Pentacoordinate Silicon Derivatives. III.[1] 2,2′,2″-Nitrilotriphenol, a New Chelating Agent

C. L. Frye, G. A. Vincent, and G. L. Hauschildt

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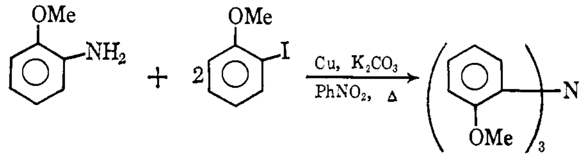
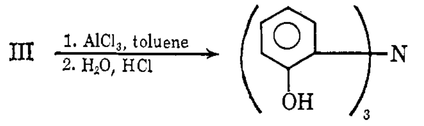
Abstract: The copper-catalyzed condensation of 2-substituted iodobenzenes with 2-substituted anilines yielded the novel 2,2′,2″-trichloro-, trimethyl-, and trimethoxytriphenylamines. Cleavage of the trimethoxy species produced 2,2′,2″-nitrilotriphenol which was shown to be an effective chelating agent, reacting with a variety of silanes ($ZSiX_3$) to form monomeric pentacoordinate derivatives, $Z\underline{Si(OC_6H_4)_3N}$; related aluminum and titanium chelates were also prepared. The use of *o*-dianisidine in the above condensation yielded N,N,N′,N′-tetrakis(2-methoxyphenyl)-3,3′-dimethoxybenzidine; cleavage afforded N,N,N′,N′-tetrakis(2-hydroxyphenyl)-3,3′-dihydroxybenzidine, a hexaol from which a dimeric pentacoordinate silicon derivative was prepared.

The recent preparation of nitrilotriethoxysilanes,[2] $Z\text{-}Si(OCH_2CH_2)_3N$, suggested the possible synthesis of related extracoordinate silicon derivatives of 2,2′,2″-nitrilotriphenol (I). This novel compound was prepared by an Ullmann-like condensation followed by ether cleavage as illustrated in the following equations.



(1)

II (65% yield)

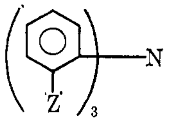


(2)

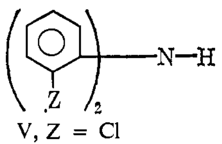
I (75% yield)

Since our search of the literature revealed no established examples of 2,2′,2″-trisubstituted triarylamines,[3] the straightforward preparation of II in such good yield was rather unexpected.[4] The extensive studies of Adams, *et al.*,[5] upon hindered biphenyls showed *o*-methoxy groups to be among the least bulky of the many examined. Triarylamine preparations with larger *ortho* substituents might therefore be expected to proceed more slowly, if steric effects are important. Indeed, 2,2′,2″-trichlorotriphenylamine (III) and 2,2′,2″-trimethyltriphenylamine (IV) formed much less readily than did II in the above copper-catalyzed condensation; factors other than sheer bulk effects are probably also involved in these rate differences.

Although in the preparation of III and IV the secondary amines (V and VI) were obvious intermediates and easily isolated, we obtained little, if any, secondary amine (VII) during the preparation of II unless a large excess of *o*-anisidine was used. Even under these conditions II was a major product. As in the related Ullmann preparation of biaryls,[6] aryl iodides were superior to other aryl halides and the presence of *spongy* copper was essential. The role of the potassium carbonate is not entirely clear; its function is presumably to combine with the by-produced hydrogen iodide to prevent the formation of unreactive amine hydriodides. In our hands, however, most other inorganic bases were unsatisfactory, leading to little or no II.

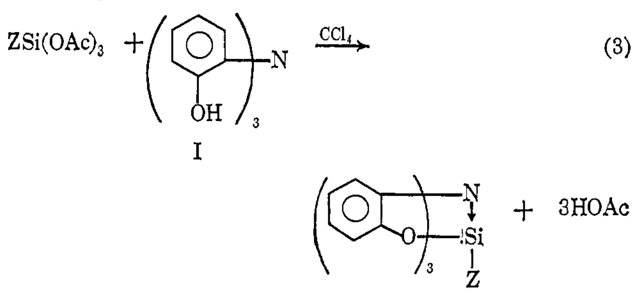


III, Z = Cl
IV, Z = Me



V, Z = Cl
VI, Z = Me
VII, Z = OMe

The anticipated utility of I as a chelating agent was confirmed by simply adding it to a CCl_4 solution of an appropriate triacetoxysilane, whereupon the expected crystalline nitrilotriphenoxysilane[7] (VIII) formed immediately, *i.e.*



(3)

I

VIII

When $HSi(OAc)_3$ was used, the desired silane (VIII, Z = H) was not obtained; this compound appears to be sufficiently "hydridic" to undergo facile protolysis with acetic acid to yield the observed acetoxy derivative (VIII, Z = OAc). Likewise, similar attempts to prepare the hydride from reaction of I with $HSi(OMe)_3$ or $HSiCl_3$ led only to the methoxy and the chloro derivatives, respectively (VIII, Z = OMe, Cl).

Since I, like other triarylamines, is nonbasic these silicon chelates may be prepared by direct reaction with the appropriate chlorosilanes without complications

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(1) Paper II: C. L. Frye, *J. Am. Chem. Soc.*, **86**, 3170 (1964).

(2) (a) C. L. Frye, G. E. Vogel, and J. A. Hall, *ibid.*, **83**, 996 (1961); (b) C. M. Samour, U. S. Patent 3,118,921 (1964); (c) A. B. Finestone, U. S. Patent 3,113,108 (1964).

(3) The recent elegant synthesis of azatriptycene constitutes a uniquely different type of 2,2′,2″-trisubstituted triarylamine in which a single *ortho* substituent is shared by three aryl groups: G. Wittig and G. Steinhoff, *Angew. Chem. Intern. Ed. Engl.*, **2**, [7] 396 (1963).

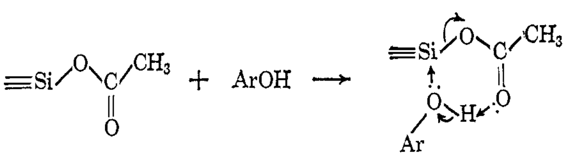
(4) The unsubstituted triphenylamine synthesis by this reaction is, of course, well known: Hager, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 544.

(5) R. Adams and H. Yuan, *Chem. Rev.*, **12**, 261 (1933); R. Shriner, R. Adams, and C. S. Marvel in "Organic Chemistry," Vol. I, H. Gilman, Ed., 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1938, p 268 ff.

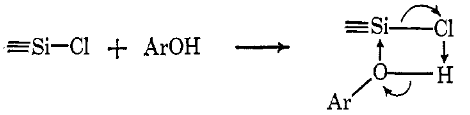
(6) P. E. Fanta, *Chem. Rev.*, 38, 139 (1946).

(7) The related nitrilotriphenoxy aluminate and titanate were also prepared by condensation of I with the appropriate metal isopropylates.

arising from by-produced amine hydrochlorides. Accordingly, $PhSi(OC_6H_4)_3N$ (*i.e.*, VIII, Z = Ph) was prepared in good yield from I and $PhSiCl_3$; however, the reaction was exceedingly slow, in striking contrast to the virtually immediate reaction of the acetoxysilane. Acetoxysilanes are generally considered to be less reactive than chlorosilanes, but the above fact shows this is *not* true for all nucleophilic reagents. When the base is a strong one such as hydroxide or alkoxide, the displacement presumably involves essentially nucleophilic attack upon the silicon with little or no electrophilic "pulling" upon the leaving group. If, however, the base is a relatively weak one such as phenol, then displacement may well involve simultaneous nucleophilic attack at the silicon and electrophilic attack upon the leaving group. We suggest that acetoxysilanes, because of their strategically located carbonyl functions, may readily undergo concerted nucleophilic–electrophilic displacement


(4)

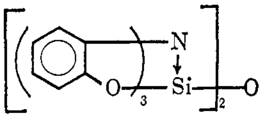
An attack of this type upon a chlorosilane is perhaps less likely because of the strained four-membered ring which would presumably be required.


(5)

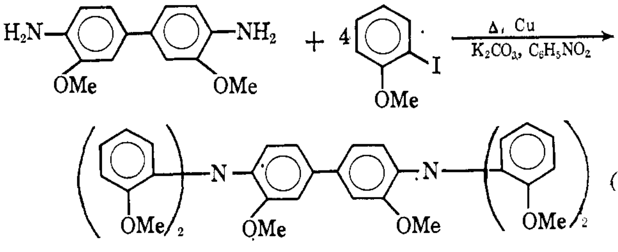
The above rationale would also explain why $PhSi(OMe)_3$ and $PhSiH_3$ were *relatively* unreactive toward I.

The actual existence of a dative bond in this series of silanes (VIII) is difficult to establish unequivocally. Our strongest argument for pentacoordination is by analogy with the structurally similar trialkanolamine derivatives in which such bonding was conclusively demonstrated.[2] Since we have been unable to isolate 2,2′,2′′-nitrilotriphenoxysilane (VIII, Z = H), we cannot cite the anticipated[2] shift of ν(Si–H) as evidence for N→Si dative bonding. Likewise, since triarylamines are neutral, we cannot observe the "delayed" protonation reaction which would otherwise be the expected consequence of such dative bonding.[2] However, this brings up an interesting point: the neutrality of triarylamines is attributed to delocalization of the nitrogen nonbonded pair of electrons by the aromatic rings. Such delocalization requires at least one of the rings to lie in such a way that its π orbital overlaps effectively with the nitrogen atomic orbital containing the nonbonded pair of electrons. With a structure in which the rings are constrained from such alignment, the nitrogen should exhibit basic character. Wittig's triarylamine,[3] azatriptycene, is an example of such a structure and is decidedly basic. Models indicate the 2,2′,2′′-nitrilotriphenoxysilanes to be of this constrained structural type, and therefore they should be basic if they are merely tetracoordinate silicon derivatives. Their definite lack of basicity is consistent with N→Si dative bonding.

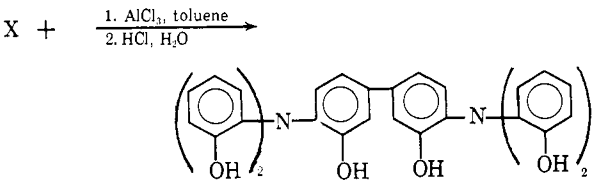
Little is known, at present, about the reactivity of the apical substituent, Z, in the nitrilotriphenoxysilanes. As noted above, we have inferred marked susceptibility to electrophilic attack for a hydrogen substituent. The nitrilotriphenoxysilyl acetate (VIII, Z = OAc) undergoes ready hydrolysis to the disiloxane (IX) when treated with moist solvents; when heated strongly it apparently undergoes pyrolytic loss of acetic anhydride to again form IX. Solvolysis of the chloro- or acetoxysilanes with methanol or phenol yields the expected methoxy- and phenoxysilanes (VIII, Z = MeO, PhO).


IX

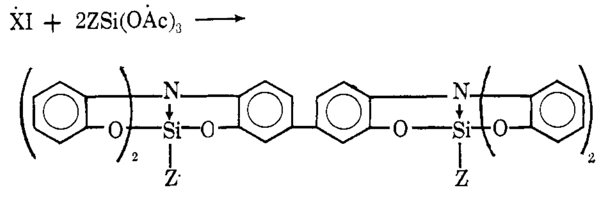
A number of dianisidine derivatives have also been prepared as shown in eq 6–8. These dianisidine derivatives were prepared in order to explore their potential as thermally stable materials. Thermogravimetric analysis[8] of three such materials confirmed their anticipated stability. In the first example (XII, Z = phenyl), sublimation without decomposition occurred at about 500°. When the acetoxy derivative of XII was similarly examined, a weight loss of 20% at 550° was observed; complete pyrolytic loss of acetic anhydride would account for most of this loss (13%). Accordingly, hydrolysis of the acetoxy species yielded a siloxane derivative of XII which, upon thermal gravimetric analysis, exhibited a weight loss of only 5% at 550°. Similar studies in air rather than helium showed appreciable oxidative decomposition at about 475°.


(6)

X (53% yield)


(7)

XI (75% yield)


(8)

XII

Experimental Section

2,2′,2′′-Trimethoxytriphenylamine (II). To a 1-l., three-necked flask fitted with a reflux condenser and Dean–Stark trap, Trubore stirrer, thermometer, and nitrogen purge line was added 64 g

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[8] W. W. Wendlandt, "Thermal Methods of Analysis," Interscience Publishers Inc., New York, N. Y., 1964, p 89.

(0.52 mole) of *o*-anisidine, 234 g (1.0 mole) of *o*-iodoanisole, 300 g of ball-milled K_2CO_3, 64 g of spongy copper powder (J. T. Baker Chemical Co.), and 200 g of nitrobenzene. The flask was then heated at reflux for about 3 hr under a nitrogen purge, removing water *via* the Dean–Stark trap. The pot contents were then cooled and extracted with hot $HCCl_3$ several times. The combined extracts were then distilled with a Nester–Faust 36-in. × 10 mm stainless steel spinning-band column. The product distils at 180–200° (0.4 mm) and is a crystalline solid which was then recrystallized from acetone, 115 g (65% yield), mp 145–147°. This product was shown by glc to be free of contamination, and the observed absence of absorption in the 2.5–3.0-μ range is consistent with the proposed tertiary amine structure. Its nmr spectrum in $DCCl_3$ showed a complex aromatic multiplet[9] at τ 2.7–3.3 and a singlet (CH_3O–) at τ 6.47 with the expected intensity ratio of 4:3. *Anal.* Calcd for $C_{21}H_{21}O_3N$: C, 75.2; H, 6.26; N, 4.18. Found: C, 75.2; H, 6.39; N, 3.93.

2,2′-Dimethoxydiphenylamine (VII).[10] To a 3-l. flask outfitted as in the previous example were added 738 g (6.00 moles) of *o*-anisidine, 468 g (2.00 moles) of *o*-iodoanisole, 800 g of nitrobenzene, 600 g of powdered K_2CO_3, and 128 g of spongy copper powder. The reactants were then heated at 200° for about 90 min at which time glc examination showed the *o*-iodoanisole to have been completely consumed and the presence of peaks believed to be secondary and tertiary amine. The contents of the flask were filtered; the filter cake was triturated with 800 ml of boiling $HCCl_3$ and this filtrate added to the first. Fractional distillation on a 36 in. × 10 mm stainless steel spinning-band column (Nester–Faust) yielded 178 g (39% yield) of the desired secondary amine, bp 150° (0.5 mm); this material was shown by glc to be a single component, and its infrared spectrum possessed a sharp singlet at 2.9 μ characteristic of secondary amines. The nmr spectrum (neat) showed a complex aromatic multiplet[9] at τ 2.6–3.9 and a singlet (CH_3O–) at τ 6.4 with the expected intensity ratio of 4.5:3 (assuming the N–H resonance to lie under the aromatic multiplet). *Anal.* Calcd for $C_{14}H_{15}O_2N$: C, 73.4; H, 6.55; N, 6.11. Found: C, 73.7; H, 6.57; N, 6.13.

This material is a liquid of unusual solubility, *i.e.*, approximately seven times its weight of hexane was required to yield complete miscibility at room temperature, and it was of similar limited miscibility with methanol. Toluene solutions yielded crystalline deposits melting at 34–36° and shown by nmr to contain about 9.3% by weight of toluene. Lengthy evacuation at room temperature resulted in liquefaction. Apparently the secondary amine forms low-melting clathrates with this solvent.

A small portion was treated with concentrated HCl to yield a crystalline hydrochloride, mp 145–146°. *Anal.* Calcd for $C_{14}H_{15}O_2N \cdot HCl$: C, 63.3; H, 6.03; N, 5.27; Cl, 13.37. Found: C, 64.1; H, 6.55; N, 5.04; Cl, 12.9. Upon brief boiling with toluene this salt decomposed to yield an oil whose infrared spectrum was identical with that of the free base (after evacuation to thoroughly remove the toluene).

The above fractional distillation also yielded 103 g (31% yield) of the tertiary amine (II).

2,2′,2′′-Nitrilotriphenol (I). A. $AlCl_3$ Cleavage[11] of II. To a 1-l, three-necked flask fitted with a Trubore stirrer (Teflon paddle), condenser, and nitrogen purge line were added 91 g (0.271 mole) of II, 500 ml of dry toluene, and 109 g (0.816 mole) of anhydrous $AlCl_3$. The addition of the $AlCl_3$ resulted in a vigorous exotherm as the etherate formed, depositing as a green-colored solid at the bottom of the flask. After heating at toluene reflux for 90 min (MeCl ↑), the toluene was decanted from the solid product which was then hydrolyzed with excess aqueous HCl (10%). The resulting solid was then isolated and recrystallized from methylene chloride to give 66 g (75% yield), mp 171–174°. Alternatively, the product may be recrystallized from toluene or from methanol–water mixtures.

An infrared spectrum (hexachlorobutadiene mull) confirmed the presence of OH (band at 2.95 μ) and the absence of OMe (no band at 3.4–3.6 μ). An nmr spectrum (DMSO) showed a complex multiplet[9] at τ 2.9–3.5 (*o*-phenylene) and a singlet at τ 1.48 in the anticipated intensity ratio of 4:1. *Anal.* Calcd for $C_{18}H_{15}O_3N$: C, 73.7; H, 5.12; N, 4.78. Found: C, 73.5; H, 5.52; N, 4.49.

B. Pyridine–HCl Cleavage of II. Ten grams (0.042 mole) of II and 15 g (0.13 mole) of pyridine hydrochloride were heated and stirred under nitrogen at 200° for 90 min. The reaction mass was then added to water and the resulting solid was recrystallized from ethanol to yield 7.5 g of material melting at about 230°. This material is believed to have been a somewhat impure pyridine hydrochloride adduct of I. Treatment of a small portion with aqueous KOH produced an immediate odor of pyridine. Extraction of the alkaline solution with hexane (to remove pyridine) followed by acidification with concentrated HCl produced a crystalline solid which was shown by melting point and infrared spectrum to be the anticipated triol (I).

The suspected adduct formation was confirmed as follows. A solution of 2.93 g (0.0100 mole) of I in 15 g of ethanol was added to a solution of 3.0 g (0.026 mole) of pyridine hydrochloride. This produced the almost immediate deposition of the crystalline 1:1 adduct which was isolated, washed first with additional ethanol and then with hexane, and finally evacuated to a constant weight of 3.82 g (93% yield), mp 244–246°. *Anal.* Calcd for $C_{23}H_{21}O_3N_2Cl$: C, 67.6; H, 5.14; N, 6.85; Cl, 8.69. Found: C, 68.6; H, 5.44; N, 6.60; Cl, 8.61.

The triacetate of I was also prepared. One gram of the crude pyridine hydrochloride I adduct was boiled for 2 hr with 4 g of NaOAc and 15 g of acetic anhydride. The resulting solution was then poured into water and boiled briefly. Upon cooling, a needle-like crystalline deposit formed and was isolated, mp 133–135°; a strong infrared absorption at 5.67 μ (ester carbonyl) was observed. *Anal.* Calcd for $C_{24}H_{21}O_6N$: C, 68.7; H, 5.01; N, 3.34. Found: C, 68.5; H, 5.00; N, 3.53.

2,2′,2′′-Nitrilotriphenoxysilanes (VIII). A. From Acetoxysilanes. Phenyl(2,2′,2′′-nitrilotriphenoxy)silane (Z = Ph). A hot solution of 2.00 g (0.0071 mole) of $PhSi(OAc)_3$ in 10 ml of CCl_4 was added to a boiling suspension of 2.00 g (0.0068 mole) of I in 25 ml of CCl_4. The reaction mixture quickly cleared momentarily before depositing a crystalline product which was removed by filtration and then evacuated free of CCl_4 and HOAc to give 2.40 g (89% yield) of the expected product. This material does not melt below 300° but does sublime when heated strongly. The infrared spectra (Nujol mull) of this and related silanes show bands at 10.70, 11.05, and 11.70 μ which appear to be characteristic of the chelate cage structure. *Anal.* Calcd for $SiC_{24}H_{17}O_3N$: C, 72.9; H, 4.30; Si, 7.10; N, 3.55. Found: C, 72.9; H, 4.49; Si, 7.04; N, 3.48.

In like fashion the following analogous compounds were also prepared.

Methyl(2,2′,2′′-nitrilotriphenoxy)silane (Z = Me). *Anal.* Calcd for $SiC_{19}H_{15}O_3N$: C, 68.5; H, 4.50; N, 4.20; Si, 8.41; mol wt, 333. Found: C, 68.1; H, 4.70; N, 4.22; Si, 8.03; mol wt (ebulliometric in toluene), 351; mp 289–290°.

Vinyl(2,2′,2′′-nitrilotriphenoxy)silane (Z = Vi). *Anal.* Calcd for $SiC_{20}H_{15}O_3N$: C, 69.6; H, 3.99; N, 4.04; Si, 8.14. Found: C, 68.7; H, 4.55; N, 3.73; Si, 7.57; mp 273–275°.

2,2′,2′′-Nitrilotriphenoxysilyl Acetate (Z = OAc). *Anal.* Calcd for $SiC_{20}H_{15}O_5N$: C, 63.6; H, 3.98; N, 3.72; Si, 7.43. Found: C, 63.0; H, 4.12; N, 3.62; Si, 7.63. A strong carbonyl absorption at 5.8 μ is present in the infrared spectrum of this material. This compound does not melt below 300° but undergoes loss of acetic anhydride resulting in the formation of the disiloxane IX. Upon brief refluxing of this acetoxysilane in methanol, the derived methoxysilane (VIII, Z = MeO) resulted. *Anal.* Calcd for $C_{10}H_{15}O_4N$: C, 65.4; H, 4.30; N, 3.90; Si, 8.15. Found: C, 65.8; H, 4.8; N, 4.07; Si, 7.99; mp 280–283°. This product is prepared more satisfactorily by refluxing a toluene solution of I and either $HSi(OMe)_3$ or $Si(OMe)_4$.

B. From Chlorosilanes. Phenyl(2,2′,2′′-nitrilotriphenoxy)silane (Z = Ph). One gram (0.0034 mole) of I and 0.72 g (0.0034 mole) of $PhSiCl_3$ were heated at reflux in 20 ml of CCl_4 for 45 min. Infrared examination of the solid which was then isolated showed it to be merely the starting triol (I). A second attempt employing a higher boiling solvent was more successful. A solution of 1.0 g (0.0034 mole) of I and 0.72 g (0.0034 mole) of $PhSiCl_3$ in 20 ml of *n*-butyl ether was boiled for 2 hr during which time HCl was evolved and a crystalline solid was gradually deposited. This solid was isolated (1 g, 74% yield) and shown, by comparison of its spectrum with that of an authentic sample, to be the anticipated phenyl(2,2′,2′′-nitrilotriphenoxy)silane.

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[9] The appearance of the *o*-phenylene multiplet of compounds I–VII is very dependent upon temperature and/or solvent choice. These changes possibly arise from altered conformation populations or from altered rates of configurational inversion of the nitrogen atom.

[10] For an earlier report of this structure, see G. Wieland and L. Chudoshilow, *J. Russ. Phys. Chem. Soc.*, **46**, 195 (1914); *Chem. Zentr.*, **1**, 2164 (1914).

[11] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc, New York, N. Y., 1953, p 171.

Chloro(2,2′,2′′-nitrilotriphenoxy)silane (Z = Cl). This chlorosilane analog was prepared in like fashion to the above phenyl derivative and recrystallized from toluene. *Anal.* Calcd for $SiC_{18}H_{12}O_3ClN$: C, 61.2; H, 3.4; N, 3.96; Cl, 10.04; Si, 7.94. Found: C, 62.2; H, 3.9; N, 3.85; Cl, 9.19; Si, 7.54. This compound sublimes at temperatures above 250° and does not melt below 300°. The derived phenoxy species was then obtained by heating the chloride with phenol, mp 230–232°. *Anal.* Calcd for $SiC_{24}H_{17}O_4N$: C, 70.4; H, 4.14; Si, 6.80. Found: C, 70.0; H, 4.21; Si, 6.85.

Bis(2,2′,2′′-nitrilotriphenoxysilyl) Oxide (IX). This novel disiloxane was prepared by adding 0.4 ml of H_2O to a refluxing slurry of 6.1 g of the acetoxysiloxane (VIII, Z = AcO) in acetonitrile. After boiling for a few minutes, tetrahydrofuran was added in sufficient quantity to dissolve all the solids present. Subsequent addition of heptane followed by boiling to displace the tetrahydrofuran caused the deposition of 5.0 g (77% yield) of IX. An infrared spectrum confirmed the absence of carbonyl absorption and the presence of a strong doublet at 8.9 and 9.1 μ ascribed to the disiloxane moiety. This material did not melt below 300°; it sublimes intact at 450° during thermogravimetric analysis. *Anal.* Calcd for $Si_2C_{36}H_{24}O_7N_2$: C, 66.2; H, 3.68; N, 4.29; Si, 8.62. Found: C, 66.1; H, 4.00; N, 4.52; Si, 8.50.

Isopropyl-2,2′,2′′-nitrilotriphenyl Titanate. A mixture of 3.00 g (0.0102 mole) of I and 2.90 g (0.0102 mole) of $(i\text{-PrO})_4Ti$ was heated at 120–150° until it had been largely transformed to a yellow solid which was then recrystallized from isopropyl alcohol, 3.3 g, 82% yield; the crystals do not melt below 300° but darken when heated strongly. This material has infrared absorption bands at 11.0, 11.5, and 12.0 μ, presumably related to the chelate cage structure. *Anal.* Calcd for $TiC_{21}H_{19}O_4N$: C, 63.2; H, 4.79; Ti, 12.1; N, 3.53. Found: C, 62.7; H, 4.93; Ti, 12.5; N, 3.52.

2,2′,2′′-Nitrilotriphenyl Aluminate. A 50-ml erlenmeyer flask containing 3.00 g (0.0102 mole) of I and 2.10 g (0.0103 mole) of $(i\text{-PrO})_3Al$ was heated at 120–150° until a dry solid resulted. This solid was then dissolved in hot isopropyl alcohol and recrystallized from ether after sufficiently concentrating the solution, 2.8 g, 75% yield; the crystals do not melt below 300°. This product contains a mole of solvated isopropyl alcohol. The anticipated absorptions in the 10–12-μ range were present (10.9, 11.6, 11.9 μ). *Anal.* Calcd for $AlC_{18}H_{12}O_3N\cdot C_3H_8O$: C, 65.9 H, 5.30; N, 3.71. Found: C, 66.1; H, 5.47; N, 3.36.

The solvated isopropyl alcohol was removed by heating in a 120° oven for 2 hr. *Anal.* Calcd for $AlC_{18}H_{12}O_3N$: C, 68.2; H, 3.79; N, 4.42. Found: C, 68.0; H, 3.90; N, 4.43.

N,N,N′,N′-Tetrakis(2-methoxyphenyl)-2,2′-dimethoxybenzidine. Into a 1-l., three-necked flask fitted with a Dean–Stark condenser, Trubore stirrer, thermometer, and nitrogen purge line was placed 48.8 g (0.200 mole) of 2,2′-dimethoxybenzidine, 200 g (0.844 mole) of *o*-iodoanisole, 220 g of powdered K_2CO_3, 150 g of nitrobenzene, and 60 g of copper powder (spongy). After heating at reflux and under nitrogen purge for 3 hr, an additional 50 g of *o*-iodoanisole was added and reflux was continued for an additional 2 hr. The reaction mixture was then cooled and 300 ml of $HCCl_3$ was added, causing a pink crystalline solid to form. The solids (copper, potassium salts, pink crystals, etc.) were then filtered from the resulting slurry and the filtrate was discarded. The solids were then leached well with hot toluene in which the pink solid was quite soluble. Upon concentration and cooling of this toluene solution, a pink crystalline solid again deposited. Recrystallization from chloroform yielded 97 g of almost colorless product, mp 173–175°. Subsequent analysis showed this compound to contain 2 moles of solvated chloroform, and on that basis the yield is 53%. *Anal.* Calcd for $C_{42}H_{40}O_6N_2$: C, 58.2; H, 4.63; N, 3.09. Found: C, 58.6; H, 4.65; N, 3.16. The chloroform is readily removed by heating in a 120° oven.

N,N,N′,N′-Tetrakis(2-hydroxyphenyl)-2,2′-dihydroxybenzidine (XI). To a 500-ml three-necked flask fitted with an air-driven Teflon paddle and a reflux condenser were added 14.2 g (0.021 mole) of X and 100 g of toluene. The subsequent addition of 16.4 g (0.126 mole) of $AlCl_3$ resulted in the exothermic formation of the insoluble etherate. After heating at reflux for 2 hr (MeCl↑), the toluene was decanted (and discarded) and the residue was hydrolyzed with excess 10% HCl. The hydrolysis mixture was extracted with ether and this extract was then devolatilized on the steam bath. The residue was washed with hot $HCCl_3$ and then recrystallized from ethanol to give pure XI, 8.0 g, 65% yield, mp 234–237°. The infrared spectrum of this material was consistent with the structure assigned (*i.e.*, OH band at 2.95 μ and no OMe band at 3.4–3.6 μ). Convincing proof of structure is provided by the extracoordinate phenylsilicon derivative (XII) prepared (*vide infra*). *Anal.* Calcd for $C_{36}H_{28}O_6N_2$: C, 74.1; H, 4.46; OH, 17.8. Found: C, 73.7; H, 4.80; OH, 18.2.

Bis[5-phenyl(2,2′,2′′-nitrilotriphenoxy)silane] (XII, Z = Ph). A boiling solution of 2.8 g (0.011 mole) of $PhSi(OAc)_3$ in 15 g of CCl_4 was added to a boiling suspension of 2.9 g (0.005 mole) of XI in 15 g of CCl_4. A clear solution resulted upon refluxing for several minutes. Upon cooling to room temperature, an almost quantitative yield of the anticipated product (4 g) deposited and was recrystallized from moist acetone. This material does not melt below 300°; infrared bands in the 10.7–11.7-μ region were consistent with the proposed dimeric cage structure. *Anal.* Calcd for $Si_2C_{48}H_{32}O_6$: C, 73.1; H, 4.06; Si, 7.12; N, 3.55. Found: C, 72.2; H, 4.36; Si, 7.33; N, 3.29.

In similar fashion starting with $Si(OAc)_4$ the acetoxy derivative was prepared. This material was then hydrolyzed to yield a siloxane soluble in tetrahydrofuran or acetone whose infrared spectrum showed it to be free of carbonyl content.

Tris(*o*-tolyl)amine (IV). To a 1-l., three-necked flask fitted with a Dean–Stark trap and condenser, air-operated Teflon paddle, nitrogen purge line, and thermometer were added 52 g (0.50 mole) of *o*-toluidine, 219 g (1.0 mole) of *o*-iodotoluene, 138 g (1.0 mole) of powdered K_2CO_3, 64 g of powdered spongy copper, and 200 g of *o*-dichlorobenzene. After refluxing for 30 hr, the metal and salts were filtered out, the filtrate was freed of solvent by distillation, and the residue was recrystallized from a small amount of acetonitrile to give 70 g (49% yield) of IV, mp 104–106°. Infrared examination confirmed the absence of the N–H moiety. The nmr spectrum showed a singlet (CH_3) at τ 8.12 and a complex multiplet[9] (*o*-phenylene) at τ 3.8–3.4 in the expected intensity ratio of 9.12. *Anal.* Calcd for $C_{21}H_{21}N$: C, 87.8; H, 7.32; N, 4.88. Found: C, 87.8; H, 7.52; N, 4.87.

Glc examination of samples taken during the above reflux period showed the buildup and subsequent decay of compound VI which was then deliberately prepared as shown in the following procedure.[12]

Bis(*o*-tolyl)amine (VI). To a 250-ml three-necked flask outfitted as in the previous example were added 25 g (0.24 mole) of *o*-toluidine, 43.6 g (0.20 mole) of *o*-iodotoluene, 27.6 g (0.20 mole) of powdered K_2CO_3, 12.6 g of powdered copper, and 30 g of *o*-dichlorobenzene. After heating at reflux for 5 hr, an additional 20 g (0.2 mole) of *o*-toluidine was added. The mixture was then refluxed for an additional 18 hr and then filtered while still hot. Fractional distillation yielded 18 g (45% yield) of material boiling at 119° (1 mm), mp 48–50°. Infrared examination revealed the absorption at 2.9 μ anticipated for the N–H moiety. The material was a single component as evidenced by glc. The nmr spectrum (CCl_4) showed singlets at τ 7.88 (CH_3) and 5.11 (N–H) and a complex multiplet[9] (*o*-phenylene) at 2.8–3.5 in the ratio of 5.94:0.85:8.0, respectively. *Anal.* Calcd for $C_{14}H_{15}N$: C, 85.3; H, 7.62; N, 7.11. Found: C, 85.6; H, 7.81; N, 7.12.

Tris(*o*-chlorophenyl)amine (III). As in the preceding preparation, 64 g (0.50 mole) of *o*-chloroaniline, 253 g (1.06 mole) of *o*-chloroiodobenzene, 138 g (1.00 mole) of K_2CO_3, 64 g of powdered copper, and 150 g of *o*-dichlorobenzene were heated at reflux for 48 hr. The reaction mixture was filtered hot and upon cooling to room temperature 67.3 g of tertiary amine (III) crystallized from the filtrate; an additional 8 g of III was obtained by extracting the salts with hot hexane. After removing the deposit of III, the *o*-dichlorobenzene filtrate was distilled yielding an additional 2.5 g of III for a total of 77.8 g (45% yield), mp 175–178°. The infrared spectra showed no band at 2.9 μ (consistent with the absence of N–H content). The nmr spectrum ($HCCl_3$) showed only the complex multiplet[9] (τ 2.5–3.2) arising from the *o*-phenylene protons. *Anal.* Calcd for $C_{18}H_{12}Cl_3N$: C, 62.0; H, 3.44; Cl, 30.6; N, 4.02. Found: C, 63.1; H, 3.92; Cl, 30.2; N, 3.89.

The above distillation also yielded 32 g of liquid shown by glc to be a single component and believed to be the secondary amine (V), bis(*o*-chlorophenyl)amine, bp 120–130° (0.1 mm), $n^{25.2}\mathrm{D}$ 1.6424. The infrared spectrum of this material possessed a sharp band at 2.94 μ, consistent with the supposed N–H content, and the nmr spectrum showed a complex 15-line multiplet[9] at τ 2.7–3.6. *Anal.* Calcd for $C_{12}H_9Cl_2N$: C, 60.5; H, 3.78; Cl, 29.8; N, 5.9. Found: C, 61.4; H, 4.09; Cl, 31.0; N, 5.6.

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(12) For a more involved procedure, see H. Wieland and A. Suesser, *Ann.*, **392**, 176 (1908).