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A variety of novel chelating 1,3-bis(2'-pyridylimino)isoindoline ligands were prepared and characterized including ligands substituted on both the pyridyl and isoindoline ring systems. Noteworthy are the first isoindoline ligands with solubility in aqueous media. A convenient preparation of 4-alkoxyphthalonitriles is reported; these compounds are readily obtained from 4-nitrophthalonitrile and are suitable starting materials for alkoxy-substituted ligands.

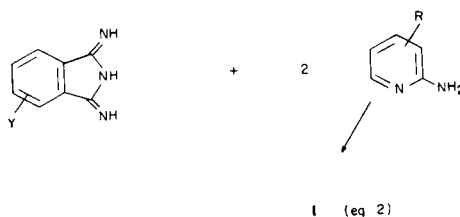
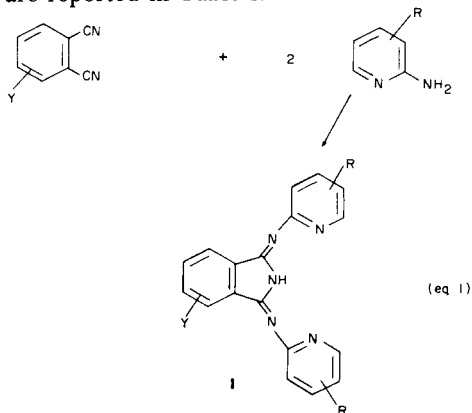
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## Introduction.

1,3-bis(2'-Pyridylimino)isoindolines have been shown to function as uninegative chelating ligands capable of complexing a large variety of transition metal ions (1-4). The ligands are capable of occupying three coplanar sites about a metal ion and, accordingly, of forming either 1:1 or 2:1 (ligand:metal) complexes depending on the coordination number and geometry of the metal ion. The utility of these ligands is enhanced by the ease with which substituents may be introduced on the pyridyl rings (5), thus allowing the controlled modification of electron donor properties and solubilities (3,4). In order to have available 1,3-bis(2'-pyridylimino)isoindoline chelating ligands with a wide range of solubility and donor properties, a series of substituted ligands was prepared. The new isoindoline ligands include those with substituents on both the pyridyl and isoindoline ring systems and the first ligand with water-solubility.

## Results and Discussion.

The isoindoline ligands **1** were prepared in a single step from two equivalents of the appropriately substituted 2-aminopyridine and one equivalent of phthalonitrile or the corresponding diimine (eq 1 and 2). Where phthalonitrile was used as the starting material, anhydrous calcium chloride was usually employed to facilitate the reaction (5). The yield and melting point data for 20 new ligands are reported in Table I.



## New Ligands from Substituted 2-Aminopyridines.

Ligands **1a-1c**, with methyl substituents on the pyridyl rings, were obtained *via* (eq 1) from the previously unreported 2-aminopyridines. 2-Amino-3,5-dimethylpyridine was obtained from treatment of 3,5-dimethylpyridine with sodium amide (6); similarly, 2-amino-3,4-dimethylpyridine and 2-amino-4,5-dimethylpyridine were obtained as a 4:1 mixture *via* treatment of 3,4-dimethylpyridine with sodium amide. The latter two isomeric aminopyridines were separated by a combination of column chromatography and fractional crystallization and are easily distinguished on the basis of <sup>1</sup>H-nmr spectra.

Ligands **1d-1g** were obtained by heating the appropriately substituted 2-aminopyridine with 1,3-diiminoisoindoline in 1-butanol at reflux (eq 2). 2-Amino-4-phenylpyridine, the starting material for **1d**, was obtained by treatment of 4-phenylpyridine with sodium amide, whereas the other three substituted 2-aminopyridines are commercially available.

## New Ligands from Substituted Phthalonitriles.

3- and 4-Methylphthalonitrile (7) undergo condensation with 2-aminopyridines (eq 1) to afford **1h** and **1i**, the first reported unsymmetrically substituted isoindoline ligands.

Tetrachlorophthalonitrile reacts in the usual manner with 2-aminopyridines to form the corresponding isoindoline ligand **1j**. However, tetrafluorophthalonitrile fails to react in the usual manner (eq 1), but rather affords a mixture of products which still exhibits a strong  $\nu$  CN in the infrared. These cyano containing products most likely result from displacement of fluoride by 2-aminopyridine or solvent; the replacement of fluoride from tetrafluorophthalonitrile by various nucleophiles had been observed earlier (8).

Table I  
Yield and Characterization Data for New Ligands

Compound	Dinitrile	Starting Materials		Molecular Formula	Yield %	Mp, °C
			2-Aminopyridine			
<b>1a</b>	Phthalonitrile	2-Amino-3,4-dimethylpyridine		C <sub>22</sub> H <sub>21</sub> N <sub>5</sub>	64	181-182
<b>1b</b>	Phthalonitrile	2-Amino-3,5-dimethylpyridine		C <sub>22</sub> H <sub>21</sub> N <sub>5</sub>	53	191-193
<b>1c</b>	Phthalonitrile	2-Amino-4,5-dimethylpyridine		C <sub>22</sub> H <sub>21</sub> N <sub>5</sub>	64	266-267
<b>1d</b>	1,3-Diiminoisoindoline	2-Amino-4-phenylpyridine		C <sub>32</sub> H <sub>25</sub> N <sub>5</sub>	46	280-282
<b>1e</b>	1,3-Diiminoisoindoline	2-Amino-3-hydroxypyridine		C <sub>18</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub>	65 (a)	246-248
<b>1f</b>	1,3-Diiminoisoindoline	2-Aminonicotinamide		C <sub>20</sub> H <sub>15</sub> N <sub>7</sub> O <sub>2</sub>	50 (a)	302-303
<b>1g</b>	1,3-Diiminoisoindoline	2-Amino-3,5-dichloropyridine		C <sub>18</sub> H <sub>9</sub> Cl <sub>4</sub> N <sub>5</sub>	42	251-252
<b>1h</b>	3-Methylphthalonitrile	2-Aminopyridine		C <sub>19</sub> H <sub>15</sub> N <sub>5</sub>	80	162-163
<b>1i</b>	4-Methylphthalonitrile	2-Aminopyridine		C <sub>19</sub> H <sub>15</sub> N <sub>5</sub>	55	176-177
<b>1j</b>	Tetrachlorophthalonitrile	2-Amino-4-methylpyridine		C <sub>20</sub> H <sub>13</sub> Cl <sub>4</sub> N <sub>5</sub>	72	246-248
<b>1k</b>	3,4-Dicyanoacetanilide	2-Amino-4-methylpyridine		C <sub>22</sub> H <sub>20</sub> N <sub>2</sub> O	14	238-240
<b>1l</b>	3,4-Dicyanosulfonanilide	2-Amino-4-methylpyridine		C <sub>21</sub> H <sub>20</sub> N <sub>6</sub> O <sub>2</sub> S	32	236-237
<b>1m</b>	4-Nitrophthalonitrile	2-Amino-4-methylpyridine		C <sub>20</sub> H <sub>17</sub> N <sub>6</sub> O <sub>2</sub>	79	230-231
<b>1n</b>	4-Methoxyphthalonitrile	2-Amino-4-methylpyridine		C <sub>21</sub> H <sub>19</sub> N <sub>5</sub> O	70	142-143
<b>1o</b>	4-Ethoxyphthalonitrile	2-Amino-4-methylpyridine		C <sub>22</sub> H <sub>21</sub> N <sub>5</sub> O	50	143-144
<b>1p</b>	4- <i>iso</i> Propoxyphthalonitrile	2-Amino-4-methylpyridine		C <sub>23</sub> H <sub>23</sub> N <sub>5</sub> O	59	142-143
<b>1q</b>	4- <i>n</i> -Butoxyphthalonitrile	2-Amino-4-methylpyridine		C <sub>24</sub> H <sub>25</sub> N <sub>5</sub> O	50	176-177
<b>1r</b>	4-(2'-Dimethylamino)ethoxyphthalonitrile	2-Amino-4-methylpyridine		C <sub>24</sub> H <sub>26</sub> N <sub>6</sub> O	25	153-154
<b>1s</b>	4-(2'-Dimethylethylammonium)-ethoxyphthalonitrile iodide	2-Amino-4-methylpyridine		C <sub>26</sub> H <sub>31</sub> IN <sub>6</sub> O	30	219-221 dec
<b>1t</b>	4-(2'-Trimethylammonium)-ethoxyphthalonitrile chloride	2-Amino-4-methylpyridine		C <sub>25</sub> H <sub>29</sub> ClN <sub>6</sub> O	(b)	213-214 dec

(a) Crude yield; all other values are for purified yields. (b) The chloride salt was obtained by anion exchange from the corresponding iodide salt.

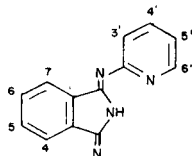
Table II  
Chemical Shift Data for Selected Ligands (a)

Compound	Chemical Shifts (b)								α-CH of Substituent	
	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>3'</sub>	H <sub>4'</sub>	H <sub>5'</sub>	H <sub>6'</sub>		
<b>1a</b>	8.06 (q)	7.61 (q)	7.61 (q)	8.06 (q)		7.39 (s)		8.26 (s)	3'-CH <sub>3</sub>	2.52
<b>1b</b>	8.08 (q)	7.63 (q)	7.63 (q)	8.08 (q)			6.90 (d)	8.27 (d)	5'-CH <sub>3</sub>	2.34
<b>1c</b>	8.03 (q)	7.60 (q)	7.60 (q)	8.03 (q)	7.24 (s)			8.32 (s)	3'-CH <sub>3</sub>	2.52
<b>1h</b>		7.41 (m) (c)	7.49 (t)	7.91 (d)	7.41 (m) (c)	7.75 (m)	7.10 (m)	8.60 (m)	4'-CH <sub>3</sub>	2.29
<b>1i</b>	7.89 (s)		7.45 (m) (c)	7.95 (d)	7.45 (m) (c)	7.76 (m)	7.11 (m)	8.66 (m)	4-CH <sub>3</sub>	2.90
<b>1l</b>	7.83 (d)		7.48 (q)	8.01 (d)	7.26 (s)		6.96 (s)	8.46 (t)	5-CH <sub>3</sub>	2.54
<b>1n</b>	7.56 (s)		7.17 (d)	7.96 (d)	7.30 (s)		6.94 (d)	8.47 (d)	4'-CH <sub>3</sub>	2.40

(a) Chemical shifts are taken from 100 MHz or 360 MHz spectra and are reported in parts per million downfield from TMS, the internal standard. The solvent is deuteriochloroform.

(b)

(c) Overlapping signal.



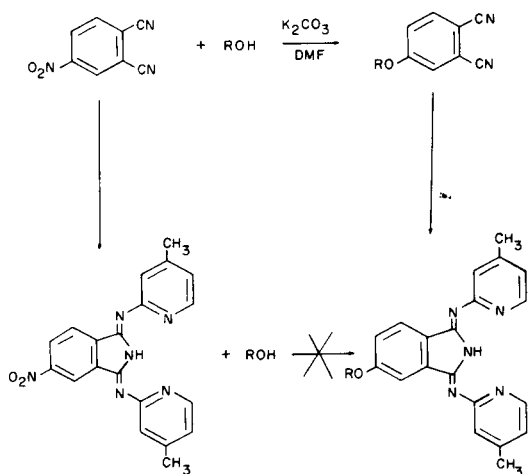
4-Nitrophthalonitrile, prepared from 4-nitrophthalic anhydride (9,10), reacts with 2-amino-4-methylpyridine (eq 1) to afford ligand **1m**, with a nitro substituent on the isoindoline ring. Commercially available 4-aminophthalonitrile, however, yielded only a mixture of products from which the expected amino-substituted ligand was not readily isolated. The failure of 4-aminophthalonitrile to

undergo the expected condensation with a 2-aminopyridine may be due either to the deactivating effect of an electron-donating amino group on the nitriles, or to competition by the amino group of 4-aminophthalonitrile in the condensation reaction. Conversion of 4-aminophthalonitrile to the corresponding acetyl and methanesulfonyl amides produced phthalonitriles which

underwent the condensation (eq 1) in the usual manner to yield ligands **1k** and **1l**, respectively.

4-Alkoxyphthalonitriles, prepared as described below, were treated with 2-amino-4-methylpyridine to afford the corresponding 5-alkoxy-substituted ligands **1n-1s** in moderate-good yields. No exchange of alkoxy groups with the solvent 1-butanol was observed. The route to 5-alkoxyisoindoline ligands illustrated in Scheme I should allow the attachment of a variety of functional groups to the ligand. Alternatively, it should provide a method for attachment of the ligand to various support materials containing primary or secondary hydroxyl groups. However, the displacement of the nitro group by alkoxide must be carried out on the phthalonitrile. Attempts to carry out the displacement by alkoxide on the nitro-substituted ligand **1m** itself were unsuccessful; even after prolonged heating at 70-80° in the presence of potassium carbonate, the starting material **1m** was recovered unchanged.

Scheme I

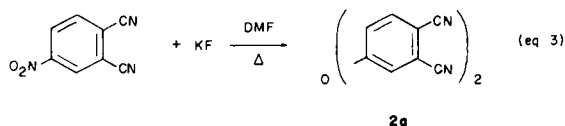


The utility of Scheme I for the preparation of specifically substituted 1,3-bis(2'-pyridylimino)isoindolines is illustrated by the preparation of ligands **1r** and **1s**. The water soluble nitriles **2f** and **2g**, prepared from 4-nitrophthalonitrile and 2-dimethylaminoethanol followed by alkylation with ethyl iodide and methyl iodide respectively, when treated with 2-amino-4-methylpyridine according to (eq. 1) afforded the first isoindoline ligands with solubility in aqueous solvent systems.

Anion exchange reactions could be carried out on the initially formed iodide salts to further modify the solubility properties of the ionic ligands. For example, the hexafluorophosphate salts possessed a higher solubility in acetone and the chloride salts exhibited a higher solubility in water. Representative salts are reported in Table I.

In an attempt to replace the nitro group by fluoride, 4-nitrophthalonitrile was treated with potassium fluoride in dimethylformamide at 70-80°. Instead of the fluoro-

phthalonitrile, the product obtained, in 70% yield, was identified as the diaryl ether **2g**, 4,4'-oxybis(phthalonitrile) (eq 3). A similar reaction was observed earlier by Markezich and Zamek (11) upon treatment of 4-nitro-*N*-methylphthalimide with potassium fluoride; these authors suggested that the nitrite ester and phenol are likely intermediates in the formation of the bis ether.



#### Characterization of the New Ligands.

All of the new ligands are yellow or gold crystalline solids with long shelf-lives. They have good thermal stability but are subject to acid hydrolysis in aqueous media. In general, electronegative substituents increase the melting points and decrease the solubility in organic solvents. The infrared spectra contain two characteristic bands at *ca.* 1640 (m-s) and *ca.* 1590 (s)  $\text{cm}^{-1}$ , which undergo changes upon chelation of a metal ion (4).  $^1\text{H}$ -nmr spectra were recorded where solubility permitted and are presented for representative ligands in Table 2. In most cases chemical shift assignments could be made for all the aryl protons. In general, for the isoindoline ring system H-4 and H-7 appear at lower field than H-5 and H-6; the pyridyl protons are shifted downfield in the order H-6' > H-4' > H-3' > H-5'.

#### 4-Alkoxyphthalonitriles.

In what appears to be a general reaction, 4-nitrophthalonitrile reacts with primary and secondary alcohols to afford the corresponding 4-alkoxyphthalonitriles. The transformation proceeds in dimethylformamide in the presence of potassium carbonate at ambient temperature in good yield; the product is easily isolated from the reaction mixture. Yield data are presented for a number of new 4-alkoxyphthalonitriles in Table III. With *t*-butyl alcohol, even after heating the reaction mixture at 70-80°, the 4-nitrophthalonitrile was recovered unchanged. Diethylamine reacted with 4-nitrophthalonitrile at ambient temperature under the usual conditions and it appeared

Table III

Preparation of 4-Alkoxyphthalonitriles

Compound	Alkoxy Substituent	Yield (%) (a)	Mp °C
<b>2a</b>	$\text{CH}_3\text{O}$ -	82	145-146
<b>2b</b>	$\text{CH}_3\text{CH}_2\text{O}$ -	73	132-133
<b>2c</b>	$(\text{CH}_3)_2\text{CHO}$ -	71	56-57
<b>2d</b>	<i>n</i> - $\text{CH}_3(\text{CH}_2)_3\text{O}$ -	89	Oil
<b>2e</b>	$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{O}$ -	61	50-51
<b>2f</b>	$\text{CH}_3\text{CH}_2(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{O} \cdot \text{I}^-$	85 (b)	156-157

(a) Yield of isolated product. (b) Prepared from **2e**.

Table IV  
Analytical Data for New Ligands

Compound	Calculated			Found		
	C	H	N	C	H	N
<b>1a</b>	74.34	5.96	19.70	74.33	5.93	19.64
<b>1b</b>	74.34	5.96	19.70	74.23	5.91	19.61
<b>1c</b>	74.34	5.96	19.70	74.31	6.02	19.71
<b>1d</b>	80.14	5.25	14.61	79.88	5.05	14.56
<b>1e</b>	65.25	3.95	21.14	65.07	3.92	21.15
<b>1f</b>	62.33	3.92	25.45	62.41	3.94	25.52
<b>1g</b>	49.46	2.07	16.02	49.74	2.24	15.89
<b>1h</b>	72.54	4.83	22.74	72.82	4.83	22.75
<b>1j</b>	51.64	2.82	15.06	51.44	2.78	15.09
<b>1k</b>	68.73	5.24	21.86	68.83	5.29	21.60
<b>1l</b> (a)	57.52	5.05	19.17	57.27	5.23	18.70
<b>1m</b>	64.52	4.33	22.58	34.39	4.32	22.64
<b>1n</b>	70.57	5.36	19.60	70.45	5.27	19.68
<b>1o</b>	71.14	5.70	18.86	71.16	5.65	18.70
<b>1p</b>	71.66	6.01	18.17	71.46	5.92	18.14
<b>1q</b>	72.15	6.31	17.53	72.07	6.28	17.49
<b>1r</b>	69.54	6.32	20.28	69.45	6.26	19.88
<b>1s</b> (a)	53.06	5.48	14.28	53.45	5.42	13.97

(a) compound is a hydrate containing one mole of water.

that 4-diethylaminophthalonitrile ( $\nu$  CN 2220  $\text{cm}^{-1}$ ) was formed in low yield, however, it was not isolated in pure form. The reactions of 4-nitrophthalonitrile with phenol (12) and with diols (13) under similar conditions at higher temperatures have been described in the literature.

The mild conditions of this preparative method can be employed to introduce various functional groups to the phthalonitrile molecule. As shown in Table III tertiary amines and aryl nitrile groups are inert under these conditions. Preliminary indications are that other functionalized alcohols, such as chloro, ether, and amido, may also be employed in this reaction. The trialkylamine **2e** is easily alkylated to form the quaternary ammonium iodide which is perhaps the first reported water-soluble phthalonitrile. These new functionalized phthalonitriles should be of value as starting materials for a variety of substituted phthalocyanines as well as the isoindoline ligands.

## EXPERIMENTAL

Infrared spectra were taken on a Perkin-Elmer 283 infrared spectrophotometer as films or as potassium bromide pellets. The nmr spectra were recorded at 100 or 360 MHz with tetramethylsilane as the internal standard; chemical shift values are reported in ppm relative to tetramethylsilane. Melting points are reported uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

### 2-Amino-3,5-dimethylpyridine.

To 40 g of sodium amide and 91.4 g of 3,5-dimethylpyridine was added 218 ml of *N,N*-dimethylaniline. After stirring several hours at room temperature under nitrogen, the mixture was heated to 175° and maintained at that temperature for 18 hours. After cooling to room temperature, the reaction mixture was poured over ice. The organic layer was separated, dried over sodium sulfate, and distilled *in vacuo* to yield 42.2 g (36%) of a colorless oil, bp 110°/10 mm, nmr (deuteriochloroform):

$\delta$  1.99 (s, 3H), 2.09 (s, 3H), 5.01 (s, 1H), 6.82 (s, 1H), 7.60 (s, 1H).

Anal. Calcd. for  $\text{C}_7\text{H}_{10}\text{N}_2$ : C, 68.85; H, 8.20; N, 22.95. Found: C, 68.90; H, 8.13; N, 22.86.

### 2-Amino-3,4-dimethylpyridine and 2-Amino-4,5-dimethylpyridine.

To 100 g (0.935 mole) of 3,4-dimethylpyridine (Aldrich) and 40 g (1.0 mole) of sodium amide (Fisher) was added 237 ml (1.86 moles) of *N,N*-dimethylaniline. The mixture was heated with stirring under argon at 145-155° for 6.5 hours. After cooling to room temperature, the reaction mixture was added to 400 ml of ice. The organic layer was separated, dried over potassium carbonate, and distilled *in vacuo*. A fraction was collected (114-118°/8 mm) which solidified on cooling. The solid (33% yield) was identified as a 3.5:1 mixture of the 3,4-dimethyl- and 4,5-dimethyl-2-aminopyridines respectively on the basis of an nmr analysis.

The major isomer was isolated by recrystallization of the distillate from heptane-benzene. The first crop obtained was pure 2-amino-3,4-dimethylpyridine, mp 82-82°; nmr (deuteriochloroform):  $\delta$  2.06 (s, 3H), 2.24 (s, 3H), 4.38 (s, 1H), 6.44 (d, 1H,  $J = 6$  Hz), 7.73 (d, 1H).

Anal. Calcd. for  $\text{C}_7\text{H}_{10}\text{N}_2$ : C, 68.85; H, 8.20; N, 22.95. Found: C, 68.85; H, 8.26; N, 23.03.

Repeated careful fractional recrystallization of the material in the mother liquor afforded a pure sample of the other isomer, 2-amino-4,5-dimethylpyridine, as white crystals, mp 113-114°; nmr (deuteriochloroform):  $\delta$  2.08 (s, 3H), 2.13 (s, 3H), 4.18 (s, 1H), 6.11 (s, 1H), 7.53 (s, 1H).

Anal. Found: C, 68.83; H, 8.17; N, 22.96.

### 3,4-Dicyanoacetanilide.

To 1 ml of acetyl chloride in 16 ml of pyridine, was added 1.5 g of 4-aminophthalonitrile; the solution was allowed to stir at room temperature. After 45 minutes a solid had deposited; the reaction mixture was added to *ca.* 200 ml of ice, stirred for 1 hour, and then filtered. After drying (55°), 1.65 g (85%) of off-white solid was obtained. The solid could be recrystallized from acetone-water to afford white crystals, mp 193-194°; ir (potassium bromide):  $\nu$  CO 1716 and 1685  $\text{cm}^{-1}$ ; nmr (dimethylsulfoxide- $d_6$ ):  $\delta$  2.18 (s, 3H), 2.40 (s, 6H), 3.36 (s, 1H).

Anal. Calcd. for  $\text{C}_{10}\text{H}_7\text{N}_3\text{O}$ : C, 64.86; H, 3.81; N, 22.69. Found: C, 64.67; H, 3.85; N, 22.55.

### 3,4-Dicyanosulfonilide.

To 1.0 g (7.04 mmoles) of 4-aminophthalonitrile in 20 ml of pyridine was added dropwise with stirring 1 ml (an excess) of methanesulfonyl chloride. After one hour the reaction mixture was poured over 200 ml of ice. The precipitate which deposited was collected, washed with water, and dried. The tan color powder was recrystallized from acetone-water, redissolved in tetrahydrofuran, and then treated with Norit. Off-white crystals, mp 183-185°, were obtained from tetrahydrofuran-methanol in 37% yield.

Anal. Calcd. for  $\text{C}_6\text{H}_4\text{N}_2\text{O}_2\text{S}$ : C, 48.86; H, 3.19; N, 18.99. Found: C, 48.83; H, 3.20; N, 18.90.

### 4-Alkoxyphthalonitriles.

These compounds were prepared from 4-nitrophthalonitrile (9,10) and the appropriate alcohol according to the procedure given below for 4-methoxyphthalonitrile. 4-Alkoxyphthalonitriles which were not solids at ambient temperature were extracted from the aqueous dimethylformamide with toluene. The toluene extract was passed through a short column of neutral alumina and then concentrated to yield the product as an oil.

### 4-Methoxyphthalonitrile.

To 2.5 mmoles of 4-nitrophthalonitrile and 5 mmoles of potassium carbonate in a Schlenk tube under argon was added 3 ml of dimethylformamide and 5 mmoles of methanol. After stirring for 25 hours at ambient temperature, 60 ml of water was added with stirring to the suspension. The precipitate was collected by filtration, washed with water, and dried to yield 337 mg of off-white powder. The powder was recrystallized from methylene chloride-hexane to afford an 82% yield of off-white crystals, mp 145-146°; ir (potassium bromide):  $\nu$  CN 2236  $\text{cm}^{-1}$ ; nmr

(deuteriochloroform):  $\delta$  2.99 (s, 3H), 7.22 (d, 1H), 7.26 (s, 1H), 7.72 (d, 1H).

*Anal.* Calcd. for  $C_9H_6N_2O_8$ : C, 68.34; H, 3.83; N, 17.72. Found: C, 68.19; H, 3.86; N, 17.99.

#### 4-Ethoxyphthalonitrile.

This compound was obtained as white crystals, mp 132-133°; ir (potassium bromide):  $\nu$  CN 2244 (sh), 2238  $cm^{-1}$ ; nmr (deuteriochloroform):  $\delta$  1.50 (t, 3H), 4.18 (q, 2H), 7.20 (d, 1H), 7.25 (d, 1H), 7.71 (d, 1H).

*Anal.* Calcd. for  $C_{10}H_8N_2O$ : C, 69.75; H, 4.68; N, 16.27. Found: C, 69.70; H, 4.58; N, 16.25.

#### 4-*i*-Propoxyphthalonitrile.

This compound was obtained in 71% yield as off-white crystals, mp 56-57°; ir (potassium bromide):  $\nu$  CN 2236  $cm^{-1}$ ; nmr (deuteriochloroform):  $\delta$  1.45 (d, 6H), 4.76 (m, 1H), 7.26 (d, 1H), 7.31 (s, 1H), 7.79 (d, 1H).

*Anal.* Calcd. for  $C_{11}H_{10}N_2O$ : C, 70.95; H, 5.41; N, 15.05. Found: C, 70.89; H, 5.48; N, 15.00.

#### 4-*n*-Butoxyphthalonitrile.

This nitrile was obtained as a yellow oil; ir (film):  $\nu$  CN 2240  $cm^{-1}$ ; nmr (deuteriochloroform):  $\delta$  1.02 (t, 3H), 1.36-2.02 (m, 4H), 4.16 (t, 2H), 7.28 (d, 1H), 7.35 (s, 1H), 7.79 (d, 1H).

*Anal.* Calcd. for  $C_{12}H_{12}N_2O$ : C, 71.97; H, 6.04; N, 13.99. Found: C, 71.85; H, 5.99; N, 13.89.

#### 4-(2'-Dimethylaminoethoxy)phthalonitrile (2e).

The nitrile was obtained as a pale yellow oil which was difficult to crystallize. However, stirring the oil with hexanes at ambient temperature resulted in the formation of a white crystalline powder, mp 50-51°; ir (film):  $\nu$  2238  $cm^{-1}$ ; nmr (deuteriochloroform):  $\delta$  2.42 (s, 6H), 2.86 (t, 2H), 4.26 (t, 2H), 7.29 (d, 1H, J = 7 Hz), 7.33 (s, 1H), 7.74 (d, 1H, J = 7 Hz).

*Anal.* Calcd. for  $C_{12}H_{13}N_3O$ : C, 66.96; H, 6.09; N, 19.52. Found: C, 66.86; H, 5.99; N, 19.61.

#### Preparation of the Iodoethane Adduct of 2e.

To 2.65 mmoles (570 mg) of nitrile 2e in 2 ml of methylene chloride was added 2 ml of iodoethane. The solution was stirred at ambient temperature. The white solid which precipitated was collected, washed with methylene chloride, and dried to afford an 85% yield (837 mg) of white crystalline ammonium salt 2f, mp 156-157°; ir (potassium bromide):  $\nu$  CN 2242  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{14}H_{18}IN_3O$ : C, 45.30; H, 4.89; N, 11.32. Found: C, 45.34; H, 4.82; N, 11.28.

#### Preparation of the Iodomethane Adduct of 2e.

The iodomethane adduct of 2e was prepared as described above and was obtained as an off-white powder. Recrystallization from methanol-toluene provided white needles, mp 176-178°.

*Anal.* Calcd. for  $C_{13}H_{16}IN_3O \cdot \frac{1}{2}H_2O$ : C, 42.23; H, 4.72; N, 11.38. Found: C, 42.10; H, 4.77; N, 11.16.

#### 4,4'-Oxybis(phthalonitrile) (2g).

A mixture of 2 mmoles of 4-nitrophthalonitrile, 4 mmoles of anhydrous potassium fluoride and 3 ml of dimethylformamide was heated at 70-80° in a Schlenk tube under argon with stirring for 48 hours. After cooling, 50 ml of water was added and the mixture was stirred. The product was collected by filtration, washed with water, and dried to afford a 70% yield of white powder. Recrystallization from acetonitrile gave an analytical sample of white crystals, mp 254-256° dec; ir (potassium bromide):  $\nu$  CN 2240  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{16}H_8N_4O$ : C, 71.11; H, 2.24; N, 20.73. Found: C, 71.28; H, 2.43; N, 20.66.

#### Preparation of 1,3-bis(2'-Pyridylimino)isoindolines.

The new ligands were prepared from the starting materials indicated in Table I by methods described below. The preparation of ligand 1d il-

lustrates the preparation from 1,3-diiminoisoindoline, the preparation of ligand 1j illustrates the preparation of ligands directly from a phthalonitrile and 2-aminopyridine, and the preparation of ligand 1r illustrates the preparation of an ionic ligand from an ionic phthalonitrile.

#### 1,3-bis(2'-(4'-Phenyl)pyridylimino)isoindoline (1d).

A mixture of 3 mmoles (435 mg) of 1,3-diiminoisoindoline and 6 mmoles (1.0 g) of 2-amino-4-phenylpyridine in 50 ml of 1-butanol was heated with stirring at reflux for 26 hours. The reaction mixture was cooled in an ice bath, filtered, and the solid obtained was washed with methanol. The crude product was recrystallized from chloroform to yield 665 mg (46%) of yellow crystals, mp 283-284°.

#### 1,3-bis(2'-(4'-Methyl)pyridylimino)-4,5,6,7-tetrachloroisoindoline (1j).

A mixture of 4 mmoles (1.064 g) of tetrachlorophthalonitrile (Columbia), 9 mmoles (972 mg) of 2-amino-4-methylpyridine, and 1 mmole of anhydrous calcium chloride in 20 ml of 1-butanol was heated with stirring at reflux for 48 hours. After cooling, the reaction mixture was allowed to evaporate at room temperature. The residue was washed with water, dried, and recrystallized from chloroform-ethanol to afford 1.34 g (72%) of yellow crystals, mp 246-248°.

#### Preparation of Ligand 1s.

To 742 mg (2 mmoles) of nitrile 2f, 486 mg (4.5 mmoles) of 2-amino-4-methylpyridine, and 222 mg (2 mmoles) of anhydrous calcium chloride was added 8 ml of 1-butanol. The mixture was heated with stirring at reflux for 3 days. After cooling to room temperature, the mixture was transferred to a beaker and the solvent was allowed to evaporate. The residue was washed consecutively with cyclohexane, methylene chloride, diethyl ether, and water. The insoluble material was air-dried to afford 340 mg (30% yield) of orange powder, mp 217-219°. Recrystallization of the powder from methanol-toluene yielded an analytically pure sample of yellow crystals, mp 219-221° dec.

#### Anion Exchange: Preparation of Ionic Ligand 1t.

A solution of the iodide salt of ligand 1t in methanol was added to a saturated solution of ammonium hexafluorophosphate in methanol. A small amount of water was added. On standing a yellow precipitate of the hexafluorophosphate salt deposited. The precipitate was collected, washed with water, and dried. A concentrated solution of the precipitate in acetone was added to a saturated solution of lithium chloride in acetone. On standing a new yellow solid deposited. Recrystallization of the solid from a methanol-toluene-acetone mixture afforded bright yellow crystals, mp (sealed capillary) 241-243° dec, which exhibited no hexafluorophosphate bands in the infrared. The hygroscopic crystals gave repeated analyses with the correct C/N ratio but with varying amounts of water.

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