Open-shell nitrene- and carbene-complexes of cobalt

*Characterisation and reactivity*

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Chapter 5

Synthesis, characterisation and application of anionic $[\text{Co}^{II}(\text{Cor})]\text{−}$ corrole complexes in ring-closing $C$–$H$ amination of an aliphatic azide.*

*We thank Paul Geuijen for his valuable contributions to this chapter.
Introduction

N-containing ring-compounds are one of the most commonly found heterocycles in natural products and pharmaceuticals.1 Synthesising such heterocycles via direct C–H amination, i.e. C–H activation combined with a C–N bond forming ring-closing step, is time and atom-efficient and hence an attractive way to make such compounds. One such strategy of doing so is via reactive metallo-nitrene intermediates.2 In this method a metal catalyst activates a nitrene precursor which leads to the formation of a metallo-nitrene intermediate. Depending on its reactivity, this metallo-nitrene intermediate can insert into challenging bonds, such as thermodynamically and kinetically stable C–H bonds. Organic azides are particularly attractive nitrene precursors in this perspective, as they are easy to synthesise and generate only N2 as a waste product in the amination step. However, only a handful of examples exist where intramolecular C–H amination reactions using organic azides to form N-heterocyclic compounds have been reported.3,4 A particular system that has shown successful activity in this type of reactivity is the [CoII(Por)] catalyst, capable of a variety of nitrene transfer reactions from azides. In addition to the classical inter- and intramolecular aziridination reactions,5 also intramolecular benzylic/allylic/benzallylic C–H amination reactions have been reported. Mechanistic studies using DFT reveal a step-wise mechanism involving an experimentally well-characterised CoIII-nitrene radical intermediate.7 DFT calculations further suggest that the rate determining step of these catalytic reactions is the activation of the azide at the metal centre,8 which has a substantial barrier. Consequently, in many of these reactions high temperatures are required.6 This is most evident in reactions involving unactivated alkyl azides (azide moiety positioned directly next to a CH2 group), which require heating to ~100 °C to activate the azide using [CoII(Por)] catalysts.9 Notably, in the azide activation step the metal centre undergoes an oxidation from cobalt(II) to cobalt(III). As such, we expected that application of ligands imposing a high electron density at cobalt could be beneficial, lowering the barrier of the rate limiting step, thus leading to faster catalytic reactions. Some earlier studies seem to confirm this hypothesis in an indirect manner,4 but the beneficial effect of electron-donating ligands on the rate of these reactions is evident from recent studies performed in our group.9 In a direct comparative study, the electron-rich [CoII(TMP)] was shown to outperform [CoII(TPP)] in the intramolecular C–H amination of aliphatic azides (Scheme 1).9 As such, we hypothesised that a ligand scaffold that retains the square planar geometry of a porphyrin but is more electron-rich could well be beneficial for the activation of aliphatic azides.

![Scheme 1. [CoII(Por)]-catalysed intramolecular C–H amination of aliphatic azides.](image)

Hence, we turned our attention to the corrole macrocycle. Corroles are tetrapyrrolic molecules, maintaining the skeletal structure of corrin. The difference with porphyrins is that in corroles one of the methine bridges (which links the pyrrole units together) has been replaced with a direct pyrrole–pyrrole bond (Figure 1). Thus, corroles have a trianionic charge when bound to transition metals and there is one less position for a meso-substituent. As a consequence, corroles have a slightly smaller metal-binding pocket, allowing for a ‘tighter grip’ on the metal. In addition, there is one less carbon in
the aromatic ring of corroles, which next to the trianionic charge of a corrole ligand further increases the electron density of corrole complexes relative to porphyrin complexes. As a result, corroles are expected to stabilize transition metals in higher oxidation states, even better so than porphyrins. Hence, this feature is expected to have a positive influence on the azide activation step, which occurs at the metal ion of the catalyst, with cobalt undergoing one-electron oxidation. Even though corrole complexes of cobalt have been extensively studied in oxidation and reduction reactions,\textsuperscript{10} mono-anionic cobalt(II)-corrole complexes have so far never been employed as metalloradical catalysts for nitrene- or carbene-insertion into C–H bonds. This provides an opportunity to study the metalloradical reactivity of mono-anionic $[\text{Co}^{III}(\text{Cor})]\text{−}$ complexes in mediating catalytic radical-type reactions in general, which go beyond the one particular nitrene-transfer reaction described in this chapter.

![Figure 1. Various tetradentate macrocyles. From left to right: Chlorin - Porphyrin - Corrole - Corrin.](image)

**Results and discussion**

To test the feasibility of corroles as ligands in cobalt-catalysed nitrene transfer reactions, we set out to synthesise three corrole ligands with electronically different substituents. These are depicted in Figure 2.

![Figure 2. Three $[\text{Co}^{III}(\text{Cor})]$ with varying substituents applied in the ring-closing C–H amination of alkyl azides.](image)

In their mono-reduced (mono-anionic) cobalt(III) form, all of these complexes should be much more electron rich than the corresponding cobalt(II) porphyrin complexes. Additionally, the electronic properties within the series of corrole complexes differs. The dibromo-substituted $[\text{Co}^{III}(\text{Br}_2\text{Cor})(\text{PPPh}_3)]$ should contain the least electron-rich corrole, the mesityl-substituted $[\text{Co}^{III}(\text{Mes}_2\text{Cor})(\text{PPPh}_3)]$ should contain the most electron-rich corrole, and the (unsubstituted) $[\text{Co}^{III}(\text{Ph}_2\text{Cor})(\text{PPPh}_3)]$ should have electronic properties in-between those of $[\text{Co}^{III}(\text{Br}_2\text{Cor})(\text{PPPh}_3)]$ and $[\text{Co}^{III}(\text{Mes}_2\text{Cor})(\text{PPPh}_3)]$. Reduction of these complexes using a suitable chemical reductant should produce the corresponding mono-anionic metalloradical $[\text{Co}^{II}(\text{Cor})]\text{−}$ complexes. For this purpose, in
order to find the right reducing agent, we first studied the electro-chemical properties of the [Co^{III}(Cor)(PPh_{3})] complexes.

**Synthesis of the [Co^{III}(Cor)(PPh_{3})] complexes**

The three corroles were synthesised via the dipyrromethane route, following the procedures reported by Gryko and co-workers\(^\text{11}\) (with some modifications). This is schematically represented in Scheme 2. Details of the synthetic procedures are described in the experimental section.

![Scheme 2. Generalised scheme for the synthesis of the corrole complexes [Co^{III}(Br_{2}Cor)(PPh_{3})], [Co^{III}Ph_{2}Cor](PPh_{3}) and [Co^{III}Mes_{2}Cor](PPh_{3})].](image)

While the crystal structure of [Co^{III}(Ph_{2}Cor)(PPh_{3})] is reported, the X-ray structural data of [Co^{III}(Br_{2}Cor)(PPh_{3})] and [Co^{III}(Mes_{2}Cor)(PPh_{3})] were previously unknown. We were able to grow crystals of these complexes. The molecular structure of [Co^{III}(Br_{2}Cor)(PPh_{3})] and some relevant bond distances derived from these measurements are shown in Figure 3. As is evident from the structure, the Co–N(corrole) bonds are significantly shorter than the Co–N(porphyrin) bonds (1.867 and 1.880 in [Co^{III}(Br_{2}Cor)(PPh_{3})] compared to 1.949 in [Co^{III}TPP]).\(^\text{12}\) This is to be expected, both based on the trionionic charge and the smaller ring size of the corrole macrocycle. For the [Co^{III}(Mes_{2}Cor)(PPh_{3})] complex the atom connectivity could be determined, confirming the structure of the formed complex. However, unfortunately the X-ray data were of insufficient quality to derive reliable information about the bond lengths of this complex. This structure is shown in the supporting information.
Redox chemistry of the [Co$^{III}$(Cor)(PPh$_3$)] complexes

Cyclic voltammetry (CV) experiments were used to study the redox behaviour of the three above described [Co$^{III}$(Cor)(PPh$_3$)] complexes.$^{13,14}$ For the application of these complexes as catalysts in nitrene transfer reactions we were particularly interested in the first reduction- and corresponding re-oxidation waves of these complexes. The first (chemically irreversible) reduction peak potential is important to choose a suitable chemical reductant, reducing the parent [Co$^{III}$(Cor)(PPh$_3$)] complexes to corresponding mono-anionic complexes without over-reduction. The corresponding re-oxidation peak potential gives direct information about the reductive power of the mono-anionic [Co$^4$(Cor)]$^-$ complexes.

The [Co$^n$(Cor)(PPh$_3$)] complexes show the expected redox behaviour, similar to that observed previously for related complexes.$^{15}$ The first one-electron reduction process is electrochemically irreversible for all these complexes, at least at the applied scan rate of 100 mV/s of the CV measurements (Figure 4A, B and C). The first reduction wave is coupled to an anodically shifted re-oxidation wave for all complexes, in an overall chemically reversible electrochemical-chemical-electrochemical-chemical (ECEC) process (Figure 4D). A second reduction peak at more negative potentials is also observed for all these complexes, which is fully reversible in all cases (see Figure 9, supporting information). In accordance with the electronic nature of the substituents, the peak potential of the first reduction process shifts to more negative potentials upon increasing the electron-donating properties of the substituents. This is summarised in Figure 4D ([Co$^n$(Mes$_2$Cor)(PPh$_3$)] < [Co$^n$(Ph$_2$Cor)(PPh$_3$)] < [Co$^n$(Br$_2$Cor)(PPh$_3$)]). Based on these peak potentials, either cobaltocene (CoCp$_2$; $E_k$ ~ −1.3 V vs Fc/Fc$^+$) or decamethylcobaltocene (CoCp$^{*2}$; $E_k$ ~ −1.9 V vs Fc/Fc$^+$) can be used as a suitable reductant for these complexes.$^{16}$ The ECEC sequence of events, explaining the observed behaviour of the first reduction process with an anodically shifted re-oxidation wave, is schematically represented in Figure 4D. One-electron reduction of the parent [Co$^{III}$(Cor)(PPh$_3$)] complex at the metal centre leads to the formation of an anionic [Co$^{II}$(Cor)(PPh$_3$)]$^- \cdot$ complex, followed by PPh$_3$ dissociation producing [Co$^I$(Cor)]$^-$. Oxidation of [Co$^I$(Cor)]$^-$ to [Co$^{III}$(Cor)] occurs at a higher redox potential than

<table>
<thead>
<tr>
<th>Bond</th>
<th>XRD (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–N1</td>
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</tr>
<tr>
<td>Co–N2</td>
<td>1.880 (5)</td>
</tr>
<tr>
<td>Co–P1</td>
<td>2.225 (3)</td>
</tr>
<tr>
<td>Br1–C12</td>
<td>1.895 (7)</td>
</tr>
<tr>
<td>Br2–C16</td>
<td>1.891 (6)</td>
</tr>
<tr>
<td>N1–C1</td>
<td>1.354 (8)</td>
</tr>
<tr>
<td>N1–C4</td>
<td>1.380 (7)</td>
</tr>
<tr>
<td>N2–C9</td>
<td>1.386 (8)</td>
</tr>
<tr>
<td>N2–C6</td>
<td>1.400 (7)</td>
</tr>
<tr>
<td>C11–C5</td>
<td>1.516 (8)</td>
</tr>
</tbody>
</table>

Figure 3. (left) displacement ellipsoid plot of [Co$^{III}$(Br$_2$Cor)(PPh$_3$)] and (right) some relevant bond distances (Å) obtained from X-ray diffraction studies. Hydrogen atoms are omitted for clarity.
reduction of \([\text{Co}^{\text{III}}(\text{Cor})(\text{PPh}_3)]\) to \([\text{Co}^{\text{III}}(\text{Cor})(\text{PPh}_3)]^-\), and is followed by re-coordination of \(\text{PPh}_3\) to regenerate the parent \([\text{Co}^{\text{III}}(\text{Cor})(\text{PPh}_3)]\) complex.

A) $\text{CV of [Co}^{\text{III}}(\text{Br}_2\text{Cor})(\text{PPh}_3)]$ in THF referenced against Fc/Fc$^+$ (using Fc$^*$ (bis(pentamethylcyclopentadienyl)iron) as internal standard).

B) EPR spectroscopic and UV-Vis spectro-electrochemical measurements (SEC) were performed to confirm the ECEC mechanism shown in Figure 4D. The SEC measurements were performed by coupling coulometric CV experiments to UV-vis measurements in an optically transparent thin layer electrochemical (OTTLE) cell. These experiments also allowed us to determine if any decomposition
occurs on the couloulmetric timescale or if any long-lived intermediates are formed during the reduction/re-oxidation events. Upon one-electron reduction, in all cases the absorbance of the soret bands undergo a bathochromic shift with the absorbance at ~380 nm decreasing in intensity with a new absorbance arising around at ~420 nm. In addition, the absorbance of the Q bands between 550 and 700 nm show an increase in intensity, probably due to a decreased difference in energy between the π-π* orbitals of the reduced complex. The rather small red-shifts observed are strongly suggestive of PPh₃ dissociation upon reduction. A representative example of the spectral changes observed upon reduction of [CoIII(Ph₂Cor)(PPh₃)] is shown in Figure 5. For similar spectra of the two other complexes, see Figure 10 (supporting information). When the complexes are allowed to re-oxidise (at the anodically shifted redox potential), the original [CoIII(Ph₂Cor)(PPh₃)] complex is cleanly regenerated from the [CoIII(Ph₂Cor)]⁻ complex, as evidenced by the UV-vis measurements. Multiple and quite sharp isosbestic points are indicative of clean interconversion of the reduced and oxidized species, without going through long-lived intermediates.

![Figure 5. UV-vis spectra obtained in the spectro-electrochemical experiments of [CoIII(Ph₂Cor)(PPh₃)].](image)

Having ascertained the reduction peak potentials of these complexes, as well as clean conversion to the reduced species, we also performed X-band electron paramagnetic resonance (EPR) studies on these complexes. Using a chemical reductant (bis(cyclopentadieny)lcobalt(II) (CoCp₂) for [CoIII(Br₂Cor)(PPh₃)] and [CoIII(Ph₂Cor)(PPh₃)] and bis(pentamethycyclopentadienyl)cobalt(II) (CoCp⁺₂) for [CoIII(Mes₂Cor)(PPh₃)]), all of these complexes could be reduced to give EPR spectra (anisotropic spectra, measured at 20 K in a MeTHF glass) characteristic for formation of cobalt(II) metalloradicals. The EPR spectra of the [CoIII(Mes₂Cor)]⁻ complex is shown in Figure 6. For EPR spectra of the other complexes, see Figure 11 (supporting information). The EPR spectrum shown in figure 6 reveals clear cobalt hyperfine couplings along the two higher g-values (g₁₁ = 3.56, A²₀₁₁ = 740 MHz; g₂₂ = 2.22, A²₀₂₂ = 260 MHz) and a sharper featureless line at the lowest g-value (g₃₃ = 1.85). No (resolved) phosphorus hyperfine couplings are visible along any of these directions in the anisotropic spectrum, in agreement with PPh₃ dissociation upon one-electron reduction of [CoIII(Mes₂Cor)(PPh₃)].

DFT optimisation of the anionic [CoI⁺(Cor)]⁻ complex clearly showed that the singly occupied molecular orbital (SOMO) is the dₓ orbital, thereby leading to different spin-orbit interactions than in the related [CoI⁺(Por)] complexes. This is in agreement with the EPR spectra being distinctly different from those of the porphyrin complexes.
Figure 6. (left) Experimental and simulated EPR spectra of the anionic [CoIII(Mes2Cor)]— complex formed upon reduction of reduced [CoIII(Mes2Cor)(PPh3)] with CoCp*2, measured at 20 K in a MeTHF glass. Microwave frequency = 9.38412 GHz, modulation amplitude = 0.1 G, power = 2 mW. (Right) DFT calculated spin density of the anionic [CoIII(Mes2Cor)]— complex showing that the unpaired electron is in a dxy orbital.

Application of anionic [CoII(Cor)]— complexes in ring-closing C-H amination of (4-azidobutyl)benzene

With access to the three mono-anionic [CoII(Cor)]— complexes, we decided to test the activity and selectivity of these complexes in the direct ring-closing reaction of (4-azidobutyl)benzene to give the heterocyclic pyrrolidine product. This is a reaction that was reported to proceed with [CoII(TMP)], selectively producing the Boc-protected pyrrolidine product. The high barrier and slow reactions associated with the cobalt-porphyrin catalysed process prompted us to test the more electron-rich mono-anionic cobalt(II)-corrole complexes as catalysts for this reaction. We argued that a more facile electron transfer from cobalt(II) to the nitrene-moiety generated at cobalt upon N2-loss from the coordinated aliphatic azide in the transition state for nitrene-radical formation (see Chapter 2) might lead to a lower barrier of the rate limiting azide activation step.

Using the same reaction conditions as reported for the [CoII(TMP)] system we performed this reaction with the [CoII(Cor)]— complexes described above. These were generated from the corresponding [CoII(Cor)(PPh3)] complexes by one-electron reduction with a suitable cobaltocene reducing agent prior to catalysis. We followed the appearance of the product and disappearance of the azide substrate in time, using NMR integrations against an internal standard. The results are summarised in Figure 7.
Scheme 3. Application of [Co\textsuperscript{III}(Cor)(PPh\textsubscript{3})] pre-catalysts in the ring-closing reaction of (4-azidobutyl)benzene.

As is evident from these reaction profiles (Figure 7), in each case the substrate azide was fully consumed and pyrrolidine product was formed (Table 1, entry 1-3). In absence of the reductant no reaction took place. This proves that it is only the reduced complex that is able to activate the azide in this reaction and not the parent complex itself (Table 1, entry 5). Also, in the absence of the Boc\textsubscript{2}O no reaction took place. The same was observed in the cobalt-porphyrin catalysed reactions, which was ascribed to product inhibition due to binding of the pyrrolidine product to cobalt(II) in absence of Boc\textsubscript{2}O, while the Boc-protected pyrrolidine does not inhibit the reaction. Product inhibition in absence of Boc\textsubscript{2}O, therefore, also seems to be an issue in the cobalt(II)-corrole catalysed reactions (Table 1, entry 4). For all three catalysts, the reaction has an initiation time of about 2 hours before the azide starts to get consumed (Figure 7). This initiation time can be attributed to the poor solubility of the charged [Co\textsuperscript{II}(Cor)]\textsuperscript{−} (cobaltocenium\textsuperscript{+}) complexes in toluene-\textsubscript{d}\textsubscript{8} solvent used in these reactions. Upon reduction of the neutral [Co\textsuperscript{III}(Cor)(PPh\textsubscript{3})] complexes to the anionic [Co\textsuperscript{II}(Cor)]\textsuperscript{−} complexes the solubility decreases drastically. This is also visually observable from the NMR tubes in which the reactions are conducted, revealing almost quantitative precipitation of the [Co\textsuperscript{II}(Cor)]\textsuperscript{−} (cobaltocenium\textsuperscript{+}) salts (Figure 13D, supporting information). After heating to 100 °C for about two hours, the complex (or a part of it) slowly gets solubilised, so it can take part in the reaction. This process is likely assisted by a slow reaction between the azide and the precipitated [Co\textsuperscript{II}(Cor)]\textsuperscript{−} (cobaltocenium\textsuperscript{+}) salts. Once the reaction starts, all azide is consumed within about six hours in each case. This is a remarkable improvement in reaction time (about 2.5 folds) as compared to the benchmark [Co\textsuperscript{II}(TMP)] system, which takes about 16 hours before all the azide is consumed.\textsuperscript{9} This proves that the more electron-rich mono-anionic [Co\textsuperscript{II}(Cor)]\textsuperscript{−} complexes are indeed faster catalysts than the corresponding neutral porphyrin complexes [Co\textsuperscript{II}(Por)].
Notably, even though all azide substrate is consumed, the yield of the pyrrolidine product is not proportional to the consumption of the azide (based on ¹H NMR). The highest yield of the pyrrolidine product (78%) was found when using the [Co⁰(Ph₂Cor)]⁻ catalyst. This means that apart from the pyrrolidine product, other side products are produced as well. This must be a complex mixture of several (non-characterised) side-products, which only give rise to small, poorly recognisable peaks in the crude ¹H NMR spectra of these reaction mixtures. So, while the activity of the system is increased, its selectivity is somewhat compromised. Formation of the linear N-Boc protected amine product (Ph(CH₂)₄NH·Boc; Scheme 3) provides only a partial explanation for the unaccounted mass-balance. While Ph(CH₂)₄NH·Boc is a known by-product in related reactions,⁴ it is only formed in minor amounts in the reactions studied here (see Table 1). A Staudinger reaction between PPh₃ liberated from the catalyst (producing the iminophosphorane) can account for a maximum loss of 5 mol% of the starting material (Scheme 4, supporting information). Hence, other (poorly defined) side products must be formed in these reactions.

As far as the relative performances of the three [Co⁰(Cor)]⁻ catalysts are concerned, the [Co⁰(Ph₂Cor)]⁻ catalyst consistently proved to give the highest yields of the desired pyrrolidine product. The [Co⁰(Br₂Cor)]⁻ catalyst gave lower yields, and the lowest yields were obtained with the [Co⁰(Mes₂Cor)]⁻ catalyst. This behaviour is counterintuitive, as we expected best reaction results for the more electron-rich [Co⁰(Mes₂Cor)]⁻ catalyst and the poorest for the least-electron rich [Co⁰(Br₂Cor)]⁻ catalyst. However, it should be noted that these yields do no correlate directly to the

**Figure 7.** Reaction profiles for the ring-closing C–H amination shown in Scheme 3. Top left: [Co⁰(Br₂Cor)]⁻; top right: [Co⁰(Ph₂Cor)]⁻ and bottom left: [Co⁰(Mes₂Cor)]⁻. Bottom right: overlay of the pyrrolidine product formation (red: [Co⁰(Br₂Cor)]⁻; blue: [Co⁰(Ph₂Cor)]⁻; black: [Co⁰(Mes₂Cor)]⁻).
relative activities, as the rates (max. slopes in Figure 7, bottom right \([\text{Co}^0(\text{Br}_2\text{Cor})^-] > [\text{Co}^0(\text{Ph}_2\text{Cor})^-] > [\text{Co}^0(\text{Mes}_2\text{Cor})^-])\) not only do not differ much, but these values are also likely to be influenced by the (slow) rate of solubilisation of the salts. It is further of importance to note that the \([\text{Co}^0(\text{Mes}_2\text{Cor})^-]\) and \([\text{Co}^0(\text{Br}_2\text{Cor})^-]\) catalysts are more sterically hindered around cobalt when compared to \([\text{Co}^0(\text{Ph}_2\text{Cor})^-]\) catalyst. As such, favourable electronic effects of electron-donating side-groups at the corrole ring of these catalysts could be (partly) counterbalanced by unfavourable steric interactions.

Next we tried to increase the efficiency of this reaction by attempting to increase the solubility of the in-situ reduced catalyst. In order to see if the solubility of the reduced catalyst could be increased by changing the polarity of the reaction mixture, we tried a few other solvents in this reaction. These results are summarised in Table 1 (entry 6-10). Unfortunately, when changing the solvent to more polar solvents like tetrahydrofuran (THF), no formation of product was observed, and upon using solvent mixtures like acetonitrile/toluene, DCM/toluene or THF/toluene the yield of the pyrrolidine product dropped drastically. In the DCM/toluene mixture 15\% of the unwanted linear product was also observed. Also with \(\text{N}-\text{butyl} \) ammonium phosphate as a phase transfer catalyst (PTC) the yield of the pyrrolidine dropped to 29\%. Hence it seems these reactions only work well in apolar aromatic solvents like toluene and benzene, at least for the \([\text{Co}^0(\text{Cor})^-]\) catalysts studied here.

**Table 1. Performance of different \([\text{Co}^0(\text{Cor})^-]\) catalysts in the intramolecular ring closing C-H amination of (4-azidobutyl)benzene to give the corresponding Boc-protected pyrrolidine.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Remarks</th>
<th>Pyrrolidine</th>
<th>Linear product</th>
</tr>
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<tr>
<td>1</td>
<td>([\text{Co}^0(\text{Br}_2\text{Cor})^-])</td>
<td>Toluene</td>
<td></td>
<td>73%</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Co}^0(\text{Ph}_2\text{Cor})^-])</td>
<td>Toluene</td>
<td></td>
<td>78%</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>([\text{Co}^0(\text{Mes}_2\text{Cor})^-])</td>
<td>Toluene</td>
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<td>64%</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>Any ([\text{Co}^0(\text{Cor})^-])</td>
<td>Toluene</td>
<td>No Boc(_2\text{O})</td>
<td>Not observed</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>Any ([\text{Co}^0(\text{Cor})^-])</td>
<td>Toluene</td>
<td>No reductant</td>
<td>Not observed</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>Any ([\text{Co}^0(\text{Cor})^-])</td>
<td>THF</td>
<td></td>
<td>Not observed</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>([\text{Co}^0\text{Ph}_2\text{Cor})^-])</td>
<td>Acetonitrile/Toluene</td>
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<tr>
<td>8</td>
<td>([\text{Co}^0\text{Ph}_2\text{Cor})^-])</td>
<td>DCM/Toluene</td>
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<td>31%</td>
<td>15%</td>
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<tr>
<td>9</td>
<td>([\text{Co}^0\text{Ph}_2\text{Cor})^-])</td>
<td>THF/Toluene</td>
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<tr>
<td>10</td>
<td>([\text{Co}^0\text{Ph}_2\text{Cor})^-])</td>
<td>Toluene</td>
<td>NBu(_4)PF(_6) added</td>
<td>29%</td>
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* Reactions were performed in 0.3 mmol scale in dry toluene at 100\°C with 5 mol\% precatalyst, 5 mol\% reducing agent, and 1.1 eq di-tert-butylidicarbonate (Boc\(_2\)O) for 16h. \(^\ast\) \(^1\)H-NMR yields are reported using mesitylene as an internal standard.

DFT calculated mechanism

Next, to confirm if indeed the azide activation step had a lower barrier for the \([\text{Co}^0(\text{Cor})^-]\) systems, we computed the energy changes of this step computationally, using DFT methods. The computations were performed at the BP86 and def2-TZVP level using the non-functionalised \([\text{Co}^0(\text{Cor})^-]\) system. The choice for this computational method is based on previous realistic mechanistic pathways calculated by us on such systems.\(^7\)\(^9\) We further incorporated Grimme’s dispersion corrections (DFT-D3) for these systems. For the substrate, we included a full model for the azide substrate (4-azidobutyl)benzene. The energies are depicted in Figure 8 (left). Indeed the transition state barrier (TS_N\(_2\)loss) for this step
is dramatically lower than that of the previously reported neutral [Co\(\text{II}(\text{Por})\)] complexes reported by us earlier \(^9\) (\(\Delta G^\dagger = +13.9\ \text{kcal mol}^{-1}\) for [Co\(\text{II}(\text{Cor})\)]\(^+\)) versus \(\Delta G^\dagger = +21.3\ \text{kcal mol}^{-1}\) for [Co\(\text{II}(\text{Por})\)].\(^9\) Thus, the hypothesis that an anionic electron-rich complex should be more efficient at azide activation compared to the neutral porphyrin complexes indeed holds true. Yet, unfortunately, the temperature needed for this reaction couldn’t be lowered by replacing the neutral [Co\(\text{II}(\text{Por})\)] complexes by any of the [Co\(\text{II}(\text{Cor})\)]\(^-\) complexes investigated here. This we attribute to the low solubility of the ionic [Co\(\text{II}(\text{Cor})\)]\(^+\) (cobaltocenium\(^+\)) salts, which immediately precipitate from toluene solutions upon reduction of the neutral complex at room temperature and only slowly re-solubilise under the catalytic reaction conditions in the presence of azide substrate at 100 °C. Thus, synthesis of a [Co\(\text{III}(\text{Cor})\)]\(^-\) complex with higher solubility in such apolar solvents (benzene or toluene) or performing ion exchange to increase solubility may well be a promising strategy to lower the temperatures for such C–H amination reactions proceeding via azide activation.

Next, we also calculated the spin-density of the corrole-based cobalt(III)-nitrene complexes. Despite the fact that the spin density of the parent complexes resides in a different d-orbital (d\(_{xy}\)) when compared to the corresponding [Co\(\text{III}(\text{Por})\)] complexes (d\(_{z^2}\)), the nitrene moiety also shows maximum spin-density at the nitrene nitrogen atom for the corrole complexes. Thus, it can be expected that mechanistically the reactions with the [Co\(\text{III}(\text{Cor})\)]\(^-\) complexes proceed via similar cobalt(III)-nitrene radical intermediates as previously reported for the [Co\(\text{II}(\text{Por})\)] complexes.\(^7, 9\)

![Figure 8](image)

**Figure 8.** (A) DFT-D3 calculated (Turbomole BP86, def2-TZVP) free energies (\(\Delta G^\text{298K}^\circ\) in kcal mol\(^{-1}\)) for the key step of azide activation by the [Co\(\text{III}(\text{Cor})\)]\(^-\) complex. (B) Spin density plot of the thus formed nitrene radical intermediate B showing maximum spin density at the nitrene nitrogen.

**Summary and Conclusion**

For nitrene transfer reactions from azides catalysed by [Co\(\text{II}(\text{Por})\)] catalysts, azide activation on the catalyst is known to be the rate limiting step. In this step the cobalt centre undergoes an oxidation from cobalt(II) to cobalt(III). Therefore, we hypothesised that the use of a ligand that retains the planar geometry of the porphyrin ligand but is more electron-rich could be beneficial for such reactions. Corroles are porphyrin-like ligands with a smaller pocket and a higher electron-density overall. Therefore, we synthesised three corrole complexes of cobalt ([Co\(\text{III}(\text{Cor})\)(PPh\(_3\))]) with electronically different substituents. As a benchmark reaction we chose the intramolecular ring-closing C–H amination reaction of (4-azidobutyl)benzene (in presence of Boc\(_2\)O) to give the saturated N-heterocycle tert-butyl-2-phenylpyrrolidine-1-carboxylate. This reaction is known to proceed with excellent yields
using the \([\text{Co}^{\text{II}}(\text{TMP})]\) catalyst, but requires a long reaction time of about 16h. The synthesised
\([\text{Co}^{\text{II}}(\text{Cor})(\text{PPh}_3)]\) complexes investigated in this study could be chemically reduced to generate the
Corrole complexes, which are catalytically active in the same ring-
closing C–H amination reaction. These reduced species were characterised by CV, EPR and UV-vis
spectro-electrochemistry. Upon reduction, all synthesised \([\text{Co}^{\text{II}}(\text{Cor})(\text{PPh}_3)]\) complexes proved not
only active in the ring-closing C–H amination reaction of (4-azidobutyl)benzene, but also to be much
faster (more than 2.5 times) than the reported \([\text{Co}^{\text{II}}(\text{TMP})]\) catalyst in the same reaction. We also
performed computational studies to confirm that the improved rates are due to lower barriers of the
rate limiting azide activation step. Indeed, DFT calculations reveal a much lower transition state barrier
for this step for the mono-anionic \([\text{Co}^{\text{II}}(\text{Cor})]^-\) complexes than for the neutral \([\text{Co}^{\text{II}}(\text{Por})]\)
complexes. Despite a different starting electronic structure, the thus produced nitrene species are best described
as nitrene-radical intermediates, with most of their spin density located at the nitrene nitrogen atom,
similar to the nitrene-radical intermediates reported for the neutral \([\text{Co}^{\text{II}}(\text{Por})]\) systems.

In conclusion, we have demonstrated for the first time in an unequivocal manner that anionic
\([\text{Co}^{\text{II}}(\text{Cor})]^-\) complexes are effective metalloradical catalysts. Moreover, we demonstrated that
increased electron-density of the corrole cobalt(II) complexes compared to porphyrin cobalt(II)
complexes has a positive impact on the rate of the ring-closing reactions of aliphatic azides to give
pyrroloidine N-heterocycles. Although the reaction temperatures couldn’t be lowered, the reaction
times were significantly decreased. In the catalysts tested in this study the reactions were about 2.5
faster than the corresponding \([\text{Co}^{\text{II}}(\text{Por})]\) catalysts. The selectivity was, however, somewhat
compromised. In future studies solubility issues will need to be tackled. With more soluble \([\text{Co}^{\text{II}}(\text{Cor})]^-\)
catalysts in hand, several other metalloradical transformations (carbene and nitrene transfer
reactions) may become feasible, and this should definitely be explored in the near future.

Supporting information, experimental and computational details

General information

All manipulations were performed under an N₂ atmosphere using standard Schlenk techniques or in a
glovebox unless otherwise mentioned. Acetonitrile and DCM were distilled under nitrogen from CaH₂.
THF and toluene were distilled under nitrogen from Na wire. CoCp₂ and CoCp*₂ were purchased from
commercial sources and stored in the glove-box. Mesitylene or trimethoxy benzene was used as
internal standard was purchased from Sigma-Aldrich. Mesitylene was degassed prior to use and stored
under molecular sieves.

\(^1\text{H NMR}\): All \(^1\text{H}\) NMR spectra were recorded on a Bruker Avance 400 (400 MHz) or Mercury 300 (300
MHz), referenced internally to residual solvent resonance of CDCl₃ (δ = 7.26 ppm).

\(^{13}\text{C (\text{H}) NMR}\): All \(^{13}\text{C}\) NMR spectra were recorded on a Bruker Avance 400 (101 MHz), or Mercury
300 (75 MHz), referenced internally to residual solvent resonance of CDCl₃ (δ = 77.2 ppm).
Abbreviations used are: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

High Resolution Mass spectra were measured on an AccuTOF LC, JMS-T100LP Mass spectrometer
(JEOL, Japan). FD/FI probe (FD/FI) is equipped with FD Emitter, Carbotec or Linden (Germany), FD 10
μm. Current rate 51.2 mA/min over 1.2 min FI Emitter, Carbotec or Linden (Germany), FI 10 μm.
Flashing current 40 mA on every spectra of 30 ms. Typical measurement conditions are: Counter electrode –10kV, Ion source 37V.

- (4-azidobutyl)benzene was synthesised according to procedure described in literature.
- **Synthesis of [Co^III(Br_2Cor)(PPh_3)]**

The corrole was made using the general dipyrromethane condensation method of Gryko et al. 11

2,6-dibromophenyl dipyrromethane (1 mmol) was dissolved with benzaldehyde (0.5 mmol) in 100 mL methanol. To this 50 mL H_2O and 5 mL concentrated (37%) HCl were added. The mixture was allowed to stir for 2 hours. The bilane intermediate was extracted with chloroform and washed with water. The organic layer was dried with Na_2SO_4, filtered and concentrated. The concentrate was diluted to a volume of 250 mL chloroform, after which p-chloranil (1.5 mmol) was added allowed to stand overnight without stirring. The mixture was then condensed and flushed though a plug of silica with dichloromethane. This gave a purple solution which was concentrated to give a purple solid which is the 5,15-bis(2,6-dibromophenyl)-10-phenylcorrole. ^1^H NMR (400 MHz, CDCl_3) δ 8.99 (d, J = 4.2 Hz, 2H), 8.59 (d, J = 4.7 Hz, 2H), 8.51 (d, J = 4.7 Hz, 2H), 8.40 (d, J = 4.2 Hz, 2H), 8.21 – 8.16 (m, 2H), 8.00 (d, J = 8.1 Hz, 4H), 7.72 (dd, J = 5.0, 1.7 Hz, 3H), 7.49 (t, J = 8.1 Hz, 2H).

5,15-bis(2,6-dibromophenyl)-10-phenylcorrole (0.1 mmol) was then refluxed for 1 hour in MeOH (60 ml) together with cobalt acetate tetrahydrate (0.2 mmol) and triphenyl phosphine (0.2 mmol). After which the solution is condensed and flushed through a silica plug with dichloromethane as eluent, collecting the deep red fractions which to give the desired cobalt(III) corrole complex. Slow evaporation from DCM yielded deep red crystals.

^1^H NMR (300 MHz, CDCl_3) δ 8.37 (t, J = 5.1 Hz, 4H), 8.27 (d, J = 6.5 Hz, 1H), 8.10 (d, J = 4.8 Hz, 2H), 8.01 (t, J = 7.9 Hz, 1H), 7.80 (dd, J = 7.6, 2.7 Hz, 7H), 7.73 (d, J = 4.9 Hz, 3H), 7.33 (dd, J = 16.3, 8.2 Hz, 3H), 7.00 (t, J = 7.5 Hz, 3H), 6.69 (td, J = 7.7, 2.3 Hz, 6H), 5.17 – 5.05 (m, 6H).

^13^C NMR (126 MHz, CDCl_3) δ 146.14, 145.61 (d, J = 3.3 Hz), 144.39 (d, J = 2.3 Hz), 143.28, 142.82, 135.88 (d, J = 3.2 Hz), 134.59, 131.00, 130.29, 130.21, 129.24 (d, J = 2.7 Hz), 127.58, 127.46 – 127.27 (m), 127.22, 126.94, 126.58, 126.45 (d, J = 2.3 Hz), 125.93, 124.68 (d, J = 2.3 Hz), 122.75, 122.09 (d, J = 4.5 Hz), 120.74 (d, J = 2.6 Hz).

HRMS (FD); m/z: Calcd. For ([M]^+) C_{35}H_{34}Br_4CoN_4P= 1160.4280, found= 1159.7722 Dalton ([M]^+),
Calcd. For (M –PPh_3)^+C_{33}H_{19}Br_3CoN_4 = 898.1362 Dalton, found= 897.7435 Dalton

- **Synthesis of [Co^III(Ph_2Cor)(PPh_3)]**

Freshly alumina filtered pyrrole (10 mmol) and benzaldehyde (5 mmol) were dissolved in 200 ml MeOH. To this 200 mL H_2O and 5 mL concentrated (37%) HCl were added, after which the reaction mixture was allowed to stir for 3 hours at room temperature. The bilane intermediate was extracted
with chloroform and washed with water. The organic layer was dried with either Na₂SO₄ and filtered. The tetrapyrrole/bilane solution was diluted to a volume of 250 mL chloroform and kept in dark conditions from this point on. It is important that these intermediates are handled in dark. p-chloranil (5 mmol) was added and the bilane was allowed to oxidize overnight with stirring. The reaction mixture was concentrated, followed by a quick flush though a silica plug with dichloromethane. Purity of the solution was checked using a TLC (in pure DCM) after which the collected the dark green/purple solution was dried, giving nearly pure corrole (302 mg, 34%).

In CDCl₃ the ¹H NMR spectra was broad, probably due to stacking. The NMR spectra was therefore recorded in CDCl₃ with the addition of a drop of MeOD to prevent stacking. NMR spectra matched those reported in literature.

The free base 5,10,15-triphenylcorrole (0.3 mmol) was refluxed for 1 hour in MeOH (180 ml) together with cobalt acetate tetrahydrate (0.6 mmol) and triphenyl phosphine (0.6 mmol) for 1 hour in dark conditions. After which the solution is condensed and flushed through a silica plug with dichloromethane as eluent, collecting the dark red fraction with the desired cobalt(III) corrole complex (91 mg, 36%).

¹H NMR (300 MHz, CDCl₃) δ 8.60 (d, J = 4.4 Hz, 2H), 8.33 (d, J = 4.8 Hz, 2H), 8.09 (d, J = 4.8 Hz, 3H), 8.03 (d, J = 4.6 Hz, 2H), 7.98 (s, 1H), 7.68 – 7.52 (m, 11H), 7.36 (d, J = 7.4 Hz, 1H), 7.06 (t, J = 7.5 Hz, 3H), 6.76 – 6.64 (m, 6H), 4.72 (dd, J = 10.7, 8.1 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 146.27, 145.57, 145.01, 141.88, 136.42, 132.12 (d, J = 9.6 Hz), 131.94, 131.74 (d, J = 9.2 Hz), 131.55, 130.92, 130.74, 129.85, 129.30, 128.55, 127.63, 127.36, 127.11 (d, J = 6.2 Hz), 127.00, 125.39, 124.11, 123.05, 118.58.

HRMS (FD); m/z: Calcd. for [(M⁺)], C₅₅H₃₈CoN₄= 844.8440 Dalton, found= 844.2140 Dalton
Calcd. For (M -PPh₃)⁺ C₃₇H₂₃CoN₄= 582.5522 Dalton, found= 582.1199 Dalton

- **Synthesis of [CoIII(Mes₂Cor)(PPh₃)]**

The corrole was made using the hindered dipyromethane condensation method of Gryko et al. ¹¹ 5-(mesityl)dipyromethane (2 mmol) was dissolved with 2,4,6-trimethoxybenzaldehyde (1 mmol) in 200 mL methanol, after which 100 ml H₂O and 10 ml concentrated (37%) HCl were added to the reaction mixture. The mixture was allowed to stir for 2 hours. The bilane intermediate was extracted with chloroform and washed with water. The organic layer was dried with either Na₂SO₄ or MgSO₄ and filtered. The tetrapyrrole/bilane solution was from here on kept under dark conditions and diluted to a volume of 500 mL chloroform. While kept in dark conditions p-chloranil (3 mmol) was added and the bilane was allowed to oxidize overnight with stirring. The mixture was then condensed and flushed though a silica plug with dichloromethane, collecting the purple solution, giving near pure corrole (115 mg, 16%). The ¹H NMR spectra were in accordance with those reported in literature.
5,15-dimesityl-10-(2,4,6-trimethoxyphenyl)corrole (0.1 mmol) was refluxed for 1 hour in MeOH (60 ml) together with cobalt acetate tetrahydrate (2 eq) and triphenyl phosphine (2 eq) for 1 hour in dark conditions. After cooling down the solution is condensed and flushed through a silica plug with DCM as eluent, collecting the deep red fraction which contains the desired cobalt(III) corrole complex. Crystallization via slow evaporation in DCM resulted in crystals.

**NMR:** when measured in pyridine the NMR spectrum matches literature, which does not show the PPh₃.¹⁹

1H NMR (300 MHz, CDCl₃) δ 8.19 (d, J = 4.6 Hz, 2H), 8.05 (d, J = 4.4 Hz, 2H), 7.91 (d, J = 4.7 Hz, 2H), 7.64 (d, J = 4.4 Hz, 2H), 7.03 (d, J = 11.4 Hz, 4H), 6.94 (d, J = 8.0 Hz, 3H), 6.64 (d, J = 7.9 Hz, 7H), 6.54 (d, J = 2.2 Hz, 1H), 6.45 (d, J = 2.2 Hz, 1H), 5.23 (t, J = 9.4 Hz, 6H), 4.09 (s, 3H), 3.66 (s, 3H), 3.17 (s, 3H), 2.50 (s, 6H), 1.74 (s, 6H).

13C NMR (126 MHz, CDCl₃) δ 161.55, 159.62, 158.89, 147.52, 145.99, 137.99, 136.77, 136.54, 136.27, 131.68 (d, J = 9.8 Hz), 128.88, 128.12, 127.81, 127.47, 127.19 (d, J = 9.9 Hz), 124.32, 123.00, 122.29, 119.23, 116.01, 114.20, 91.15, 90.89, 56.33, 55.71, 55.40, 29.86, 21.47, 20.42, 19.94.

**HRMS (FD); m/z:** Calcd. For ([M]+) C₆₄H₅₆CoN₄O₃P = 1018.3422 Dalton, found = 1018.3451 Dalton

Calcd. For (M-PPh₃)+ C₅₄H₄₁CoN₄O₃S = 756.2511 Dalton, found = 756.2512 Dalton

- **X-ray single crystal determination**

[Co₃⁺(Br₂Cor)(PPh₃)] C₅₅H₃₄Br₂CoN₄P Fw = 1160.36, purple-black rough fragment, 0.25 x 0.14 x 0.05 mm, orthorhombic, Pnma (no. 62), a = 16.5436(17), b = 19.975(2), c = 13.5943(15) Å, α = 90 °, V = 4492.4(8) Å³, Z = 4, Dc = 1.716 g cm⁻³, μ = 4.020 mm⁻¹. In total, 22100 reflections were measured on a Bruker D8 Quest Eco diffractometer, equipped with a TRIUMPH monochromator and a CMOS PHOTON 50 detector (θ = 0.71073 Å) up to a resolution of (sin θ/λ)max = 0.84 Å⁻¹ at a temperature of 150(2) K. The intensity data were integrated with the Bruker APEX2 software.²⁰ Absorption correction and scaling was performed with SADABS.²¹ (0.46–0.75 correction range). In total, 4069 reflections were unique (Rint = 0.110), of which 2829 were observed (I > 2σ(I)). The structure was solved with direct methods using the program SHELXS-97²² and refined with SHELXL-2013 against F² of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. R1/wR2 [I > 2σ(I)]: 0.0581/0.1682. S = 1.025. Residual electron density between -1.174 and 0.677 e Å⁻³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.
[Co$^{III}$(Mes$_2$Cor)(PPh$_3$)] unfortunately the crystal diffracted poorly. But the connectivity between the atoms could be clearly seen to ascertain the structure.

- CV measurements

Cyclic voltammograms were recorded using a Metrohm Autolab AUT85221 potentiostat in conjunction with Nova 1.8.17 at a scan rate of 0.1 V/s. The electrodes used were a glassy-carbon working electrode, a platinum counter electrode and a silver reference electrode. A solution of 0.3 M n-Bu$_4$NPF$_6$ in dry THF was used as the electrolyte, and potentials were referenced to FeCp$_2$ by using FeCp$_2^*$ ($E^{0/2} = -0.45$ vs FeCp$_2$ in THF)$^{14}$ as an internal reference.

CV measurements of the three [Co$^{III}$(Cor)(PPh$_3$)] complexes showing the two reduction waves:

Figure 9. CV plots with both reduction peaks for [Co$^{III}$(Br$_2$Cor)(PPh$_3$)] (left), Co$^{III}$(Ph$_2$Cor)(PPh$_3$)
 (centre) and [Co$^{III}$(Mes$_2$Cor)(PPh$_3$)] (right) referenced to FeCp$_2$ by using FeCp$_2^*$ ($E^{0/2} = -0.45$ vs FeCp$_2$ in THF)$^{14}$ as an internal standard.

- UV-vis spectro-electrochemical measurements

UV-Vis spectro-electrochemistry was performed by using an Autolab95 pgstat10 and a Hewlett Packard 8453 spectrometer. Absorbance spectra were recorded with UV-visible chemstation B.05.02. A solution of 0.3 M n-Bu$_4$NPF$_6$ in dry THF was used as the electrolyte. The concentration of the corrole complexes was roughly 5*10$^{-4}$ M. The scan speed used was 0.02 V/s. SpectraGryph 1.0.6 was used for processing the spectra.

An initial UV/VIS spectrum was recorded before applying any voltage in order to record the spectrum of the neutral compound in THF itself. Following this, the CV was started with further UV/VIS measurements taken every 0.1 V or until the spectrum started showing significant changed in which case spectra were taken every 0.05 V. This continued until either −1.0 V was reached or the spectrum no longer showed any changes when the applied potential was increased. For the back oxidation a
similar strategy was followed. By initially taking spectra every 0.1 V until changes in the spectra started to show, after which new spectra were recorded every 0.05 V until 0 V was reached again.

- UV-vis spectra of the $[\text{Co}^{\text{III}}(\text{Br}_2\text{Cor})(\text{PPh}_3)]$ and $[\text{Co}^{\text{II}}(\text{Br}_2\text{Cor})]^{-}$ species (left) and the $[\text{Co}^{\text{III}}(\text{Mes}_2\text{Cor})(\text{PPh}_3)]$ and $[\text{Co}^{\text{II}}(\text{Mes}_2\text{Cor})]^{-}$ species (right) obtained in an OTTLE-cell.

Figure 10. UV-vis spectra of the $[\text{Co}^{\text{III}}(\text{Br}_2\text{Cor})(\text{PPh}_3)]$ and $[\text{Co}^{\text{II}}(\text{Br}_2\text{Cor})]^{-}$ species (left) and the $[\text{Co}^{\text{III}}(\text{Mes}_2\text{Cor})(\text{PPh}_3)]$ and $[\text{Co}^{\text{II}}(\text{Mes}_2\text{Cor})]^{-}$ species (right) obtained in an OTTLE-cell.

- EPR studies

Inside a glove box, 0.005 mmol of the cobalt corrole complex and 0.75 eq cobaltocene or decamethylcobaltocene (for $[\text{Co}^{\text{III}}(\text{Mes}_2\text{Cor})(\text{PPh}_3)]$) were dissolved in dry 1.5 ml methyl-THF and 0.5 ml DMSO after which 0.2 mL of this solution was transferred into an EPR tube. The sample was then measured at 20K. After the initial measurements, the tubes were opened and the contents exposed to air for ~2 minutes after which the tubes were closed and the samples measured again at 20K.
- EPR spectra of the anionic [Co\(\text{III}(\text{Br}_2\text{Cor})\)]\(^-\) and [Co\(\text{III}(\text{Ph}_2\text{Cor})\)]\(^-\) complexes.

Figure 11. EPR spectra (20K) of the anionic [Co\(\text{III}(\text{Br}_2\text{Cor})\)]\(^-\) complex (top left, with and without exposure to air) and the anionic [Co\(\text{III}(\text{Ph}_2\text{Cor})\)]\(^-\) complex (top right, with and without exposure to air). Bottom left EPR spectra (20K) of [Co\(\text{III}(\text{Mes}_2\text{Cor})\)]\(^-\).

Figure 12. EPR of spectrum cobaltocene only in methyl-THF measured at 20K.

Scheme 4. Possible pathway of azide degradation via formation of an iminophosphorane on reaction with PPh\(_3\).
• **General procedure for the catalytic reactions.**

Reactions were performed in 0.3 mmol scale. To a flame dried and nitrogen filled Schlenk tube were added catalyst 5 mol%, 1 eq (4-azidobutyl)benzene, 1.1 eq di-tert-butyl dicarbonate (Boc₂O) and 5 mol% reductant (cobaltocene) in dry toluene (5.0 ml). The mixture was then stirred for 16 hours at 100°C. After drying either mesitylene or 1,3,5-trimethoxybenzene was then added to use as external standard to determine the yield via NMR. 6.1 ppm or 6.8 ppm were used as reference for 1,3,5-trimethoxybenzene or mesitylene respectively. Product peaks at 5-4.75 ppm in CDCl₃ were to determine yield of the product.

NMR scale reactions were performed using the same method but in 0.06 mmol scale and in toluene-d₈. Product appearance was monitored by integrating the peaks at 5-4.75 ppm and azide consumption was monitored via the decreasing peaks at 3.34 and 2.74 ppm.

![Figure 13. Stacked ¹H NMR spectra of reaction progress in time of (4-azidobutyl)benzene with (a) [Co²⁺(Br₂Cor)PPh₃], (b) [Co²⁺(Ph₂Cor)PPh₃] and (c) [Co²⁺(Mes₂Cor)PPh₃]. Product appearance was monitored by emerging peaks at 5-4.75 ppm and azide consumption was monitored via the disappearing peaks at 3.34 and 2.74 ppm (d) The reaction mixture before (left) and after (right) heating. Precipitation of the reduced catalyst was observed before heating the reaction mixture.](image)

**DFT Studies**

Geometry optimizations were carried out with the Turbomole program package coupled to the PQS Baker optimizer via the BOpt package. We used unrestricted ri-DFT-D3 calculations at the BP86 level, in combination with the def2-TZVP basis set, and a small (m4) grid size. Grimme’s dispersion
corrections (version 3, disp3, ‘zero damping’) were used to include Van der Waals interactions. All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterised by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The nature of the transition states was confirmed by following the intrinsic reaction coordinate.

**Table 2. Energies of optimised geometries shown in Figure 8.**

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References and notes


All redox potentials are reported against the ferrocene/ferrocenium (Fc/Fc+) redox couple. Decamethylferrocene was used as an internal standard (E = 0.427 V vs. Fc/Fc+ in THF).


In these spectra, contamination by an asymptotic signal was observed which increased in intensity on exposure to air. This signal probably arises from oxygen binding to the reduced species as is reported also for other related complexes.


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