Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Peripherally Substituted Phthalocyanines

M. J. Chen[a]; J. W. Rathke[a]; S. Sinclair[a]; D. W. Slocum[b]
[a] Argonne National Laboratory, Argonne, Illinois [b] Department of Chemistry, Western Kentucky University, Bowling Green, Kentucky

To cite this Article Chen, M. J. , Rathke, J. W. , Sinclair, S. and Slocum, D. W.(1990) 'Peripherally Substituted Phthalocyanines', Journal of Macromolecular Science, Part A, 27: 9, 1415 — 1430
To link to this Article: DOI: 10.1080/00222339009349702
URL: http://dx.doi.org/10.1080/00222339009349702

J. MACROMOL. SCI.—CHEM., A27(9–11), pp. 1415–1430 (1990)

PERIPHERALLY SUBSTITUTED PHTHALOCYANINES

M. J. CHEN,* J. W. RATHKE, S. SINCLAIR, and D. W. SLOCUM*,†

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, Illinois 60439

ABSTRACT

Peripherally substituted phthalocyanine (Pc) systems render more accessible the desirable properties of the Pc system, i.e., high thermal and oxidative stability as well as significant complexity ability of transition metals. After brief examination of existing synthetic methods, two new routes to substitution of the peripheral protons of the Pc system are described: (1) directed metalation of the Pc system itself followed by derivatization, and (2) directed metalation of phthalonitrile followed by derivatization and Pc formation. Each of these methods is further distinguished by providing exclusively substitution at the α-positions of the Pc nucleus. Several of the compounds have been isolated and characterized using the techniques of HPLC; ^{1}H, ^{13}C, and ^{29}Si NMR; and mass spectroscopy. These multisubstituted Pc systems are much more soluble in organic solvents than is the parent system. Such soluble macromolecules are of interest to the energy research community because of a variety of possible applications, notably the preparation of sensors, electrode coatings, catalysts, and soluble oxygen transports.

†Current address: Department of Chemistry, Western Kentucky University, Bowling Green, Kentucky 42101.

INTRODUCTION

Phthalocyanine (Pc) was first discovered by Braun and Tcherniac shortly after the beginning of the 20th century [1]; the copper and iron derivatives were subsequently isolated and identified in the 1920s [2]. Each of the discoveries was an accident. It remained for Linstead and his coworkers to ascertain the structure of Pc and subsequently of several of the metal-containing Pc's in the early 1930s [3].

For many years variously substituted phthalocyanines were synthesized for use in the dye and colorant fields with commercial applications ranging from textiles to ballpoint pen inks. In the last 25 years, increasing investigation of magnetic, catalytic, redox, and photochemical properties of metal-containing Pc's has resulted in new applications (or potential ones) outside of the dye and colorant fields. For these applications the solubility, or the lack thereof, of the various Pc's is of significant importance [4].

Our primary interest in Pc's is in their potential applications in homogeneous catalysis. The development of this field has been greatly impeded by the low solubility, usually little more than 10^{-5} M, of simple Pc's in common organic solvents. The similarity between the structures of Pc's and porphyrins (Fig. 1) and the extensive use of the latter and related systems in oxygen transport (hemoglobin) and in catalyzing other vital biological reactions (chlorophyll, cytochrome c, vitamin B_{12}, etc.) suggest that Pc's may also be active catalysts for such reactions. In addition, the higher thermal stability of Pc's can lead to facilitation of catalytic reactions at higher temperatures at which most other bio-mimicking homogeneous catalysts are not stable.

The Pc system's insolubility stems from its ability to form stacked oligomers possessing considerable molecular weights. To increase the solubility of Pc systems significantly, two approaches are possible, one being to incorporate solubilizing substituents, the other being to alter the molecule in such a manner that its stacking ability is reduced. Certain substituents, positioned appropriately, can dramatically increase the solubility of Pc systems by utilizing a combination of these two effects.

These considerations prompted a review of the synthetic methods which can lead to peripherally substituted Pc's. The peripheral aromatic protons of the Pc nucleus [5] can be substituted to provide a variety of Pc derivatives via two distinct routes, namely, by substitution of the aromatic protons of the phthalo precursors and by direct substitution of the Pc

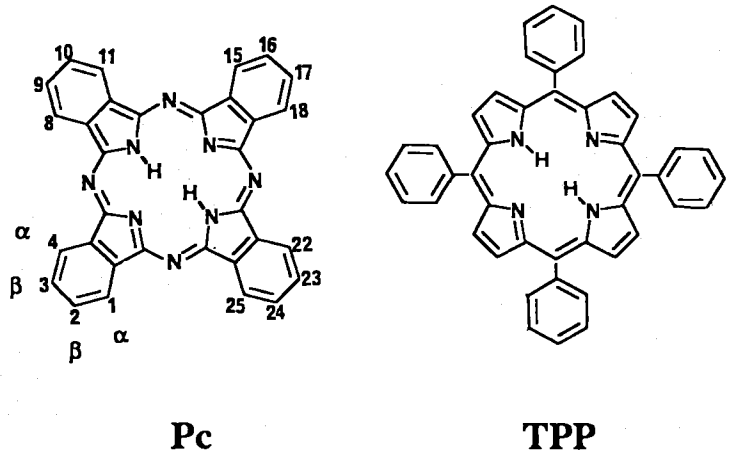


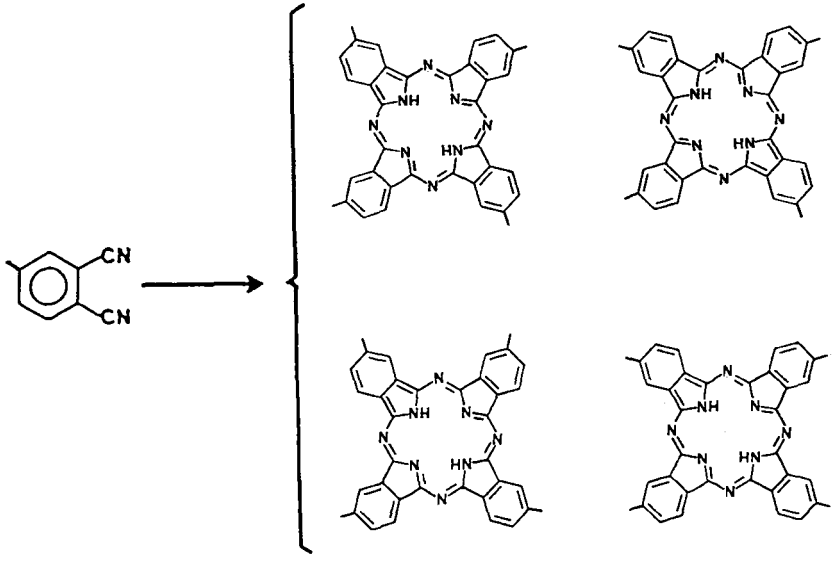
FIG. 1. Structures of phthalocyanine (Pc) and tetraphenylporphyrin (TPP). The systematic numbering of the peripheral aromatic protons is shown; protons numbered 1, 4, 8, 11, 15, 18, 22, and 25 are designated "α," and the remaining peripheral protons are designated "β."

nucleus. For the purpose of increasing the solubility of various Pc's, substitution of the protons closer to the isoindole nitrogen, those designated "α," are preferred over those designated "β" since bulky α-position substituents will be more efficient in hindering agglomeration. The systematic numbering of the Pc nucleus as well as the designation of the α- and β-positions are shown in Fig. 1 [6].

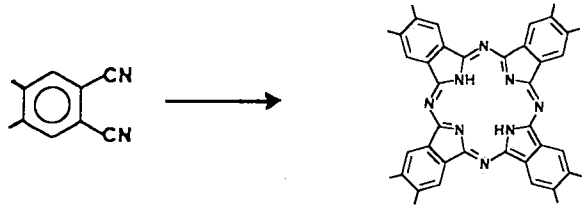
Direct electrophilic substitution of the peripheral aromatic protons of Pc has been accomplished in a number of cases. Pc behaves in effect as a deactivated nitrogen-containing heterocycle, the best known example of which is the pyridine molecule. Thus electrophilic substitutions must be effected under much more vigorous conditions than those for benzene. Nonselective electrophilic sulfonation, chlorosulfonation, chlorination, and bromination of Pc have been accomplished. Two to four sulfonyl groups can be introduced per molecule, depending on the sulfonating conditions. Chlorine and bromine can be introduced into the copper Pc system in much greater numbers, perhalo derivatives in fact having been prepared [7]. In the few examples where some regioselectivity has been observed, β-substitution has been preferred. It is difficult to ascertain whether this preference is attributable to a steric or an electronic effect.

Many articles have been published describing Pc's prepared by the tetramerization of a phthalo precursor. Scheme 1 illustrates the formation of the mixture of four tetra-β-substituted Pc's which results from the tetramerization of a 4-substituted phthalonitrile derivative, while Scheme 2 shows the octa-β-substituted Pc afforded by tetramerization of a 4,5-disubstituted phthalo precursor. These substituents range from simple nitro, alkoxy, and related groups [8] to cyclic examples such as those containing crown ether substituents [9] as well as more elaborated peripherally dimerized systems [10]. Few examples of Pc's bearing only α-substituents are known, and fewer yet are known where all the α-protons have been substituted. This can be attributed to the difficulty in preparing a 3-substituted phthalo derivative and the even greater difficulty in preparation of a 3,6-disubstituted phthalo derivative.

As noted earlier, substitution at the α-position is preferred to that at the β-positions to solubilize various Pc's. In this paper we discuss the new methods of synthesis that we have employed to prepare Pc's substituted only at the α-positions. As our investigation has progressed, both a new procedure for direct substitution of the Pc nucleus and a new procedure



SCHEME 1.



SCHEME 2.

for preparation of 3-substituted and 3,6-disubstituted phthalo precursors have been developed.

RESULTS AND DISCUSSION

Heteroatom facilitated *ortho*-lithiation reactions (directed metalations) have been used extensively to introduce substituents into aromatic systems *ortho* to the heteroatom-containing substituent [11]. Directed metalation reactions have been utilized in this investigation to synthesize several α-substituted Pc's. These new Pc's possess solubilities orders of magnitude greater than their unsubstituted analogs.

Direct Trimethylsilylation of H_2Pc

The *in-situ* reaction of lithium diisopropylamide (LDA) or lithium 2,2,6,6-tetramethylpiperidide (LiTMP) with PcH_2 in the presence of excess chlorotrimethylsilane results in a product solution which after hydrolysis affords a mixture of $(Me_3Si)_xPcH_2$ where $x = 2, 3, 4$ [12]. Table 1 summarizes a study of the effect of variation of temperature and reactant ratios for this reaction. Typical HPLC chromatograms are shown in Fig. 2 along with their respective assignments. A better than 90% selectivity toward the tetrasubstituted Pc can be obtained by using a very high (16 : 1) ratio of reagents to Pc.

The absence of any $(Me_3Si)_xPcH_2$ with $x > 4$ requires an explanation. This limiting number of four peripheral substituents suggests that substitution has taken place only at α-positions and that, of the eight α-protons, only one of the two in each of the four "outer" pockets between two adjacent isoindole units can be replaced by the bulky trimethylsilyl group. Four isomeric tetrasubstituted Pc's are predicted by this analysis.

TABLE 1. Reaction Conditions in the Formation of $(Me_3Si)_xPc$

Reaction[a] temperature, °C	Total reaction time, h	Equivalents of Me_3SiCl	Equivalents of LiTMP	g product (x = 2, 3, 4) / g Pc reactant
−78	1.3	8	8	0
−78, RT	64	8	8	0.700
−78, RT	1	32	16	0.738
0[b]	1.6	32	16	0.471
−78, −20	2.5	28	14	0.583
−25	1.5	35	17	0.585

[a]When two temperatures are given, the first is the temperature for the addition of LiTMP to the H_2Pc/Me_3SiCl mixture and the second is the final reaction temperature.

[b]PcH_2 added to the $LiTMP/Me_3SiCl$ solution.

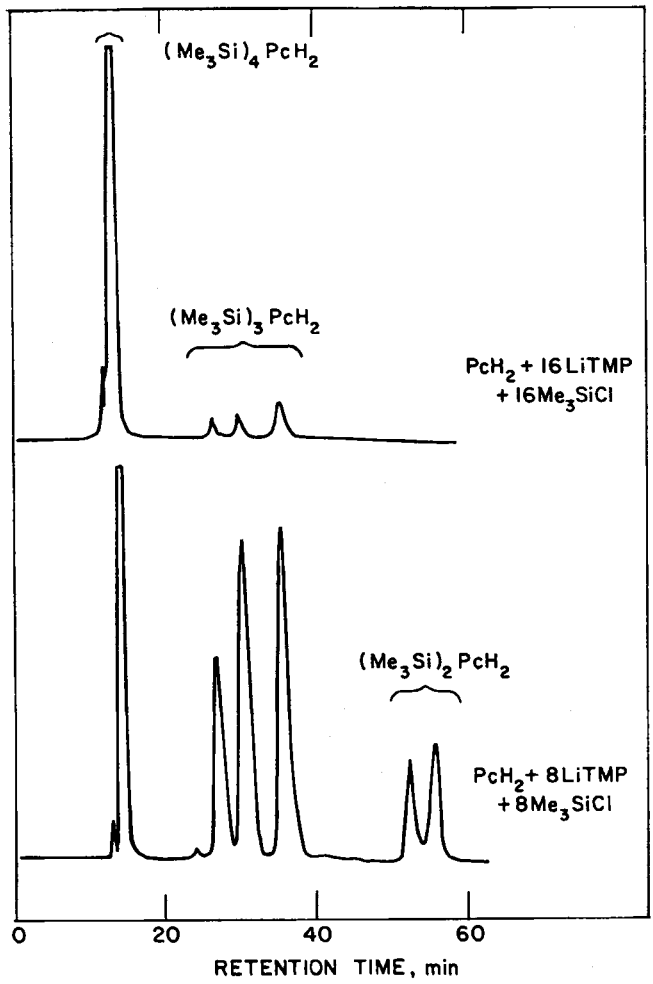


FIG. 2. Typical HPLC traces of product mixtures of $(Me_3Si)_xPcH_2$ from an Alltech econosphere NH_2 column (250 mm × 4.6 mm) with *n*-heptane (0.5 mL/min) as the liquid phase.

The structures of these four isomers along with their respective statistical populations are illustrated in Fig. 3.

That there are indeed four tetrasubstituted isomers is demonstrated by the following observations. Although only one HPLC peak was observed for $(Me_3Si)_4PcH_2$, the $^{29}Si\{^1H\}$ spectrum of this fraction clearly illustrates the isomeric make-up of this mixture. Careful consideration of the silicon

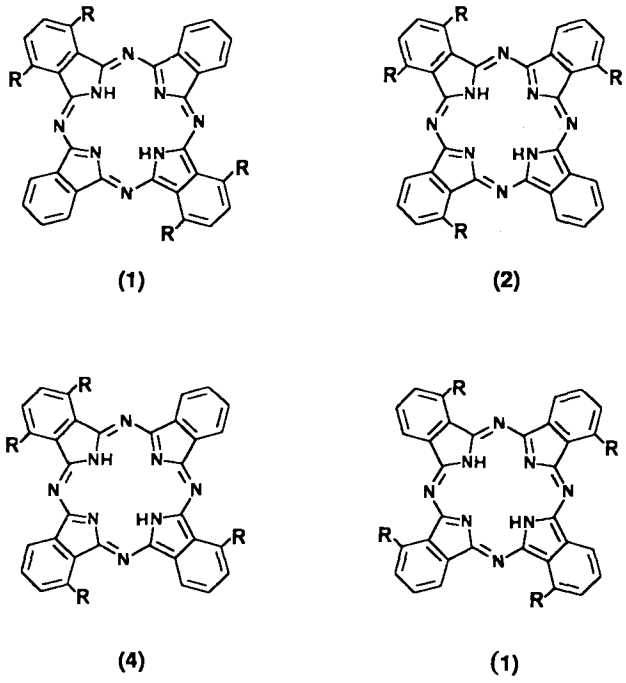


FIG. 3. The statistical distribution of the tetrakis(trimethylsilyl) Pc's given the selection rules outlined in the text. The predicted relative abundances of each are indicated by the numbers in parentheses.

environments of the four isomers reveals that there are eight distinct signals of equal intensity that can be anticipated for this spectrum. Consistent with this hypothesis, the spectrum obtained (Fig. 4) exhibits eight resonances, the intensities of which vary within a factor of 3. The ^{1}H-NMR spectrum, which exhibits three multiplets at δ8.10–8.30 (β-H), δ8.35–8.53 (β-H), and δ9.40–9.70 ppm (α-H) in the ratio 1 : 1 : 1 is also consistent with substitution of half of the α-H's with Me_3Si— groups.

Further support for the α-substitution nature of this reaction is afforded by an NMR study of the Pc isolated after LiTMP-catalyzed D-exchange with 2,2,6,6-tetramethylpiperidine-d^1. Of the two multiplets for the aromatic protons exhibited by $PcLi_2$, δ9.33–9.41 ppm representing the α-protons and δ7.98–8.05 ppm representing the β-protons, the former is significantly attenuated while the latter becomes a singlet due to the absence of α-proton coupling.

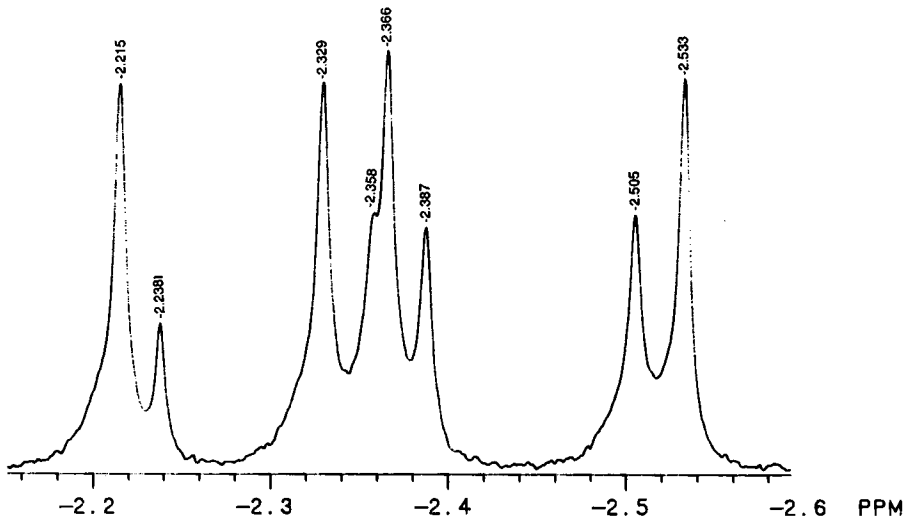
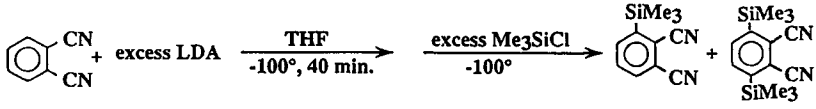


FIG. 4. $^{29}Si\{^1H\}$-NMR spectrum (59.7 MHz; TMS δ = 0) of $(SiMe_3)_4PcH_2$ in $CDCl_3$.

Synthesis of α-Substituted Pc's from 3-Substituted Phthalo Precursors

As indicated above, substituted phthalo precursors can be tetramerized to afford substituted Pc's. If a 3-substituted phthalonitrile is utilized, four possible tetra-α-substituted Pc's can be obtained. However, if the bulky trimethylsilyl group is the substituent and the one-bulky-group-per-outer-pocket rule applies, only one of these is possible.

To accomplish such a tetramerization, a method to prepare 3-substituted phthalo precursors is required. A procedure toward this end has been devised and is presently undergoing investigation. Directed metalation of phthalonitrile and treatment with chlorotrimethylsilane yields a mixture of both 3-trimethylsilyl and 3,6,-bis(trimethylsilyl) derivatives, depending on the ratio of the reactants [13] (Scheme 3). However, *in-situ* trapping such as was outlined for direct metalation of Pc is not necessary (it may

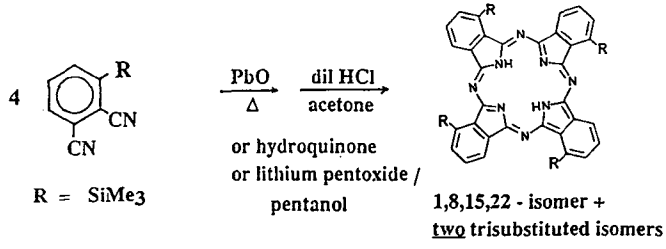


SCHEME 3.

not be necessary for Pc either). Both derivatives have been prepared by a conventional two-step metalation/derivatization sequence as well as by the *in-situ* trapping method. Apparently the monolithiated and dilithiated phthalonitriles are sufficiently stable at $-100°C$ that derivatization can be effected after a build-up of the desired lithio intermediate. This opens up the possibility of synthesizing a variety of α-substituted Pc's incorporating a variety of substituents, a possibility which remains to be exploited.

Initial efforts to prepare metal-containing Pc's from these precursors have begun. The 3,6-bis(trimethylsilyl)phthalonitrile affords no Pc formation under a variety of tetramerization conditions, and it affords only very low yields of trimethylsilyl-derivatized Pc's upon co-tetramerization with phthalonitrile. The main product from these experiments is Pc itself. Apparently the one-trimethylsilyl-group-per-outer-pocket rule applies in the failure to attain an all α-octatrimethylsilyl Pc. The co-tetramerization experiments reveal the fact that phthalonitrile reacts with itself much faster than it reacts with a phthalonitrile substituted in both α-positions.

On a more positive note, tetramerization of 3-trimethylsilylphthalonitrile has been effected under a variety of conditions (Scheme 4). The most intriguing of the tetramerization techniques is the template cyclization around lead oxide. Lead(II) has an ionic radius of approximately 1.75 Å, whereas the cavity in Pc has a radius of 1.35 Å, i.e., the Pc cavity is a bit too small to provide a good fit for Pb(II) [14]. Therefore, use of PbO in a Pc template synthesis affords an isolable metal complex which readily gives the free base Pc upon mild hydrolysis. Moreover, this method of tetramerization of the three attempted provides the greatest selectivity toward isolation of the tetrasubstituted Pc. In all three reactions there was obtained relatively modest amounts of a mixture of the two possible tris products. This observation, as well as others, indicates that detrimethylsi-



SCHEME 4.

lylation takes place at elevated temperatures. When this sample template cyclization is run with $CoCl_2$, a 44% yield of the product $(Me_3Si)_4Pc$-Co(II) is obtained with very little product from detrimethylsilylation being observed. This synthesis is not as general since the Co(II) ion cannot be removed.

The structure of the tetramerization product is unique in that it is, to our knowledge, the first tetrasubstituted Pc that can be specifically named. Consideration of the one-trimethylsilyl-group-per-outer-pocket rule predicts that the tetrasubstituted product of this cyclization will possess the specific structure 1,8,15,22-tetrakistrimethylsilyl Pc. A mass spectrum of the material exhibited an M-1 ion at 801.7. Conclusive proof of the substitution pattern of the *all*-α-trimethylsilyl groups is revealed by the ^{1}H-NMR spectrum. Three specific proton absorptions can be seen (Fig. 5) with the low field doublet being assigned to the remaining α-proton and the triplet being assigned to the β-proton in the middle. The compound gives a single ^{29}Si resonance at δ2.366 ppm which corresponds precisely with one of the resonances exhibited by the mixture of tetrasubstituted isomers (Fig. 4).

While this work was in progress, two communications appeared describing a new method of specifically preparing octa-substituted Pc's with the substituents all in the α-position [15]. This method involves three principal steps: (1) bis metalation of furan, followed by alkylation; (2) a

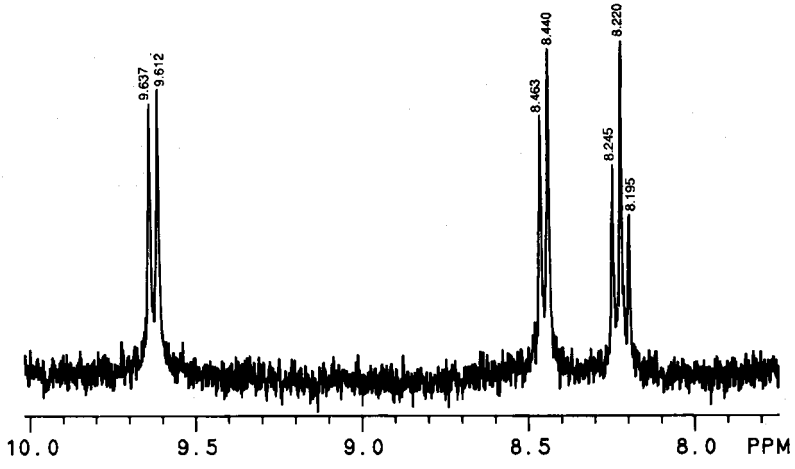


FIG. 5. ^{1}H-NMR spectrum of the aromatic region of 1,8,15,22-$(Me_3Si)_4PcH_2$ in $CDCl_3$.

Diels-Alder reaction; and (3) aromatization. The resulting 3,6-bisalkylated phthalonitrile can be obtained in only modest yield due primarily to low conversions encountered in Step (1).

Our studies, along with this novel technique described by Cook and coworkers [15], demonstrate that several new avenues of Pc synthesis have been opened up which utilize metalation and directed metalation procedures. Moreover, these new avenues provide exclusive α-substitution patterns and provide Pc complexes of greatly increased solubility in organic solvents.

EXPERIMENTAL

Preparation of 3,6-Bis(trimethylsilyl)phthalonitrile

To a stirred solution of 17.7 g (165 mmol) lithium diisopropylamide (LDA) in dry THF (500 mL) at $-100°C$ (bath temperature) under argon was added dropwise a solution of 10.0 g (78 mmol) 1,2-dicyanobenzene in dry THF (125 mL). After 40 min at $-100°C$, 21.6 mL (170 mmol) chlorotrimethylsilane was added. The reaction mixture was allowed to come slowly to room temperature before the solvent was removed with a rotary evaporator. The mixture was extracted with methylene chloride and the extract was washed with aqueous NaCl to remove salt by-products. The crude product was purified by column chromatography on a silica gel column with CH_2Cl_2 as the eluent, followed by recrystallization from petroleum ether to give 7.4 g (35%) of the product, mp 120–122°C.

Analysis. Calculated for $C_{14}H_{20}N_2Si_2$: C, 61.71; H, 7.40; N, 10.28; Si, 20.62%. Found: C, 61.93; H, 7.11; N, 10.03; Si, 21.09% ^1H NMR ($CDCl_3$ ppm): δ7.8 (s, 2H), 0.5 (s, 18H); ^{13}C NMR (CS_2, ppm): δ146.7 (C—Si), 136.9 (unsubstituted ring C), 121.8 (C—CN), 116.2 (CN), −1.5 (CH_3).

Preparation of 3-Trimethylsilylphthalonitrile

A solution of 90 g (0.70 mol) phthalonitrile (not completely dissolved) and 75 mL (0.59 mol) chlorotrimethylsilane in 150 mL THF was prepared in a 2-L three-neck flask equipped with an addition funnel and a mechanical stirrer. A solution of 0.195 *M* LiTMP was prepared by the reaction of 45 mL of 2,2,6,6-tetramethylpiperidine (TMP) and 105 mL of 2.5 *M* *n*-BuLi in hexane followed by addition of 1.2 L THF. The dropwise addi-

tion of the LiTMP solution was carried out at room temperature under an argon atmosphere. After the addition was completed, a few milliliters H_2O was added to quench the reaction. The solvent was removed by rotary evaporation.

Most of the unreacted phthalonitrile was removed by recrystallization in 600 mL toluene. The filtrate was rotary-evaporated and the residue was recrystallized in 150 mL of 9 : 1 heptane/toluene to remove more of the remaining phthalonitrile. The filtrate was then purified by chromatography on a basic alumina column with a 4 : 1 heptane/CH_2Cl_2 eluent. The crude product was further purified by recrystallization from petroleum ether to give 31 g (20%) of the product, mp 54–56°C [16].

Analysis. Calculated for $C_{11}H_{12}N_2Si$: C, 65.95; H, 6.04; N, 13.98; Si, 14.02%. Found: C, 65.60; H, 6.17; N, 13.90; Si, 13.01% ^{1}H NMR ($CDCl_3$, ppm): δ7.84, dd, 1H, $J_{5,6}$ = 7.5 cps, $J_{4,6}$ = 1.4 cps; δ7.78, dd, 1H, $J_{5,4}$ = 7.8 cps, $J_{6,4}$ = 1.4 cps; δ7.67, dd, 1H; δ0.47, s, 9H.

Preparation of 1,8,15,22-(Me_3Si)$_4$PcCo(II)

A solution of 1.014 g (5.06 mmol) 3-trimethylsilylphthalonitrile and 0.164 g (1.26 mmol) $CoCl_2$ in 2.0 mL ethylene glycol was refluxed for 3 h under N_2. After the solution had cooled, water was added and the product extracted with CH_2Cl_2. The CH_2Cl_2 extracted was dried over anhydrous $MgSO_4$ followed by rotary evaporation of the solvent. The crude product was chromatographed on a column made up of activated basic alumina, using as eluent first 25% CH_2Cl_2/heptane followed by CH_2Cl_2. Removal of the solvent afforded 480 mg (44%) of the product which was further purified by recrystallization from ethanol.

Analysis. Calculated for $C_{44}H_{48}N_8Si_4Co$: C, 61.44; H, 5.63; N, 13.03; Si, 13.06; Co, 6.85%. Found: C, 60.52; H, 5.73; N, 13.30, Si, 13.06; Co, 6.35%. ^{1}H NMR ($CDCl_3$, ppm): δ4.06 (s, 36H, CH_3), 10.93 (s, 4H, β-H), 11.15 (s, 4H, central β-H), 16.99 (s, 4H, α-H).

Preparation of Trimethylsilylated Phthalocyanines by *in-situ* Trapping of Lithiated Phthalocyanines

A solution of 0.530 g (1.03 mmol) H_2Pc and 1.1 mL (8.67 mmol) chlorotrimethylsilane in 20 mL dry THF was cooled in a dry ice/acetone bath. To this was added dropwise a solution of LiTMP, prepared from 3.1 mL of 2.5 *M* *n*-BuLi in hexane and 1.4 mL (8.29 mmol) TMP in 35 mL

THF. Upon completion of the addition, the solution was allowed to warm to room temperature and the solvent was removed by rotary evaporation. The solid residue was extracted with CH_2Cl_2 and the combined extracts were acidified with dilute HCl. After the layers were separated, the CH_2Cl_2 solution was dried and concentrated. The crude product mixture was chromatographed on a basic alumina column first with CCl_4 and then with $CHCl_3$ as eluents. Three fractions in the order $x = 4$, 3, and 2 were collected. After rotary evaporation of each of the fractions, the residues were sublimed at 320°C to afford $(Me_3Si)_xPcH_2$ in yields of 13, 18, and 3%, respectively, for $x = 4$, 3, and 2. Analyses for these compounds are recorded in Ref. 12.

ACKNOWLEDGMENTS

This research was supported by the Office of Chemical Sciences, Division of Basic Energy Sciences, U.S. Department of Energy. We thank Professor J. Halpern for helpful discussion and Carol M. Fendrick, Randy A. Watson, Kevin S. Kinter, and Joe R. Bernard for assistance with the research. Special thanks are due Mrs. Miriam Weiss for her labors with this manuscript.

REFERENCES

[1] A. Braun and J. Tcherniac, *Ann. Ber., 40*, 2709 (1907).

[2] (a) H. De Diesbach and E. Von der Weid, *Helv. Chim. Acta, 10*, 886 (1927). (b) A. G. Dandridge, H. A. Drescher, and J. Thomas (to Scottish Dyes Ltd.), British Patent 322,169 (November 18, 1929).

[3] (a) R. P. Linstead, *Br. Assoc. Adv. Sci. Rep.*, p. 465 (1933). (b) C. E. Dent, R. P. Linstead, and A. R. Lowe, *J. Chem. Soc.*, p. 1033 (1934) and preceding papers.

[4] (a) F. H. Moser and A. L. Thomas, *The Phthalocyanines*, Vols. I and II, CRC Press, Boca Raton, Florida, 1983. (b) L. J. Boucher, in *Coordination Chemistry of Macrocyclic Compounds* (G. A. Melson, ed.), Plenum, New York, 1979, p. 461. (c) A. B. P. Lever, *Pure Appl. Chem., 58*, 1467 (1986).

[5] The *peripheral* aromatic protons of the Pc nucleus are those numbered 1, 2, 3, 4, 8, 9, 10, 11, 15, 16, 17, 18, 22, 23, 24, and 25, i.e., *all* the protons on the perimeter of the molecule. This designation is

consistent with the terminology used in Ref. 4a. This revises the terminology used in our preliminary communication (Ref. 12).

[6] We use here the designation of α- and β-positions in the sense that they are used in 5-membered heterocyclic ring systems such as pyrrole. Thus a Pc formed by the tetramerization of a 4-substituted phthalonitrile can be designated the $\beta,\beta',\beta'',\beta'''$-isomer, a designation which conveys the fact that the molecule is a mixture of the four possible statistical isomers (see Scheme 1).

[7] For a comprehensive review of sulfonation and halogenation of the Pc nucleus, see Ref. 4a, Volume I, Chapters 2 and 5; and Volume II, Chapter 2. Perfluoro and periodo Pc's have also been reported [17], but their preparation does not involve the direct introduction of the respective halogen into the Pc nucleus.

[8] Reference 4a, Volume I.

[9] O. E. Sielcken, L. A. van de Kuil, W. Drenth, and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, p. 1232 (1988); N. Kobayashi and Y. Nishiyama, *Ibid.*, p. 1462 (1986).

[10] C. C. Leznoff, H. Lam, S. M. Marcuccio, W. A. Nevin, P. Janda, N. Kobayashi, and A. B. P. Lever, *Ibid.*, p. 699 (1987); C. C. Leznoff, H. Lam, W. A. Nevin, N. Kobayashi, P. Janda, and A. B. P. Lever, *Angew. Chem., Int. Ed. Engl., 26*. 1021 (1987).

[11] (a) D. W. Slocum and D. I. Sugarman, in *Polyamine-Chelated Alkali Metal Compounds* (A. W. Langer, ed., Advances in Chemistry Series, No. 130), American Chemical Society, Washington, D.C., 1974, p. 222. (b) H. W. Gshwend and H. R. Rodriguez, *Org. React., 26*, 1 (1979). (c) B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon, London, 1974. (d) L. Brandsma and H. Verkruijsse, *Preparative Polar Organometallic Chemistry 1*, Springer-Verlag, Berlin, 1987.

[12] M. J. Chen, C. M. Fendrick, R. A. Watson, K. S. Kinter, and J. W. Rathke, *J. Chem. Soc., Perkin Trans. I*, p. 1071 (1989).

[13] For a study of the directed metalation of benzonitrile and of 1,2-dicyanobenzene, see T. D. Krizan and J. C. Martin, *J. Org. Chem., 47*, 2681 (1982).

[14] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, p. 1719 (1936).

[15] (a) M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown, and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, p. 1086 (1987). (b) M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown, and A. J. Thomson, *Ibid.*, p. 1148 (1987).

[16] A melting point of 89°C has previously been reported for this compound: H. Hopft and P. Gallegra, *Helv. Chim. Acta, 51*, 253 (1968).
[17] (a) J. M. Birchall, R. N. Haszeldine, and J. O. Morley, *J. Chem. Soc. (C)*, p. 2667 (1970). (b) T. Nishi, K. Arishima, and H. Hiratsuka, Japanese Kokai Tokkyo Koho JP 61, 32,051 [86 32,051]; *Chem. Abstr., 105*, 88745s (1986).