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## Cobalt PNC<sup>NHC</sup> 'pincers': ligand dearomatisation, formation of dinuclear and N<sub>2</sub> complexes and promotion of C-H activation†

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**Studies of ligand dearomatisation in cobalt phosphino-picoline *N*-heterocyclic carbene (PNC<sup>NHC</sup>)-type pincers have revealed the formation of dinuclear cobalt complexes by either side-arm metalation or C-H activation at the NHC backbone; in the latter case, the product complex, featuring an 'anionic dicarbene', originated from a dearomatised Co<sup>I</sup>-N<sub>2</sub> complex.**

The development of base-metal, notably iron<sup>1</sup> and cobalt,<sup>2</sup> homogeneous catalysts with improved properties and green credentials stimulates new insights into the underlying fundamental organometallic chemistry. Since 3d metals are prone to react *via* one-electron processes, concepts encompassing metal-ligand cooperation in catalysis, *i.e.* with redox-active or proton-responsive ligands, gain growing appeal.<sup>3</sup> Thus, bis(arylimidazol-2-ylidene)pyridine (C<sup>NHC</sup>NC<sup>NHC</sup>) alkyl cobalt complexes have shown remarkable activity in catalytic hydrogenation,<sup>4</sup> and coordinated bis-(phosphinomethyl)pyridine (PNP) is renowned for promoting metal-ligand cooperation with various metals through aromatisation-dearomatisation steps.<sup>5</sup> Presently, there is no reported example that demonstrates cobalt-PNP cooperation in catalysis with pyridine-based ligands, although such steps are plausible,<sup>6</sup> and have been established for aliphatic-PNP-Co complexes.<sup>7</sup> However, dearomatised Co<sup>I</sup> PN<sub>a</sub>P\* (N<sub>a</sub> = anionic amido N donor, P\* = vinyl P donor) complexes, including one with a dinitrogen coligand,<sup>8</sup> have been recently studied in stoichiometric, metal-centred reactions.<sup>8-9</sup>

Tuning the metal-ligand synergism using structural tools opens new ways for catalyst discovery and development. In this context, it is conceivable that ligand dearomatisation may benefit from trifunctional donor sets that can modulate the  $\alpha$ -

methylene protons acidity, provide precise stereoelectronic tuning of the metal and may exhibit hemilability.<sup>10</sup> Accordingly, the phosphino-picoline-NHC (PNC<sup>NHC</sup>)<sup>11</sup> donor set may extend the growing versatility of the pincer ligand family.

Herein, we present novel reactivity that we ascribe to the ease of PNC<sup>NHC</sup> dearomatisation (Scheme 1): (a) the <sup>CY</sup>PNC<sup>NHC</sup> deprotonation/dearomatisation and Co<sup>II</sup> coordination of <sup>CY</sup>P\*<sub>3</sub>C<sup>NHC</sup> brought about by Co-N aminolysis of the [Co{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] precursor; (b) a competing bridging coordination mode of the dearomatised (<sup>CY</sup>P\*<sub>3</sub>C<sup>NHC</sup>) leading to dinuclear species; (c) a Co<sup>I</sup>(<sup>CY</sup>P\*<sub>3</sub>C<sup>NHC</sup>) moiety weakly binding N<sub>2</sub>, and (d) the activation of a C-H bond at the backbone of the NHC heterocycle, which is accompanied by re-aromatisation of the pincer skeleton.

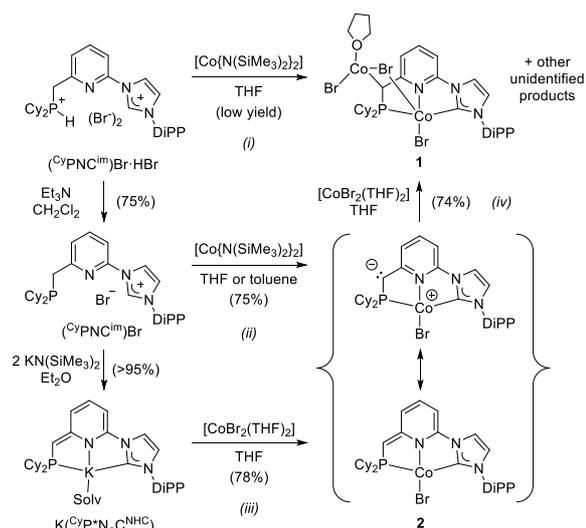
Aminolysis of [Co{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]<sup>12</sup> with imidazolium salts has been employed as a selective and facile route to access NHC-Co<sup>II</sup> complexes.<sup>13</sup> However, this aminolysis with precursors to the <sup>CY</sup>PNC<sup>NHC</sup> pincer is sensitive to their exact nature and the experimental conditions. Thus, the reaction of (<sup>CY</sup>PNC<sup>im</sup>)Br·HBr<sup>11</sup> with [Co{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (Scheme 1, (i)) afforded a brown air-sensitive solid in low yield as the only identified product. Its X-ray structure (Fig. 1) revealed the formation of the unexpected dinuclear Co<sup>II</sup> complex [Co<sub>2</sub>(<sup>CY</sup>PNC<sup>NHC</sup>)Br<sub>3</sub>]·THF (1·THF), by abstraction of three protons from the pro-ligand, rather than of the anticipated mononuclear [Co(<sup>CY</sup>PNC<sup>NHC</sup>)Br<sub>2</sub>] pincer complex. The structure of **1** features a central Co<sup>II</sup> (Co1) in a slightly distorted square pyramidal environment ( $\tau \cong 0.19$ ),<sup>14</sup> the basal donors being the ( $\kappa$ P, $\kappa$ N, $\kappa$ C<sup>NHC</sup>) pincer and a terminal bromide, and the apical donor being the  $\mu_2$ -Br. The coordination geometry at the lateral Co<sup>II</sup> (Co2) is distorted tetrahedral with one sp<sup>3</sup>-hybridised  $\alpha$ -C benzylic donor, one bridging and one terminal bromides, and one THF ligand. The Co2-C21 bond distance of 2.116(8) Å is at the high end of the Co-alkyl bonds reported.<sup>15</sup> The aromatic nature of the picoline ring was confirmed from the relevant bond distances (See Table S2 for comparison of bond distances of the complexes reported herein).

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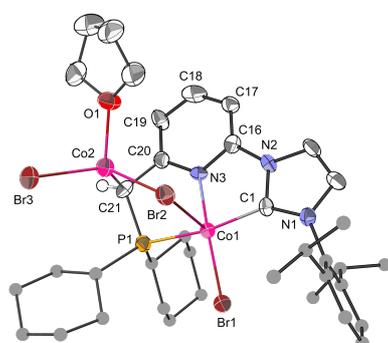


**Scheme 1** Synthetic routes to access the cobalt(II) complexes **1** and **2**.

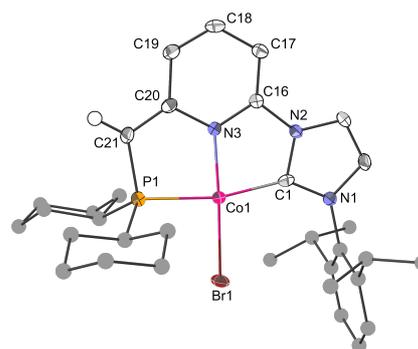
Complex **1** is paramagnetic; the value of  $\mu_{\text{eff}} = 4.8 \pm 0.2 \mu_{\text{B}}$  in THF (Evans' method), supports some antiferromagnetic coupling between two high-spin  $\text{Co}^{\text{II}}$  centres (see ESI).

To gain insight into the formation of **1**, the aminolysis of  $[\text{Co}\{\text{N}(\text{SiMe}_3)_2\}_2]$  with the phosphine-picoline-imidazolium bromide ( $^{\text{Cy}}\text{PNC}^{\text{im}}\text{Br}$ ) (Scheme 1, (ii)) was studied, which led to good yields of the air-sensitive, dark-red, paramagnetic ( $\mu_{\text{eff}} = 2.1 \pm 0.2 \mu_{\text{B}}$  Evans' method, consistent with low spin  $d^7 \text{Co}^{\text{II}}$ )  $[\text{Co}(\text{CyP}^*\text{N}_a\text{C}^{\text{NHC}})\text{Br}]$  (**2**). Its structure (Fig. 2) revealed a  $\text{Co}^{\text{II}}$  centre in a nearly square planar environment, chelated by the  $(\kappa\text{P}, \kappa\text{N}, \kappa\text{C}^{\text{NHC}})$  anionic  $^{\text{Cy}}\text{P}^*\text{N}_a\text{C}^{\text{NHC}}$ . All relevant bond distances are in support of a dearomatised picoline structure, which is to be contrasted to the aromatic backbone in **1** (Table S2).

The formation of **2** can be rationalised by the deprotonation of both the azolium NCHN and the  $\alpha\text{-CH}_2\text{P}$  of ( $^{\text{Cy}}\text{PNC}^{\text{im}}\text{Br}$ ). Plausible pre-coordination of  $\text{Br}^-$  (azolium counterion),<sup>13b</sup> and/or of P-, N-neutral donors may amplify the basicity of the co-coordinated base  $\text{N}(\text{SiMe}_3)_2$ , enhance the  $\alpha\text{-CH}_2\text{P}$  acidity, and bring the relevant reactive centres in close proximity. The stabilisation of the ensuing  $^{\text{Cy}}\text{P}^*\text{N}_a\text{C}^{\text{NHC}}$  anion and the increased negative charge at the  $\alpha\text{-CHP}$  in **2** are well described by the mesomeric forms in Scheme 1. Complex **2** was also directly obtained by transmetalation of  $\text{K}(\text{P}^*\text{N}_a\text{C}^{\text{NHC}})^{11}$  with  $[\text{CoBr}_2(\text{THF})_2]$  (Scheme 1, (iii)).



**Fig. 1** The structure of **1** with thermal ellipsoids at 40% probability (the C atoms of the Cy and DiPP rings are depicted as spheres). H atoms are omitted except the  $\alpha\text{-CH}$  (C21).

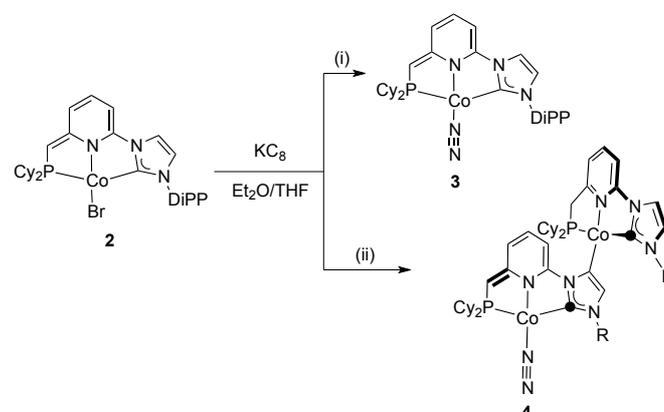


**Fig. 2** The structure of **2** with thermal ellipsoids at 40% probability (the C atoms of the Cy and DiPP rings are depicted as spheres). H atoms are omitted except the  $\alpha\text{-CH}$  (C21).

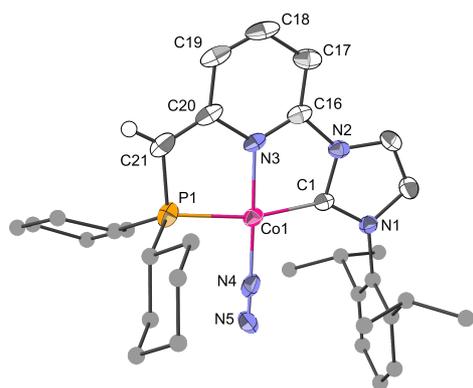
In view of the facile formation of **2**, the occurrence of **1** can also be rationalised by the rapid trapping by **2** of the  $\text{CoBr}_2$  formed *in situ* at the initial stages of the aminolysis. This was verified by the independent rational synthesis of **1**, treating a THF solution of crude **2** with a THF solution of  $[\text{CoBr}_2(\text{THF})_2]$  (Scheme 1, (iv)). The brown solid isolated showed an identical NMR signature to **1**. Pincer side-arm metalation has so far been described at the  $\alpha\text{-CHP}$  of PNP in  $[\text{Cr}(\text{P}^{\text{h}}\text{PN}^{\text{h}}\text{P})\text{Cl}_3]$  (by Al alkyls) and of PCP in  $[\text{Pt}(\text{CF}_3\text{PC}^{\text{CF}_3}\text{P})\text{Cl}]$  (by  $\text{Pt}^{\text{II}}$ );<sup>16</sup> side-arm metalations of coordinated bidentate chelating phosphino-picolines have been described in rare cases.<sup>17</sup>

The two routes leading to **2** offer versatile complementary alternatives to access dearomatised pincer complexes, in particular if the use of strong, non-selective external alkylolithium bases to deprotonate the ligand scaffold needs to be avoided (*e.g.* with 3d metals).<sup>9,13a,18</sup>

Reduction of **2** with stoichiometric amount of  $\text{KC}_8$  led to different  $\text{Co}^{\text{I}}$  complexes depending on the reaction conditions (Scheme 2). Upon addition of  $\text{KC}_8$ , a fast colour change from red-brown to dark blue-green was observed. When the reaction was carried out at  $-40^\circ\text{C}$  in  $\text{N}_2$ -saturated solvents followed by evaporation of the volatiles in a stream of  $\text{N}_2$ , the dark blue crystalline, diamagnetic air-sensitive  $[\text{Co}(\text{CyP}^*\text{N}_a\text{C}^{\text{NHC}})(\text{N}_2)]$  (**3**) was isolated and characterised spectroscopically (multinuclear NMR, see ESI) and crystallographically (Fig. 3).



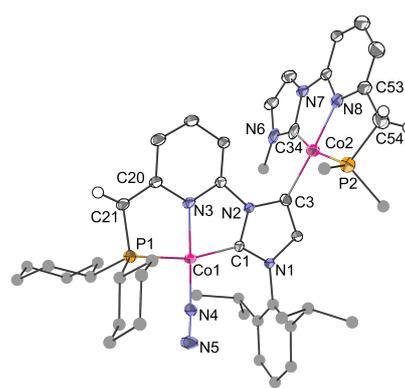
**Scheme 2** Reduction of **2** with  $\text{KC}_8$  (i) in  $\text{N}_2$ -saturated solvents; (ii) under  $\text{N}_2$ -depleted conditions (see text).



**Fig. 3** The structure of **3** with thermal ellipsoids at 40% probability (the C atoms of the Cy and DiPP rings are depicted as spheres). H atoms are omitted except the  $\alpha$ -CH (C21).

The structure of **3** comprises a Co centre in a square planar environment constituted by the monoanionic ( $\kappa$ P, $\kappa$ N, $\kappa$ C<sup>NHC</sup>) pincer and a terminal N<sub>2</sub> ( $\kappa$ N). The dearomatised ligand structure was undoubtedly inferred from the metrical data, which are comparable to those observed in **2** (cf. Table S2). Compared to the related [Co(<sup>t</sup>BU<sup>t</sup>P\*<sup>N</sup><sub>a</sub><sup>t</sup>BU<sup>t</sup>P)(N<sub>2</sub>)],<sup>8</sup> the Co-N4 bond (1.789(3) Å) is 0.05 Å longer and the N4-N5 separation (0.987(3) Å) is ca. 0.14 Å shorter, revealing reduced back-donation from the Co(<sup>CY</sup>P\*<sup>N</sup><sub>a</sub><sup>C</sup><sup>NHC</sup>) fragment and no 'structural activation' of the coordinated N≡N. However, the N≡N separation, shorter than in free N<sub>2</sub> (1.098 Å), is perplexing in view of the expected  $\pi$ -backbonding<sup>19</sup> from the electron-rich Co<sup>I</sup> centre. Such short distances have been reported and rationalised as crystallographic artefact or minor disorder that could not be modelled.<sup>20</sup> We cannot overtly apply any of these explanations to the current system. Despite the 'anomaly' in the metrical data of the coordinated N<sub>2</sub>, the  $\nu$ (N≡N) in the IR spectrum at 2057 cm<sup>-1</sup> confirms N<sub>2</sub> coordination and backbonding. Surprisingly, this value is higher (by 36 cm<sup>-1</sup>) than the corresponding  $\nu$ (N≡N) in [Co(<sup>t</sup>BU<sup>t</sup>P\*<sup>N</sup><sub>a</sub><sup>t</sup>BU<sup>t</sup>P)(N<sub>2</sub>)],<sup>8</sup> in apparent contradiction with the better  $\sigma$ -donor ability of NHC vs. PR<sub>3</sub>.<sup>21</sup> Similar observations have been reported with Fe<sup>0</sup> complexes and explained by competing backbonding involving the Fe-N<sub>pyr</sub> antibonding orbital.<sup>20b</sup> Noteworthy, **3** was stable for several weeks at room temperature and under N<sub>2</sub> atmosphere both in the solid state and in C<sub>6</sub>D<sub>6</sub> solution, contrasting with the easy decomposition of related complexes.<sup>22</sup> However, heating under vacuum led to intractable thermolysis products. To the best of our knowledge, there is only one precedent of Co-N<sub>2</sub> pincer complex with NHC donors.<sup>4</sup>

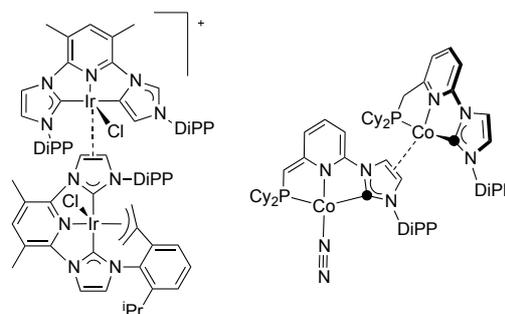
Reduction of **2** with KC<sub>8</sub> at room temperature yielded a second product which was isolated after *evaporation of the volatiles under vacuum* and crystallisation from toluene. Crystallographic characterisation revealed it to be the dinuclear complex [Co(<sup>CY</sup>P\*<sup>N</sup><sub>a</sub><sup>C</sup><sup>NHC</sup>)(Co(<sup>CY</sup>PNC<sup>NHC</sup>))](N<sub>2</sub>) (**4**), which comprises two subunits with chelated Co<sup>I</sup> centres in distorted square planar coordination geometries (Fig. 4). The metrical data for the Co(<sup>CY</sup>P\*<sup>N</sup><sub>a</sub><sup>C</sup><sup>NHC</sup>)(N<sub>2</sub>) ( $\kappa$ P, $\kappa$ N, $\kappa$ C<sup>NHC</sup>, $\kappa$ N<sub>2</sub>) subunit are very similar to those observed in **3**. The second subunit, Co(<sup>CY</sup>PNC<sup>NHC</sup>)( $\kappa$ P, $\kappa$ N, $\kappa$ C<sup>NHC</sup>), features a pincer



**Fig. 4** The structure of **4** with thermal ellipsoids at 40% probability (the C atoms of the Cy and DiPP rings are depicted as spheres). H atoms except the  $\alpha$ -CH and C atoms of the Cy and DiPP of the upper ligand bar those attached to P and N have been omitted.

coordination with a 're-aromatised' skeleton and an sp<sup>3</sup>-hybridised  $\alpha$ -CH<sub>2</sub>P (C53-C54=1.483(7) Å, C53-C54-P2 =110.6(3)°). The NHC plane is tilted by 7.9° relative to that of the pyridine. Interestingly, the C34-Co2 bond distance (1.760(5) Å is the shortest C<sup>NHC</sup>-Co distance reported.<sup>15</sup> The amido-cobalt N3-Co1 bond is slightly shorter than the corresponding neutral pyridine-cobalt N8-Co2 (1.904(3) and 1.918(4) Å, respectively). Examination of the <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum of **4** revealed singlets at  $\delta$  48.3 and 42.3. Noteworthy, no anomalous chemical shift ( $\delta \geq 10$  ppm) was observed in the <sup>1</sup>H-NMR spectrum, ruling out redox non-innocence (*i.e.* not a Co<sup>II</sup> centre engaged in an antiferromagnetic coupling with a ligand radical anion).<sup>4</sup> The  $\alpha$ -CH<sub>2</sub>P as well as the alkyl DiPP protons are diastereotopic owing to hindered rotation around the N8-Co2-C3 bond.

The di-metalated NHC ring can be viewed as 'ditopic carbanionic carbene' (anionic 'dicarbene' NHDC) coordinated through the 'normal' and the 'abnormal' position.<sup>23</sup> This constitutes the first example of a 'dicarbene' complex of cobalt and only the second occurrence of 'abnormal' Co-NHC coordination.<sup>24</sup> NHDC have been generated by deprotonation/metalation<sup>25</sup> or chemical reduction of NHC ligands<sup>26</sup> but Ru-promoted C-H activation<sup>27</sup> and Pd-mediated C-H and C-I activation<sup>28</sup> have also been described. Although a detailed mechanism for the formation of **4** requires further investigation, the concomitant re-aromatisation of the picoline moiety of the second subunit points to C-H activation *via* metal-ligand cooperation under N<sub>2</sub>-depleted conditions.



**Fig. 5**  $\eta^2$ -Ethylene-like interaction described for an Ir<sup>I</sup>-Ir<sup>III</sup> C<sup>NHC</sup>NC<sup>NHC</sup> pincer complex (left)<sup>29</sup> and postulated intermediate for the formation of **4** (right).

Noteworthy, C-H activation on pincer ligands has been described upon reduction under Ar of related  $[\text{Fe}(\text{C}^{\text{NHC}}\text{NC}^{\text{NHC}})\text{Br}_2]^{20\text{b}}$  and aliphatic-PNP-Co<sup>I</sup> complexes.<sup>22</sup> It is plausible that formation of **4** could be preceded by initial  $\eta^2$ -ethylene-like interaction between the unsaturated NHC backbone and the Co<sup>I</sup>, analogous to the coordination mode described in an Ir<sup>I</sup>-Ir<sup>III</sup> C<sup>NHC</sup>NC<sup>NHC</sup> pincer analogue (Fig. 5).<sup>29</sup> However, homolytic pathways leading to **4** cannot be excluded.

In conclusion, the dearomatisation of the PNC<sup>NHC</sup> in **2** and **3** is crucial for the formation of the dinuclear complexes, either through metalation at the nucleophilic  $\alpha$ -CHP side-arm or by C-H activation of the NHC backbone, the latter presumably being facilitated by metal-ligand cooperation. In view of the increasing involvement and importance of dearomatised complexes in catalysis, the reactivity reported here is of broader relevance.

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