

Convenient synthesis of phthalocyanines with disilazanes under mild conditions

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Dedicated to Professor S. Swaminathan on his 80th birthday
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Abstract

We have previously reported convenient synthesis of metallo- and metal-free phthalocyanines under mild conditions by heating phthalimides, phthalic anhydrides, and phthalonitriles with hexamethyldisilazane. This paper deals with a convenient method for the preparation of Cu- and Zn-phthalocyanines as well as metal-free phthalocyanines by using disilazane derivatives with high boiling points.

Keywords: Metallophthalocyanine, metal-free phthalocyanine, hexamethyldisilazane, tetramethyldiphenyldisilazane, dimethyltetraphenyldisilazane

Introduction

A great deal of attention has been paid to optical and electronic properties of chemically and thermally stable phthalocyanines for developing new functionalized materials,¹ e.g. optical information recording media, organic semiconductors for laser beam printers,² agents for photodynamic therapy,³ NO_x^{4,5} and halogen⁵ gas and pH sensors.⁶ Generally, metallo-phthalocyanines⁷ as well as metal-free phthalocyanines⁸ have been synthesized from phthalonitrile derivatives under basic conditions. Urea is used in the production of phthalocyanines from less expensive starting materials such as phthalic acids, phthalic anhydrides and phthalimides but the reaction needs severe conditions which often cause the formation of undesirable by-products.⁹

Recently, we have reported that hexamethyldisilazane¹⁰ (HMDS) is an excellent reagent for the construction of the phthalocyanine framework from phthalimides, phthalic anhydrides, and phthalonitriles.¹¹ Various metallophthalocyanines can be prepared under mild conditions on

heating with HMDS. HMDS also realized the first synthesis of metal-free phthalocyanines from phthalimides and phthalic anhydrides. HMDS is a nitrogen source and it also accelerates dehydration in the formation of the phthalocyanine framework. The reaction using phthalimides or phthalic anhydrides as starting materials can be efficiently performed at 150 °C; however, the reaction should be carried out in a sealed vessel because of the low boiling point of HMDS. We now report a successful use of disilazane derivatives having high boiling points in place of HMDS in the preparation of phthalocyanines on heating without using a sealed vessel.

Results and Discussion

The reaction of phthalimides with various disilazane derivatives was examined. The results are shown in Table 1. As previously reported,^{11b} HMDS **1a** gives Cu-phthalocyanine **Cu-2** in 71% yield by heating phthalimide with 0.25 equiv of Cu(OTf)₂ and DMF at 150 °C for 10 h (entry 1). The boiling point of HMDS is 126 °C and bis(trimethylsilyl) ether, which is one of the products formed during the reaction, has even lower boiling point. The reaction should be performed in a sealed vessel to maintain the reaction temperature at 150 °C. Thus, the reaction with disilazanes having higher boiling points was examined. The reaction was carried out as in the case using HMDS except that it was done under atmospheric pressure. A mixture of phthalimide, disilazane, Cu(OTf)₂, and DMF in a molar ratio of 1.0:4.0:0.25:1.0 was heated at 150 °C for 10 h. The 8- and 5-membered cyclic derivatives **1b** and **1c** afforded **Cu-2** in 35 and 42% yields, respectively (entries 2 and 3). The boiling point of the corresponding disilyl ethers, which are supposed to be one of the products formed during the formation of the Pc framework, are also shown for reference in Table 1. Both 1,1,3,3-tetramethyl-1,3-diphenyldisilazane **1d** and 1,3-dimethyl-1,1,3,3-diphenyldisilazane **1e** having high boiling points showed high yields of **Cu-2** after heating at 150 °C for 10 h under atmospheric pressure (entries 4 and 5). Since disilyl ethers corresponding to **1d** and **1e** also have boiling points higher than 150 °C, the reaction temperature could be maintained at 150 °C.

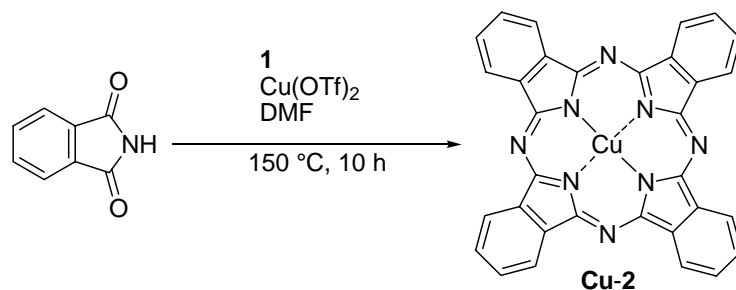
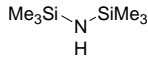
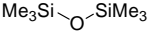
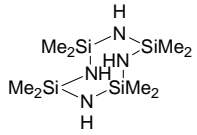
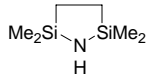
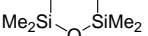
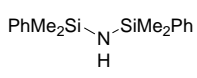
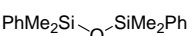
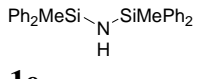
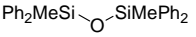


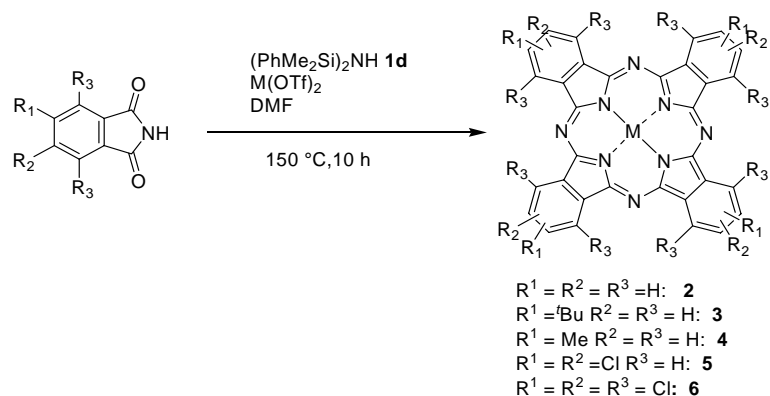
Table 1. Formation of Cu-phthalocyanine **Cu-2** on treatment of phthalimide with various disilazanes, Cu(OTf)₂, and DMF

Entry	Disilazane	bp	Reaction Apparatus ^a	Yield of Cu-2 (%)	Disilyl Ethers bp
1	 1a	126 °C	A	71 ^b	 99 °C
2	 1b	225 °C	B	35	
3	 1c	92 °C/ 185 mmHg	B	42	 124 °C
4	 1d	96 °C/ 0.1 mmHg	B	76	 96 °C/ 0.1 mmHg
5	 1e	218 °C/ 1.5 mmHg	B	75	 155 °C/ 13 mmHg

^a The reaction was performed at 150 °C for 10 h in a sealed vessel (A), or under atmospheric pressure (B).

^b Ref. 11b.

The preparation of various phthalocyanines was next examined using the disilazane **1d** (Table 2). Zn-Phthalocyanine **Zn-2** was obtained in the reaction of phthalimide with Zn(OTf)₂ (entry 1). Cu-Phthalocyanines were prepared by heating various phthalimides with disilazane **1d** and Cu(OTf)₂ under the reaction conditions similar to the above. Thus, Cu-phthalocyanines **Cu-3-6** having a variety of substituents were produced in good yields from 4-*tert*-butyl, 4-methyl, 4,5-dichloro-, and 3,4,5,6-tetrachlorophthalimides (entries 2-5). Phthalocyanine derivatives **Cu-3** and **Cu-4** were obtained as a mixture of regioisomers which were not separated. The reaction of phthalimides with **1d** in the absence of a metal salt gave **H₂-2** in 40% yield (entry 6). Addition of (NH₄)₂SO₄ improved the yield (entry 7). The role of (NH₄)₂SO₄ is not clear, but it would activate the disilazane and/or the phthalimide to promote the formation of the phthalocyanine framework. When Cu(OTf)₂ and Zn(OTf)₂ are used, it is not necessary to use (NH₄)₂SO₄ because these triflates and/or TfOH liberated during the reaction would activate the disilazane and phthalimide.^{11b,c} Peripherally substituted metal-free phthalocyanines **H₂-3** and **H₂-4** could also be prepared (entries 8 and 9).

**Table 2.** Reaction of **1** with disilazane **1d**

Entry	Phthalimide			M(OTf) ₂	Additive	Product	Yield (%)
	R ₁	R ₂	R ₃				
1	H	H	H	Zu(OTf) ₂	-	Zu-2	38
2	t-Bu	H	H	Cu(OTf) ₂	-	Cu-3	81
3	Me	H	H	Cu(OTf) ₂	-	Cu-4	65
4	Cl	Cl	H	Cu(OTf) ₂	-	Cu-5	27
5	Cl	Cl	Cl	Cu(OTf) ₂	-	Cu-6	11
6	H	H	H	-	-	H₂-2	40
7	H	H	H	-	(NH ₄) ₂ SO ₄	H₂-2	61
8	t-Bu	H	H	-	(NH ₄) ₂ SO ₄	H₂-3	15
9	Me	H	H	-	(NH ₄) ₂ SO ₄	H₂-4	59

In summary, unsubstituted or peripherally substituted Cu- and Zn-phthalocyanines and metal-free phthalocyanines were conveniently prepared from phthalimides on treatment with disilazane derivatives having high boiling points.

Experimental Section

Preparation of Cu-phthalocyanine Cu-2 with 1,1,3,3-tetramethyl-1,3-diphenyldisilazane.

Phthalimide (100 mg, 0.68 mmol), copper(II) triflate (69 mg, 0.17 mmol), 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (790 μL , 777 mg, 2.7 mmol), and DMF (50 μL , 0.68 mmol) were mixed in a round-bottom flask equipped with a reflux condenser. The mixture was heated at 150 °C under argon. A dark blue solid immediately appeared. After being heated for 10 h, the mixture was cooled and filtered. The solid was washed with methanol and then dissolved in concentrated H₂SO₄ (5 mL). The solution was poured into water (100 mL). The resulting blue precipitates were filtered and washed successively with dilute H₂SO₄, water, and methanol. The solid was

further purified by extraction with methanol by Soxhlet's extractor to give 75 mg (76%) of **Cu-2** as a blue solid.

Preparation of Cu-phthalocyanine Cu-2 with 1,3-dimethyl-1,1,3,3-tetraphenyldisilazane. A mixture of phthalimide (100 mg, 0.68 mmol), copper(II) triflate (69 mg, 0.17 mmol), 1,3-dimethyl-1,1,3,3-tetraphenyldisilazane (1.0 g, 2.7 mmol), and DMF (50 μ L, 0.68 mmol) was heated at 150 °C for 10 h. Workup and purification as above gave 74 mg (75%) of **Cu-2** as a blue solid.

Preparation of Cu-phthalocyanine Cu-2 with 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane. A mixture of phthalimide (100 mg, 0.68 mmol), copper(II) triflate (69 mg, 0.17 mmol), 2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane (1.0 mL, 867 mg, 2.7 mmol), and DMF (50 μ L, 0.68 mmol) was heated at 150 °C for 10 h. Workup and purification as above gave 41 mg (42%) of **Cu-2** as a blue solid.

Preparation of Cu-phthalocyanine Cu-2 with 2,2,4,4,6,6,8,8-octamethylcyclotetrasilazane. A mixture of phthalimide (100 mg, 0.68 mmol), copper(II) triflate (69 mg, 0.17 mmol), 1,1,3,3,5,5,7,7-octamethylcyclotetrasilazane (795 mg, 2.7 mmol), and DMF (50 μ L, 0.68 mmol) was heated at 150 °C for 10 h to give 34 mg (35%) of **Cu-2** as a blue solid.

Preparation of Zn-phthalocyanine Zn-2 with 1,1,3,3-tetramethyl-1,3-diphenyldisilazane. A mixture of phthalimide (100 mg, 0.68 mmol), zinc triflate (69 mg, 0.17 mmol), 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (790 μ L, 777 mg, 2.7 mmol), and DMF (50 μ L, 0.68 mmol) was heated at 150 °C for 10 h to give 37 mg (38%) of **Zn-2** as a blue solid.

Preparation of tetra-tert-butyl-Cu-phthalocyanine Cu-3. A mixture of 4-tert-butylphthalimide (140 mg, 0.69 mmol), copper(II) triflate (69 mg, 0.17 mmol), 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (800 μ L, 787 mg, 2.8 mmol), and DMF (50 μ L, 0.68 mmol) was heated at 150 °C for 10 h. A dark purple solid immediately appeared. After being heated for 10 h, the mixture was cooled and filtered. The solid was washed with methanol and then dissolved in concentrated H₂SO₄ (5 mL). The solution was poured into water (100 mL). The resulting blue precipitates were filtered and washed successively with dilute H₂SO₄, water, and methanol. The solid was further purified by silica gel column chromatography (benzene/THF=99/1) to give 112 mg (81%) of **Cu-3** as a blue solid.

Preparation of tetramethyl-Cu-phthalocyanine Cu-4. A mixture of 4-methylphthalimide (110 mg, 0.68 mmol), copper(II) triflate (69 mg, 0.17 mmol), 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (790 μ L, 787 mg, 2.8 mmol), and DMF (50 μ L, 0.68 mmol) was heated at 150 °C for 10 h. Workup and purification as shown in the preparation of Cu-2 with 1,1,3,3-tetramethyl-1,3-diphenyldisilazane gave 70 mg (65%) of **Cu-4** as a blue solid.

Preparation of octachloro-Cu-phthalocyanine Cu-5. A mixture of 4,5-dichlorophthalimide (145 mg, 0.67 mmol), copper(II) triflate (68 mg, 0.17 mmol), 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (780 μ L, 767 mg, 2.7 mmol), and DMF (50 μ L, 0.68 mmol) was heated at 150 °C for 10 h. Usual workup and purification gave 39 mg (27%) of **Cu-5** as a blue solid.

Preparation of hexadecachloro-Cu-phthalocyanine Cu-6. A mixture of 3,4,5,6-tetrachlorophthalimide (195 mg, 0.68 mmol), copper(II) triflate (69 mg, 0.17 mmol), 1,1,3,3-

tetramethyl-1,3-diphenyldisilazane (790 μL , 777 mg, 2.7 mmol), and DMF (50 μL , 0.68 mmol) was heated at 150 $^{\circ}\text{C}$ for 10 h. Usual workup and purification gave 21 mg (11%) of **Cu-6** as a blue solid.

Preparation of H₂-phthalocyanine H₂-2. (A) A mixture of phthalimide (100 mg, 0.68 mmol), 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (790 μL , 777 mg, 2.7 mmol), and DMF (50 μL , 0.68 mmol) was heated at 150 $^{\circ}\text{C}$ for 10 h to give 39 mg (40%) of **H₂-2** as a blue solid. (B) The same procedure as in A except the addition of ammonium sulfate (9 mg, 0.07 mmol) gave 59 mg (61%) of **H₂-2**.

Preparation of tetra-tert-butyl-H₂-phthalocyanine H₂-3. A mixture of 4-tert-butylphthalimide (140 mg, 0.69 mmol), ammonium sulfate (9 mg, 0.07 mmol), 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (800 μL , 787 mg, 2.8 mmol), and DMF (50 μL , 0.68 mmol) was added. Then, the mixture was heated at 150 $^{\circ}\text{C}$ for 10 h. Workup and purification by silica gel column chromatography as above gave 19 mg (15%) of **H₂-3** as a blue solid.

Preparation of tetramethyl-H₂-phthalocyanine H₂-4. A mixture of 4-methylphthalimide (110 mg, 0.68 mmol), ammonium sulfate (9 mg, 0.07 mmol), 1,1,3,3-tetramethyl-1,3-diphenyldisilazane (790 μL , 787 mg, 2.8 mmol), and DMF (50 μL , 0.68 mmol) was heated at 150 $^{\circ}\text{C}$ for 10 h. Usual workup and purification as above gave 57 mg (59%) of **H₂-4** as a blue solid.

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