Cobalt Corrole Activation of Azides

Application of [Co(Corrole)]⁻ Complexes in Ring-Closing C–H Amination of Aliphatic Azides via Nitrene Radical Intermediates

Monalisa Goswami,[a] Paul Geuijen,[a] Joost. N. H. Reek,[a] and Bas de Bruin*[a]

Abstract: The synthesis, characterisation and application of anionic [CoII(Cor)]⁻ (Cor = corrole) metalloradicals in the ring-closing C–H amination of an aliphatic azide in the presence of Boc₂O (Boc = tert-butyloxycarbonyl) to give the corresponding Boc-protected N-heterocyclic product tert-butyl 2-phenylpyrrolidine-1-carboxylate are reported. This is the first example of the use of metalloradical cobalt(II) corrole complexes in nitrene-transfer reactions. On the basis of DFT calculations, the reaction is proposed to proceed via discrete open-shell nitrene radical intermediates bearing most of their spin density at the nitrene nitrogen atom. The [CoII(Cor)]⁻ complexes are substantially faster catalysts than the corresponding neutral [CoII(porphyrin)] complexes when applied in the same ring-closing C–H amination reaction under identical reaction conditions. Increasing the electron density at cobalt(II) therefore has a positive influence on the reaction rate.

Introduction

Nitrogen-containing ring compounds are among the most commonly found heterocycles in natural products and pharmaceuticals.[1] Synthesising such heterocycles by direct C–H amination, that is, 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 strategy to achieve this goal is via reactive metallo-nitrene intermediates.[2] In this method a metal catalyst activates a nitrene precursor to form 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.[3] Organic azides are particularly attractive nitrene precursors in this regard, as they are easy to synthesise and generate only N₂ as a waste product in the amination step.[3,4] However, only a handful of examples in which organic azides are used in intramolecular C–H amination reactions to form N-heterocyclic compounds have been reported.[5,6] Particular systems of relevance to the results described in this paper that have proven to be successful in C–H bond amination are cobalt(II) porphyrin (Por) catalysts (Scheme 1). These [CoII(Por)] catalysts are in general capable of a variety of nitrene-transfer reactions from azides. In addition to the inter- and intramolecular aziridination reactions,[7] also a variety of intermolecular[8] and intramolecular[9] benzylic/allylic/benzallylic C–H amination reactions have been reported. Typically, activated azides are used as the substrates in these reactions, such as carbamoyl, sulfonyl or phosphoryl azides.[10] DFT mechanistic studies revealed a stepwise mechanism involving an experimentally well characterised CoIII nitrene radical intermediate.[11] DFT calculations further suggested that the rate-determining step of these catalytic reactions is the activation of the azide at the metal centre,[12] which has a substantial barrier. Consequently, in many of these transformations high reaction temperatures are required.[7–13] This is most evident in reactions involving unactivated alkyl azides (azide moiety positioned directly next to a CH₂ group), which require heating to at least around 100 °C to activate the azide with [CoII(Por)] catalysts.[13] The generalised mechanism proposed for these reactions involves rate-limiting azide activation followed by hydrogen-atom transfer from a benzylic C–H bond to the thus-formed nitrene radical. A subsequent radical rebound step, followed by dissociation and trapping of the cyclic amine by Boc₂O (Boc = tert-butyloxycarbonyl) to produce the Boc-protected product, completes the catalytic cycle.

Scheme 1. [CoII(Por)]-catalysed intramolecular C–H amination of aliphatic azides mediated by [CoII(Por)] complexes.
(Scheme 2).\textsuperscript{[13]} Notably, in the azide-activation step the metal centre is oxidised from cobalt(II) to cobalt(III) to generate the required nitrene radical intermediate. Hence, we expected that application of ligands imposing a higher electron density at the cobalt centre could be beneficial in leading to faster catalytic reactions by lowering the barrier of the rate-limiting N\textsubscript{2}-dissociation step. Some earlier studies seem to confirm this hypothesis in an indirect manner,\textsuperscript{[6]} but the beneficial effect of electron-donating ligands on the rate of these reactions is evident from recent studies performed by us.\textsuperscript{[13]} In a direct comparative study, the electron-rich [Co\textsuperscript{II}(TMP)] was shown to outperform [Co\textsuperscript{II}(TPP)] in the intramolecular C–H amination of aliphatic azides (Scheme 1).

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. Hence, we turned our attention to the corrole macrocycle. Corroles are tetrapyrrolic compounds related to porphyrins. The difference to porphyrins is that in corroles one of the methine bridges that link 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 position less to attach the meso substituents. As a consequence, corroles have a slightly smaller metal-binding pocket allowing for a “tighter grip” on the metal centre. In addition, there is one less carbon atom in the aromatic ring of corroles, which, besides the trianionic charge of a corrole ligand, substantially increases the electron density of the metal centre in corrole complexes compared to the corresponding porphyrin complexes. As a result, corroles are expected to stabilize transition metals in higher oxidation states, even better so than porphyrins. This feature is expected to have a positive influence on the azide-activation step at the metal centre of the catalyst, in which cobalt(II) undergoes one-electron oxidation. Previously, corrole complexes of cobalt have been extensively studied,\textsuperscript{[14]} amongst others for water oxidation and oxygen reduction reactions. However, monoanionic 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 monoanionic [Co\textsuperscript{II}(Cor)]\textsuperscript{+} complexes in mediating catalytic radical-type reactions in general, and in particular for the nitrene-radical ring-closing C–H amination reactions described herein.

Results and Discussion

To test the feasibility of corroles as ligands in cobalt(II)-catalysed nitrene-transfer reactions, we synthesised three corrole ligands with electronically different substituents (Figure 2).
between those of [CoIII(Br2Cor)(PPh3)] and [CoIII(Mes2Cor)(PPh3)]. Reduction of these complexes with a suitable chemical reductant should produce the corresponding monoanionic metallo-radical [CoII(Cor)]− complexes. To find the right reducing agent for reduction of cobalt(III) to cobalt(II), we first studied the electrochemical properties of the [CoIII(Cor)(PPh3)] complexes. The three corroles were synthesised via the dipyrromethane route, following the procedures reported by Gryko and co-workers with some minor modifications (Scheme 3).[16] Details of the synthetic procedures are described in the Experimental Section.

While the crystal structure of [CoIII(Ph2Cor)(PPh3)] has been reported, the X-ray structural data of [CoIII(Br2Cor)(PPh3)] and [CoIII(Mes2Cor)(PPh3)] were previously unknown. We were able to grow crystals of these complexes. The molecular structure of [CoIII(Br2Cor)(PPh3)] and some relevant bond lengths are shown in Figure 3. The Co–N(corrole) bonds are significantly shorter than Co–N(porphyrin) bonds {1.867 and 1.880 in [CoIII(Br2Cor)(PPh3)] vs. 1.949 in [CoII(TPP)]}.[17] This is expected, because of the trianionic charge and the smaller ring size of the corrole macrocycle.

For [CoIII(Mes2Cor)(PPh3)] the atom connectivity could be satisfactorily determined and confirmed the structure of the complex. However, the X-ray data of [CoIII(Mes2Cor)(PPh3)] were of insufficient quality to derive any reliable information about the bond lengths. This structure is shown in the Experimental Section (Figure 9).

Cyclic voltammetry (CV) was used to study the redox behaviour of the three above-mentioned [CoIII(Cor)(PPh3)] complexes.[18,19] For the application of these complexes as catalysts in nitrene-transfer reactions, we were particularly interested in the first reduction waves and the corresponding re-oxidation waves of these complexes. The first (chemically irreversible) reduction peak potential is important for choosing a suitable chemical reductant that reduces the parent [CoIII(Cor)(PPh3)] complexes to corresponding monoanionic [CoII(Cor)(PPh3)] complexes without over-reduction. The corresponding re-oxidation peak potential gives direct information about the reductive power of the corresponding monoanionic [CoII(Cor)]− complexes after PPh3 dissociation.[20]

The [CoIII(Cor)(PPh3)] complexes show the expected redox behaviour, similar to that observed previously for related complexes.[20] The first one-electron reduction process is electrochemically irreversible for all these complexes, at least at the applied scan rate of 100 mV s−1 of the CV measurements (Figure 4A–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 S1). 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 (Table 1): [CoIII(Mes2Cor)(PPh3)] < [CoIII(Ph2Cor)(PPh3)] < [CoIII(Br2Cor)(PPh3)]. On the basis of these peak potentials, cobaltocene (CoCp2; \(E^{1/2}_{1/2} \approx –1.3\) V vs. Fc0/+) or decamethylcobaltocene (CoCp*2; \(E^{1/2}_{1/2} \approx –1.9\) V vs. Fc0/+) can be used as a suitable reductant for these complexes.[21] The ECEC sequence of events explaining the observed behaviour of the first reduction process with an anodically shifted re-oxidation wave is schematically shown in Figure 4D. One-electron reduction of the parent [CoIII(Cor)(PPh3)] complex at the metal centre leads to the formation of an anionic [CoII(Cor)(PPh3)]− complex, followed by PPh3 dissociation producing [CoII(Cor)]−. Oxidation of [CoII(Cor)]− to [CoIII(Cor)] occurs at a higher redox potential than reduction of [CoIII(Cor)(PPh3)] to [CoII(Cor)(PPh3)]−, and is followed by re-coordination of PPh3 to regenerate the parent [CoIII(Cor)(PPh3)] complex.[20]

EPR spectroscopic and UV/Vis spectro-electrochemical (SEC) measurements were performed to confirm the ECEC mecha-
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Figure 4. (A) CV of [CoIII(Br2Cor)(PPh3)], (B) CV of [CoIII(Ph2Cor)(PPh3)], (C) CV of [CoIII(Mes2Cor)(PPh3)] in THF referenced against Fc0/+ [with bis(pentamethylcyclopentadienyl)iron (Fc*) as internal standard]. (D) Schematic representation of different species present during the reduction and re-oxidation events during the CV scan.

Table 1. Peak currents for the first reduction and the corresponding re-oxidation wave of the three complexes referenced against the Fc0/+ couple, measured in THF by using Fc* as internal standard (colour codes follow those of Figure 4).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{red}}^{\text{peak}}$ [V]</th>
<th>$E_{\text{ox}}^{\text{peak}}$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CoIII(Br2Cor)(PPh3)]</td>
<td>-1.06</td>
<td>-0.56</td>
</tr>
<tr>
<td>[CoIII(Ph2Cor)(PPh3)]</td>
<td>-1.15</td>
<td>-0.59</td>
</tr>
<tr>
<td>[CoIII(Mes2Cor)(PPh3)]</td>
<td>-1.34</td>
<td>-0.79</td>
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Having determined the reduction peak potentials of these complexes and their clean conversion to the reduced species, we performed X-band EPR studies. Using a chemical reductant ([CoCp2 for [CoIII(Br2Cor)(PPh3)] and [CoIII(Ph2Cor)(PPh3)] and CoCp*2 for [CoIII(Mes2Cor)(PPh3)]), all of these complexes could be reduced to give species with EPR spectra [anisotropic spectra, measured at 20 K in a 2-methyltetrahydrofuran (MeTHF) glass] characteristic for formation of cobalt(II) metalloradicals. The EPR spectrum of [CoII(Mes2Cor)]− is shown in Figure 6. For EPR spectra of the other complexes, see Figure S3. The EPR spectrum shown in Figure 6 reveals clear cobalt hyperfine couplings along the two higher $g$ values ($g_{11} = 3.56$, $A_{\text{Co}11} = 740$ MHz; $g_{22} = 2.22$, $A_{\text{Co}22} = 260$ MHz) and a sharper, almost featureless line at the lowest $g$ value ($g_{33} = 1.85$). 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)].

Figure 5. UV/Vis spectra obtained in the spectro-electrochemical experiments on [CoIII(Ph2Cor)(PPh3)].
DFT optimisation of the anionic [Co\textsuperscript{II}(Cor)]\textsuperscript{−} complex clearly showed that the SOMO is the d\textsubscript{xy} orbital (Figure 6, bottom), and this leads to different spin–orbit interactions than in related [Co\textsuperscript{III}(Por)] complexes. This is in agreement with the EPR spectra of the corrole being distinctly different from those of the related porphyrin complexes\textsuperscript{[24]}. We tested the activity and selectivity of the three monoanionic [Co\textsuperscript{II}(Cor)]\textsuperscript{−} complexes in the direct ring-closing reaction of (4-azidobutyl)benzene to give the N-heterocyclic pyrrolidine product. This reaction was reported to proceed with [Co\textsuperscript{II}(TMP)]\textsuperscript{−} to selectively produce the Boc-protected pyrrolidine product tert-butyl 2-phenylpyrrolidine-1-carboxylate\textsuperscript{[13]}. The high barrier and slow reactions associated with the Co(Por)-catalysed process prompted us to test the more electron rich monoanionic cobalt(II) corrole complexes as catalysts for this reaction. We argued that more facile electron transfer from cobalt(II) to the nitrene moiety generated at cobalt upon N\textsubscript{2} loss from the coordinated aliphatic azide in the transition state for nitrene-radical formation might lead to a lower barrier of the rate-limiting azide-activation step. Thus, using the same reaction conditions as reported for the [Co\textsuperscript{II}(TMP)]\textsuperscript{−} system, we performed this reaction with the [Co\textsuperscript{II}(Cor)]\textsuperscript{−} complexes described above. These were generated from the corresponding [Co\textsuperscript{III}(Cor)(PPh\textsubscript{3})\textsuperscript{−}] complexes by one-electron reduction with a suitable cobaltocene reducing agent prior to catalysis. We monitored the appearance of the product and disappearance of the azide substrate with
time using NMR integrations against an internal standard (Figure 7).

In each case the azide substrate was fully consumed and pyrrolidine product was formed (Table 2, entries 1–3). In the absence of the reductant no reaction took place. This proves that it is only the reduced (CoII) complex that is able to activate the azide in this reaction and not the parent CoIII complex itself (Table 2, entry 5).

Also, in the absence of Boc2O 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(III) in absence of Boc2O, while the Boc-protected pyrrolidine does not inhibit the reaction. Product inhibition in absence of Boc2O therefore also seems to be an issue in the cobalt(III)-corrole-catalysed reactions (Table 2, entry 4). For all three catalysts, the reaction has an initiation time of about 2 h before azide consumption starts (Figure 7).

We ascribe this initiation time to the poor solubility of the [CoII(Cor)]– (cobaltocenium+) salts in the low-polarity [D2]toluene solvent used in these reactions. Upon reduction of the neutral [CoII(Cor)(PPh3)] complexes to the anionic [CoII(Cor)]– complexes, the solubility decreases drastically, which was also visibly observable in the NMR tubes in which the reactions were monitored {near-quantitative precipitation of the [CoII(Cor)]– (cobaltocenium+) salts is evident from a photograph of the NMR tube shown in Figure S5}. After heating to 100 °C for about 2 h in the presence of the azide, (part of) the complex is slowly solubilised, after which it can take part in the reaction. This process is most likely facilitated by a slow heterogeneous reaction between the azide and the precipitated [CoII(Cor)]– (cobaltocenium+) salt. After the initiation lag time, the azide is fully consumed within about 6 h for all three corrole complexes investigated. This is a remarkable improvement in reaction rate (ca. 2.5-fold) compared to the benchmark [CoII(TMP)] system, which requires about 16 h before all the azide is consumed. This proves that the more electron rich monoanionic [CoII(Cor)]– complexes are indeed more active catalysts than the corresponding neutral porphyrin [CoII(Por)] complexes.

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 spectra). The highest yield of the pyrrolidine product (78%) was obtained with the [CoII(Ph2Cor)]– catalyst. Hence, apart from the pyrrolidine product other, side products are produced as well. These are a mixture of several (uncharacterised) compounds that only give rise to small, poorly recognisable peaks in the 1H NMR spectra of the crude 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)4-NHBoc provides only a partial explanation for the unaccounted mass balance. While Ph(CH2)4-NHBoc is a known by-product in related reactions, it is only formed in minor amounts in the reactions studied here (see Table 2). A Staudinger reaction of PPh3 liberated from the catalyst producing the iminophosphorane can account for at most 5 mol-% loss of the starting material. Hence, some other unidentified side products must be formed in these reactions.

As far as the relative performance of the three [CoII(Cor)]– catalysts is concerned, [CoII(Ph2Cor)]– consistently gave the highest yields of the desired pyrrolidine product. The [CoII(Br2Cor)]– catalyst gave lower yields, and the lowest yields were obtained with the [CoII(Mes2Cor)]– catalyst. This behaviour is counterintuitive, as we expected best reaction results for the more electron rich [CoII(Mes2Cor)]– catalyst and the poorest for the least-electron rich [CoII(Br2Cor)]– catalyst. However, these yields do not correlate directly to the relative activities, as the rates (max. slopes in Figure 7, bottom right [CoII(Br2Cor)]– > [CoII(Ph2Cor)]– > [CoII(Mes2Cor)]–) not only do not differ much, but these values are also likely to be influenced by the (slow and potentially different) rates of solubilisation of the salts. Furthermore, the [CoII(Mes2Cor)]– and [CoII(Br2Cor)]– catalysts are more sterically hindered around cobalt than the [CoII(Ph2Cor)]– catalyst. Thus, favourable electronic effects of electron-donating side groups at the corrole ring of these catalysts could well be (partly) counterbalanced by unfavourable steric interactions.

Next we tried to improve the efficiency of this reaction by attempting to increase the solubility of the in-situ-reduced catalyst. To determine whether the solubility of the reduced catalyst could be increased by changing the polarity of the reaction mixture, we tried a few other solvents (Table 2, entries 6–10). However, on changing to more polar solvents such as THF, no product formation was observed, and with solvent mixtures
such as acetonitrile/toluene, CH₂Cl₂/toluene and THF/toluene, the yield of the pyrrolidine product dropped drastically. In the CH₂Cl₂/toluene mixture 15% of the unwanted linear product was also observed. Also, with N-butylammonium phosphatase as phase-transfer catalyst the yield of the pyrrolidine dropped to 29% (Table 2, entry 10). Hence, it seems these reactions only work well in low-polarity aromatic solvents such as toluene and benzene, at least for the [Co⁴(Cor)]⁺ catalysts studied here.

DFT Calculations

Next, to confirm whether indeed the azide-activation step has a lower barrier for the anionic [Co⁴(Cor)]⁺ systems compared to the corresponding neutral [Co⁴(Por)] systems, we computed the free-energy barrier of this step using DFT methods. The calculations were performed at the BP86 and def2-TZVP level of theory for the non-functionalised [Co⁴(Cor)]⁺ system. The choice of this computational method is based on previous studies showing realistic calculated barriers for several metalloradical reactions of [Co⁴(Por)] systems. We further incorporated Grimme’s dispersion corrections (DFT-D3) for these systems. For the substrate, we included a full model of the azide substrate (4-azidobutyl)benzene. The free energies are depicted in Figure 8 (top). Indeed the transition state barrier (TS_N₂loss) for this step is butyl)benzene. The free energies are depicted in Figure 8 (top). Thus, the hypothesis that an anionic electron-rich cobalt(II) corrole complex should be more efficient in the activation of the azide than a corresponding neutral cobalt(II) porphyrin complex indeed holds true. Yet, unfortunately, the temperature needed for this reaction could not be lowered by replacing the neutral [Co⁴(Por)] complexes by any of the [Co⁴(Cor)]⁺ complexes investigated here. We attribute this behaviour to the low solubility of the ionic [Co⁴(Cor)]⁺ (cobaltocenium⁺) salts, which immediately precipitate from the toluene solutions upon reduction of the neutral complex at room temperature and are only slowly solubilised under the catalytic reaction conditions in the presence of azide substrate at 100 °C. Thus, synthesis of [Co⁴(Cor)]⁺ complexes with higher solubilities in such low-polarity solvents (benzene or toluene) or replacing the cobaltocenium⁺ counterions by, for example, tetraalkylammonium cations to increase the solubility may well be a promising strategy to lower the reaction temperatures of the C–H amination reactions in future studies.

We also calculated the spin density of the corrole-based cobalt(III) nitrene complexes. Although the spin density of the parent corrole cobalt(II) complex resides in a different d orbital (dₓᵧ) than in the corresponding [Co⁴(Por)] complex (dₓz), a very similar nitrene radical moiety is formed upon azide activation by the anionic [Co⁴(Cor)]⁺ system. As found earlier for the corresponding [Co⁴(Por)(N[R]) system,[¹³] the spin density of the [Co⁴(Cor)(N[R])]⁻ intermediate is concentrated at the nitrene nitrogen atom (Figure 8, bottom). Thus, it can be expected that the reactions with the anionic [Co⁴(Cor)]⁺ complexes are mechanistically related to those proposed previously (Scheme 2), and most likely proceed via similar corrole(III)/nitrene radical intermediates, as previously reported for the neutral [Co⁴(Por)] systems.

Conclusions

We have demonstrated that anionic [Co⁴(Cor)]⁻ complexes are effective metalloradical catalysts for ring-closing C–H amination of (4-azidobutyl)benzene in the presence of Boc₃O to give the corresponding Boc-protected N-heterocyclic pyrrolidine product (tert-butyl 2-phenylpyrrolidine-1-carboxylate). The [Co⁴(Cor)(PPh₃)] complexes investigated in this study could be chemically reduced to generate the corresponding mononionic [Co⁴(Cor)]⁻ complexes, which are catalytically active in the ring-closing C–H amination reaction of the aliphatic azide. These reduced species were characterised by CV, EPR and UV/Vis spectro-electrochemistry. We demonstrated that the increased electron density of the corrole cobalt(II) complexes compared to porphyrin cobalt(II) complexes increases the rate of the ring-closing C–H amination reaction. Although the reaction temperatures could not be lowered, the reaction times were significantly decreased. In the catalysts tested in this study the reactions were about 2.5 faster than with the corresponding [Co⁴(Por)] catalysts. However, the selectivity was somewhat compromised. 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 [Co⁴(Por)] systems. In future studies solubility issues will need to be tackled. With more
soluble [Co(L(Cor))]^+ catalysts in hand, several other metallo-radical transformations (carbene- and nitrene-transfer reactions) may become feasible.

**Experimental Section**

All manipulations were performed under an N2 atmosphere by using standard Schlenk techniques or in a glove box unless otherwise mentioned. Acetonitrile and CH2Cl2 were distilled under nitrogen from CaH2; THF and toluene were distilled under nitrogen from Na wire. CoCP2 and CoCP2+ were purchased from commercial sources and stored in the glove box. Mesitylene or trimethoxybenzene was used as standard internal standard. All 1H NMR spectra were recorded with a Bruker Avance 400 (400 MHz) or Mercury 300 (300 MHz) spectrometer, referenced internally to the residual protic-solvent resonance of CDCl3 (δ = 7.26 ppm). 13C NMR spectra were recorded with a Bruker Avance 400 (101 MHz), or Mercury 300 (75 MHz) spectrometer, referenced internally to CDCl3 (δ = 77.2 ppm). High-resolution mass spectra were measured with an Acquity LC-MS TQ-SLM Mass spectrometer (JEOL, Japan). The FD/FI probe was equipped with FD Emitter, Carbotec or Lindenberg (Germany), FD 10 μm. Current rate 51.2 mA min\(^{-1}\) over 1.2 min FI Emitter, Carbotec or Lindenberg (Germany), FI 10 μm. Flashing current 40 mA on every spectrum of 30 ms. Typical measurement conditions: Counter electrode –10 kV, ion source 37 V. (4-Azidobutyl)pyrrole/3,5-dibromo-2,6-dimethoxybenzaldehyde (1 mmol) was added and oxidation of the bilane intermediate was allowed to proceed overnight with stirring. The reaction mixture was concentrated and washed with water. The organic layer was dried with Na2SO4 and filtered. The tetrapyrole/bilane solution was diluted to a volume of 250 mL of chloroform and kept in the dark from this point on (it is important that these intermediates are handled in the dark). p-Chloranil (5 mmol) was added and oxidation of the bilane intermediate was allowed to proceed overnight with stirring. The reaction mixture was concentrated and quickly flushed through a silica plug with dichloromethane. The purity of the solution was checked by TLC (pure CH2Cl2), after which the collected dark green-purple solution was dried to give nearly pure corrole (302 mg, 34 %). In CDCl3 the 1H NMR spectra was broad, probably due to stacking. NMR spectra matched those reported in the literature.[6]

**Synthesis of [Co(Ph2Cor)(PPh3)]**

2,6-Dibromophenyl dipyrromethane (1 mmol) and benzaldehyde (0.5 mmol) were dissolved in methanol (100 mL), and H2O (50 mL) and concentrated (37 %) HCl (5 mL) were added. The mixture was stirred for 2 h. The bilane intermediate was extracted with chloroform and washed with water. The organic layer was dried with Na2SO4 and filtered. The tetrapyrole/bilane intermediate was extracted with chloroform and washed with water. The organic layer was dried with Na2SO4 and filtered. The tetrapyrole/bilane solution was diluted to a volume of 250 mL of chloroform and kept in the dark from this point on (it is important that these intermediates are handled in the dark). p-Chloranil (5 mmol) was added and oxidation of the bilane intermediate was allowed to proceed overnight with stirring. The reaction mixture was concentrated and flushed through a silica plug with dichloromethane. The purity of the solution was checked by TLC (pure CH2Cl2), after which the collected dark green-purple solution was dried to give nearly pure corrole (302 mg, 34 %). In CDCl3 the 1H NMR spectra was broad, probably due to stacking. NMR spectra matched those reported in the literature.[6]

The free base 5,10,15-triphenylcorrole (0.3 mmol) was heated to reflux for 1 h in MeOH (180 mL) with cobalt acetate tetrahydrate (0.6 mmol) and tripheophosphine (0.6 mmol) for 1 h in the dark, after which the solution was concentrated and flushed through a silica plug with dichloromethane as eluent. The deep red fraction containing the desired cobalt(III) corrole complex was collected (91 mg, 36 %).

1H NMR (300 MHz, CDCl3); δ = 8.37 (t, J = 5.1 Hz, 4 H), 8.27 (d, J = 6.5 Hz, 1 H), 8.10 (d, J = 4.8 Hz, 2 H), 8.01 (t, J = 7.9 Hz, 1 H), 7.81 (dd, J = 7.6, 2.7 Hz, 7 H), 7.73 (d, J = 4.9 Hz, 3 H), 7.33 (dd, J = 16.3, 8.2 Hz, 3 H), 7.00 (t, J = 7.5 Hz, 3 H), 6.69 (dd, J = 7.7, 2.3 Hz, 6 H), 5.17–5.05 (m, 1–6 H) ppm. 13C NMR (126 MHz, CDCl3); 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), 127.35, 122.75, 122.09 (d, J = 4.5 Hz, 120.74 (d, J = 2.6 Hz) ppm. HRMS: calcd. for C53H53Br5CoP4N8 [M+Na]+ 1160.4280, found 1159.7722; calcd. for C53H53Br5CoN4 [M–PPh3]+ 898.1362, found 897.7435.

**Synthesis of [Co(L)(Mes2Cor)(PPh3)]**

Freshly alumina filtered pyrrole (10 mmol) and benzaldehyde (5 mmol) were dissolved in MeOH (200 mL), and H2O (200 mL) and concentrated (37 %) HCl (5 mL) were added, after which the reaction mixture was stirred for 3 h at room temperature. The bilane intermediate was extracted with chloroform and washed with water. The organic layer was dried with Na2SO4 and filtered. The tetrapyrole/bilane solution was diluted to a volume of 250 mL of chloroform and kept in the dark from this point on (it is important that these intermediates are handled in the dark). p-Chloranil (5 mmol) was added and oxidation of the bilane intermediate was allowed to proceed overnight with stirring. The reaction mixture was concentrated and quickly flushed through a silica plug with dichloromethane. The purity of the solution was checked by TLC (pure CH2Cl2), after which the collected dark green-purple solution was dried to give nearly pure corrole (302 mg, 34 %). In CDCl3 the 1H NMR spectra was broad, probably due to stacking. NMR spectra matched those reported in the literature.[6]

The free base 5,10,15-triphenylcorrole (0.3 mmol) was heated to reflux for 1 h in MeOH (180 mL) with cobalt acetate tetrahydrate (0.6 mmol) and triphenylphosphine (0.6 mmol) for 1 h in the dark, after which the solution was concentrated and flushed through a silica plug with dichloromethane as eluent. The deep red fraction containing the desired cobalt(III) corrole complex was collected (91 mg, 36 %).

1H NMR (300 MHz, CDCl3); δ = 8.33 (d, J = 4.4 Hz, 2 H), 8.00 (d, J = 4.8 Hz, 2 H), 8.09 (d, J = 4.8 Hz, 2 H), 7.98 (s, 1 H), 7.68–7.52 (m, 11 H), 7.36 (d, J = 7.4 Hz, 1 H), 7.06 (d, J = 7.5 Hz, 3 H), 6.76–6.64 (m, 6 H), 4.72 (dd, J = 10.7, 8.1 Hz, 6 H) ppm. 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 ppm. HRMS (FD): calcd. for C53H53Br5CoP4N8 [M+Na]+ 844.8440, found 844.2140; calcd. for C53H53Br5CoN4 [M–PPh3]+ 582.5522, found 582.1199.

**Synthesis of [Co(L)(Mes2Cor)(PPh3)]**

The corrole was made by using the hindered dipyrromethane condensation method of Gryko and co-workers.[16] 5-Mesityl dipyrromethane (2 mmol) and 2,4,6-trimethoxybenzaldehyde (1 mmol) were dissolved in methanol (200 mL), after which H2O (100 mL) and
concentrated (37 %) HCl (10 mL) were added. The mixture was stirred for 2 h. The bilane intermediate was extracted with chloroform and washed with water. The organic layer was dried with Na₂SO₄ or MgSO₄ and filtered. The tetrapyrrole/bilane solution was from here on kept in the dark, and diluted to a volume of 500 mL with chloroform. p-Chloranil (3 mmol) was added in the dark, and oxidation of the bilane intermediate was allowed to proceed overnight with stirring. The mixture was then concentrated and flushed through a silica plug with dichloromethane, and the purple solution was collected to give nearly pure corrole (115 mg, 16 %). The ¹H NMR spectra were in accordance with those reported in the literature.[26] 5,15-Dimesityl-10-(2,4,6-trimethoxyphenyl)corrole (0.1 mmol) was heated to reflux for 1 h in MeOH (60 mL) with cobalt acetate tetrahydrate (2 equiv.) and triphenylphosphine (2 equiv.) for 1 h in the dark. After cooling, the solution was condensed and flushed through a silica plug with CH₂Cl₂ as eluent, and the red fraction containing the CH₂Cl₂ cobalt(III) corrole complex was collected. Crystallization by slow evaporation of a solution in DCM resulted in crystals. The NMR spectrum in pyridine matches that in the literature, which does not show a signal for the PPh₃ ligand.[26] Crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. [Co[Br₂Cor][PPh₃]]: The crystal diffracted poorly, but the connectivity between the atoms could be clearly resolved to ascertain the molecular structure shown in Figure 9.

5,15-Dimesityl-10-(2,4,6-trimethoxyphenyl)corrole (0.1 mmol) was heated to reflux for 1 h in MeOH (60 mL) with cobalt acetate tetrahydrate (2 equiv.) and triphenylphosphine (2 equiv.) for 1 h in the dark. After cooling, the solution was condensed and flushed through a silica plug with CH₂Cl₂ as eluent, and the red fraction containing the CH₂Cl₂ cobalt(III) corrole complex was collected. Crystallization by slow evaporation of a solution in DCM resulted in crystals. The NMR spectrum in pyridine matches that in the literature, which does not show a signal for the PPh₃ ligand.[26] Crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. [Co[Br₂Cor][PPh₃]]: The crystal diffracted poorly, but the connectivity between the atoms could be clearly resolved to ascertain the molecular structure shown in Figure 9.

CV Measurements: Cyclic voltammograms were recorded with a Metrohm Autolab AUT85221 potentiostat in conjunction with Nova 1.8.17 at a scan rate of 0.1 V s⁻¹. The electrodes used were a glassy carbon working electrode, a platinum counter electrode and a silver reference electrode. A solution of 0.3 M nBu₄NPF₆ in dry THF was used as the electrolyte, and potentials were referenced to FeCp₂⁺⁻ by using FeCp₂⁺⁻ (E°₁/₂ = –0.45 vs. FeC⁺⁻) in THF[15] as internal reference. These CVs are shown in Figure S1.

Spectro-Electrochemistry: UV/Vis spectro-electrochemistry was performed with 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 nBu₄NPF₆ in dry THF was used as the electrolyte. The concentration of the corrole complexes was roughly 5 × 10⁻⁴ M. The scan speed was 0.02 V s⁻¹. SpectraGraphy 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 to show significant changes, in which case spectra were taken every 0.05 V. This was continued until either −1.0 V was reached or the spectrum no longer showed any changes when the applied potential was increased. For the backoxidation a similar strategy was followed, by initially taking spectra every 0.05 V. This was continued until the spectrum started to show significant changes, in which case spectra were taken every 0.05 V. This was continued until either −1.0 V was reached or the spectrum no longer showed any changes when the applied potential was increased. For the backoxidation 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. These spectra are shown in Figure S2.

EPR Studies: In a glove box, 0.005 mmol of the cobalt corrole complex and 0.75 equiv. of cobaltocene or decamethylcobaltocene (for [Co[Mes₂Cor][PPh₃]]) were dissolved in dry MeTHF (1.5 mL) and DMSO (0.5 mL), after which 0.2 mL of the resulting solution was transferred to an EPR tube. The spectrum was then measured at 20 K. After the initial measurements, the tubes were opened and the contents exposed to air for ca. 2 min, and then which the tubes were closed and the spectra measured again at 20 K to check for possible effects of minor oxygen leakage. The spectra were recorded on a Bruker EMX-plus spectrometer equipped with a helium cryostat. For additional EPR spectra, see Figure S3.
General Procedure for the Catalytic Reactions: Reactions were performed on 0.3 mmol scale. To a flame-dried and nitrogen-filled Schlenk tube were added catalyst (5 mol-%), (4-azidobutylibenzene (1 equiv.), Boc₂O (1.1 equiv.) and reductant (5 mol-% cobaltocene) in dry toluene (5.0 mL). The mixture was stirred for 16 h at 100 °C. After drying, mesitylene or 1,3,5-trimethoxybenzene was added as external standard to determine the yield by NMR spectroscopy (6.1 or 6.8 ppm, respectively). Product peaks at 5–4.75 ppm in CDCl₃ were used to determine the yield of the product. NMR-scale reactions were performed using the same method but on 0.06 mmol scale and in [D₈]toluene. Product appearance was monitored by means of the decreasing peaks at δ = 3.34 and 2.74 ppm. See Figure S5, for details.

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