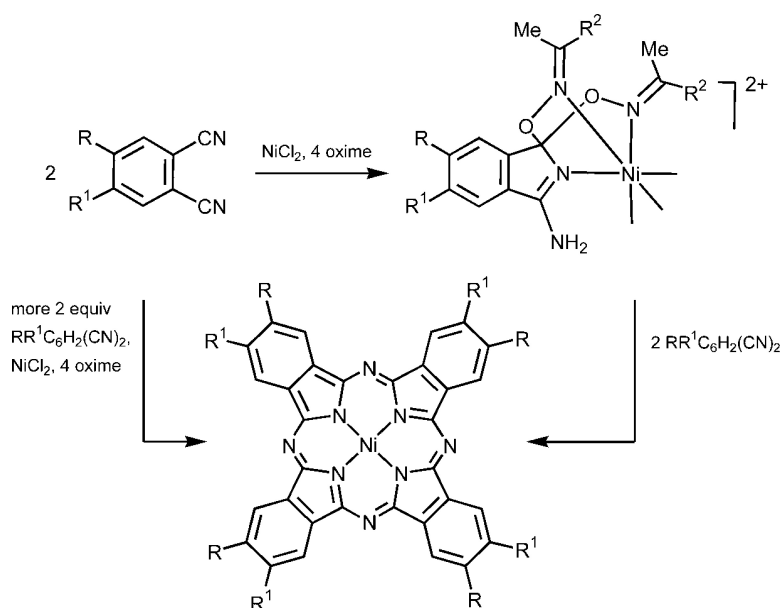


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## An Efficient Synthesis of Phthalocyanines Based on an Unprecedented Double-Addition of Oximes to Phthalonitriles

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Phthalocyanines (Pcs) and their complexes are compounds of high industrial importance with a variety of applications,<sup>1–3</sup> especially in modern technologies. Surprisingly, the approaches<sup>2,4</sup> for their syntheses have not changed substantially since the early studies by Linstead.<sup>5</sup> The most important method is based on the template reaction between a source of metal (metal, salt, alkoxide, or metal salt/organic amine) and phthalonitrile (PN), C<sub>6</sub>H<sub>4</sub>-1,2-(CN)<sub>2</sub>, upon reflux in C3–C8 alcohols at 100–200 °C or in 2-(*N,N*-dimethylamino)ethanol at 135 °C.<sup>2,4</sup> In particular, NiPcs can be synthesized from PNs in the presence of Ni<sup>2+</sup> salt and an amine (e.g., quinoline,<sup>6</sup> DMF,<sup>7</sup> (*N,N*-dimethylamino)ethanol,<sup>8</sup> 1,8-diazabicyclo[5.4.0]undec-7-ene,<sup>8</sup> and urea<sup>9</sup>), hydroquinone,<sup>10</sup> or alkali.<sup>11</sup> The majority of methods are performed at elevated temperatures and are both energy- and time-consuming; additional activation by microwave<sup>12</sup> or UV irradiation<sup>13</sup> has been achieved but requires special instrumentation. There are only a few reports on the synthesis of metalla-Pcs under rather mild conditions: (i) treatment with metal salts and hexamethyldisilazane in DMF;<sup>14</sup> (ii) condensation of PNs to the corresponding nonmetalated Pcs in the presence of solid NaOMe in dry THF followed by their reaction with metal sources;<sup>15</sup> and (iii) condensation of PNs with lithium 2-(*N,N*-dimethylamino)ethoxide in 2-(*N,N*-dimethylamino)ethanol.<sup>16</sup> All these methods, despite their advantages, involve moisture-sensitive reagents and dry solvents.

We report herein a novel reaction which gives an efficient method for the preparation of Pcs and their complexes from PN or its derivatives. The method utilizes low-cost reagents of hydrolytic stability, high simplicity, and easy accessibility, i.e., oximes, and proceeds via an unprecedented double addition of oximes to the nitrile group.

When NiCl<sub>2</sub>·2H<sub>2</sub>O<sup>17</sup> (1 equiv) is refluxed with an oxime MeR<sup>2</sup>C=NOH (4 equiv, R<sup>2</sup> = Me, Et) and a PN RR<sup>1</sup>C<sub>6</sub>H<sub>2</sub>(CN)<sub>2</sub> (2 equiv, R/R<sup>1</sup> = H/H, Cl/Cl, H/NO<sub>2</sub>) in acetone for 1 d, an unusual complex (**1**<sup>2+</sup>–**4**<sup>2+</sup>, route A, Scheme 1; the relative position of R/R<sup>1</sup> is shown conditionally) is released as its dichloride salt (80–70% isolated yield), a slightly grayish (almost colorless) solid. The crystal structures of [1]Cl<sub>2</sub>–[3]Cl<sub>2</sub> (Figure 1 for [3]Cl<sub>2</sub>; for [1]Cl<sub>2</sub> and [2]Cl<sub>2</sub> see Supporting Information) revealed that two ketoximes were added to one nitrile group of the PN, forming a chelated moiety resembling one in oxime-based clathrochelates.<sup>18</sup>

Despite the wealth of chemistry associated with the metal-mediated addition of a variety of nucleophiles to nitriles,<sup>19–21</sup> the observed addition of two nucleophiles to one nitrile group is the first example of that kind; previously only 1:1-type additions were

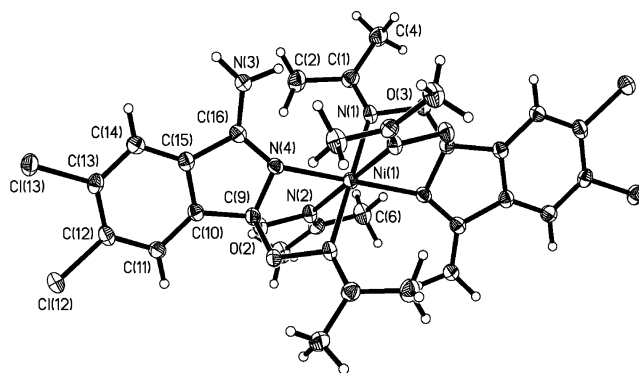
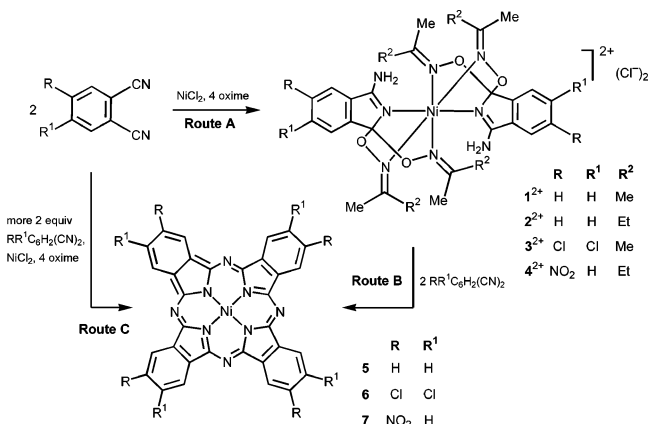


Figure 1. Thermal ellipsoid plot of [3]<sup>2+</sup>.

### Scheme 1

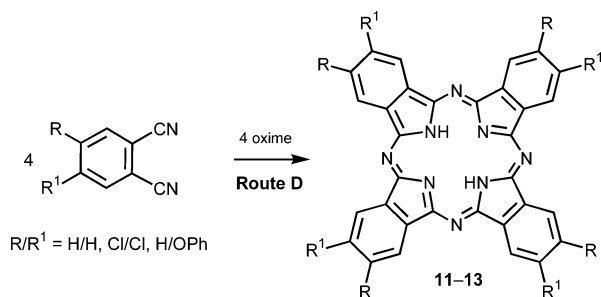


observed. Moreover, this novel type of addition is all the more so surprising because (i) it has recently been reported<sup>22</sup> that PN couples with a thioether dioxime at a Ni(II) center to form an imine-appended macrocycle upon conventional<sup>19,22</sup> addition of one oxime OH to one C≡N of PN; (ii) we observed that ketoximes at Ni(II) react with RCN to form (imidoylamidine)Ni(II) complexes.<sup>17</sup>

The complexes [1]Cl<sub>2</sub>·2H<sub>2</sub>O and [2]Cl<sub>2</sub>·2H<sub>2</sub>O, on heating in the solid state, undergo an intense blue coloration by converting into NiPc **5** (30–20% isolated yield upon vacuum sublimation) following heating at 200 °C for 8 h. The formation of the phthalocyanine complexes **5**, **6**, and **7** (derived from [1]Cl<sub>2</sub>·2H<sub>2</sub>O or [2]Cl<sub>2</sub>·2H<sub>2</sub>O; [3]Cl<sub>2</sub>·2H<sub>2</sub>O; or [4]Cl<sub>2</sub>·2H<sub>2</sub>O, correspondingly; the relative position of R/R<sup>1</sup> for **7** is shown conditionally) is much more efficient when (i) [1]Cl<sub>2</sub>·2H<sub>2</sub>O–[4]Cl<sub>2</sub>·2H<sub>2</sub>O is heated with 2 equiv of the corresponding PN RR<sup>1</sup>C<sub>6</sub>H<sub>2</sub>(CN)<sub>2</sub> (200 °C, 8 h, yields 60–50%) (route B, Scheme 1) or the reaction is performed in refluxing methanol (ca. 65 °C, 24 h, yield ca. 60%) or (ii) NiCl<sub>2</sub>·2H<sub>2</sub>O is

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Scheme 2



reacted with 4 equiv of oxime and 4 equiv of **PN** (100 °C, 8 h, yield ca. 75%) (route C, Scheme 1). These routes illustrate a novel approach to metal phthalocyanines involving oximes. Route B in methanol is the one that operates under the mildest conditions (65 °C), but route C is even more attractive since it provides a single-pot method, proceeds still under rather mild conditions, and, as the others (routes A and B), does not require dry reagents and solvents.

We also succeeded in conducting the oxime-mediated cyclotetramerization of **PNs** ( $\text{C}_6\text{H}_4\text{-1,2-(CN)}_2$ ,  $\text{C}_6\text{H}_2\text{-1,2-(CN)}_2\text{-4,5-(Cl)}_2$ , or  $\text{C}_6\text{H}_3\text{-1,2-(CN)}_2\text{-4-OPh}$ ) in the absence of any metal source to achieve metal-free Pcs **11** and **12** (route D, Scheme 2). The reaction proceeds under conditions similar to those in route C, with isolated yields of ca. 65–60% (lower by ca. 10–15% relative to NiPcs whose formation is promoted by the metal **PN** activating and template effects).

The cyclotetramerization of **PN** to give metal-free Pc requires both a two-electron reduction and the addition of two protons ( $+2e^-/+2\text{H}^+$  process). Thus, reducing reagents and  $\text{H}^+$  donors as hydroquinone and 1,2,3,6-tetrahydropyridine are effective when the reaction is performed in the melt (ca. 275 °C).<sup>2</sup> The application for the synthesis of Pcs, achieved in this work for the first time, of the so-called “simple” oximes, which combine reducing and  $\text{H}^+$ -donor properties (on one hand) with the broad commercial availability, low cost, and low toxicity or nontoxicity<sup>23</sup> (on the other hand), provides further benefits.

Our preliminary data indicate that Pcs of other metals, e.g., Cu(II), Zn(II), and Cd(II), can be obtained by the described method, which can also be extended to the syntheses of *unsymmetrical* (i) metal Pcs and (ii) metal-free Pcs. Synthesis (i) is accomplished via route B by reacting complexes  $[\mathbf{1}]^{2+}$ – $[\mathbf{4}]^{2+}$  with **PNs**  $\text{R}^3\text{R}^4\text{C}_6\text{H}_2\text{(CN)}_2$  that are different from the **PNs** used for their preparation, e.g., reaction of  $[\mathbf{1}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$  or  $[\mathbf{2}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$  (1 equiv) with 4,5-dichlorophthalonitrile (2 equiv) to achieve **8**, reaction of  $[\mathbf{2}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$  (1 equiv) with 4-nitrophthalonitrile (2 equiv) or  $[\mathbf{4}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$  (1 equiv) with phthalonitrile (2 equiv) to give **9**, reaction of  $[\mathbf{4}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$  (1 equiv) with 4-methylphthalonitrile (2 equiv) to afford **10** (in these products, two of the  $\text{R/R}^1$  pairs in **5** or **7** have been replaced by  $\text{R}^3/\text{R}^4$ ). This synthesis can afford a mixture of unsymmetrical metal Pcs with symmetrical ones since  $[\mathbf{1}]^{2+}$ – $[\mathbf{4}]^{2+}$  convert into the corresponding symmetrical metal Pcs on heating

(see above). Synthesis (ii) proceeds via route D by starting with an unsymmetrical substituted **PN**, e.g., the preparation of **13** from  $\text{C}_6\text{H}_3\text{-1,2-(CN)}_2\text{-4-OPh}$ .

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**Supporting Information Available:** Experimental details and analytical data; X-ray crystallographic data, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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