coordinate Bis(iminopyrrolyl) Complexes of Cobalt(II) containing PMe<sub>3</sub> and THF Ligands. *Inorg. Chem.* 2008, 47, 8896–8911. (c) Gomes, C. S. B.; Carabineiro, S. A.; Gomes, P. T.; Duarte, M. T. Octahedral Co(III) complexes of 2-(phenylimino)-pyrrolyl ligands: Synthesis and structural characterization. *Inorg. Chim.* Acta 2011, 367, 151–157. (d) Cruz, T. F. C.; Figueira, C. A.; Waerenborgh, J. C.; Pereira, L. C. J.; Gomes, P. T. *Polyhedron*, 2018, in press, DOI: 10.1016/j.poly.2018.06.026.

(16) Dawson, D. M.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. Synthesis and reactivity of sterically hindered iminopyrrolato complexes of zirconium, iron, cobalt and nickel. *J. Chem. Soc., Dalton Trans.* **2000**, *4*, 459–466.

(17) (a) Figueira, C. A.; Lopes, P. S.; Gomes, P. T. Synthesis of 2-Arylpyrroles Via Catalytic Dehydrogenation of 2-Aryl-1-pyrrolines in the Presence of Palladium-supported on Alumina. *Tetrahedron* **2015**, *71*, 4362–4371. (b) Figueira, C. A.; Lopes, P. S.; Gomes, C. S. B.; Veiros, L. F.; Gomes, P. T. Exploring the influence of steric hindrance and electronic nature of substituents in the supramolecular arrangements of 5-(substituted phenyl)-2-formylpyrroles. *CrystEngComm* **2015**, *17*, 6406–6419.

(18) For example: (a) Reid, S. D.; Blake, A. J.; Wilson, C.; Love, J. B. Syntheses and Structures of Dinuclear Double-Stranded Helicates of Divalent Manganese, Iron, Cobalt, and Zinc. *Inorg. Chem.* **2006**, *45*, 636–643. (b) Love, J. B.; Blake, A. J.; Wilson, C.; Reid, S. D.; Novak, A.; Hitchcock, P. B. The syntheses and structures of Group 1 expanded dipyrrolides: the formation of a 12-rung amidolithium circular ladder. *Chem. Commun.* **2003**, 1682–1683.

(19) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. Advanced Inorganic Chemistry; 6th ed., Wiley: 1999; p 821.
(b) Greenwood, N. N.; Earnshaw, A. Chemistry of the Elements, 2nd ed., Elsevier Butterworth-Heinemann: 1997; p 1113.

(20) Yang, L.; Powell, D. R.; Houser, R. P. Structural variation in copper(I) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index,  $\tau_4$ . Dalton Trans. **2007**, 955–964.

(21) Ding, B.; Yang, E.-C.; Zhao, X.-J.; Wang, X. G. A linear trinuclear cobalt(II) complex with 4-(2-pyridine)-1,2,4-triazole: synthesis, structure and characterization. *J. Coord. Chem.* **2008**, *61*, 3793–3799.

(22) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **2016**, *72*, 171–179.

(23) For example: (a) Bkouche-Waksman, P. I.; L'Haridon, P. Structure du composé CoCl<sub>2</sub>.2.5C<sub>2</sub>H<sub>5</sub>OH et classification de composés d'addition de métaux divalents. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1977, 33, 11-21. (b) Jakonen, M.; Hirva, P.; Nivajärvi, T.; Kallinen, M.; Haukka, M. Surface-Assisted Synthesis and Behavior of Dimetallic Mixed-Metal Complexes  $[M_2Cl_2(\mu-Cl)_4(CO)_6M'(L)_2]$  (M = Ru, Os; M' = Fe, Co; L = CH<sub>3</sub>CH<sub>2</sub>OH, H<sub>2</sub>O). Eur. J. Inorg. Chem. 2007, 2007, 3497-3508. (c) Zheng, Y.-Z.; Speldrich, M.; Schilder, H.; Chen, X.-M.; Kögerler, P. A tetranuclear cobalt(II) chain with slow magnetization relaxation. Dalton Trans. 2010, 39, 10827-10829. (d) James, M.; Horvat, J. The crystal structure and magnetic properties of the 1-dimensional dihalide-bridged polymers dichlorobis(thiazole)cobalt(II) and dibromobis(thiazole)-cobalt(II). J. Phys. Chem. Solids 2002, 63, 657-663. (e) Masaki, M. E.; Prince, B. J.; Turnbull, M. M. Transition Metal Halide Salts and Complexes of 2-Aminopyrimidine: Cobalt(II) and Nickel(II) compounds, Crystal Structures of Bis(2-Aminopyrimidinium) $MX_4$  [M = Co, Ni; X = Cl, Br] and 2-Aminopyrimidinium(+2) [NiBr<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]Br<sub>2</sub>. J. Coord. Chem. 2002, 55, 1337-1351. (f) Hierso, J.-C.; Ellis, D. D.; Spek, A. L.; Bouwman, E.; Reedijk, J. Unique chains of alternating octahedral and tetrahedral cobalt(II) sites: crystal structures of the novel chloro-bridged complexes  $[Co_4(\mu-Cl)_6Cl_2(THF)_4(MeOH)_2]_n$  and  $[{Co_4(\mu-Cl)_6Cl_2(THF)_4(MeOH)_2}]_n$ Cl)<sub>6</sub>Cl<sub>2</sub>(THF)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>}<sub>2</sub>THF]<sub>n</sub>. Chem. Commun. 2000, 1359–1360. (g) Adams, C. J.; Kurawa, M. A.; Orpen, A. G. Coordination chemistry in the solid state: synthesis and interconversion of pyrazolium salts, pyrazole complexes, and pyrazolate MOFs. Dalton Trans. 2010, 39, 6974–6984. (h) Lawandy, M. A.; Huang, X.; Wang, R.-J.; Li, J.; Lu, J. Y.; Yuen, T.; Lin, C. L. Two-Dimensional Coordination Polymers with One-Dimensional Magnetic Chains: Hydrothermal Synthesis, Crystal Structure, and Magnetic and Thermal Properties of  $[MCl_2(4,4'-bipyridine)]$  (M = Fe, Co, Ni, Co/Ni). Inorg. Chem. 1999, 38, 5410-5414. (i) von Hänisch, C.; Fenske, D.; Weigend, F.; Ahlrichs, R. A Square As<sub>4</sub> and a Prismatic As<sub>6</sub> Structure as Complex Ligands. Chem. - Eur. J. 1997, 3, 1494-1498

(24) Nöth, H.; Wrackmeyer, B. Nuclear Magnetic Resonance Spectroscopy of Boron Compounds. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer: 1978; p 316.

(25) Zhu, D.; Janssen, F. F. B. J.; Budzelaar, P. H. M.  $(Py)_2Co(CH_2SiMe_3)_2$  As an Easily Accessible Source of "CoR<sub>2</sub>. Organometallics **2010**, 29, 1897–1908.

(26) Sobota, P.; Olejnik, Z.; Utko, J.; Lis, T. Synthesis, magnetic properties and structure of the  $[Co_4(\mu_3-Cl)_2(\mu_2-Cl)_4Cl_2(THF)_6]$  complex. *Polyhedron* **1993**, *12*, 613–616.

(27) (a) Evans, D. F. The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc.* **1959**, 2003–2005. (b) Sur, S. K. Measurement of Magnetic Susceptibility and Magnetic Moment of Paramagnetic Molecules in Solution by High-Field Fourier Transform NMR Spectroscopy. *J. Magn. Reson.* **1989**, *82*, 169–173.

(28) SMART Software for the CCD Detector System Version 5.625; Bruker AXS Inc., Madison, WI, USA, 2001.

(29) SAINT Software for the CCD Detector System, Version 7.03; Bruker AXS Inc., Madison, WI, USA, 2004.

(30) Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 1996.

(31) Burla, M. C.; Caliandro, R.; Carrozzini, B.; Cascarano, G. L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G. Crystal structure determination and refinement via SIR2014. *J. Appl. Crystallogr.* **2015**, *48*, 306.

(32) (a) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3-8.
(b) Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt

graphical user interface for SHELXL. J. Appl. Crystallogr. 2011, 44, 1281–1284.

(33) (a) Farrugia, L. J. WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837–838. (b) Farrugia, L. J. WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **2012**, *45*, 849–854.

(34) (a) Burnett, M. N., Johnson, C. K. ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustration; Oak Ridge National Laboratory, 1996; Report ORNL-6895. (b) Farrugia, L. J. ORTEP-3 for Windows – a version of ORTEP-III with a Graphical User Interface (GUI). J. Appl. Crystallogr. 1997, 30, 565.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.01; Gaussian, Inc., Wallingford, CT, 2009.

(36) (a) Handy, N. C.; Cohen, A. J. Left-right correlation energy. *Mol. Phys.* **2001**, *99*, 403–412. (b) Hoe, H.-M.; Cohen, A.; Handy, N. C. Assessment of a new local exchange functional OPTX. *Chem. Phys. Lett.* **2001**, *341*, 319–328.

(37) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865–3868. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1997**, 78, 1396.

(38) (a) Swart, M. Accurate Spin-State Energies for Iron Complexes. J. Chem. Theory Comput. 2008, 4, 2057–2066. (b) Conradie, J.; Ghosh, A. Electronic Structure of Trigonal-Planar Transition-Metal-Imido Complexes: Spin-State Energetics, Spin-Density Profiles, and the Remarkable Performance of the OLYP Functional. J. Chem. Theory Comput. 2007, 3, 689–702. (c) Conradie, J.; Ghosh, A. DFT Calculations on the Spin-Crossover Complex Fe(salen)(NO): A Quest for the Best Functional. J. Phys. Chem. B 2007, 111, 12621– 12624.

(39) (a) McLean, A. D.; Chandler, G. S. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z = 11-18. J. Chem. Phys. 1980, 72, 5639-5648. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. J. Chem. Phys. 1980, 72, 650-654. (c) Wachters, A. J. H. Gaussian Basis Set for Molecular Wavefunctions Containing Third-Row Atoms. J. Chem. Phys. 1970, 52, 1033. (d) Hay, P. J. Gaussian basis sets for molecular calculations. The representation of 3d orbitals in transition-metal atoms. J. Chem. Phys. 1977, 66, 4377-4384. (e) Raghavachari, K.; Trucks, G. W. Highly correlated systems. Excitation energies of first row transition metals Sc-Cu. J. Chem. Phys. 1989, 91, 1062-1089. (f) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning, R. C.; Radom, L. Extension of Gaussian-2 theory to molecules containing third-row atoms Ga-Kr. J. Chem. Phys. 1995, 103, 6104. (g) McGrath, M. P.; Radom, L. Extension of Gaussian-1 (G1) theory to brominecontaining molecules. J. Chem. Phys. 1991, 94, 511-516.

(40) (a) Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Accuracy of energy-adjusted quasirelativistic ab initio pseudopotentials. *Mol. Phys.* **1993**, *78*, 1211–1224. (b) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. Energy-adjusted pseudopotentials for the actinides. Parameter sets and test calculations for thorium and thorium monoxide. *J. Chem. Phys.* **1994**, *100*, 7535–7542. (c) Leininger, T.; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P. The accuracy of

the pseudopotential approximation. II. A comparison of various core sizes for indium pseudopotentials in calculations for spectroscopic constants of InH, InF, and InCl. J. Chem. Phys. **1996**, 105, 1052–1059.

(41) (a) Modern Theoretical Chemistry, 3rd ed.; Dunning, T. H., Jr., Hay, P. J., Schaefer, H. F., Eds.; Plenum: New York, 1976; Vol. 3, p 1. (b) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. **1985**, 82, 270. (c) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys. **1985**, 82, 284. (d) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J. Chem. Phys. **1985**, 82, 299.

(42) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. A set of f-polarization functions for pseudo-potential basis sets of the transition metals Sc-Cu, Y-Ag and La-Au. *Chem. Phys. Lett.* **1993**, 208, 111.