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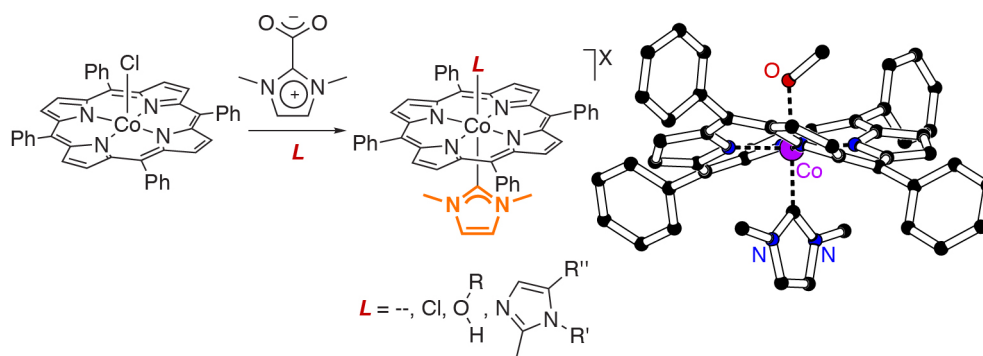
## N-heterocyclic carbene bonding to cobalt porphyrin complexes

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**Abstract:** N-heterocyclic carbene (NHC) coordination to a cobalt(III) center embedded in a porphyrin scaffold has been accomplished by decarboxylation from N,N'-dimethylimidazolium-2-carboxylate in the presence of Co(TPP)Cl (TPP = 5,10,15,20-tetraphenylporphyrin). The distal chloride ligand in the resulting complexes Co(NHC)(TPP)Cl was successfully substituted with imidazoles and alcohols. Single crystal X-ray diffraction of the latter complexes Co(NHC)(TPP)(ROH) (R = Me, Et) revealed a pronounced ruffling of the porphyrin macrocycle due to the two *ortho* methyl groups in the carbene ligand and because of the relatively short distance between the cobalt center and the carbene ligand. Spectroscopic investigations support a substantial porphyrin dearomatization upon NHC bonding.



**Keywords:** cobalt, N-heterocyclic carbene, porphyrin, imidazole, steric strain, ligand substitution

## Introduction

The development of N-heterocyclic carbenes as ligands for transition metal chemistry has undoubtedly been one of the most significant advances in modern inorganic and organometallic chemistry [1]. Even though NHCs are formally neutral donor ligands and have indeed initially been compared to phosphines [2], they are distinctly different from classical coordination ligands that bind the metal center via a heteroatom-centered lone pair or a  $\pi$  bond [3]. Coordination ligands engage in what is often referred to as a dative bond to the metal center, indicating a largely ionic contribution and hence a kinetic lability of the bond, which may be detrimental to some (catalytic) processes (ligand loss, complex decomposition), yet beneficial or even essential for other reaction pathways (cyclometalation, transient and reversible formation of coordinatively unsaturated and catalytically competent species). As a consequence, the metal-ligand bonding in these complexes is often thermodynamically controlled, allowing simple and powerful principles to be established such as the hard-soft-acid-base concept [4].

In contrast, the bonding between a NHC and a metal center comprises a much higher covalent contribution [5]. Metal bonding is thus, generally, under kinetic control, and the NHC-metal bond is kinetically inert, *i.e.* reversible ligand dissociation does typically [6] not occur [7]. While this bonding situation has clear implications, *e.g.* on supramolecular chemistry and catalytic cycles, it also indicates that NHCs may form complexes with a significantly larger number of metals than for example soft phosphines, or hard alkoxides. Indeed, NHC complexes have been reported with metals across the entire periodic table, including actinides and lanthanides [8], (alkali) earth metals [9], main group metals [10], and all types of d-block transition metals [11]. Despite this unique diversity, the organometallic chemistry of NHC ligands has been largely dominated by platinum group metal complexes (in particular Ru, Rh, Ir, and Pd) [12], and by coinage metal complexes [13]. The 3<sup>rd</sup> row homologues of the

platinum group metals have been investigated much less [14], and in particular NHC cobalt complexes have been rare [15]. The low popularity may origin, in parts, from the fact that a number of classical synthetic methods are less applicable to 3<sup>rd</sup> row transition metals (*e.g.* transmetalation from NHC silver intermediates, oxidative addition routes). Perhaps equally relevant may be the coordinative lability of cobalt in terms of redox processes and ligand substitutions. Indeed, only a handful of NHC cobalt complexes have been reported and most of them are sensitive and require careful handling [15].

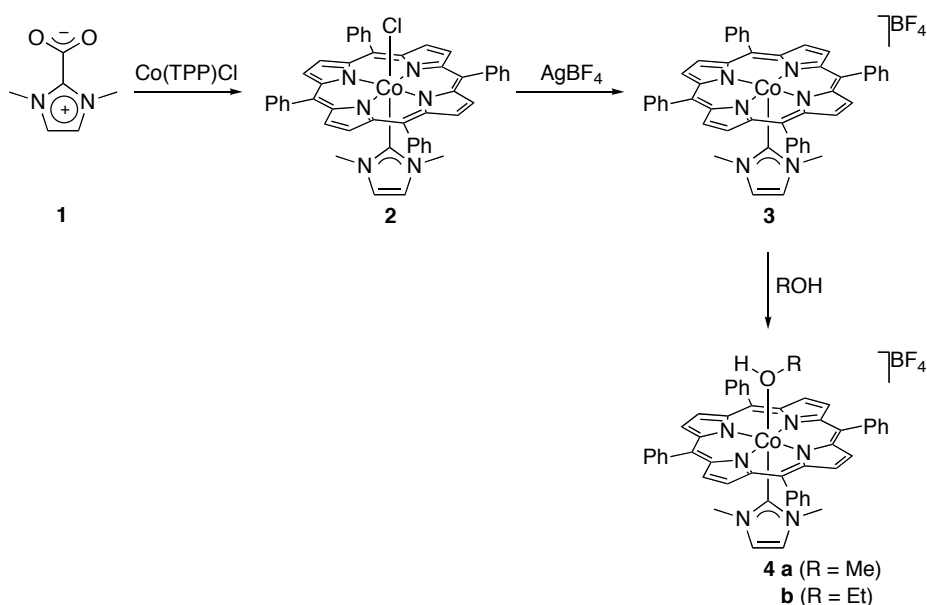
We reasoned that the lability of the complexes may be reduced upon immobilizing the cobalt center in a rigid scaffold. Porphyrins appear particularly attractive for this purpose [16], as they stabilize the diamagnetic cobalt(III) center and prevent undesired redox-processes at the metal [17]. In addition, coordination of a NHC leaves one labile coordination site opposite to the carbene, which should eventually allow the strong *trans* effect of the NHC ligand to be exploited. Here we report on the synthesis and structural characterization of air-stable NHC cobalt complexes.

## Results and discussion

The air-stable NHC cobalt complex **2** was successfully prepared by reacting the imidazolium carboxylate **1** [18] in the presence of equimolar amounts of *meso*-tetraphenylporphyrin cobalt(III) chloride (TPP–CoCl; Scheme 1). Complex formation was indicated by the intense purple color, which is reflected in the UV-vis spectrum by the Soret band ( $\lambda_{\text{max}}$  434 nm) and two absorption maxima for the Q band ( $\lambda_{\text{max}}$  560 and 595 nm). A split of the Q band into two resolved absorptions has been noted previously when using sterically demanding 2-substituted imidazoles in related TPP–Co complexes [19]. Structural evidence in solution was obtained by NMR spectroscopy. Bonding of the NHC ligand to the cobalt center was

indicated by the presence of two singlets in 1:3 ratio at  $\delta_{\text{H}}$  5.06 and  $-0.63$  ppm, attributed to the heterocyclic protons and the N-CH<sub>3</sub> wingtip groups, respectively. The extraordinary high-field shift of these signals ( $\Delta\delta$  approximately  $-2$  and  $-5$  ppm, respectively) when compared to other complexes containing the *N,N'*-dimethylimidazolyliene (IMe) ligand [18] is obviously a direct consequence of the porphyrin ring current and thus a clear indication for carbene bonding to the TPP-Co unit. The integral ratio between the TPP signals and the NHC ligand are commensurate with a single carbene bound to the TPP-Co unit. The <sup>13</sup>C NMR chemical shifts were less sensitive to the ring current effects and the resonances for both the C4/C5 and the N-CH<sub>3</sub> carbons are not unusual ( $\delta_{\text{C}}$  123.7 and 32.5, respectively). Complex **2** was also the exclusive product when performing the reaction in the presence of a large excess of **1**, suggesting that in contrast to imidazole coordination [19], bonding of a second NHC ligand to the cobalt porphyrin core is unfavorable. Complex **2** is air-stable in solution and in the solid state for weeks, hence contrasting the stability of various other NHC cobalt complexes [15].

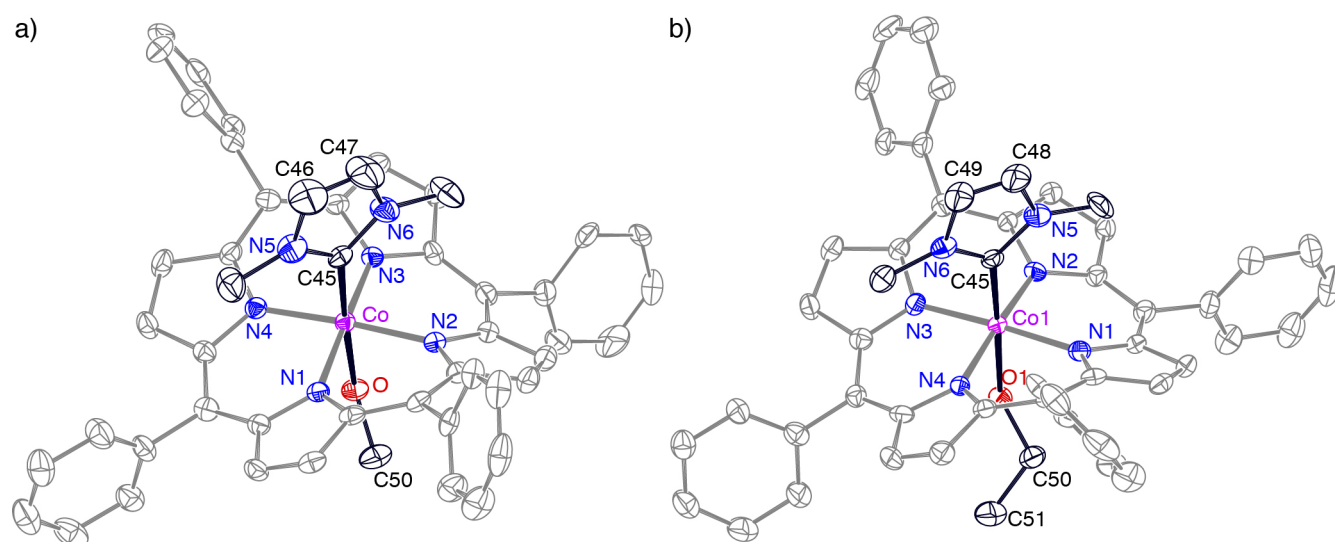
**Scheme 1**



The chloride ligand in complex **2** was readily abstracted by AgBF<sub>4</sub> (Scheme 1). Under dry conditions (CHCl<sub>3</sub> solution), complex **3** was the only detectable product. Complex **3** features either a penta-coordinate cobalt(III) center, or an octahedral geometry including weak coordination of the BF<sub>4</sub><sup>−</sup> anion. Elemental analysis data do not suggest coordination of a small ligand, *e.g.* adventitious water. Complex **3** is sensitive to Lewis bases and afforded the octahedral complexes **4a** and **4b** in the presence of MeOH and EtOH, respectively. The <sup>1</sup>H NMR resonances of the NHC ligand were diagnostic for confirming the effective replacement of the chloride anion by a weaker bound ligand. Thus, the NCH<sub>3</sub> wingtip resonance is shifted downfield by 0.12 (±1) ppm. Likewise, the heterocyclic C<sub>NHC</sub>–H frequencies are considerably less shielded in complexes **3** and **4** and appear in the 5.35–5.38 ppm range (*cf* 5.06 in **2**). A similar effect was noted for the heterocyclic porphyrin protons, which shift from 8.83 to 8.95 ppm upon chloride abstraction. These observations are in agreement with a more electropositive cobalt center in complexes **3** and **4** and hence a more pronounced  $\sigma$  donation of the TPP ligand to the metal center, which depletes electron density in the TPP fragment and hence reduces the ring current. In the spectra of all complexes **2–4**, the TPP ligand appeared as a C<sub>4</sub>-symmetric unit. No desymmetrization due to NHC coordination was noted, suggesting that ligand rotation about the C<sub>NHC</sub>–Co bond is relatively fast in solution [20].

Complexes **4a** and **4b** were analyzed by single crystal X-ray diffraction. The ORTEP plots of the formally cationic complexes (Fig. 1) reveal an octahedral cobalt center with the TPP ligand occupying the equatorial position and the NHC ligand and ROH coordinating through oxygen on the axial positions. Crystals of **4b** contained two crystallographically independent cations in the unit cell. The metric data around the cobalt center are identical in both complexes within standard deviations. Analysis of the global structure reveals in both complexes a staggered orientation of the NHC ligand with respect to the equatorial Co–N<sub>TPP</sub> bonds (Fig. 2a), suggesting little metal–NHC  $\pi$  bond interactions [21]. As a consequence of

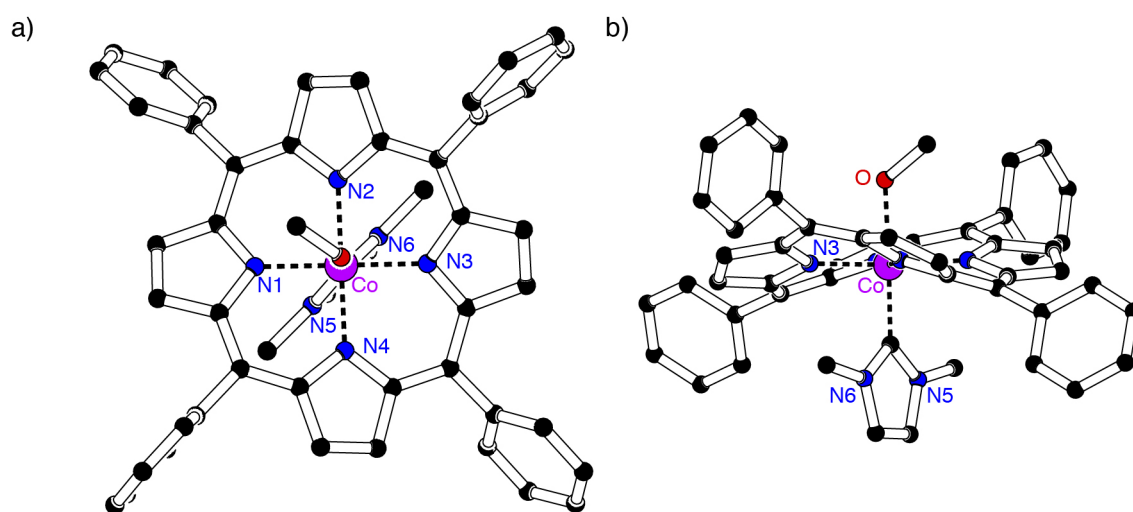
this arrangement, two phenyl groups are pushed towards the ROH side of the porphyrin ring, while the other two phenyl groups are twisted towards the empty space on the NHC side, resulting in a pronounced saddle conformation of the porphyrin with a superimposed ruffling to alleviate the steric interactions. The distinct orientation of the NHC ligand as well as the distortion in the porphyrin macrocycle renders the complex essentially (but not crystallographically) C<sub>2</sub>-symmetric. This specific structural arrangement is, however, not preserved in solution and rotation of the NHC ligand appears to be fast (see above).



**Fig. 1.** Ortep representations (50% ellipsoids, hydrogen atoms, non-coordinating BF<sub>4</sub><sup>−</sup> anion and co-crystallized solvent molecules omitted), of **4a** (a; only one of two disordered conformations of one phenyl group shown) and **4b** (b; only one of the two independent molecules in the unit cell shown).

On an atomic level, it is worth noting that the Co–C<sub>NHC</sub> bond distance is within expectation (Co–C 1.93 Å) and does not seem to be elongated due to the rigid porphyrin skeleton (Table 1). It is, however, significantly shorter than typical Co–N bonds of proximal pyridine or imidazole ligands, which are around 2.20 Å [22]. The closer distance in the NHC complexes may reflect the higher covalent contribution of the cobalt-ligand bond and may provide a rationale for the substantial distortion in the porphyrin skeleton. All C<sub>NHC</sub>–Co–N bond angles are slightly but consistently larger than 90° (average angle is 92.5±1.0° in **4a** and **4b**), while

the O–Co–N bond angles are all smaller than 90° (average angle is 87.5±2.0° in both structures), thus reflecting considerable distortion. Hence, the steric demand due to the two methyl wingtip groups at the metal center appears to be alleviated by a slight move of the cobalt center out of the least square plane of the four porphyrin nitrogens towards the NHC ligand (0.085 Å and 0.084 Å for **4a** and **4b**, respectively) [23]. The ruffled structure is caused by the significant deviation of the *meso* carbons out of this least square plane by 0.70 to 0.87 Å in both structures.



**Fig. 2.** Pluton drawing of the top and side-view of the complex cation of **4a**, visualizing a) the staggered orientation of the NHC ligand with respect to the equatorial Co–N<sub>TPP</sub> bonds, and b) the saddle conformation due to repulsive interactions between two phenyl groups and the N–CH<sub>3</sub> groups of the NHC ligand.

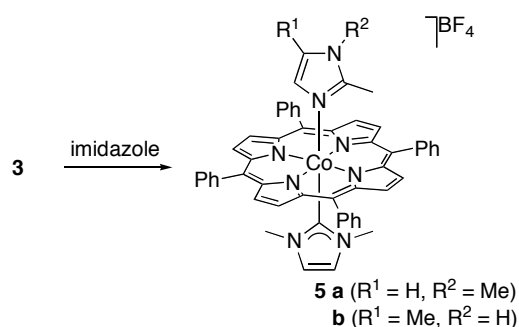
**Table 1.** Selected bond lengths (Å) and angles (°) for complexes **4a** and **4b**

	<b>4a</b>	<b>4b</b>		<b>4a</b>	<b>4b</b>
Co–C <sub>NHC</sub>	1.930(3)	1.933(4)	C <sub>NHC</sub> –Co–O	176.95(13)	177.38(15)
Co–O	2.059(2)	2.067(3)	C <sub>NHC</sub> –Co–N1	92.52(12)	91.55(14)
Co–N1	1.933(3)	1.923(3)	C <sub>NHC</sub> –Co–N2	91.82(13)	94.34(15)
Co–N2	1.918(2)	1.914(3)	C <sub>NHC</sub> –Co–N3	91.87(13)	91.91(15)
Co–N3	1.934(3)	1.935(3)	C <sub>NHC</sub> –Co–N4	93.94(12)	92.17(15)
Co–N4	1.923(3)	1.911(3)	O–Co–N1	89.28(10)	88.86(13)
			O–Co–N2	85.75(10)	88.24(13)
			O–Co–N3	86.34(10)	86.69(11)
			O–Co–N4	88.48(10)	85.25(12)



The specific bonding features presumably prevent the coordination of another NHC ligand to complexes **2** or **3**. Likewise, we have not been successful to coordinate a larger NHC ligand, *e.g.* with butyl wingtip groups, to the cobalt center in Co(TPP)Cl. However, bonding of a less strongly coordinating ligands like alcohols (complexes **4a** and **4b**) is obviously feasible. Moreover, imidazole coordination was demonstrated by the isolation of complexes **5** upon reacting complex **3** with one equivalent of 1,2-dimethylimidazole or 2,4-dimethylimidazole and subsequent purification by preparative thin layer chromatography (Scheme 2). Imidazole and NHC coordination in complexes **5a** and **5b** was supported by the diagnostic resonances in their  $^1\text{H}$  NMR spectra. Specifically, the NHC protons were shifted to higher field compared to complexes **3** and **4** and are nearly identical to those of the chloride complex **2** (for **5a**, *viz* 5.03 and  $-0.64$  ppm) or even further shifted to 4.84 and  $-0.67$  ppm for the  $\text{C}_{\text{NHC}}\text{-H}$  and  $\text{N-CH}_3$  groups in **5b**, respectively. In addition, signals due to the bound imidazole ligand were observed in the expected integral ratio and diagnostically shifted to high field due to the porphyrin ring current.

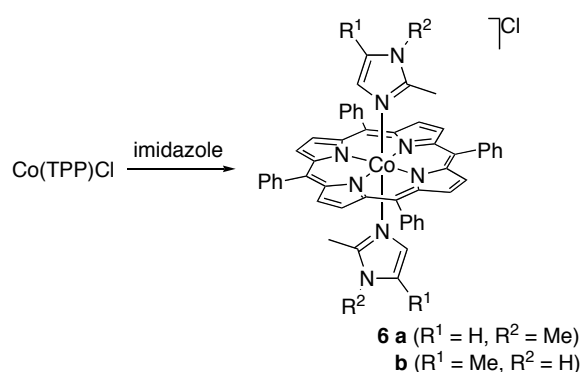
## Scheme 2



A potential disproportionation reaction was excluded based on analytical data of complexes **6** comprising two imidazole ligands bound to the Co(TPP) unit (Scheme 3). These complexes were obtained according to previously published methods by using two molequiv. imidazole [19,24]. NMR signal integration was in full agreement with the presence of two imidazole

ligands at the cobalt center. The chemical shifts for complexes **6a** and **6b** were distinctly different from those recorded for the corresponding mixed-ligand complexes **5**. Specifically, the signals due to the *meso*-phenyl groups collapse into a single broad resonance in complexes **5** while the *ortho* protons are distinctly different from the *meta*- and *para*-positioned protons in complexes **6** ( $\delta\Delta$  ca. 0.1 ppm). In addition, the resonances for the protons  $\alpha$  to the cobalt-bound nitrogen (*i.e.* C4–H in **a**, C5–H in **b**) are located at higher field in bis(imidazole) complexes **6** than in the carbene complexes **5**. The weaker ring current exposure of the imidazole ligands in complexes **5** may be a direct consequence of the stronger *trans* influence of the NHC ligand as compared to the imidazole. In addition, a stronger porphyrin deformation accompanied by a partial reduction of the aromatic character may be more significant in the NHC complexes due to the presence of two *ortho* substituents in the NHC ligand (as opposed to only one in the C2-substituted imidazoles) paired with the relatively short Co–C<sub>NHC</sub> bond.

### Scheme 3



### Conclusions

New porphyrin cobalt(III) complexes comprising a proximal N-heterocyclic carbene (NHC) ligand were synthesized and fully characterized. The NHC bonding has significant steric and electronic implications. In particular, the presence of substituents on both *ortho* positioned

nitrogens paired with the strong Co–C<sub>NHC</sub> bond imparts a substantial distortion of the porphyrin macrocycle, which may be exploited for the labilization of otherwise tightly bound ligands in distal position. Based on the critical role of metalloporphyrin derivatives as cofactors in a number of biological processes and since metalloporphyrins have shown promising catalytic activity in a variety of synthetic oxidation processes, it will be interesting to investigate the catalytic scope of these carbene cobalt complexes. Preliminary experiments suggest useful activity in the oxidation of olefins and a full account on these studies will be reported in due course.

## Experimental part

**General.** Complex Co(TPP)Cl [25] was prepared according to published procedures. Solvents were dried by passage through solvent purification columns (CH<sub>2</sub>Cl<sub>2</sub>) or by distillation from P<sub>2</sub>O<sub>5</sub> (CHCl<sub>3</sub>), Mg/I<sub>2</sub> (MeOH), or CaH<sub>2</sub> (MeCN). All other reagents are commercially available and were used as received. Unless otherwise stated, NMR spectra were recorded at 25 °C on Varian spectrometers operating at 300 or 400 MHz (<sup>1</sup>H NMR) and 75 or 100 MHz (<sup>13</sup>C{<sup>1</sup>H} NMR), respectively. Chemical shifts (δ in ppm, coupling constants *J* in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the microanalytical laboratory of University College Dublin, Ireland.

**Complex 2.** A solution of TPPCoCl (0.200 g, 0.283 mmol) in dry MeCN (20 mL) was stirred with *N,N'*-dimethylimidazolium-2-carboxylate (0.040 g, 0.283 mmol) for 12 h at room temperature. All volatiles were removed under reduced pressure and the residue was purified by column chromatography (SiO<sub>2</sub>; CHCl<sub>3</sub>). The last fraction was collected and dried in vacuo to give the title product as a purple solid. Yield 0.18 g, 79%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.83 (s, 8H, H<sub>pyr</sub>), 7.87 (s, 8H, H<sub>Ph</sub>), 7.65 (s, 12H, H<sub>Ph</sub>), 5.06 (s, 2H, H<sub>NHC</sub>), –0.63 (s, 6H, NCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 143.81 (C<sub>pyr</sub>), 139.88 (C<sub>Ph</sub>), 134.38 (C<sub>pyr</sub>), 133.61, 128.04, 127.09 (3 × C<sub>Ph</sub>), 123.70 (C<sub>NHC</sub>), 120.25 (C–Ph), 32.54 (NCH<sub>3</sub>), carbene carbon not resolved. Anal. Calcd for

$\text{C}_{49}\text{H}_{36}\text{N}_6\text{CoCl}$  (803.4)  $\times \text{H}_2\text{O}$ : C, 71.66; H, 4.66; N, 10.23. Found: C, 71.99; H, 4.23; N, 10.02.

**Complex 3.** A solution of **2** (0.200 g, 0.249 mmol) in dry  $\text{CHCl}_3$  (15 mL) was stirred with  $\text{AgBF}_4$  (0.048 g, 0.25 mmol) for 2 h at room temperature. The mixture was filtered through Celite. All volatiles were removed from the filtrate under reduced pressure and the residue was purified by preparative thin layer chromatography ( $\text{SiO}_2$ ;  $\text{CHCl}_3$ ). Yield 0.178 g, 84%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.92 (s, 8H,  $\text{H}_{\text{pyr}}$ ), 7.85 (s, 8H,  $\text{H}_{\text{Ph}}$ ), 7.70 (s, 12H,  $\text{H}_{\text{Ph}}$ ), 5.38 (s, 2H,  $\text{H}_{\text{NHC}}$ ), -0.52 (s, 6H,  $\text{NCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.00 ( $\text{C}_{\text{pyr}}$ ), 138.67 ( $\text{C}_{\text{Ph}}$ ), 134.77 ( $\text{C}_{\text{pyr}}$ ), 132.77, 128.88, 127.72 ( $3 \times \text{C}_{\text{Ph}}$ ), 126.91 ( $\text{C}_{\text{NHC}}$ ), 123.14 ( $\text{C-Ph}$ ), 32.86 ( $\text{NCH}_3$ ), carbene carbon not resolved. Anal. Calcd for  $\text{C}_{49}\text{H}_{36}\text{BCoF}_4\text{N}_6$  (854.59): C, 68.87; H, 4.25; N, 9.83. Found: C, 69.09; H, 4.21; N, 9.69.

**Complex 4a.** A solution of **3** (0.100 g, 0.12 mmol) in dry  $\text{CHCl}_3$  (20 mL) and MeOH (0.02 ml, 0.4 mmol) was stirred for 1 h at room temperature. All volatiles were removed under reduced pressure. The crude product (0.095 g, 92%) was recrystallized from  $\text{CHCl}_3$ /pentane.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.95 (s, 8H,  $\text{H}_{\text{pyr}}$ ), 7.86 (s, 8H,  $\text{H}_{\text{Ph}}$ ), 7.71 (s, 12H,  $\text{H}_{\text{Ph}}$ ), 5.35 (s, 2H,  $\text{H}_{\text{NHC}}$ ), 3.78 (s, 1H, OH), 1.25 (s, 3H,  $\text{OCH}_3$ ), -0.51 (s, 6H,  $\text{NCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.06 ( $\text{C}_{\text{pyr}}$ ), 138.56 ( $\text{C}_{\text{Ph}}$ ), 135.02 ( $\text{C}_{\text{pyr}}$ ), 132.87, 129.02, 127.78 ( $3 \times \text{C}_{\text{Ph}}$ ), 126.65 ( $\text{C}_{\text{NHC}}$ ), 123.07 ( $\text{C-Ph}$ ), 36.11 ( $\text{OCH}_3$ ), 32.86 ( $\text{NCH}_3$ ), carbene carbon not resolved. Anal. Calcd for  $\text{C}_{50}\text{H}_{40}\text{N}_6\text{CoOBF}_4$  (886.63)  $\times 2\text{CHCl}_3$ : C, 55.50; H, 3.76; N, 7.47. Found: C, 55.19; H, 3.52; N, 7.26.

**Complex 4b.** Complex **4b** was obtained according to the same procedure as described for **4a**, starting from **3** (0.100 g, 0.12 mmol) and EtOH (0.02 ml, 0.4 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (20 mL) and after recrystallization from  $\text{CH}_2\text{Cl}_2$ /pentane. Yield 0.98 g, 93%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.96 (s, 8H,  $\text{H}_{\text{pyr}}$ ), 7.86 (s, 8H,  $\text{H}_{\text{Ph}}$ ), 7.71 (s, 12H,  $\text{H}_{\text{Ph}}$ ), 5.37 (s, 2H,  $\text{H}_{\text{NHC}}$ ), 3.83 (s, H, OH), 1.25 (br, 2H,  $\text{OCH}_2$ ), 0.87 (t, 3H,  $\text{CH}_3\text{CH}_2\text{OH}$ ), -0.50 (s, 6H,  $\text{NCH}_3$ ). Anal. Calcd for  $\text{C}_{51}\text{H}_{42}\text{BCoF}_4\text{N}_6\text{O}$  (900.66)  $\times 2\text{CH}_2\text{Cl}_2$ : C, 59.46; H, 4.33; N, 7.85. Found: C, 59.02; H, 4.11; N, 7.63.

**Complex 5a.** A solution of **3** (0.100 g, 0.12 mmol) in dry  $\text{CHCl}_3$  (20 mL) was stirred with 1,2-dimethylimidazole (0.011 g, 0.12 mmol) for 2 h at room temperature. All volatiles were

removed under reduced pressure and the residue was purified by preparative thin layer chromatography (SiO<sub>2</sub>; CHCl<sub>3</sub>). Yield 0.095 g, 85 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.86 (s, 8H, H<sub>pyr</sub>), 7.64 (br, 20H, H<sub>ph</sub>), 5.03 (s, 2H, H<sub>NHC</sub>), 4.62 (s, 1H, H<sub>im</sub>), 2.08 (s, 3H, N<sub>im</sub>-CH<sub>3</sub>), -0.21 (s, 1H, H<sub>im</sub>), -0.64 (s, 6H, N<sub>NHC</sub>-CH<sub>3</sub>), -2.20 (s, 3H, C<sub>im</sub>-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 142.17 (C<sub>pyr</sub>), 141.15 (C<sub>im</sub>), 139.16 (C<sub>ph</sub>), 135.08 (C<sub>pyr</sub>), 134.70 (C<sub>im</sub>-Me), 133.81 (C<sub>im</sub>-Me), 133.34, 128.13, 127.12 (3 × C<sub>ph</sub>), 122.15 (C<sub>NHC</sub>), 121.35 (C-Ph), 32.53 (NCH<sub>3</sub>), 8.33, 6.03 (N<sub>im</sub>-CH<sub>3</sub> and C<sub>im</sub>-CH<sub>3</sub>), carbene carbon not resolved. Anal. Calcd for C<sub>54</sub>H<sub>44</sub>BCoF<sub>4</sub>N<sub>8</sub> (950.72): C, 68.22; H, 4.66; N, 11.79. Found: C, 68.43; H, 4.21; N, 11.47.

**Complex 5b.** According to the procedure described for **5a**, complex **5b** was obtained from **3** (0.100 g, 0.12 mmol) and 2,4-dimethylimidazole (0.011 g, 0.12 mmol). Yield 0.97 g, 87%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.81 (s, 8H, H<sub>pyr</sub>), 8.03 (s, H, N<sub>im</sub>-H), 7.62 (s, 20H, H<sub>ph</sub>), 4.84 (s, 2H, H<sub>NHC</sub>), 0.61 (s, 3H, C<sub>im</sub>-CH<sub>3</sub>), -0.52 (s, 1H, H<sub>im</sub>), -0.67 (s, 6H, NCH<sub>3</sub>), -2.15 (s, 3H, C<sub>im</sub>-CH<sub>3</sub>). Anal. Calcd for C<sub>54</sub>H<sub>44</sub>BCoF<sub>4</sub>N<sub>8</sub> (950.72): C, 68.22; H, 4.66; N, 11.79. Found: C, 68.34; H, 4.54; N, 11.45.

**Complex 6a.** A solution of Co(TPP)Cl (0.080 g, 0.11 mmol) and 1,2-dimethylimidazole (0.051 g, 0.23 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was stirred at room temperature for 16 h. All volatiles were removed under reduced pressure and the residue was purified by preparative thin layer chromatography (SiO<sub>2</sub>; CHCl<sub>3</sub>). Yield 0.94 g, 93%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.98 (s, 8H, H<sub>pyr</sub>), 7.79 (s, 8H, H<sub>ph</sub>), 7.67 (s, 12H, H<sub>ph</sub>), 4.71 (s, 2H, H<sub>im</sub>), 2.07 (s, 6H, NCH<sub>3</sub>), -0.32 (s, 2H, H<sub>im</sub>), -2.20 (s, 6H, C-CH<sub>3</sub>). Anal. Calcd for C<sub>54</sub>H<sub>44</sub>ClCoN<sub>8</sub> (899.37): C, 72.11; H, 4.93; N, 12.46. Found: C, 72.01; H, 4.75; N, 12.16.

**Complex 6b.** Complex **6b** was obtained as described for **6a** from TPPCoCl (0.188 g, 0.27 mmol) and 2,4-dimethylimidazole (0.051 g, 0.53 mmol). Yield 0.210 g, 88 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.46 (s, 2H, N<sub>im</sub>-H), 8.77 (s, 8H, H<sub>pyr</sub>), 7.64 (s, 8H, H<sub>ph</sub>), 7.55 (s, 12H, H<sub>ph</sub>), 0.20 (s, 6H, C-CH<sub>3</sub>), -0.83 (s, 2H, H<sub>im</sub>), -2.38 (s, 6H, C-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 142.00 (C<sub>pyr</sub>), 141.68 (C<sub>im</sub>-Me), 139.84 (C<sub>ph</sub>), 134.52 (C<sub>pyr</sub>), 133.68, 127.71, 126.76 (3 × C<sub>ph</sub>), 120.80 (C<sub>im</sub>-Me), 118.65 (C<sub>im</sub>-H), 118.64 (C<sub>ph</sub>), 7.93, 6.44 (2 × CH<sub>3</sub>). Anal. Calcd for C<sub>54</sub>H<sub>44</sub>ClCoN<sub>8</sub> (899.37): C, 72.11; H, 4.93; N, 12.46. Found: C, 71.98; H, 4.90; N, 12.29.

**Crystallographic details.** Crystal data were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector. Crystals were measured with monochromated Mo-K $\alpha$  radiation (0.71073 Å). A twice redundant dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed [26]. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F<sup>2</sup> for all data using SHELXL-97 [27]. Hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. For complex **4a** SAME and SADI restraints were used to get corresponding disorder parts into similar shapes. Further crystallographic details are compiled in Table 2. CCDC 828899 (**4a**) and 828900 (**4b**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 2.** Crystal data and structure refinement for **4a** and **4b**.

	<b>4a</b>	<b>4b</b>
Empirical formula	C <sub>50</sub> H <sub>40</sub> BCoF <sub>4</sub> N <sub>6</sub> O × 2 CHCl <sub>3</sub>	C <sub>51</sub> H <sub>42</sub> BCoN <sub>6</sub> OF <sub>4</sub> × 2 CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	1125.36	1070.50
Temperature /K	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (#19)	P2 <sub>1</sub> (#4)
Unit cell dimensions		
a /Å	16.5323(2)	16.2566(3)
b /Å	17.4695(2)	17.8133(3)
c /Å	17.8208(2)	17.3187(3)
β /deg	90	91.219(1)
Volume /Å <sup>3</sup>	5146.84(10)	5014.08(15)
Z	4	4
Calcd density /g cm <sup>-3</sup>	1.452	1.418
μ /mm <sup>-1</sup>	0.705	0.616
Crystal size / mm <sup>3</sup>	0.27 × 0.19 × 0.11	0.32 × 0.18 × 0.15
Reflections collected, indep	27576, 8167 (R <sub>int</sub> = 0.0317)	65184, 20471 (R <sub>int</sub> = 0.0331)
Max., min. transmission	0.964, 0.924	0.957, 0.916
Restraints, parameters, GooF	21, 749, 1.079	1, 1266, 1.027

R [ $I > 2\sigma(I)$ ]	R1 = 0.0409, wR2 = 0.1011	R1 = 0.0529, wR2 = 0.1463
R (all data)	R1 = 0.0468, wR2 = 0.1032	R1 = 0.0631, wR2 = 0.1515
Absolute structure parameter <sup>a)</sup>	0.014(14)	−0.017(12)
Largest diff. peak, hole /e Å <sup>3</sup>	0.755, −0.662	1.162, −0.721

<sup>a)</sup> see reference [28]

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### Figure captions:

**Fig. 1.** Ortep representations (50% ellipsoids, hydrogen atoms, non-coordinating  $\text{BF}_4^-$  anion and co-crystallized solvent molecules omitted), of **4a** (a; only one of two disordered conformations of one phenyl group shown) and **4b** (b; only one of the two independent molecules in the unit cell shown).

**Fig. 2.** Pluton drawing of the top and side-view of the complex cation of **4a**, visualizing a) the staggered orientation of the NHC ligand with respect to the equatorial  $\text{Co-N}_{\text{TPP}}$  bonds, and b) the saddle conformation due to repulsive interactions between two phenyl groups and the  $\text{N-CH}_3$  groups of the NHC ligand.