DIRECT SYNTHESIS OF DISUBSTITUTED AROMATIC POLYIMINE CHELATES

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Summary. The reaction of an alkyl- or aryl-lithium with 1,10-phenanthroline followed by hydrolysis and rearomatisation with manganese dioxide gives good yields of the 2,9-disubstituted product. This synthetic method has been extended to other polyimines such as 2,2'-bipyridine, 2,2',6',2"-terpyridine and 1,8-naphtyridine.

Chelating polyimines of the 1,10-phenanthroline family with vicinal nitrogen substituents are mainly restricted to the dimethylated molecule¹. The recent finding that rhodium and iridium complexes of 2,9-dimethyl-1,10-phenanthroline, or their water soluble derivatives, are efficient water gas shift catalysts² has prompted us to develop a synthetic route to other 2,9-disubstituted phenanthrolines. The introduction of sterically hindering substituents could potentially lead to coordination-unsaturated complexes which can then interact specifically with small substrates. In addition, if two or more ligands wrap around the metal center and interpenetrate each other, one would obtain complexes containing a metal efficiently protected from its environment. The preparation of aromatic polyimines with vicinal nitrogen substituents by a Skraup-type synthesis has failed except for methylated compounds. Although the results described in the literature concerning the reaction of phenyl lithium with 1,10-phenanthroline (phen) as a synthetic route to 2,9diphenyl 1,10-phenanthroline (dp-phen) were negative³, we obtained a 70% yield of the desired product by direct synthesis, as described in equation (1):



To our knowledge, this procedure represents the first synthesis on a preparative scale of this, until now, ignored dp-phen ligand⁴. Due to the apparent contradiction between the literature³ and our results, various experimental conditions have been tried. Surprisingly, the yield of isolated dp-phen is almost entirely independent on the solvent used (hexane, ether, THF). In addition, no salt effect was observed: identical results were obtained with either commercial PhLi containing LiBr or freshly prepared salt free PhLi⁵. However, the nature of the dehydrogenating agent used after PhLi addition and hydrolysis is of prime importance. The use of KMnO₄ or Ph-NO₂ gives much lower yields of dp-phen than MnO₂⁶.

The preparation of other 2,9-disubstituted phenanthrolines by reacting various aryl- or alkyl-lithium has been carried out with acceptable yields, as indicated in Table !.

Starting Compound	Reagent	Product	Melting Point	Yield X	Chromatographic method: support, eluant
1,10-phenanthroline (phen)	PhLi (C ₆ H ₆ -ether, 3/1)	2,9-diphenyl 1,10- phenanthroline (dp-phen)	183-184 ^(a)	70	Silica, hexane-CH ₂ Cl ₂ (1/1)
1,10-phenanthroline (phen)	n-Buli (hexane)	2,9-di n-butyl 1,10- phenanthroline (dn-Bu-phen)	53-55	56	Silica, hexane-CH ₂ Cl ₂ (9/1)
l,10-phenanthroline (phen)	t-BuLi (pentane)	2,9-di t-butyl 1,10-phenanthroline (dt-Bu-phen)	157-159	36	Silica, hexane-CH ₂ Cl ₂ (8/2)
4,7-diphenyl 1,10-phenanthroline (4,7-dp-phen)	PhLi (C ₆ H ₆ -ether, 3/1)	2,4,7,9-tetraphenyl 1,10-phenanthroline (tp-phen)	>260 ^(b)	80	Silica, hexane-CH ₂ Cl ₂ (1/1)

Table 1. Synthesis of 2,9-disubstituted phenanthrolines

(a) literature³: 185-186; (b) literature³: 318-319.

The direct introduction of phenyl substituents α to the nitrogen atoms has also been performed with other polyimines. The starting compounds and the products obtained are presented in the figure and the preparative data are collected in Table 2.





R=H : terpy

R=Ph: dp-terpy

 $R_{1} = R_{2} = H$: napy $R_{1} = H, R_{2} = Ph$: p-napy $R_{1} = R_{2} = H$: dp-napy

R = Ph : dp-bipy

R = H ; bipy

Starting Compound	Product	Melting Point	Yield X	Chromatographic method: support, eluant
2,2'-bipyridine (bipy)	6,6'-diphenyl 2,2'-bipyridine (dp-bipy)	176-177 ^(b)	35	Silica, hexane-ether (9/1)
2,2',6',2"-terpyridine (terpy)	6,6"-diphenyl 2,2',6',2"-ter- pyridine (dp-terpy)	202-204	21	Silica, hexane-toluene (1/1)
1,8-naphtyridine (napy)	2-phenyl 1,8-naphtyridine (p-napy)	115-116	65	(c)
2-phenyl 1,8-naphtyridine (p-napy)	2,7-diphenyl 1,8-naphtyridine (dp-napy)	207-208	80	Alumina, hexane-ether (1/1)

Table 2. Synthesis of phenylated aromatic polyimines: preparative data^(a).

(a) The reagent is PhLi (1,5 M in C₆H₆-ether, 3/1); see text for experimental details. ^(b) literature⁷: 176-178. ^(c) The product was purified by recristallization from ether.

The following experimental procedure is representative. To a stirred suspension of starting aromatic imine (2 mmoles) in anhydrous toluene (7 ml), the desired aryl- or alkyl-lithium (8 mmoles; solvent indicated in Table 1) is added dropwise under argon. The rate of addition is adjusted in order to maintain the reaction temperature around 30°C. The dark red mixture is stirred at room temperature overnight, after which 10 ml H_20 are slowly added at 0°C under argon. The organic phase is separated, the aqueous phase is extracted three times with 40 ml CH_2Cl_2 and the organic fractions collected. 20 g MnO_2 (Merck, catalogue number 805958) are added to the intense yellow solution. The mixture is stirred at room temperature for 30 min. when partial decoloration occurs. The reaction is easily monitored by thin layer chromatography (silica). Addition of magnesium sulfate (20 g) and additional stirring for 30 min. is followed by filtration and evaporation of the filtrate. The residue is chromatographically separated as indicated in Tables 1 and 2. ¹H and ¹³C NMR spectra, C,H,N analysis and electronic spectra of the compounds prepared verify their structure.

The yields reported in Tables I and 2 are moderate to good: phen (or its 4,7-diphenyl derivative) is a better reagent than the other aromatic imines shown in Table 2. This is probably due to its highly condensed aromatic character. The introduction of two phenyl rings⁷ or two butyl substituents⁸ α to the nitrogen atoms of bipy has been reported ($\sim 5\%$ and 41% yield respectively) as well as that of one methyl or one phenyl at the 6 position⁸. The dramatic improvement obtained with our method especially for synthesis of dp-bipy⁷ might be due to the oxidizing agent used in the rearomatisation step as well as to the temperature of PhLi addition. 2,7-diphenyl 1,8-naphtyridine (dp-napy) was prepared in good yield by stepwise introduction of the two phenyl rings, but no diphenylated compound was obtained by direct treatment of napy with four equivalents of PhLi.

Terpy turned out to give lower yields of diphenylated compound than phen or bipy; this is in agreement with its less pronounced electrophilic character with respect to bipy, as reported earlier by others⁹.

The synthetic method described in the present report should allow the straightforward preparation of multifunctional or macrocyclic ligands built on classical polyimine chelates such as phenanthroline or its analogues. Acknowledgement.

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