

## Article

# Generation of Cobalt-Containing Nanoparticles on Carbon via Pyrolysis of a Cobalt Corrole and Its Application in the Hydrogenation of Nitroarenes

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**Abstract:** We report on the manufacture of a state-of-the-art heterogeneous non-noble metal catalyst, which is based on a molecularly well-defined phosphine-tagged cobalt corrole complex. This precursor compound is readily synthesized from convenient starting materials while the active material is obtained through wet-impregnation of the pertinent metalliferous macrocycle onto carbon black followed by controlled pyrolysis of the loaded carrier material under an inert gas atmosphere. Thus, the obtained composite was then applied in the heterogeneous hydrogenation of various nitroarenes to yield a vast array of valuable aniline derivatives that were conveniently isolated as their hydrochloride salts. The introduced catalytic protocol is robust and user-friendly with the entire assembly of the reaction set-up enabling the conduction of the experiments on the laboratory bench without any protection from air.

**Keywords:** base metal catalysis; heterogeneous hydrogenation; cobalt; corrole; pyrolysis

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## 1. Introduction

The synthesis of aniline from nitroarenes is a highly relevant industrial process considering the high demand of aromatic amines for the production of pharmaceuticals, dyestuffs, agrochemicals, and isocyanates for making polyurethanes. Traditionally, the given nitro reduction is realized through the stoichiometric Béchamp reaction, which deploys highly corrosive hydrochloric acid and excess iron powder [1]. Since this route produces a significant amount of inorganic waste, it is worthwhile, for both economic and ecological reasons, to resort to catalytic methods utilizing H<sub>2</sub> gas as the principal reductant. In this case, the pertinent chemical transformation is rendered more cost- and atom-efficient, given the low price of hydrogen and the fact that only water is formed as the by-product [2–5].

Concerning homogeneous approaches, the published procedures report the use of precious metals such as Au [6], Ir [7], Pd [8,9], Pt [10], Rh [11], or Ru [12–14], whereas non-noble, metal-based strategies center around the implementation of Fe [12,15,16], Mn [17], or Co [18] as catalytically active metal centers in the complexes that mediate the desired reaction.

Regarding heterogeneous catalysis, the first reports by Beller and coworkers dealing with the title reaction brought about by carbonaceous N-doped catalysts accessible

through pyrolytic syntheses from suitable metal-ligand assemblies [19–21] have significantly forwarded the field of heterogeneous base-metal redox catalysis. Expanding upon these seminal works, an impressive number of reports dealing with both the manufacture of related cobalt-containing hybrid materials and their application in the nitroarene reduction, either relying on gaseous  $H_2$  or selected transfer reagents (hydrazine, formic acid), has appeared in recent years [22–45]. With respect to the catalyst performance of such supported heteroatom-doped solids, it was borne out through experiments that the activity is directly proportional to the *N*-content of the composite that brings about the desired transformation [46]. Consequently, the use of nitrogen-rich (chelating) *N*-donor ligands is an effective tool for the preparation of decent heterogeneous catalysts that are activated through controlled thermal heat treatment of a molecularly well-defined metal complex.

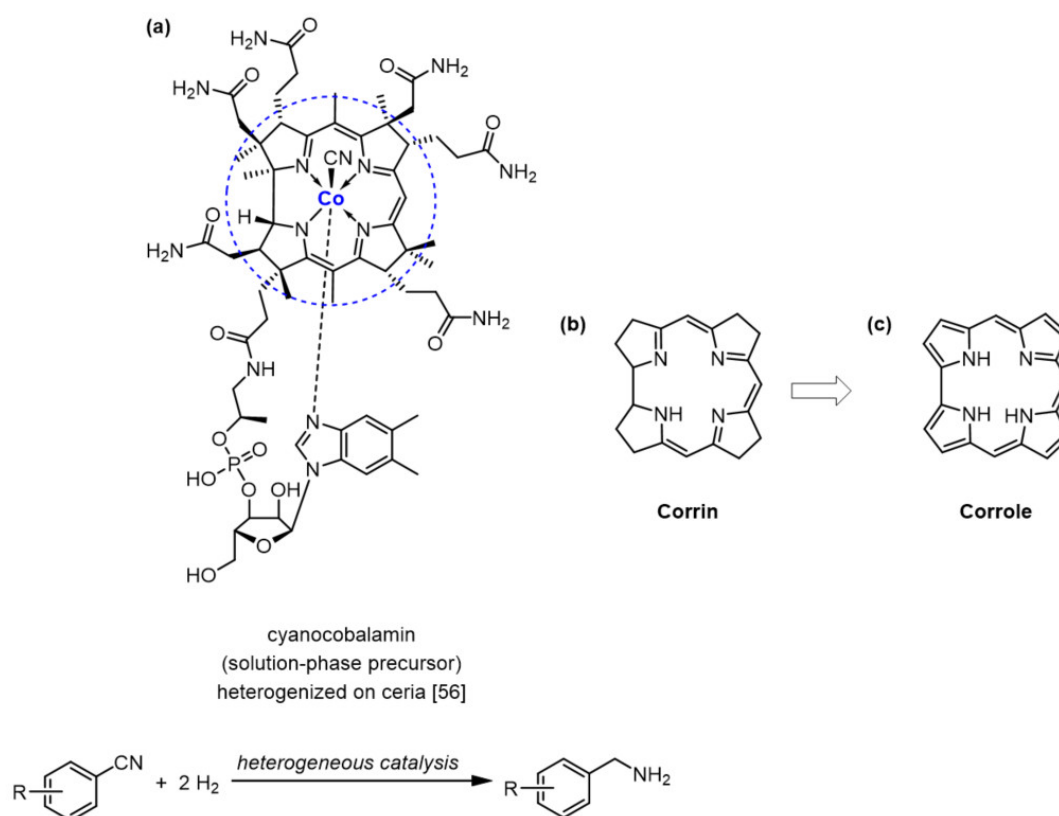
In addition to the above-mentioned strategy, pyrolysis-free approaches relying on cobalt are also well-documented in pertinent literature protocols, and a variety of Co-based solids have been demonstrated to effectively drive the hydrogenation of nitroarenes [47–52]. Finally, the highly reactive but pyrophoric and nonselective Raney® Ni, as well as the expensive Pd-on-charcoal, can also be used for the reduction of aromatic nitro compounds to afford anilines [3].

Notwithstanding the great success of composites that are based on certain annealed coordination compounds, their manufacture entails a time-consuming complexation step that is carried out in solution prior to wet-impregnation of the support. Thus, it seemed worthwhile to employ a prefabricated (and, ideally, commercially available) complex that already incorporates the catalytically active metal and a nitrogen-rich ligand to guarantee good performance. In this regard, cost-effective cyanocobalamin (vitamin  $B_{12}$ , Figure 1a) represents a sound choice, and specific materials derived therefrom have found promising applications as catalysts in fuel cells [53], in the oxygen reduction-reaction (ORR) [54], and in the hydrogen evolution reaction (HER) [55]. Furthermore, in the context of organic synthesis, mesoporous carbon prepared from this coenzyme was shown to foster the formation of imines that constitute vital intermediates in the production of pharmaceuticals [56]. In addition, ceria-supported and pyrolytically-activated cyanocobalamin was employed in the heterogeneous hydrogenation of nitrile derivatives to afford valuable benzylamines (Figure 1a) [57].

Although pristine cobalt-based cobalamins indeed serve as reasonable (solution phase) precursors for the fabrication of heterogenized catalysts, their thermal heat treatment entails the inevitable annihilation of precious stereocenters that are located in the pendent sidechains of the molecules. Hence, the overall pyrolysis processes conducted with such biomolecules suffer from very low atom efficiencies. As a consequence of this, the development of more rational production methods for related solid composite materials is highly sought after.

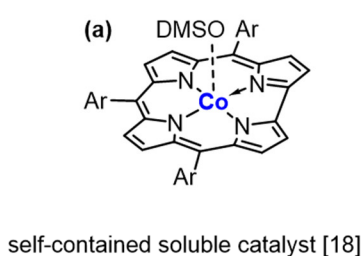
Guided by the very close structural resemblance of the vitamin  $B_{12}$  core structure (corrin, Figure 1b) and the corrole framework (Figure 1c), as well as the facile synthetic access to the latter, we decided to test the suitability of this porphyrin-related macrocycle class as a source for the manufacture of pyrolysis-based heterogeneous non-noble metal catalysts.

In general, the syntheses and in-depth characterization of corroles, including their metalliferous congeners—especially those containing cobalt—constitutes a well-established body of science [58–63], and certain metal corrole complexes were previously successfully applied for the design of catalysts applicable for water splitting [64], redox-transformations involving gaseous  $O_2$  [65–67], and  $CO_2$  electroreduction [68,69]. Quite recently, with respect to molecular catalysis, a DMSO-tagged cobalt-corrole complex was demonstrated to affect the title transformation (Figure 2a) [18]. Lastly, related Co-corrolates were developed into sensors suitable for the detection of CO gas [70], as well as ions such as nitrite and nitrate ions [71,72].

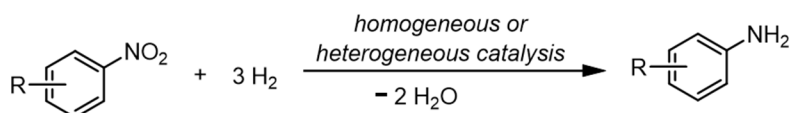
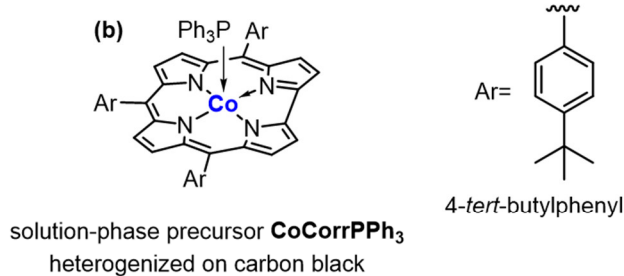


**Figure 1.** (a) Naturally occurring vitamin B<sub>12</sub> (cyanocobalamin) has previously been applied as a precursor compound for the preparation of a solid ceria-supported catalyst that facilitated the pressure hydrogenation of benzonitrile derivatives. (b) Structural drawing of the corrin base frame upon which vitamin B<sub>12</sub> and kindred bioactive macrocyclic metal complexes are built upon. (c) Molecular structure of the corrole scaffold that herein serves as the key motif for the design of a carbonaceous N-doped heterogeneous hydrogenation catalyst based on cobalt.

#### Previous work:



#### This work:



**Figure 2.** (a) A molecularly well-defined cobalt-corrole complex was shown to bring about the homogeneous hydrogenation of nitroarenes to afford a variety of aniline derivatives [18]. (b) Herein, a pre-fabricated phosphine-tagged cobalt corrole, which can be considered as a curtailed vitamin B<sub>12</sub> analog, was merged with carbon black (Vulcan® XC 72 R) and then pyrolytically activated to catalyze the same nitroarene-to-aniline hydrogenation.

Apart from the favorable *N*-content of the bare corrole backbone (*vide supra*), the architecture of the entire Co-corrole assembly allows for the accommodation of an additional axial ligand that incorporates heteroatoms other than nitrogen (Figure 2b). This feature, in turn, offers the intriguing possibility of specifically co-doping the full-fledged catalyst at the early easy-to-modify molecular level. In this respect, special emphasis is placed on phosphorus since this element is well known to ameliorate the redox activity (including the hydrogenation activity) of the respective catalysts [73–92].

Herein, we introduce the fabrication of a solid, carbon black-supported *N*, and a *P* co-doped catalyst that was prepared from a triphenylphosphine-ligated cobalt corrole through controlled pyrolysis in an argon atmosphere. Thus, the prepared composite was then utilized in the highly relevant heterogeneous pressure hydrogenation of nitroarenes to yield the corresponding aniline derivatives, which were readily precipitated from the filtered reaction solution as their hydrochlorides (*vide infra*).

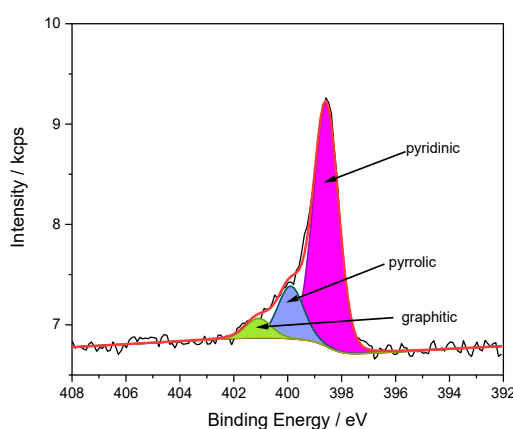
## 2. Results and Discussion

### 2.1. Catalyst Preparation and Characterization

Imbuing a commercial Vulcan® XC 72 R powder with an ethanolic solution of pre-synthesized **CoCorrPPh<sub>3</sub>** (see Figure 2 for the structural drawing), subsequent removal of the volatiles under reduced pressure, and the ensuing annealing of the modified support at 800 °C under an inert gas atmosphere (argon) furnished the catalytically active compound CoCorrPPh<sub>3</sub>@Vulcan-800. The experimental details for the manufacture of this heterogeneous catalyst are outlined in Section 3.1.

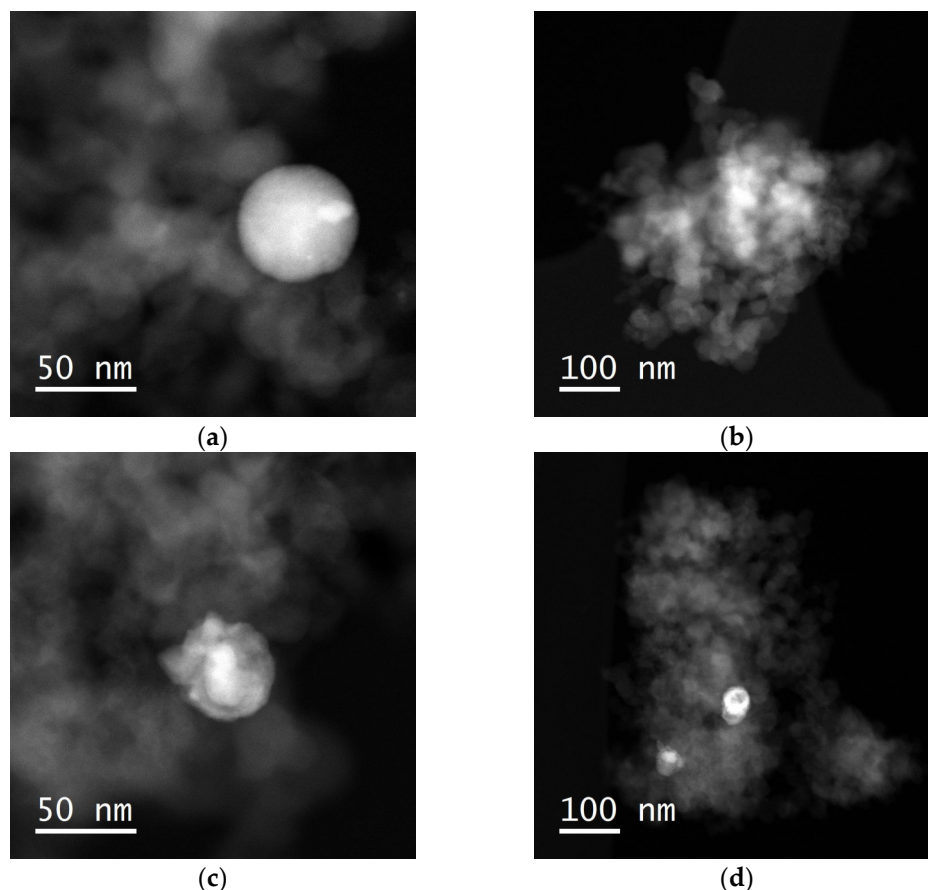
In order to obtain qualitative information about the surface composition of the pyrolytically synthesized cobalt catalyst, we employed the use of XPS. Deconvolution of the pertinent N 1s spectrum (Figure 3) exposed three individual peaks that are ascribed to pyridinic-, pyrrolic-, and graphitic-type nitrogen (with the intensity of the respective signals decreasing in the order listed). Owing to the partial overlap of the spectroscopic features, it was not possible to unequivocally quantify the single contributions of the three N species to the total nitrogen content. Notwithstanding this fact, the results of the XPS analysis proved that nitrogen is indeed incorporated into the Vulcan® matrix upon thermally induced conversion of the corrole framework.

The full range of the recorded X-ray photoelectron spectrum as well as an enlarged portion displaying the cobalt-related region are depicted in Figures S1 and S2, respectively (see the supporting information part).



**Figure 3.** High-resolution N 1s spectra (XPS) of the pyrolytically-activated CoCorrPPh<sub>3</sub>@Vulcan-800 catalyst showing three different nitrogen modifications, i.e., pyridinic (major share), pyrrolic (medium share), and graphitic (minor share); the total (surface) N content amounted to 1.3 atom-%.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used to gain deeper insight into the morphology of CoCorrPPh<sub>3</sub>@Vulcan-800 (Figure 4). The images reveal relatively large cobalt-based particles that are widely distributed over the surface of the Vulcan® carrier material. Furthermore, the composition of these particles is not uniform, which is, for instance, indicated in Figure 4c.



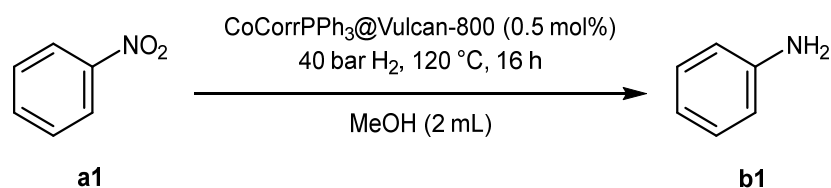
**Figure 4.** (a)–(d). Selected HAADF-STEM images of the catalytically active composite CoCorrPPh<sub>3</sub>@Vulcan-800.

Energy-Dispersive X-ray Spectroscopy (EDX) was deployed to establish both the chemical constitution and the architecture of the metalliferous particles. Upon evaluation of the EDX spectra, we infer that there are cobalt containing particles being composed of a cobalt phosphide core that is surrounded by a cobalt oxide shell (Figure S3).

## 2.2. Catalytic Tests

To assess the catalytic performance of the heterogenized cobalt corrolate in the hydrogenation of nitrobenzene (Figure 5), we applied free, thermally decomposed **CoCorrPPh<sub>3</sub>** as well as Vulcan®, ceria-, silica-, and alumina-supported modifications thereof (Table 1). The solely heat-treated metal complex already gave rise to a 60% substrate conversion (Entry 5), whereas attaching the pyrolyzed metal corrole assembly onto the Vulcan® powder improved this value by almost 20% (Entry 1). The other investigated carrier materials, i.e., CeO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>, were all heavily outperformed by the canonical Vulcan® XC 72 R (3–26% conversion of nitrobenzene, Entries 2–4).

Of note, the pristine and non-pyrolyzed solution phase precursor **CoCorrPPh<sub>3</sub>** represents a hydrogenation catalyst on its own that facilitates the given nitrobenzene-to-aniline reduction to a provable extent (Entry 6) [18]. Quite remarkably, the activity of the phosphine-ligated cobalt corrole ceases on mere immobilization on Vulcan® without subsequent pyrolysis of the impregnated material (Entry 7).



**Figure 5.** Model hydrogenation of nitrobenzene to aniline effected by CoCorrPPh<sub>3</sub>@Vulcan.

**Table 1.** Dependence of the catalyst activity on the chemical nature of the support. Reaction conditions: nitrobenzene (0.25 mmol), catalyst (0.5 mol%), H<sub>2</sub> (40 bar), MeOH (2 mL), 120 °C, 16 h, and *n*-hexadecane as an internal standard (18 mg). The indication of the catalyst quantity is based on the bulk metal content as determined by the elemental analysis.

| Entry | Catalyst                                               | Pyrolysis T (°C) | Conversion (%) |
|-------|--------------------------------------------------------|------------------|----------------|
| 1     | CoCorrPPh <sub>3</sub> @Vulcan                         | 800              | 79             |
| 2     | CoCorrPPh <sub>3</sub> @CeO <sub>2</sub>               | 800              | 26             |
| 3     | CoCorrPPh <sub>3</sub> @SiO <sub>2</sub>               | 800              | 7              |
| 4     | CoCorrPPh <sub>3</sub> @Al <sub>2</sub> O <sub>3</sub> | 800              | 3              |
| 5     | CoCorrPPh <sub>3</sub>                                 | 800              | 60             |
| 6     | CoCorrPPh <sub>3</sub>                                 | non-pyrolyzed    | 7              |
| 7     | CoCorrPPh <sub>3</sub> @Vulcan                         | non-pyrolyzed    | 0              |

Having identified the ideal support for the given cobalt-catalyzed nitrobenzene hydrogenation, we investigated the influence of the catalyst amount on the substrate conversion (Table 2). Using loadings as low as 0.10 mol% and 0.25 mol% still enabled detectable conversions of 9% and 25%, respectively (Entries 1 and 2), while increasing the portion to 0.5 mol% allowed for a decent 79% (Entry 3). Finally, application of 1 mol% of CoCorrPPh<sub>3</sub>@Vulcan-800 completely converted the NO<sub>2</sub> motif in the model compound **a1** (Entry 4). Rewardingly, we established that a proper catalyst amount of 0.5 mol% per nitro group generally suffices for decent product formation (*vide infra*).

**Table 2.** Influence of the catalyst amount on the nitrobenzene-to-aniline hydrogenation. Reaction conditions: nitrobenzene (0.25 mmol), H<sub>2</sub> (40 bar), CoCorrPPh<sub>3</sub>@Vulcan-800 catalyst, MeOH (2 mL), 120 °C, 16 h, and *n*-hexadecane as internal standard (18 mg).

| Entry | Catalyst (mol%) | Conversion (%) |
|-------|-----------------|----------------|
| 1     | 0.10            | 9              |
| 2     | 0.25            | 25             |
| 3     | 0.50            | 79             |
| 4     | 1.00            | >99            |
| 5     | no catalyst     | 0              |

Next, the effect of the pyrolysis temperature regarding the CoCorrPPh<sub>3</sub>-impregnated Vulcan<sup>®</sup> carrier on the catalyst performance was probed (Table 3). We commenced with 400 °C, whereby an onset value of 22% conversion was observed. Upon constantly increasing the oven temperature, the catalyst activity successively increased to culminate with a 79% conversion at 800 °C (Entry 4). This result is well in line with the outcome of the Thermogravimetric Analysis (TGA) (Figure S4 in the supporting information part). Importantly, going beyond this temperature causes a steep decline of the nitrobenzene conversion by 25% (Entry 5); as expected, the non-pyrolyzed samples did not produce any aniline product (Entry 6).

**Table 3.** Hydrogenation of nitrobenzene; optimization of the pyrolysis temperature. Reaction conditions: nitrobenzene (0.25 mmol), CoCorrPPh<sub>3</sub>@Vulcan-X (0.5 mol%), H<sub>2</sub> (40 bar), MeOH (2 mL), 120 °C, 16 h, and *n*-hexadecane as internal standard (18 mg). X denotes the pyrolysis temperature in °C.

| Entry | Catalyst                       | Pyrolysis T (°C) | Conversion (%) |
|-------|--------------------------------|------------------|----------------|
| 1     | CoCorrPPh <sub>3</sub> @Vulcan | 400              | 22             |
| 2     | CoCorrPPh <sub>3</sub> @Vulcan | 600              | 46             |
| 3     | CoCorrPPh <sub>3</sub> @Vulcan | 700              | 69             |
| 4     | CoCorrPPh <sub>3</sub> @Vulcan | 800              | 79             |
| 5     | CoCorrPPh <sub>3</sub> @Vulcan | 900              | 54             |
| 6     | CoCorrPPh <sub>3</sub> @Vulcan | non-pyrolyzed    | 0              |

We then went on to study the impact of the reaction medium on the activity of the solid CoCorrPPh<sub>3</sub>@Vulcan-800 composite catalyst (Table 4). The model reaction performs best in a protic polar media (Entries 1–3), whereas in the common THF the nitrobenzene conversion sharply dropped to a poor 14% (Entry 4); in nonpolar solvents (*n*-heptane, toluene) as well as in chloroform, the catalytic activity fully collapsed (Entries 5–7). Owing to the good solubility of anilinium chloride in water, the corresponding product yield was rather poor (55%) and hence, we decided to use methanol throughout this work as this solvent gave excellent results (Entry 2).

**Table 4.** Hydrogenation of nitrobenzene: optimization of the solvent. Reaction conditions: nitrobenzene (0.25 mmol), CoCorrPPh<sub>3</sub>@Vulcan-800 (0.5 mol%), H<sub>2</sub> (40 bar), solvent (2 mL), 120 °C, 16 h, *n*-hexadecane as an internal standard (18 mg).

| Entry | Solvent           | Conversion (%)                       |
|-------|-------------------|--------------------------------------|
| 1     | MeOH              | 79                                   |
| 2     | MeOH              | >99 <sup>1</sup> , (96) <sup>1</sup> |
| 3     | H <sub>2</sub> O  | >99 <sup>1</sup> , (55) <sup>1</sup> |
| 4     | THF               | 14                                   |
| 5     | <i>n</i> -heptane | 0                                    |
| 6     | toluene           | 0                                    |
| 7     | CHCl <sub>3</sub> | 0                                    |

<sup>1</sup> 1 mol% of catalyst was used, no internal standard was added, isolated yields of the corresponding hydrochloride salts are given in parentheses.

### 2.3. Scope and Limitations

After the systematic variation of the reaction parameters (*vide supra*), we intended for the elaboration of a general application protocol for the given heterogeneous cobalt catalyst (Scheme 1). The parent nitrobenzene **a1**, as well as its bis-congener **a2**, were neatly converted to afford the desired ammonium salts in an excellent yield (96% and 97%, respectively). However, placing the strong electron donating NH<sub>2</sub> functionality in direct proximity to the nitro motif (**a3**) slightly hampered the product formation (90%) that was exacerbated when two additional Me groups (**a4**) were present in the phenyl ring (79%). Yet, putting two small alkyl rests next to the nitro group (**a5**) re-established the almost quantitative formation of the desired anilinium derivative. Furthermore, we noticed that *N*-methylation of an adjacent amino group (**a6**) practically had the same effect in terms of product yield (75%) as if the arene ring had been alkylated twice (**a4**).

To our delight, the given heterogeneous catalyst system is tolerant of nitrile groups and, accordingly, the CN-tagged aniline **b7** was isolated in an excellent yield (95%). On the other hand, if an *ortho*-hydroxymethyl tether was located in the aryl moiety (**a8**) then the reaction outcome was inferior (20%). Strikingly, equipment of the phenyl ring with a pure OH group (**a9–a11**) in either position drastically increased the extent of product formation (76–85%).

An outstanding characteristic of the present pyrolytically-activated cobalt catalyst is its ability to sharply discriminate between the target NO<sub>2</sub> and a ketone motif. With an *o*- or *p*-acetyl group (**a12**, **a14**), nearly perfect chemoselectivity was observed (99% and 92% yield, respectively), though the same CH<sub>3</sub>CO fragment in the *meta*-position provided only a mediocre formation of the wanted product, **c13** (69%).

With respect to the industrially relevant halide-functionalized substrates **a15**–**a24**, the best results were obtained with Cl- and Br-containing nitrobenzenes, particularly when the pertinent halogen atoms were fixed in the *meta*- or *para*-position (91% and 93% for the chloro-derivative, whereas 95% and 83% for the bromo-kindred); in the case of the *ortho*-congeners, the yields amounted to 84% for the Cl- and 61% for the Br-bearing substrate (**a15** and **a18**), respectively. [93] This markedly diminished product generation is likely to result from the steric hindrance that is imparted to the nitro group by the immediate vicinity of the respective halide substituent. Considering this detrimental size effect of the halogen atoms alone, it is, however, counterintuitive that the *o*-fluoro compound **a21** produced the required salt to an even lesser extent (54%). Given the fact that the F-atom is considerably smaller than its group, the VII homologs, the expected yield of salt **c21** is expected to be higher than (or at least the same as) 84%. Regarding the iodo-based substrates, the H<sub>2</sub>-driven nitro-to-amine conversion severely suffered from hydro-dehalogenation and the outcome for the relevant position isomers **a22**–**a24** was moderate to poor (28–66%), with the *meta*-compound giving rise to the best result.

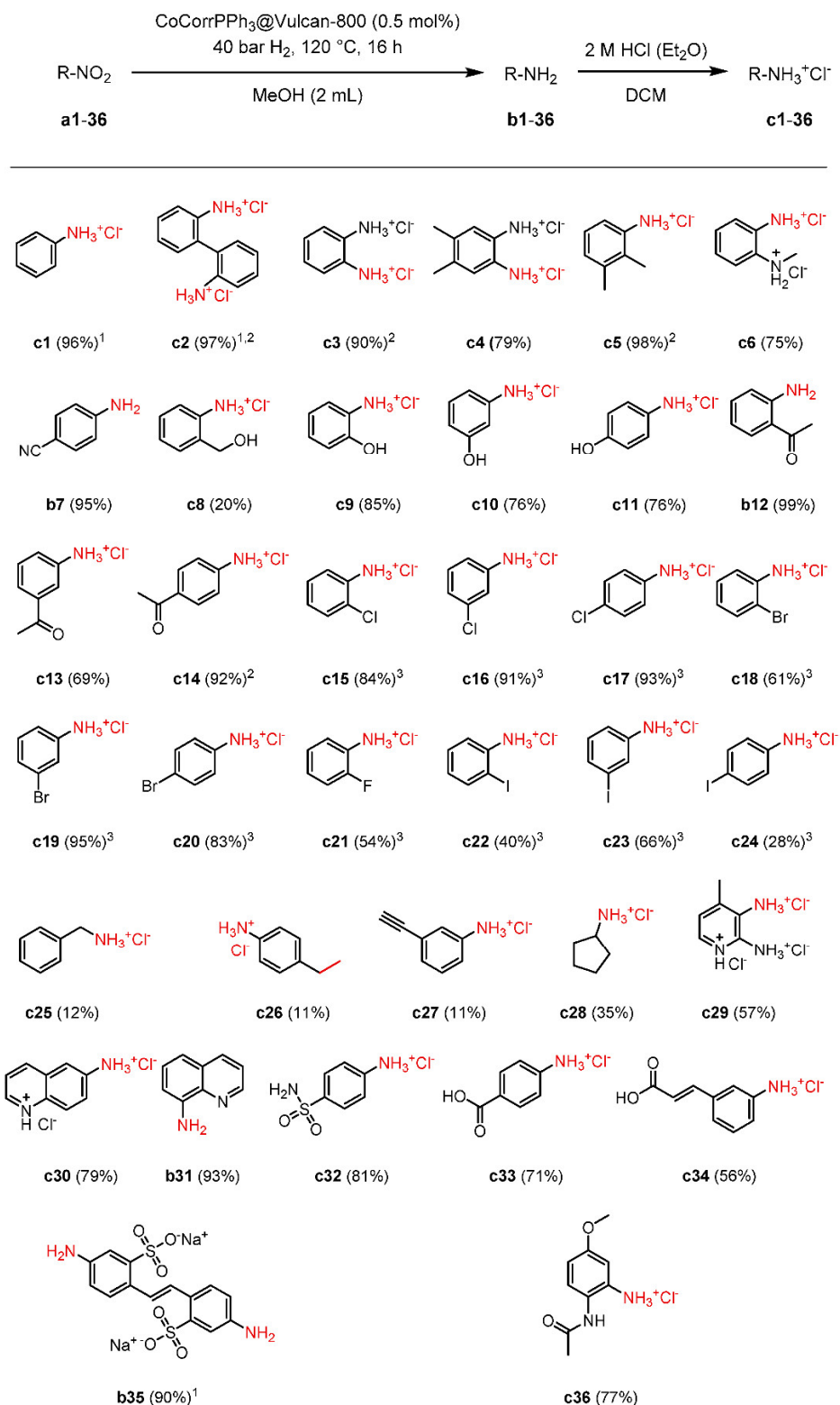
We then applied the given hydrogenation method to the CH<sub>2</sub>-extended nitrobenzene **a25** and, surprisingly, the activity of the used solid cobalt catalyst nearly completely ceased (12% **c25**). This experimental finding highlights the necessity for a direct arene-NO<sub>2</sub> linkage to enable proper product formation. Furthermore, the presence of vinyl (**a26**) or alkynyl groups (**a27**) at the periphery of the used starting material proved to be deleterious for the amine formation too (11% yield in both cases). Compound **a27** with its C≡C bond was at least chemoselectively reduced and leaving the triple bond untouched, whereas both the **a26** nitro group and the C≡C motif were reduced. In addition to this, the alicyclic species **a28** and the multi-functionalized pyridine **a29** produced similar unsatisfactory results (35% and 57%, respectively).

Continuing with the *N*-heterocyclic substrates, we found that nitro-tagged quinolines **a30** and **a31** permitted legitimate reaction outcomes with the *peri*-substituted congener, giving rise to an even and very good yield of the free amine **b31**, which exceeded 90%. Moreover, the sulfonamide-based nitrobenzene **a32** is strongly compatible with the given hydrogenation protocol and the respective product was obtained in decent amounts (81%). To our delight, the solid CoCorrPPh<sub>3</sub>@Vulcan-800 catalyst is reconciled with the presence of pendent carboxylic acids (substrates **a33** and **a34**), which are notoriously recalcitrant substrates for base metal-catalyzed hydrogenation reactions. Moreover, for substrate **a34**, the catalyst did not exhibit any activity towards the activated double bond.

One of the most important performance characteristics of our catalyst system is the provision of a brisk and atom-efficient route to disodium-4,4'-diamino-2,2'-stilbenedisulfonate **b35**, which is a key compound for the production of optical brighteners. [94]

Finally, we found that this catalytic protocol also duly accommodates reducible amide bonds, as was proven upon application of a representative acetamido-tagged substrate (77% **c36**).





**Scheme 1.** The complete scope of anilinium salts and free (heterocyclic) anilines that were made accessible through the CoCorrPPh<sub>3</sub>@Vulcan-800-catalyzed heterogeneous hydrogenation of the respective nitroarenes. In one case, i.e., compound **c28**, a cycloaliphatic ammonium salt was produced. The percent value in parentheses refers to the isolated yield of the corresponding organic ammonium salt. <sup>1</sup>The catalyst amount was doubled (1.0 mol%). <sup>2</sup>The reaction time was 20 h. <sup>3</sup>The reaction time was reduced to 5 h.

## 2.4. Recyclability Tests

For the reusability test of CoCorrPPh<sub>3</sub>@Vulcan-800, we applied 4-nitrobenzonitrile as the model substrate to additionally verify whether the chemoselectivity of the transformation is retained upon performing the hydrogenation of the given starting material several times (nine runs) with one particular catalyst loading (Table 5). Upon finishing two cycles, the catalyst activity was still very good (Entries 1–2), whereas after the third iteration a marked decrease to 59% conversion was observed. After the fifth run, a value of 44% was observed, which remained, quite remarkably, almost constant until the end of the series (Entries 5–9). Analyses of the reaction solutions revealed that in neither case was the nitrile motif reduced, and thus, the selectivity of the spent Co-catalyst was unaffected upon multiple uses.

**Table 5.** Recycling experiments for the liquid phase hydrogenation of 4-nitrobenzonitrile, facilitated by CoCorrPPh<sub>3</sub>@Vulcan-800. Reaction conditions: 4-nitrobenzonitrile (0.5 mmol), catalyst (0.5 mol%), H<sub>2</sub> (40 bar), MeOH (2 mL), 120 °C, 16 h, and *n*-hexadecane as the internal standard (18 mg).

| Entry | Run | Conversion (%) |
|-------|-----|----------------|
| 1     | 1   | >99            |
| 2     | 2   | 90             |
| 3     | 3   | 59             |
| 4     | 4   | 49             |
| 5     | 5   | 44             |
| 6     | 6   | 40             |
| 7     | 7   | 39             |
| 8     | 8   | 37             |
| 9     | 9   | 36             |

## 3. Experimental

All chemicals were purchased from different commercial suppliers (Merck, Darmstadt, Germany; Fluorochem, Hadfield, UK; Acros Organics, Vienna, Austria; Alfa Aesar, Kandel, Germany; BLDPharm, Shanghai, China; VWR, Radnor, PA, USA; Roth, Karlsruhe, Germany; TCI, Oxford, UK; and Chem Lab, Zedelgem, Belgium) and used as received without further purification. The catalyzed hydrogenation reactions were carried out in a steel autoclave (Parr, Moline, IL, USA) (300 mL) that was pressurized with H<sub>2</sub> gas (5.0 purity, Linde Gas GmbH). Routine GC-MS analyses were carried out on a GC-MS QP-2020 (Shimadzu, Kyōto, Japan) device (He carrier gas, 5.0 purity, Linde Gas GmbH), whereas the HR-MS measurements were performed on a QTOF 6520 (Agilent, Santa Clara, CA, USA). The NMR data were collected on Avance III (Bruker, Billerica, MA, USA) spectrometers (300 MHz, 500 MHz) while the applied spectrometer frequencies of the various nuclei were as follows: 300 MHz (<sup>1</sup>H NMR) and 75.5 MHz (<sup>13</sup>C{<sup>1</sup>H} NMR) on the 300 MHz machine, whereas 470.5 MHz (<sup>19</sup>F NMR) on the 500 MHz spectrometer; the chemical shifts are listed in ppm on the δ-scale and axis calibration is based on the residual nondeuterated solvent signal that was used as a reference. The XPS data were acquired on a VG ESCALAB220iXL instrument (Thermo Fisher Scientific, Waltham, MA, USA, 1486.68 eV Al K<sub>α</sub> radiation). The scanning transmission electron microscopy (STEM) micrographs were conducted on a probe aberration-corrected JEM-ARM200F electron microscope (JEOL, Tokyo, Japan, CEOS corrector) equipped with a JED-2300 (JEOL) energy-dispersive X-ray spectrometer that has a silicon drift detector (dry SD60GV). A high-angle annular dark field (HAADF) and an annular bright field (ABF) detector were used for general imaging. The solid sample was deposited without any pretreatment on a holey, carbon supported Cu grid (mesh 300) and transferred to the microscope. For the CHN analyses, a Microanalysator TruSpec (Leco, Geleen, Netherlands) machine was employed, whereas the metal content was determined via Atomic Absorption Spectroscopy using (PerkinElmer, Waltham, MA, USA) an AAS Analyst 300 device. Eventually, the TGA

curves were recorded on a Pyris Series TGA4000 (PerkinElmer, Waltham, MA, USA) thermogravimetric analyzer.

### 3.1. Procedure for the Pyrolytic Synthesis of the Supported Cobalt-Corrole-Based Heterogeneous Catalyst

Initially, the soluble precursor complex **CoCorrPPh<sub>3</sub>** (206 mg, 0.2 mmol) was dissolved in EtOH (30 mL), followed by a portioned addition of 1.00 g of the solid support (CeO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, or Vulcan® XC 72 R) to this solution within a period of 30 min. The obtained suspension was then refluxed (6 h) and, after evaporation of the solvent under reduced pressure, the remaining solid was further dried in vacuo. Hereafter, the resultant **CoCorrPPh<sub>3</sub>**-support composite was finely grinded using mortar and pestle (both made of agate), upon which the formed powder was carefully pyrolyzed in an Austromat® 624 furnace at the required temperature (Ar atmosphere, 2 h). Thus, the obtained, full-fledged catalyst is referred to as CoCorrPPh<sub>3</sub>@support-X, where X denotes the applied pyrolysis temperature (°C).

### 3.2. General Procedure for the Catalytic Hydrogenation Reactions

The catalyzed hydrogenation reactions were carried out in glass vials (4 mL), each of which was charged with solid CoCorrPPh<sub>3</sub>@Vulcan-800 (12 mg, if not stated otherwise, i.e., 0.5 mol% based on a bulk Co content of 1.16% by weight), nitro compound (0.5 mmol), solvent (2 mL), as well as a magnetic stirring bar—in that order and without any protection from air. Each reaction vessel was sealed with a septum cap, which was then pierced with a steel canula. Hereafter, the vials were placed in a drilled Al plate that was transferred into the autoclave, upon which the latter was flushed with H<sub>2</sub> (3×40 bar) before being pressurized to the desired value. Afterwards, the autoclave was placed on a heating plate whereupon the stirring rate (1000 rpm) and the required temperature were adjusted. Upon completion of the reaction, the autoclave was allowed to reach room temperature, and, after that, the steel vessel was carefully de-pressurized. Subsequently, the catalyst was separated by centrifugation whereby the collected solid was washed five times with methanol. Eventually, the combined supernatants were evaporated to dryness under reduced pressure and further dried in vacuo.

### Safety Statement Concerning the Use of Pressurized Hydrogenation Gas

The pressurized H<sub>2</sub>-containing steel bottle (200 bar, 50 L) was placed and lashed in a safety storage cabinet that is equipped with a tapping unit, whereby the gas cylinder was attached to a control panel that allowed for fine-tuning of the required H<sub>2</sub> pressure. The autoclave charging procedure was performed in a fume hood with an integrated sensor, which was wired to a magnetic valve. The latter promptly interrupts the gas feed in case of any H<sub>2</sub> leakage that might occur during the filling procedure. Moreover, optical and acoustic alerts are triggered whenever free flammable (and toxic) gas is detected inside the hood.

### 3.3. General Procedure for the Isolation of the Organic Ammonium Salts

The corresponding hydrochloride salts of the prepared amines (Section 3.2) were, if desired, obtained by the initial treatment of the crude product with etheric HCl (2 mL, 2 M in Et<sub>2</sub>O). The formed precipitate was filtered off, washed with dichloromethane (DCM) (3 × 0.5 mL), and finally dried in vacuo.

#### 4. Conclusions

We herein communicated the straightforward manufacture and characterization (XPS, EDX, and HAADF-STEM) of an immobilized cobalt-based catalyst that was prepared through pyrolytic synthesis of a Vulcan® XC 72 R-supported heteroleptic Co-corrole complex. The given functional solid was applied in the heterogeneous hydrogenation of a broad variety of nitroarenes to furnish the corresponding anilines, which were conveniently isolated as their hydrochloride salts. In addition, the introduced synthetic protocol provided excellent chemoselectivity under exceptionally low catalyst loadings (0.5 mol% per nitro group based on the bulk Co content) that were generally applied for the establishment of the product portfolio, irrespective of the complexity of the used substrates.

Since the reaction assembly is readily prepared under open-flask conditions without the need for time-consuming operating steps in containment systems (glovebox, -bags, etc.), this hydrogenation method is well-suited for the practically oriented synthetic chemist.

Finally, the fact that homoleptic metal corrole complexes still have vacant coordination sites allows for the deliberate introduction of foreign atoms into the catalyst matrix. This trait paves the way for the design of composite materials with tailor-made properties.

**Supplementary Materials:** The following supporting information can be downloaded at: [www.mdpi.com/article/10.3390/catal12010011/s1](http://www.mdpi.com/article/10.3390/catal12010011/s1), Effect of temperature and H<sub>2</sub> pressure, dependence on the reaction time, control experiments, Maitlis' hot filtration test, catalyst characterization (EA, XPS, EDX, and TGA), synthesis and characterization of **CoCorrPPh<sub>3</sub>**, characterization of the isolated products (yield, <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR, HR-MS).

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