



Short communication

# Highly organic phase soluble polyisobutylene-bound cobalt phthalocyanines as recyclable catalysts for nitroarene reduction



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## ABSTRACT

A cobalt phthalocyanine (CoMPc) containing covalently linked polyisobutylene (PIB) groups as phase anchors that is both highly soluble in nonpolar organic solvents and phase selectively soluble in a liquid/liquid separation step is shown to be an effective recyclable homogeneous catalyst for nitroarene reduction in a semi-thermomorphic system. Electron-donating and electron-withdrawing substituents in the nitroarene are tolerated in this aniline synthesis and the catalyst is recyclable up to 10 cycles with little leaching and no detectable loss in reactivity after 10 cycles.

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## 1. Introduction

Aromatic amines are important organic compounds due to their use in the syntheses of dyes [1], pesticides [2], pharmaceuticals [3,4], and polymers [5]. Reduction of nitro compounds is one of most widely used routes to this class of compounds. Classically reduction of nitroarenes to form anilines uses hydrogenation with Pd/C [6]. More recently, there has been an increase in interest in homogeneous catalysts that use more earth abundant metals [7–9], that are recyclable [10,11], or that use alternatives to hydrogen as the penultimate reductant [12–15].

Metallophthalocyanines (MPcs) were originally developed as pigments [16] but are now also used as photosensitizers, photodynamic therapy agents, and in molecular electronics [17,18]. MPcs can also be used as catalysts. However, their use in homogeneous catalysis is less common than is the case for porphyrins [19–21]. MPcs are less commonly used as homogeneous catalysts because MPcs have solubility that is in the range of  $10^{-5}$  to  $10^{-7}$  M in organic solvents [22], a limitation that renders their use as homogeneous catalysts problematic. Our success in synthesis of PIB-bound MPcs that dissolve in hydrocarbon polymers and the activity of several MPcs as heterogeneous catalysts for nitroarene reduction [23,24] suggested to us that PIB-modified MPcs could be recyclable homogeneous catalysts and that this hypothesis could be tested by examining their use in nitroarene hydrogenation. Our hypothesis about the solubility and activity of PIB-modified MPcs has been proven correct and we have shown here that a PIB-bound

CoMPc catalyst can be used as a homogeneous catalyst for nitroarene reduction and that this catalyst can be quantitatively separated from products and recycled as discussed below.

## 2. Experimental

## 2.1. General procedures

Vinyl terminated PIB (Glissopal 1000) was provided by BASF [25]. Other reagents and solvents were purchased from commercial sources and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Inova 300 or 500 MHz NMR spectrometers. IR spectra were obtained using a Shimadzu Affinity-1S IR spectrometer. UV–Visible spectra were recorded on a Shimadzu UV-2600 spectrophotometer. A NexION 300D Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine the Co metal content in **6**.

2.2. Synthesis of **2–6**

The syntheses of **2–6** are detailed in the supplemental information along with  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data.

2.3. General procedure for nitroarene reduction using hydrazine hydrate with **6** as a homogeneous catalyst

A biphasic mixture of 1 mmol of nitroarene and 0.4 mol% of catalyst **6** was prepared using 5 mL of heptane and 5 mL of anhydrous ethylene glycol in a Schlenk tube. Then 5 equivalent of hydrazine hydrate were added and the biphasic solution was stirred at 110 °C under a  $\text{N}_2$

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atmosphere for 24 h. While the original biphasic mixture never became a single phase during this process, the ethylene glycol phase visually appeared to increase in volume due to some heptane dissolution. In addition, some of the PIB-bound MPc complex visually was present in that phase. After the reaction was complete, the biphasic mixture was cooled down to ambient temperature. The polar ethylene glycol-rich phase was separated from the heptane solution of the MPc and the product was isolated by chromatography from this polar phase. The catalyst in the heptane phase was recycled for further experiments after addition of fresh reagents and fresh ethylene glycol.

**4-Chloroaniline.**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.10 (2 H, d,  $J = 8.8$  Hz), 6.60 (2 H, d,  $J = 8.8$  Hz), 3.50–3.80 (2 H, br);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.90, 129.08, 123.12, 116.20.

**4-Bromoaniline.**  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.23 (2 H, d,  $J = 8.4$  Hz), 6.56 (2 H, d,  $J = 8.4$  Hz), 3.60–3.70 (2 H, br);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.37, 131.97, 116.67, 110.15.

**4-Aminobenzoic acid.**  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ ),  $\delta$  7.59 (2 H, d,  $J = 8.5$  Hz), 6.54 (2 H, d,  $J = 8.5$  Hz), 5.70–5.84 (2 H, br);  $^{13}\text{C NMR}$  (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  168.42, 153.64, 131.88, 117.41, 113.34.

**4-Aminotoluene.**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.02 (2 H, d,  $J = 8.5$  Hz), 6.65 (2 H, d,  $J = 8.5$  Hz), 3.50–3.60 (2 H, br), 2.30 (3 H, s);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.74, 129.63, 127.59, 115.13, 20.34.

**4-tert-Butylaniline.**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.19 (2 H, d,  $J = 9.0$  Hz), 6.65 (2 H, d,  $J = 9.0$  Hz), 3.50–3.60 (2 H, br), 1.28 (9 H, s);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.70, 141.32, 125.97, 114.87, 33.83, 31.46.

**4-Aminophenol.**  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ ),  $\delta$  8.50–8.55 (1 H, br), 6.46 (2 H, d,  $J = 9.0$  Hz), 6.42 (2 H, d,  $J = 9.0$  Hz);  $^{13}\text{C NMR}$  (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  148.79, 140.89, 116.19, 116.111.

**1,4-Diaminobenzene.**  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ ),  $\delta$  6.57 (4 H, s), 3.25–3.40 (4 H, br);  $^{13}\text{C NMR}$  (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  138.56, 116.70.

**1-Aminonaphthalene.**  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.82–7.89 (2 H, m), 7.48–7.55 (2 H, m), 7.34–7.41 (2 H, m), 6.79–6.82 (1 H, m), 4.10–4.20 (2 H, br);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.00, 134.28, 128.44, 126.26, 125.75, 124.74, 123.53, 120.72, 118.83, 109.57.

### 3. Results and discussions

In our initial studies, we first repeated others' work that used an insoluble CoMPc as a heterogeneous catalyst in ethylene glycol to reduce 4-chloronitrobenzene using hydrazine hydrate as the reducing agent [26]. However, extension of this work using the PIB-supported CoMPc **1** (Fig. 1) [27] in this same solvent or in mixtures of polar solvents and heptane failed or led to incomplete reduction of 4-chloronitroarene after 24 h at 80 °C (cf. Table S1). We addressed this problem by preparing a CoMPc with PIB groups connected to the phthalocyanine core by electron-withdrawing groups (Scheme 1). Starting with a thiol-ene reaction of vinyl-terminated PIB [28,29] with thioacetic acid, PIB

thioacetate **2** was prepared. Hydrolysis of **2** formed the thiol PIB-SH **3** [30] that was allowed to react with 4-nitrophthalonitrile in a nucleophilic aromatic substitution reaction to form the PIB-thiophthalonitrile **4** [31]. Oxidation of **4** with *m*-chloroperbenzoic acid formed the PIB<sub>1240</sub> sulfonyl phthalonitrile **5** [32]. Tetracyclization of **5** in the presence of  $\text{CoCl}_2$  then formed the desired PIB<sub>1240</sub>-bound MPc **6** [33]. The phthalocyanine **6** so formed is a mixture of species with PIB in different orientations in the four quadrants of the phthalocyanines. As a result, analysis affords a nondescript  $^1\text{H NMR}$  spectrum. However, **6** was characterized by inductively coupled mass spectroscopy (ICP-MS) and UV-Visible spectroscopy. ICP-MS analysis of a 1 g sample of **6** showed that it contained 0.0087 g of cobalt. This corresponds to an  $M_n$  of 6770 Da that is higher than expected based on a  $^1\text{H NMR}$  spectroscopic analysis of the  $M_n$  of **5**. This analysis of **5** compared the integrated intensity of a known amount of 1,1,2,2-tetrachloroethane internal standard to the integration for the signals for the three aryl protons of **5** at 8.34, 8.29, and 8.07  $\delta$  and the two protons in the  $-\text{CH}_2\text{SO}_2$  doublet of doublets of **5** at 3.13 and 2.99  $\delta$  of the PIB group and showed that **5** had a d.p. of 22 (a  $M_n$  of 1430 Da). This degree of polymerization is higher than that of the starting thioacetate **2** which by a  $^1\text{H NMR}$  analysis had PIB groups with a d.p. of 20. The difference between **2** and **5** reflects fractionation of the PIB-bound species during the synthesis and purification steps in Scheme 1. The purification steps leading to isolation of **6** either formed **6** with PIB groups with d.p.s. of 26 or formed some **6b** that did not contain Co. If we conservatively assume no further fractionation occurred in forming **6** from **5**, we calculate that **6** is ca. 87% metalated. Complex **6** has a  $\lambda_{\text{max}}$  at 669 nm that is slightly higher than that reported previously for **1** ( $\lambda_{\text{max}} = 675$  nm) (Fig. S1). This peak corresponds to the Q band of the MPc. The shift of the Q band of **6** at 675 to the 669 nm band of **1** is consistent with the introduction of an electron-withdrawing sulfonyl substituent.

Gratifyingly, the conversion of 4-chloronitrobenzene to 4-chloroaniline was 100% based on  $^1\text{H NMR}$  spectroscopy when complex **6** was used as catalyst in the presence of 5 equivalents of hydrazine hydrate instead of **1** (Scheme 2). In these experiments, the reduction was carried out over a period of 24 h at 110 °C using a 1/1 (vol/vol) mixture of a  $4.0 \times 10^{-4}$  M heptane solution of **6** and ethylene glycol. Under these reactions conditions, the solution never becomes monophasic but it is rather partially thermomorphic – the volume of the denser phase visually increases and some of **6** dissolves in this phase based on a slight color change of the ethylene glycol rich phase. Fully thermomorphic systems including a 3/1 heptane/ethanol mixture, heptane/glyme (1/1, vol/vol) and heptane/*n*-propanol (1/1, vol/vol) were also examined but reductions in these solvent mixtures only led to 83–95% conversion of the nitroarene to aniline. Other thermomorphic systems using *N,N*-dimethylformamide, benzyl alcohol, and glycerol with heptane were even less successful. Control experiments without any catalyst or with a PIB-bound metal free phthalocyanine formed no product aniline. Thus, in subsequent studies of the generality and recyclability of **6** in reductions of nitroarenes at 110 °C, **6** was selected as the catalyst, 5 equivalents of hydrazine hydrate was used as the reducing agent, and 1/1 (vol/vol) mixture of heptane and ethylene glycol was used as the solvent mixture.

The generality of this reduction and recyclability of these catalysts was tested with varied aryl substituents on nitroarenes as shown in Table 1. 4-Chloro- and 4-bromonitrobenzene gave high isolated yields and complete conversion of the starting nitroarene. Yields of 4-methyl- and 4-*tert*-butylaniline were slightly lower in cycle 1, possibly due to the solubility of these aniline products in the heptane phase. Nitroarenes with electron donating substituents like hydroxy and amino substituents also were quantitatively converted to aniline products affording comparable isolated yields. Reduction of 1-nitronaphthalene was also successful. However, this reduction product is a known carcinogen so repetitive cycles were not performed. Consistent yields cycle-to-cycle were however observed for all the nitroarenes studied, reflecting the high thermal and chemical stability associated

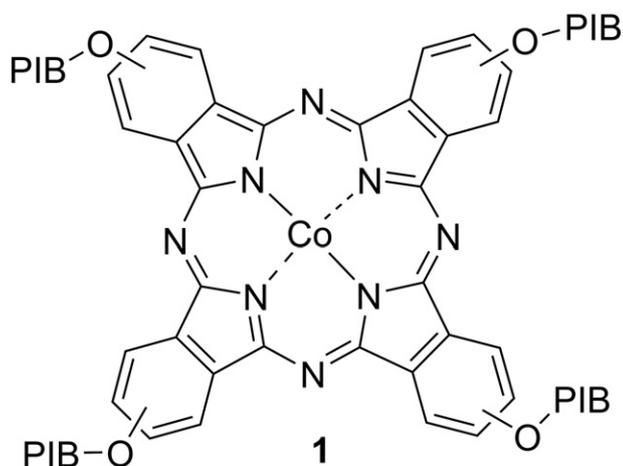


Fig. 1. A PIB-bound CoMPc complex that is soluble at 10 wt% in heptane or  $\text{CH}_2\text{Cl}_2$  at 25 °C.

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