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# OXIDATIVE DIMERIZATION OF SUBSTITUTED *o*-METHYLPHENYL ISOCYANIDES; SYNTHESIS OF BIDENTATE BIS-ISONITRILE AND CYCLIC TETRADENTATE TETRAKIS-ISONITRILE LIGANDS

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## Summary

Substituted *o*-methylphenyl isocyanides (**1**) were oxidatively dimerized via the corresponding *o*-lithiomethylphenyl isocyanides (**2**) by means of 1,2-dibromoethane to give 1,2-bis(2-isocyanophenyl)ethane derivatives (**3**). 1,2-Bis(2-isocyano-3-methylphenyl)ethane (**3e**), a coupling dimer of 2,6-xylyl isocyanide (**1e**), was further dimerized via its dilithiated intermediate to give a cyclic tetramer of 2,6-xylyl isocyanide (**1e**), which may be a cyclic tetradentate ligand for transition metal compounds.

## Introduction

Nucleophilic carbon–carbon bond formation with α-metalated isocyanides, coupled with subsequent intramolecular ring closure at the isocyano carbon, has provided a useful method for the synthesis of heterocycles [1]. In the preceding papers [2], we reported methods for the synthesis of some heterocycles including indoles on the basis of the selective lithiation at the *o*-methyl group of *o*-methylphenyl isocyanide (**1a**). This paper describes a new preparation of bidentate bis-isonitrile and cyclic tetradentate tetrakis-isonitrile ligands by oxidative coupling of *o*-methylphenyl isocyanides (**1**). This novel oxidative dimerization of substituted *o*-methylphenyl isocyanides (**1**) to 1,2-bis(2-isocyanophenyl)ethane derivatives (**3**) was carried out simply by treatment with 1,2-dibromoethane of the *o*-(α-lithiomethyl)phenyl isocyanides (**2**) generated in situ.

1,2-Bis(2-isocyano-3-methylphenyl)ethane (**3e**) thus prepared, which is a coupling dimer of 2,6-xylyl isocyanide (**1e**), was also selectively lithiated at both methyl groups on the aromatic rings by lithium diisopropylamide (LDA). The resulting 1,2-bis(2-isocyano-3-lithiomethylphenyl)ethane intermediate (**11**) was convertible to

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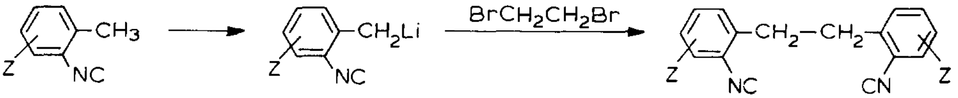
heterocyclic compounds, which corresponds to dimers of those prepared previously from *o*-lithiomethylphenyl isocyanide (**2a**) [2]. Furthermore, the oxidative cyclodimerization of 1,2-bis(2-isocyano-3-methylphenyl)ethane (**3e**) via its dilithiated intermediate (**11**) gave the cyclic tetra-isocyanide **15**, a tetramer of 2,6-xylyl isocyanide (**1e**), which may be a cyclic tetradentate ligand for transition metals. Complexations of **15** with some transition metal compounds are also described [3].

## Results and discussion

On treatment with 1,2-dibromoethane, *o*-lithiomethylphenyl isocyanides (**2a–2e**), which are generated in situ from *o*-methylphenyl isocyanides (**1a–1e**) and 2 equivalents of LDA in diglyme at −78°C according to a procedure reported [2], were quickly dimerized to give 1,2-bis(isocyanophenyl)ethanes (**3a–3e**) in good yields.

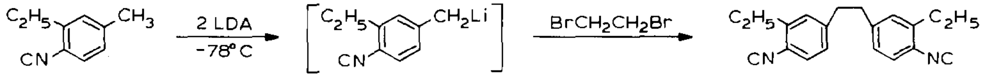


(1) (2) (3)

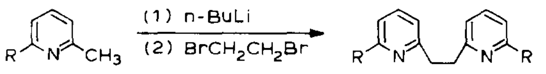
The oxidative dimerization of *o*-methylphenyl isocyanides (**1**) may be reasonably explained in terms of one electron oxidation of the *o*-(lithiomethyl)phenyl isocyanides (**2**) followed by recombination of the resulting benzylic radical. The use of bromine and carbon tetrabromide instead of 1,2-dibromoethane in the present reaction gave the dimer **3** but in lower yields.

*o*-Alkylphenyl isocyanides such as *o*-ethylphenyl isocyanide (**1f**) and 5,6,7,8-tetrahydro-1-naphthyl isocyanide (**1h**) were also dimerized in moderate yields by a similar procedure except that lithium 2,2,6,6-tetramethylpiperidide (LTMP) was used for the lithiation of **1f** and **1h**. Some oxidative dimerizations of substituted *o*-methylphenyl isocyanides (**1**) are summarized in Table 1.

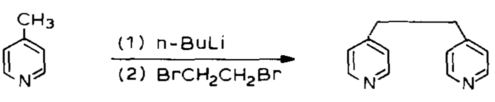
The application of the present oxidative dimerization is furthermore demonstrated by the following related examples. 2-Ethyl-4-methylphenyl isocyanide (**4**) gave a coupling dimer (**6**) in good yield, which was derived via lithiation at the 4-methyl group of **4**. 2- and 4-Methylpyridines, **7** and **9** respectively, were also oxidatively dimerized via their lithiomethylpyridines to the corresponding 1,2-dipyridylethanes (**8** and **10**).



(4) (5) (6) (75%)



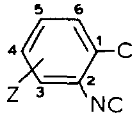
(7) (8a: R = H (57%); 8b: R = CH3 (78%))



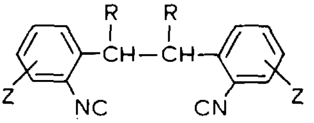
(9) (10) (35%)

TABLE 1

OXIDATIVE DIMERIZATIONS OF SUBSTITUTED *o*-METHYLPHENYL ISOCYANIDES



(1)



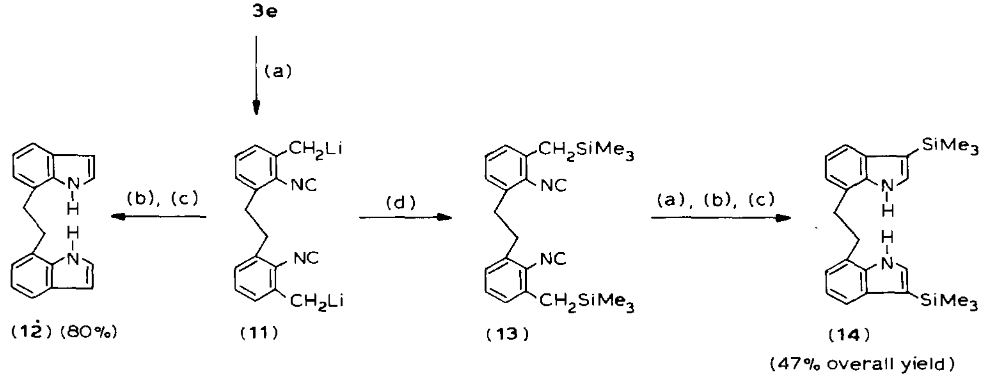
(3) (Yield %)[a]

| R | Z | | | |
|---|---|---|---|---|
| H | H | **1a** | 94 | **3a** |
| H | 5-$CH_3$ | **1b** | 80 | **3b** |
| H | 5-Cl | **1c** | 87 | **3c** |
| H | 5-$CH_3O$ | **1d** | 49 | **3d** |
| H | 3-$CH_3$ | **1e** | 69 | **3e** |
| $CH_3$ | H | **1f** | 60 | **3f** [b] |
| $CH_3S$ | H | **1g** | 48 | **3g** [b] |
| -$(CH_2)_3$- | | **1h** [c] | 41 | **3h** [b] |

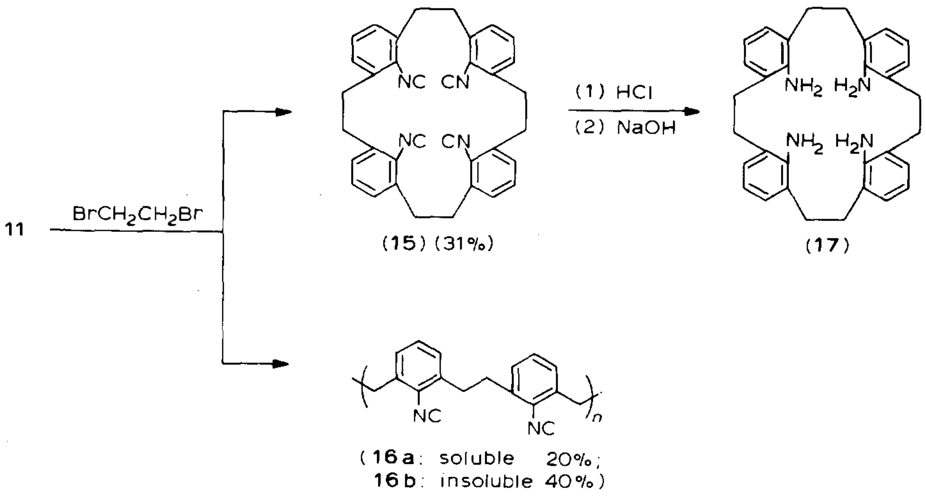
[a] Isolated yields. [b] Diastereomeric mixture. [c] 5,6,7,8-Tetrahydro-1-naphthyl isocyanide.

As may be expected, 1,2-bis(2-isocyano-3-methylphenyl)ethane (**3e**) underwent selective lithiation at the two methyl groups on treatment with 4 molar equivalents of LDA at −78°C. The 1,2-bis(2-isocyano-3-lithiomethylphenyl)ethane (**11**) generated in situ, was converted to dimeric indole derivatives according to the procedure reported [2] for the preparations of indoles from *o*-methylphenyl isocyanide, as shown in Scheme 1.

Moreover, the dilithiated di-isocyanide **11** was dimerized on treatment with dibromoethane to give the cyclic tetra-isocyanide **15** ($\nu$(C≡N) 2105 $cm^{-1}$), tetramer of 2,6-xylyl isocyanide, in 31% isolated yield together with soluble and insoluble poly-isocyanides **16** (20% and 40% yields). The cyclic tetra-isocyanide **15** was hydrolyzed by aqueous HCl to give cyclic tetra-amine **17** in 65% yield after neutralization with aqueous NaOH.



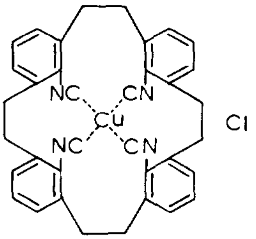
SCHEME 1. (a) 4LDA, −78°C; (b) −78°C to r.t.; (c) $H_2O$; (d) 4 $Me_3SiCl$.



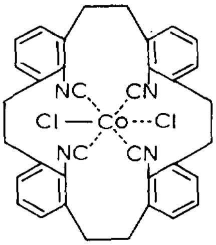
Finally, transition metal complexation [3] with the cyclic tetra-isocyanide **15** is mentioned. A suspension of $Cu^{I}Cl$ in chloroform was treated with cyclic tetra-isocyanide **15** to form a stable 1/1 coordination complex (**18**) in an almost quantitative yield, which exhibited a single IR absorption $\nu(N{\equiv}C)$ at 2145 $cm^{-1}$. The structure of the copper(I) isonitrile complex **18** was assigned by analogy with tetrakis(phenylisocyano)copper(I) chloride, $(PhNC)_4Cu^+\ Cl^-$, already known [4] as well as by combustion analysis.

The copper(I) isonitrile complex **18**, which was very stable and could be stored for a long period without change, behaves different from tetrakis(phenylisocyano)copper(I) chloride, which is readily converted to a stable tris(phenylisocyano)copper(I) chloride, $(PhNC)_3CuCl$, even on reprecipitation from a chloroform and ether solution [4]. Decomplexation of **18** was, however, carried out by treatment with KCN or magnesium metal, resulting in quantitative recovery of the cyclic tetra-isocyanide ligand **15**.

Similarly, $Co^{II}Cl_2$ was treated with the cyclic tetra-isocyanide **15** to produce a cobalt(II) complex (**19**), which is compared with $(PhNC)_4Co^{II}Cl_2$ as reported [5]. The cyclic tetra-isocyanide nickel(0) complex **20** [6] was prepared by a ligand exchange reaction of nickel(0) tetracarbonyl with cyclic tetra-isocyanide **15**. The ligand displacement rapidly proceeded with vigorous evolution of carbon monoxide. The same nickel(0) complex **20** was also obtained by a ligand exchange reaction of tetrakis(2,6-dimethylphenyl isocyano)nickel(0) [7] with cyclic tetra-isocyanide **15**.



(18)



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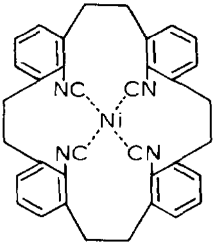

(20)

## Experimental

Substituted *o*-alkylphenyl isocyanides (**1**) were prepared by dehydration of the corresponding *N*-arylformamides according to the procedure reported by Ugi [8]. n-Butyllithium (1.6 *M* in hexane) was purchased from Aldrich Inc. Other organic reagents and solvents was commercially available and distilled in nitrogen before use. CuCl, $CoCl_2$ and $Ni(CO)_4$ were also commercially available and were used without purification.

### *1,2-Bis(2-isocyanophenyl)ethane (3a)*

176 mg (1.5 mmol) of *o*-methylphenyl isocyanide (**1a**) was added to a well stirred solution of 3 mmol of LDA in 4 ml of diglyme at −78°C and the mixture was stirred for 30 min at the same temperature. 260 mg (3 mmol) of 1,2-dibromoethane was added at −78°C to the red solution. The red color of **2a** soon turned light yellow. The resulting mixture was quenched with aqueous $NH_4Cl$ and extracted with ether. The ether extract was washed with water, dried over anhydrous $Na_2SO_4$ and evaporated in vacuo. The residual solid was recrystallized from ethanol to give 1,2-bis(2-isocyanophenyl)ethane (**3a**) (m.p. 118–120°C) in 94% yield. Found: C, 82.56; H, 5.33; N, 12.18. $C_{16}H_{12}N_2$ calcd.: C, 82.73; H, 5.21; N, 12.06%. IR (KBr disk): 2115 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 3.07 (s, 4H), 7.28 (s, 8H) ppm.

Oxidative dimerizations of other *o*-alkylphenyl isocyanides (**1** and **4**) were carried out according to the procedure described above except that lithium 2,2,6,6-tetramethylpiperidide (LTMP) was used in place of LDA for lithiations of **1f**, **1g** and **1h**.

### *1,2-Bis(2-isocyano-5-methylphenyl)ethane (3b)*

M.p. 128–129°C from EtOH. Found: C, 82.89; H, 6.11; N, 10.54. $C_{18}H_{16}N_2$ calcd.: C, 83.04; H, 6.20; N, 10.76%. IR (KBr disk): 2115 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 2.25 (s, 6H), 2.90 (s, 4H), 6.8–7.2 (m, 6H) ppm.

### *1,2-Bis(2-isocyano-5-chlorophenyl)ethane (3c)*

M.p. 168–171°C from EtOH. Found: C, 63.70; H, 3.48; N, 9.17. $C_{16}H_{10}N_2Cl_2$ calcd.: C, 63.81; H, 3.35; N, 9.30%. IR (KBr disk): 2125 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 3.00 (s, 4H), 7.17 (m, 6H) ppm.

### *1,2-Bis(2-isocyano-5-methoxyphenyl)ethane (3d)*

M.p. 162–163°C from EtOH. Found: C, 73.81; H, 5.30; N, 9.53. $C_{18}H_{16}N_2O_2$ calcd.: C, 73.95; H, 5.52; N, 9.58%. IR (KBr disk): 2105 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 3.04 (s, 4H), 3.79 (s, 6H), 6.55–6.85 (m, 4H), 7.15–7.44 (m, 2H) ppm.

### *1,2-Bis(2-isocyano-3-methylphenyl)ethane (3e)*

M.p. 151–154°C from MeOH. Found: C, 83.24; H, 6.45; N, 10.51. $C_{18}H_{16}N_2$ calcd.: C, 83.04; H, 6.20; N, 10.76%. IR (KBr disk): 2120 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 2.43 (s, 6H), 3.02 (s, 4H), 7.05 (m, 6H) ppm.

### *2,3-Bis(2-isocyanophenyl)butane (3f)*

A 1/1 diastereomeric mixture. Found: C, 83.30; H, 6.01; N, 10.88. $C_{18}H_{16}N_2$ calcd.: C, 83.04; H, 6.20; N, 10.76%. IR (KBr disk): 2115 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 1.09 and 1.44 (d of d, 6H), 3.5 (m, 2H), 6.9–7.5 (m, 8H) ppm.

### *1,2-Bis(2-isocyanophenyl)-1,2-di(methylthio)ethane (3g)*

A 3/2 diastereomeric mixture. M.p. 144–147°C from EtOH. Found: C, 66.38; H, 5.12; N, 8.51. $C_{18}H_{16}N_2S_2$ calcd.: C, 66.63; H, 4.97; N, 8.63%. IR (KBr disk): 2120 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 1.75 and 1.89 (d of s, 6H), 2.52 and 2.61 (d of s, 2H), 6.9–7.7 (m, 8H) ppm.

### *1,1'-Diisocyano-5,5',6,6',7,7',8,8'-octahydro-8,8'-binaphthyl (3h)*

M.p. 226–228°C from EtOH. Found: C, 84.73; H, 6.33; N, 8.68. $C_{22}H_{20}N_2$ calcd.: C, 84.58; H, 6.45; N, 8.97%. IR (KBr disk): 2105 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 1.20–2.50 (m, 8H), 2.50–3.25 (m, 4H), 3.26–3.63 (m, 2H), 6.63–7.33 (m, 6H) ppm.

### *1,2-Bis(3-ethyl-4-isocyanophenyl)ethane (6)*

TLC (silica gel-$C_6H_6$) $R_f = 0.63$. Found: C, 83.42; H, 6.82; N, 9.55. $C_{20}H_{20}N_2$ calcd.: C, 83.29; H, 6.99; N, 9.71%. IR (neat): 2120 $cm^{-1}$; NMR ($CCl_4$ with $Me_4Si$): $\delta$ 1.20 (t, 6H), 1.68 (q, 4H), 1.80 (s, 4H), 6.8–7.2 (m, 3H) ppm.

### *1,2-Di-2-pyridylethane (8a)*

1.5 mmol of butyllithium (1.6 *M* hexane solution) at −20°C was added to a well stirred solution of 140 mg (1.5 mmol) of 2-methylpyridine in 2 ml of ether and the mixture was stirred for 30 min. 282 mg (1.5 mmol) of 1,2-dibromoethane was added to the red solution. The red color of the reaction mixture immediately turned yellow. The mixture was quenched with water and extracted with ether. The ether extract was dried and distilled to give 1,2-di-2-pyridylethane (**8a**) (b.p. 108°C/0.6 Torr; m.p. 40–42°C) in 57% yield. Found: C, 78.42; H, 6.50; N, 15.11. $C_{12}H_{12}N_2$ calcd.: C, 78.23; H, 6.57; N, 15.21%. IR (neat): 1588, 1563, 1474 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 3.24 (s, 4H), 6.9–7.4 (m, 6H), 8.5–8.7 (m, 2H) ppm.

In a similar way, 2,6-dimethylpyridine (**7b**) and 4-methylpyridine (**9**) were oxidatively dimerized.

### *1,2-Bis(6-methyl-2-pyridyl)ethane (8b)*

M.p. 48°C from hexane. Found: C, 79.44; H, 7.38; N, 13.33. $C_{14}H_{16}N_2$ calcd.: C, 79.21; 7.60; N, 13.20%. IR (KBr disk): 1593, 1577, 1456 $cm^{-1}$; NMR ($CCl_4$ with $Me_4Si$): $\delta$ 2.50 (s, 6H), 3.16 (s, 4H), 6.79 (d, 4H), 7.32 (dd, 2H) ppm.

### *1,2-Di-4-pyridylethane (10)*

B.p. 95°C/0.6 Torr; m.p. 105–108°C. Found: C, 78.12; H, 6.48; N, 15.35. $C_{12}H_{12}N_2$ calcd.: C, 78.23; H, 6.57; N, 15.21%. IR (neat): 1598, 1416 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 2.77 (s, 4H), 6.93 (dd, 4H), 8.37 (dd, 4H) ppm.

### *1,2-Bis-7-indolylethane (12)*

390 mg (1.5 mmol) of **3e** in 5 ml of diglyme was added to a well stirred solution of 6 mmol of LDA in 8 ml of diglyme at −78°C. The red solution of 1,2-bis[2-isocyano-3-(lithiomethyl)phenyl]ethane (**11**) was allowed to warm up to room temperature, and then quenched with aqueous $NH_4Cl$ and extracted with ether. The ether extract was evaporated, and chromatographed on silica gel with benzene to give 1,2-bis-7-indolylethane (**12**) (TLC $R_f = 0.70$; m.p. 201°C) in 80% yield. Found: C, 83.12; H, 6.02; N, 10.49. $C_{18}H_{16}N_2$ calcd.: C, 83.04; H, 6.20; N, 10.76%. IR (KBr

disk): 3385 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 3.15 (s, 4H), 6.3 (m, 2H), 6.7–7.5 (m, 8H), 7.7 (broad 2H) ppm.

*1,2-Bis[2-isocyano-3-(trimethylsilylmethyl)phenyl]ethane (13)*

4.10 mg (4 mmol) of trimethylchlorosilane was added to a well stirred solution of 1 mmol of **11** described above at −78°C. After 30 min stirring, the mixture was quenched with water and extracted with ether. The ether extract was evaporated and subjected to preparative TLC on silica gel to give **13** (TLC (silica gel/$C_6H_6$) $R_f = 0.87$; m.p. 102–103°C) in 74% yield. Found: C, 71.39; H, 8.12; N, 7.17. $C_{24}H_{32}N_2Si_2$ calcd.: C, 71.24; H, 7.97; N, 6.92%. IR (KBr disk): 2105, 1250, 855 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 0.06 (s, 18H), 2.31 (s, 4H), 3.08 (s, 4H), 6.9–7.4 (m, 6H).

*1,2-Bis[3-(trimethylsilyl)7-indolyl]ethane (14)*

**14** (TLC (silica gel/$CHCl_3$) $R_f = 0.92$) was prepared in 64% yield from **13** in a similar manner to the preparation of 1,2-bis-7-indolylethane (**12**). Found: C, 70.97; H, 8.01; N, 6.91. $C_{24}H_{32}N_2Si_2$ calcd.: C, 71.24; H, 7.97; N, 6.92%. IR (KBr disk): 3450, 1245, 835 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 0.17 (s, 18H), 3.20 (s, 4H), 6.54 (d, 2H), 7.0–7.7 (m, 8H) ppm.

*Cyclodimerization of 1,2-bis(2-isocyano-3-methylphenyl)ethane (3e), cyclic tetra-isocyanide 15*

1040 mg (4 mmol) of **3e** in 20 ml of diglyme was added to a well stirred solution of 16 mmol of LDA in 120 ml of diglyme at −78°C and the mixture was stirred for 30 min at the same temperature. 3 g (16 mmol) of 1,2-dibromoethane to the red mixture was added dropwise. The red color faded gradually, but did not disappear completely. The mixture was stirred for 7 h at −78°C and poured into aqueous $NH_4Cl/CHCl_3$ with stirring. The resulting mixture was filtered to remove polymeric isocyanide. The chloroform layer was washed with water and dried over anhydrous $Na_2SO_4$. After the chloroform solution was evaporated in vacuo, the residual solid was subjected to preparative TLC to give 320 mg (31%) of crude cyclic tetra-isocyanide **15**, which was purified by recrystallization from $C_6H_6$/MeOH (1/1) (m.p. 260°C (dec.)). Found: C, 83.94; H, 5.64; N, 10.58. $C_{36}H_{28}N_4$ calcd.: C, 83.69; H, 5.46; N, 10.85%. IR (KBr disk): 2105 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 3.08 (s, 16H), 6.9–7.4 (m, 12H); Mass spectrum: 516 ($M^+$).

*Conversion of cyclic tetra-isocyanide 15 to cyclic tetra-amine 17*

1.8 ml of concentrated hydrochloride was added to a solution of 115 mg (0.22 mmol) of cyclic tetra-isocyanide **15** in 5.5 ml of $MeOH/CHCl_3$ (3/2). The mixture was heated under reflux for 30 h, and evaporated. The residue was suspended in 4 ml of $MeOH/H_2O$, neutralized with aqueous NaOH, and then extracted with $CHCl_3$. The extract was evaporated and chromatographed on silica gel with $CHCl_3$/AcOEt (1/1) to give 68 mg (65%) of cyclic tetra-amine **17** (TLC $R_f = 0.59$; m.p. 244–246°C). Found: C, 80.84; H, 7.58; N, 11.58. $C_{32}H_{36}N_4$ calcd.: C, 80.63; H, 7.61; N, 11.76%. IR (KBr disk): 3425, 3350, 1620 $cm^{-1}$; NMR ($CDCl_3$ with $Me_4Si$): $\delta$ 2.63 (s, 16H), 3.04 (s, 8H), 6.2–6.8 (m, 12H) ppm.

*Complexation of cyclic tetra-isocyanide 15 with $Cu^ICl$*

100 mg (0.19 mmol) of **15** in 1 ml of chloroform was added to a suspension of

19.2 mg (0.19 mmol) of $Cu^ICl$ in 2.5 ml of chloroform. The mixture was stirred overnight at room temperature, and then filtered and washed with $CHCl_3$ to remove any unreacted **15**. The solid was dissolved in $MeOH/CHCl_3$, filtered and reprecipitated with $C_6H_{14}/CHCl_3$ (10/1) to give an almost quantitative yield of a cyclic tetra-isocyanide copper(I) chloride complex (**18**) (m.p. 250°C (dec.)). Found: C, 70.08, H, 4.55; N, 8.91; Cl, 5.84. $C_{36}H_{28}N_4ClCu$ calcd.: C, 70.23; H, 4.58; N, 9.10; Cl, 5.76%. IR (KBr disk): 2145 $cm^{-1}$.

*Decomplexation of 18*

(a) 39 mg (0.6 mmol) of potassium cyanide was added to a well stirred solution of 62 mg (0.1 mmol) of $Cu^ICl$ complex **18** in 2 ml of methanol. A white solid soon precipitated. The mixture was stirred for 3 h at room temperature and filtered. The filtrate was evaporated and chromatographed on silica gel with $CHCl_3$ to give cyclic tetraisocyanide **15**. (b) A suspension of 50 mg (0.08 mmol) of $Cu^ICl$ complex **18**, and 20 mg (0.8 mg atom) of Mg metal in 2 ml of THF was stirred overnight at room temperature. The mixture was filtered and washed with THF. The solid was chromatographed on silica gel with $CHCl_3$ to give cyclic tetra-isocyanide, **15**.

*Complexation of cyclic tetra-isocyanide 15 with $Co^{II}Cl_2$*

A mixture of 52 mg (0.1 mmol) of **15** and 13 mg (0.1 mmol) of $Co^{II}Cl_2$ in 5 ml of ethanol was stirred overnight at room temperature. The mixture was filtered and washed with EtOH and then $CHCl_3$ to give analytically pure cyclic tetra-isocyanide cobalt(II) dichloride complex **19**. Found: C, 66.89; H, 4.09; N, 8.29; Cl, 10.99. $C_{36}H_{28}N_4Cl_2Co$ calcd.: C, 66.88; H, 4.37; N, 8.67; Cl, 10.97%. IR (KBr disk): 2175 $cm^{-1}$.

*Ligand displacement of $Ni(CO)_4$ with cyclic tetra-isocyanide 15*

8.8 mg (0.052 mmol) of $Ni(CO)_4$ was added to a well stirred solution of 27 mg (0.052 mmol) of **15** in 3 ml of benzene. The reaction proceeded with vigorous evolution of carbon monoxide. After the evolution of carbon monoxide ceased, the mixture was heated at 50°C for 1 h and evaporated. The residual solid was analytically pure and the IR spectrum was consistent with the cyclic tetra-isocyanide nickel(0) complex **20**. Found: C, 75.02; H, 4.79; N, 9.15. $C_{36}H_{28}N_4Ni$ calcd.: C, 75.15; H, 4.91; N, 9.74%. IR (KBr disk): 1994, 2030 $cm^{-1}$.

Similarly, the ligand displacement reaction of tetrakis(2,6-dimethylphenylisocyano)nickel(0) [7] with cyclic tetra-isocyanide **15** was carried out and yielded **20**.

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