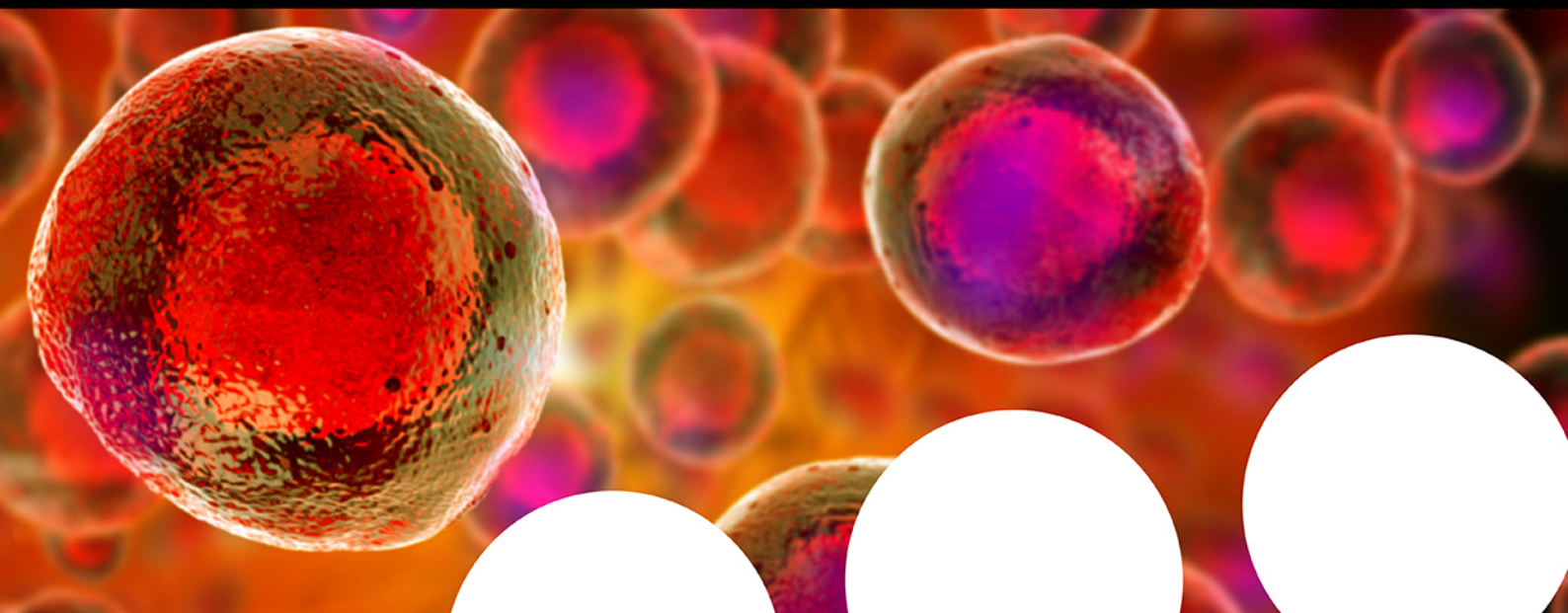


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# Cobalt Porphyrin-Catalysed Synthesis of Azobenzenes by Dehydrogenative Coupling of Anilines

Caterina Damiano,<sup>\*,[a]</sup> Matteo Cavalleri,<sup>[a]</sup> Nicola Panza,<sup>[a]</sup> and Emma Gallo<sup>\*,[a]</sup>

Dedicated to Professor Cesare Gennari on the occasion of his 70th birthday

The demand for azobenzenes has exponentially grown due to their wide range of applications in textile, medical, and dye industries. Here we report a procedure to synthesise azobenzenes by the dehydrogenative coupling of anilines in the presence of Co<sup>II</sup>(TPP) (TPP = dianion of tetraphenyl porphyrin) catalyst and 4-nitrophenyl azide oxidant species. Differently substituted azobenzenes were obtained in yields up to 72% together with 4-nitrophenyl amine, which is the stoichiometric

by-product of the process. The procedure displayed a good sustainability due to the almost quantitative recovery of pure 4-nitrophenyl amine that can be transformed again into the desired azide to pave the way for an efficient circular process. Experimental data supported the occurrence of a radical mechanism mediated by putative nitrene radical cobalt intermediate.

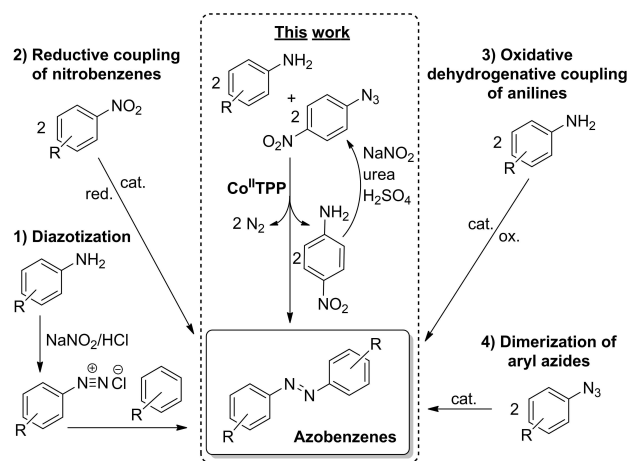
## Introduction

Since their discovery in 1834,<sup>[1]</sup> aromatic azo compounds, also called azobenzenes, have gained high attention due to their structural and electronic properties. The extended  $\pi$ -electron delocalization due to conjugation between the N=N bond and the aromatic rings has rendered this class of compounds very attractive for synthetic and optical applications, to the point of making azobenzenes indispensable for textile, medical, and dye industries. In fact, aromatic azo compounds are widely employed as pigments, dyes<sup>[2]</sup> indicators, food additives, drug delivery systems<sup>[3]</sup> as well as precursors for the synthesis of chemicals, polymers and natural products.<sup>[4–6]</sup> More recently, azobenzenes have also found promising applications in electronics, non-linear optics and molecular machine developments<sup>[7–9]</sup> thanks to the *trans-cis* isomerization of N=N double bond, which can take place under opportune UV-light irradiations.<sup>[10]</sup> As a result, the demand for azobenzenes has exponentially grown and a plethora of synthetic strategies<sup>[11]</sup> have been developed to make accessible a wide variety of aromatic azo compounds.

The four main classes of synthetic methodologies yielding azobenzenes are: 1) diazotization; 2) reductive coupling of

nitrobenzenes; 3) oxidative dehydrogenative coupling of anilines and 4) dimerization of aryl azides (Scheme 1).

The traditional diazotization process provides a two-steps reaction in which an unstable diazonium salt, formed in the first step from a primary amine, yields the desired azobenzene by reacting with an aromatic electrophile, such as phenols or anilines. Even if this method guarantees the synthesis of differently substituted azobenzenes, the high production of wastes, the instability of the diazonium intermediate and the harsh experimental conditions usually required, make the diazotization methodology unattractive for industrial applications. Thus, in order to reduce the waste production and employ milder reaction conditions, alternative synthetic routes, such as the reductive coupling of nitrobenzenes and the oxidative dehydrogenative coupling of anilines, have been largely investigated in the presence of both homogeneous<sup>[12–16]</sup> and heterogeneous<sup>[17–21]</sup> catalysts. More recently, electro-<sup>[22]</sup> and photocatalytic systems<sup>[23–26]</sup> have also proven to be efficient for



Scheme 1. Synthetic routes to obtain azobenzenes.

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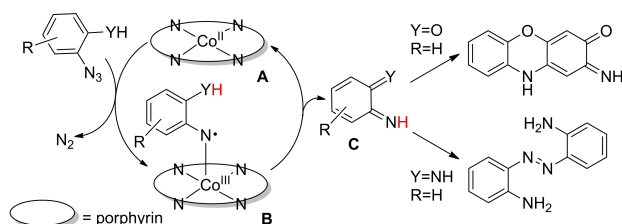
both the reductive coupling of nitrobenzenes and oxidative dehydrogenative coupling of anilines.

On the other hand, the synthesis of azobenzenes by the metal-catalysed dimerization of aryl azides ( $\text{ArN}_3$ ) have been less investigated. Aryl azides are well-known as “energetic reagents”<sup>[27]</sup> in nitrene transfer reactions due to their ability to insert the nitrene moiety ( $\text{ArN}$ ) into organic molecules by releasing molecular nitrogen as the sole by-product. Despite the broad use of  $\text{ArN}_3$  as aza-reagents<sup>[28]</sup> and the well-known formation of azobenzenes as by-products of nitrene transfers,<sup>[29–30]</sup> very few examples of catalytic synthesis of azobenzenes from aromatic azides have been published. Among the reported procedures,<sup>[31–35]</sup> those mediated by cobalt(II) porphyrins, efficient catalysts in promoting the aryl azide activation,<sup>[29,36–43]</sup> represent interesting methods to synthesise azobenzenes. The homocoupling of *ortho*-substituted aryl azides<sup>[35,44]</sup> was ascribed to the capacity of cobalt porphyrin species to assist H-atom transfer (HAT)<sup>[45–46]</sup> reactions through the well-known formation of radical nitrene intermediates.<sup>[47–50]</sup> As reported by B. De Bruin and co-authors<sup>[35,44]</sup> the radical nitrene **B**, formed by the reaction of Co(porphyrin) **A** with azide, can abstract a hydrogen atom from the vicinal YH substituent forming the reactive intermediate **C**, whose homocoupling reaction affords phenoxazinones or azobenzenes depending if Y is an O or NH functionality, respectively (Scheme 2).

Inspired by the ability of the radical nitrene species **B** to abstract a hydrogen atom from an aromatic amino group, we investigated the capacity of cobalt porphyrin nitrene species to act as hydrogen acceptors in the dehydrogenative coupling of anilines. Here we report the ability of the putative cobalt porphyrin nitrene species, obtained by the reaction of  $\text{Co}^{\text{II}}(\text{TPP})$  (TPP = dianion of tetraphenyl porphyrin) with 4-nitrophenyl azide, in catalysing the synthesis of differently substituted azobenzenes by using corresponding anilines as starting materials (Scheme 1). Surprisingly, 4-nitroaniline **1b**, deriving from the reduction of the azide oxidant reagent, was never involved in the coupling reaction.

## Results and Discussion

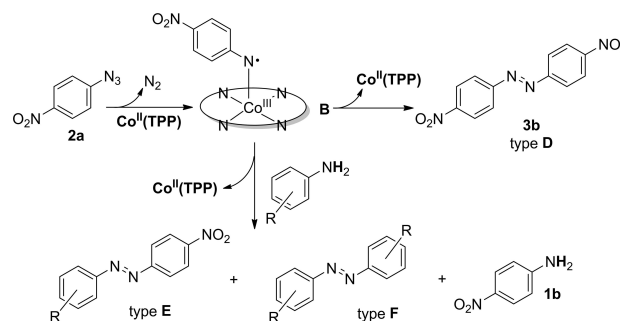
Considering the reaction mechanism shown in Scheme 2 and the intrinsic nature of 4-nitrophenyl azide **2a** in generating radical nitrene species,<sup>[51]</sup> we investigated the possibility that the cobalt nitrene intermediate **B**, generated by the reaction of **2a** with  $\text{Co}^{\text{II}}(\text{TPP})$ , could either be involved in a dimerization



Scheme 2. Activation of *ortho*-substituted aryl azides by Co(porphyrin).<sup>[35,44]</sup>

process leading 4-nitrophenyl diazene **3b** or be responsible for the hydrogen atom abstraction from aromatic amines, forming either the mixed nitrene/aniline type **E** product or the homocoupling product of anilines (type **F**) (Scheme 3). The stoichiometric by-product of the HAT reaction should be 4-nitroaniline **1b**.

In order to verify if all the compounds reported in Scheme 3 can be formed in the presence of  $\text{Co}^{\text{II}}(\text{TPP})$ , the model reaction between aniline **1a** and 4-nitrophenyl azide **2a** was performed in presence of 3% mol of the cobalt catalyst. The <sup>1</sup>H NMR and mass spectroscopy analysis of the reaction mixture revealed the formation of product **3a** (type **F**), deriving from the homocoupling of aniline **1a**, and the presence of **1b**. Neither 4-nitrophenyl diazene **3b** nor type **E** diazene molecule was formed (Scheme 3). This result can be ascribed to the preferred formation of **3a** with respect to the formation of other azobenzenes, as revealed by monitoring the decrease of the IR  $\text{N}_3$  absorbance peak of **2a** at  $2122\text{ cm}^{-1}$  in the presence or in the absence of **1a**. According to the  $\text{Co}^{\text{II}}(\text{TPP})$  ability to activate aryl azides, in both cases the **2a** concentration decreased during the reaction time (6 hours). However, the reaction carried out in the presence of **1a** was more efficient (94% of azide conversion, reaction a in Figure 1) with respect to the



Scheme 3. Possible reaction pathways of the cobalt-catalysed reaction between  $\text{ArNH}_2$  and azide **2a**.

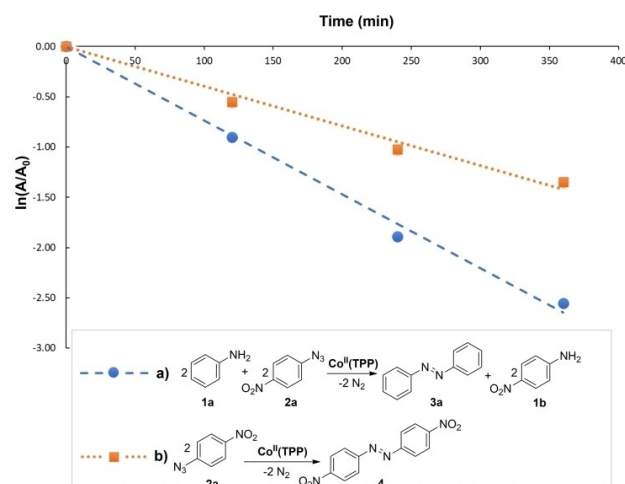


Figure 1. Conversion of 4-nitrophenyl azide **2a** in the presence (reaction a) and in the absence (reaction b) of aniline **1a**.

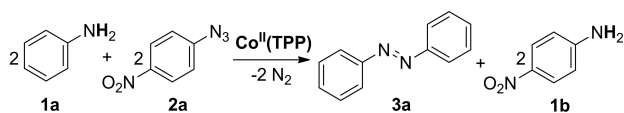
reaction run in its absence (73 % of azide conversion, reaction b in Figure 1) to support the hypothesis that aniline should play an active role in the cobalt imido reactivity (see below, Scheme 6).

It should be noted that the flash chromatography purification of the cobalt-catalysed reaction between **1a** and **2a** allowed the isolation of **3a** and of a stoichiometric amount of 4-nitroaniline **1b**, whose formation was due to the dehydrogenative coupling of **1a** by the nitrene intermediate **B** (Scheme 4).

To confirm the catalytic role of  $\text{Co}^{\text{II}}(\text{TPP})$ , the reaction between **1a** and **2a** was carried out in the absence of the catalyst and neither the azide conversion nor the **3a** formation was observed. In addition, the chemical stability of **1a** when it was treated with the sole  $\text{Co}^{\text{II}}(\text{TPP})$  suggested that the coupling of anilines requires the presence of the H-acceptor nitrene species acting as a sacrificial oxidant. Thus, the molar aniline/azide ratio was fine-tuned in the presence of 3% mol of  $\text{Co}^{\text{II}}(\text{TPP})$ . As showed in Table 1, the **3a** yield increased from 42% (entry 2, Table 1) to 64% (entry 3, Table 1) when, instead using an equimolar **1a/2a** amount, a slight excess of azide (**1a/2a** = 1:1.5) was employed. On the other hand, a further increase of the azide amount (**1a/2a** = 1:2) had a negative effect on the reaction productivity and the reaction yield dropped to 26%. This last result could be associated to the competitive dimerization of the 4-nitrophenyl azide **2a**, which can occur at higher rate when a high azide concentration was applied, in accordance with the first order dependence of the **3b** formation with respect to the azide concentration (reaction b in Figure 1).<sup>[40]</sup> The formation of **3b** was detected by TLC (thin layer chromatography) analysis.

It is important to note that the used catalytic loading of 3% mol was lower than those generally used for other metal-catalysed dehydrogenative couplings of anilines.<sup>[13–14,52]</sup>

The scope of the reaction was then investigated by testing different azides and aromatic amines and using the amine/azide



Scheme 4. Reaction of aniline **1a** with azide **2a** catalysed by  $\text{Co}^{\text{II}}(\text{TPP})$ .

Table 1. Optimisation of the aniline:azide ratio. <sup>[a]</sup>		
Entry	<b>1a/2a</b> ratio	<b>3a</b> yield [%] <sup>[b]</sup>
1	1:0.5	21
2	1:1	42
3	1:1.5	64
4	1:2	26

[a] Reactions were performed under nitrogen atmosphere by refluxing aniline **1a**, 4-nitrophenyl azide **2a** and  $\text{Co}^{\text{II}}(\text{TPP})$  (3% mol) in dry benzene for 7 hours. [b] Isolated yields, calculated on a half of the initial aniline moles.

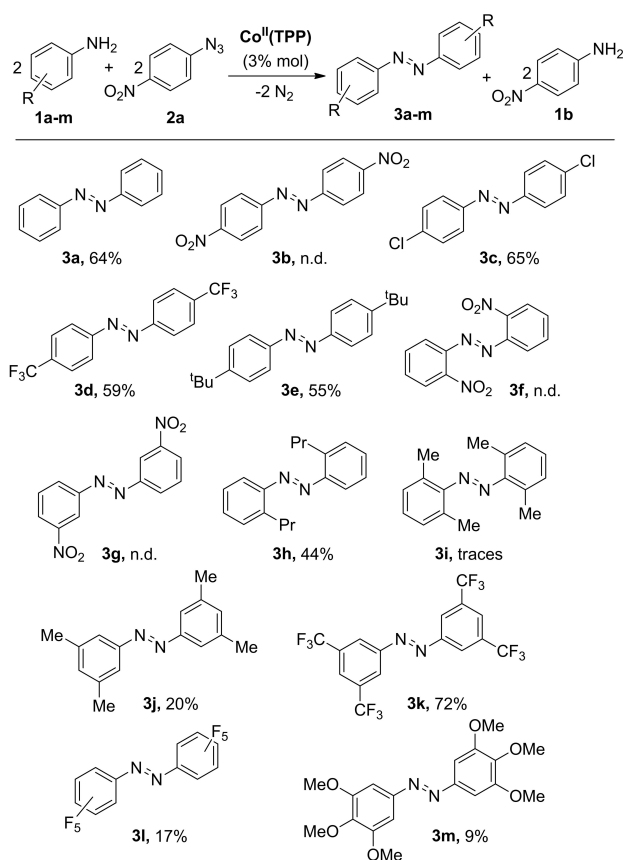
ratio of 1:1.5. First, the reactivity of different azides in assisting the  $\text{Co}^{\text{II}}(\text{TPP})$ -catalysed **1a** dehydrogenation was investigated moving from the simplest sodium azide ( $\text{NaN}_3$ ) to aryl azides bearing in *para* position either an EWG (electron withdrawing group) or EDG (electron donating group) substituent. As expected, the inorganic  $\text{NaN}_3$  was not activated by  $\text{Co}^{\text{II}}(\text{TPP})$  indicating that the aniline dehydrogenative coupling requires the assistance of organic azides. However, while 4-nitrophenyl azide **2a** resulted efficient for synthesising **3a**, the use of other aryl azides did not allow the reaction to proceed well. The desired compound **3a** was obtained in traces (8% yield) in the presence of 4-trifluoromethylphenyl azide (**2b**) and when 4-*tert*-butylphenyl azide (**2c**) or 3,5-dinitrophenyl azide (**2d**) were employed, no azide conversion was observed. These data indicated that the reaction performance was independent from the electronic characteristics of aryl azides and the reaction seems to be productive only in the presence of **2a**. Thus, the high capacity of 4-nitrophenyl azide **2a** in assisting the aniline dehydrogenation can be due to the presence of the nitro aromatic substituent, which is responsible for a higher stabilization of the radical cobalt imido intermediate by resonance with the nitro substituent in the aromatic *para* position.<sup>[51]</sup>

As a consequence, 4-nitrophenyl azide **2a** was employed to investigate the reactivity of differently substituted aromatic amines in the presence of  $\text{Co}^{\text{II}}(\text{TPP})$ . Reactions were performed under nitrogen atmosphere by refluxing the aromatic amine, **2a** and  $\text{Co}^{\text{II}}(\text{TPP})$  in dry benzene for 7 hours. In all the reactions a complete **2a** conversion was observed and 4-nitroaniline **1b** was found as by-product. All the isolated yields, calculated on a half of the initial aniline moles, are reported in Scheme 5.

As reported in Scheme 5 the presence of EWGs or EDGs groups at the *para* position of the aromatic amine did not affect the reaction productivity and azobenzenes **3a**, **3c**, **3d** and **3e** were always obtained in similar yields (65%–55% yield, Scheme 5). Surprisingly, all the nitro-substituted anilines (**1b**, **1f** and **1g**) resulted inactive, independently of the position where the  $\text{NO}_2$  substituent is placed on the aromatic ring. The high chemical stability of nitroanilines prevented their involvement in dehydrogenation processes and explains why 4-nitroaniline **1b** was always recovered unreacted at the end of the synthesis of all the diazocompounds listed in Scheme 5 (see below for a possible explanation).

Then, the steric effect was evaluated by studying the reactivity of anilines opportunely substituted in *ortho* and *meta* positions. Achieved data demonstrated that the steric hindrance in *ortho* positions strongly influenced the reaction productivity. In fact, the reaction yield decreased to 44% (product **3h**) by employing the *ortho*-propyl aniline **1h** as the starting reagent. A more pronounced effect was observed by using aniline substituted with methyl groups in both *ortho* positions (**1i**), which caused the downfall of the reaction yield and only traces of the desired product **3i** were detected. The efficiency of the synthesis of products **3j** and **3k**, deriving from *meta*-substituted aromatic amines, was strongly dependent on both electronic and steric factors. While employing 3,5-dimethyl aniline **1j** as substrate, the corresponding azobenzene **3j** was obtained in 20% yield, the replacement of methyl groups with





**Scheme 5.** Synthesis of azobenzenes **3 a–3 m** by the  $\text{Co}^{\text{II}}(\text{TPP})$ -catalysed dehydrogenative coupling of aromatic amines.

trifluoromethyl ones caused an increment of the reaction performance and the product **3 k** was obtained in the good 72% yield. These results suggested a stronger inductive effect when EWGs are placed in *meta* positions with respect to the presence of the same group ( $\text{CF}_3$ ) at the *para*-position (compound **3 d**). The prevalence of the electronic effect over the steric one was also observed by employing pentafluoroaniline **1 l** as starting reagent. Despite the presence of fluorine atoms at both *ortho* positions, which could create an unfavourable steric hindrance, the desired product **3 l** was formed in 17% yield thanks to the positive effect of EWGs. Finally, a very low yield was achieved in the synthesis of product **3 m** (9%) in which the three methoxy groups, beside generating a strong steric hindrance, have a well-known coordination ability<sup>[53–54]</sup> that can inhibit the activity of the cobalt catalyst.

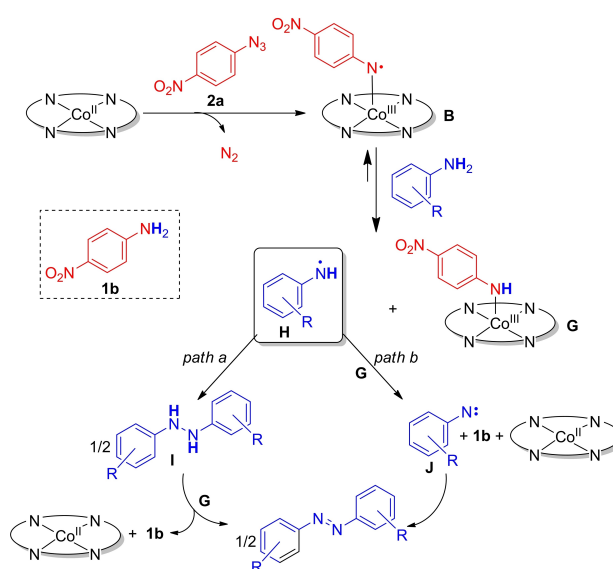
Unfortunately,  $\text{Co}^{\text{II}}(\text{TPP})$ /4-nitrophenyl azide combination was efficient only when substituted anilines were used as reagents and no reaction was observed by using aliphatic amines, such as *t*butylamine and triethylamine.

It should be noted that the purification of diazocompounds **3** reported in Scheme 5 allowed recovering 4-nitroaniline **1 b** in high yields (up to 85%) alongside traces of the azobenzene **3 b** when the reaction occurred in diazocompound yields lower than 44%. This is an important point for increasing the

procedure sustainability because the recovered **1 b** can be reconverted into 4-nitrophenyl azide **2 a** that can be reintroduced in the catalytic cycle. Therefore, in view of the importance of applying circular procedures, the so formed **1 b** could be used to restore the sacrificial oxidant reagent **2 a** azide, also using sustainable synthetic procedures such as flow chemistry technologies.<sup>[55]</sup>

Finally, considering the usual radical nature of  $\text{Co}^{\text{II}}(\text{TPP})$ -catalysed syntheses, we carried out the model reaction forming **3 a** under air conditions or in the presence of the radical trapping agent TEMPO (2,2,6,6-tetramethylpiperidinyloxy). While only a decrease of the reaction productivity was observed by performing the reaction under air (43% versus 64% yield of the reaction performed under nitrogen), the addition of TEMPO inhibited the reaction and the formation of **3 a** was not observed to support the probable occurrence of a radical process. To support the involvement of radical cobalt intermediates similar to **B** of Scheme 3, the model reaction between **1 a** and **2 a** was executed by replacing  $\text{Co}^{\text{II}}(\text{TPP})$  with  $\text{Ru}^{\text{II}}(\text{TPP})\text{CO}$ , which is not usually involved in radical reactions,<sup>[56]</sup> also in this case the desired azobenzene **3 a** was not formed. In addition, in order to propose a plausible reaction mechanism of the azobenzene formation catalysed by  $\text{Co}^{\text{II}}(\text{TPP})$ , a possible positive *trans*-effect of an axial aniline ligand was investigated. The model reaction between **1 a** and **2 a** was performed in the presence of a 30% mol of 4-nitroaniline **1 b** which, being never converted into corresponding azobenzene **3 b**, could only act as an axial ligand during the reaction. However, very similar catalytic performances were observed in the presence or in the absence of **1 b** (see Figure S2) to rule out a probable activating role of a coordinated amine in the azobenzene formation.

In view of the obtained results, a possible reaction mechanism for the  $\text{Co}^{\text{II}}(\text{TPP})$ -catalysed synthesis of azobenzenes by dehydrogenative coupling of anilines is proposed in Scheme 6. We suggest that the cobalt nitrene intermediate **B**,



**Scheme 6.** Proposed mechanism for  $\text{Co}^{\text{II}}(\text{TPP})$ -catalysed synthesis of azobenzenes by the dehydrogenative coupling of anilines.

generated by the reaction of **2a** with  $\text{Co}^{\text{II}}(\text{TPP})$ , can rapidly abstract a hydrogen atom from aniline to form the amido complex **G** and the radical species **H**. At this point, the so-formed intermediate **H** might undergo two different pathways. In *path a* (Scheme 6), intermediate **H** might form compound **I** by a radical N-N coupling with itself, and then the dehydrogenation of **I** (through consecutive HAT steps) by **G** yields the desired product **3a**, alongside **1b** and  $\text{Co}^{\text{II}}(\text{TPP})$ . On the other hand, in *path b* of Scheme 6, intermediate **H** may undergo a HAT process to the amido complex **G** forming **1b**,  $\text{Co}^{\text{II}}(\text{TPP})$  and the free nitrene **J** that can couple with itself to produce the final azobenzene **3a**. As shown in Scheme 6, the mentioned HAT processes always produce 4-nitroaniline **1b** as the stoichiometric by-product deriving from the employed azide **2a**.

The proposed mechanism can also give a plausible explanation of the lack of reactivity that was observed when nitro-substituted anilines were used as starting materials. The well-known stability of nitro-containing radical species can be responsible for the formation of a long-lived **H** intermediate which, instead of producing the desired azo-derivatives (by paths a or b), can be involved in a reversible reaction reforming **B**.

## Conclusion

In conclusion, we reported the activity of  $\text{Co}^{\text{II}}(\text{TPP})$  and 4-nitrophenyl azide **2a** in promoting the synthesis of azobenzenes by the dehydrogenative coupling of anilines. Experimental data revealed that **2a** acted as an oxidative agent that was transformed into the corresponding 4-nitroaniline **1b** by a HAT process leading to the dehydrogenative coupling of anilines. The good activity of **2a** can be ascribed to the electronic nature of the 4-nitrophenyl azide that favours the formation of stable radical cobalt nitrene intermediate. The study of the substrate scope evidenced the ability of  $\text{Co}^{\text{II}}(\text{TPP})$  to catalyse the synthesis of differently substituted azobenzenes in yields up to 72%. Both electron-rich and electron poor anilines were reactive as well as reagents showing a moderate steric hindrance around the amino group. Even if 4-nitrophenyl azide was used as a sacrificial reagent of the reaction, the corresponding reduced product **1b** could be recovered and easily reconverted into the starting azide to improve the sustainability and circularity of the methodology.

These results represent the starting point to develop an alternative approach for the synthesis of azobenzenes by using low-cost cobalt porphyrin catalysts, commercially available anilines and azide **2a** as the oxidant species that can be regenerated at the end of the catalytic process, even in flow conditions.

## Experimental Section

**General methods:** Unless otherwise specified, all the reactions were carried out under nitrogen atmosphere by employing standard Schlenk techniques and magnetic stirring. Benzene was distilled over sodium and benzophenone and kept under nitrogen. *Meso*-

tetraphenylporphyrin  $\text{TPPH}_2$  was synthesised by following Lindsey's procedure.<sup>[57]</sup>  $\text{Co}^{\text{II}}(\text{TPP})$ ,<sup>[45]</sup>  $\text{Ru}^{\text{II}}(\text{TPP})\text{CO}$ ,<sup>[53]</sup> 4-nitrophenyl azide **2a**,<sup>[54]</sup> 4-trifluoromethylphenyl azide **2b**,<sup>[58]</sup> 4-tert-butylphenyl azide **2c**,<sup>[54]</sup> and 3,5-dinitrophenyl azide **2d**<sup>[59]</sup> were synthesised by following previously reported procedures. All the other starting materials were commercial products and used as received. NMR spectra were recorded at room temperature on a Bruker Avance 400-DRX spectrometer operating at 400 MHz for  $^1\text{H}$ , at 101 MHz for  $^{13}\text{C}$  and at 376 MHz for  $^{19}\text{F}$ . Chemical shifts (ppm) are reported relative to TMS.  $^1\text{H}$  NMR signals of the compounds described in the following were attributed by 2D NMR techniques. Assignments of the resonances in  $^{13}\text{C}$  NMR were made by using the APT pulse sequence, HSQC and HMBC techniques. Infrared spectra were recorded on a Varian Scimitar FTS 1000 spectrophotometer. UV/Vis spectra were recorded on an Agilent 8453E instrument. Mass spectra and elemental analyses were recorded in the analytical laboratories of Milan University.

### General catalytic procedure for the synthesis of azobenzenes:

**Method A:** In a typical run,  $\text{Co}^{\text{II}}(\text{TPP})$  (8.20 mg, 0.012 mmol) was dissolved in 10.0 mL of distilled benzene under nitrogen and the opportune aniline (0.406 mmol) and 4-nitrophenyl azide **2a** (0.100 g, 0.608 mmol) were added. To assess the initial azide concentration by IR spectroscopy, an aliquot of the reaction mixture (0.150  $\mu\text{L}$ ) was taken from the solution before starting the reaction. Then, the reaction mixture was refluxed using a preheated oil bath (100 °C) for 7 hours. The azide conversion was monitored by IR spectroscopy, observing the disappearance of the signal of **2a** at 2122  $\text{cm}^{-1}$ . At the end of the reaction, the mixture was cooled to room temperature and the solvent evaporated under reduced pressure. The reaction crude was purified by flash chromatography ( $\text{SiO}_2$ ) (see SI for details). The isolated product was dried under vacuum and characterized (see SI for analytical data). **Method B:** The reaction was performed as described above under air instead than under nitrogen.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Azobenzene · Amines · Azides ·  $\text{Co}(\text{TPP})$  · Dehydrogenative coupling

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