Pergamon

Tetrahedron Letters, Vol. 38, No. 47, pp. 8159-8160, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10223-4

Synthesis of Free and Ruthenium Coordinated 5,6-Diamino-1,10-phenanthroline

Swamy Bodige and Frederick M. MacDonnell*

Department of Chemistry and Biochemistry
The University of Texas at Arlington, Arlington, Texas 76019

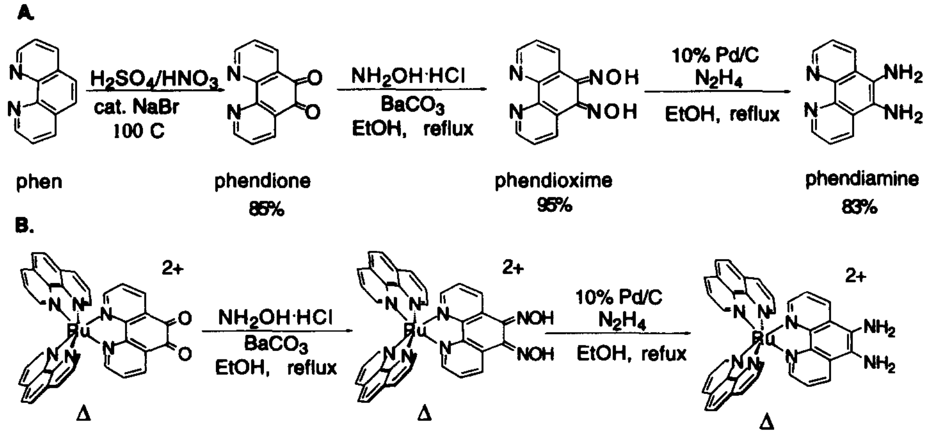
Abstract: A new preparative route to 5,6-diamino-1,10-phenanthroline is described which triples the isolated yields found in existing syntheses (67% *vs.* 22% from 1,10-phenanthroline) and utilizes mild reaction conditions. The method is general and can even be used on chiral metal complexes containing the appropriate starting material/ligand, 1,10-phenanthroline-5,6-dione, with retention of stereochemistry. © 1997 Elsevier Science Ltd.

1,10-Phenanthroline (phen) and its derivatives play important roles as molecular scaffolding for supramolecular assemblies.[1,2] One especially important and desirable class of derivatives are those which retain the twofold symmetry of this ligand and thereby avoid some of the stereochemical problems associated with their tris chelated metal complexes, namely formation of *mer* and *fac* isomers. 5,6-Diamino-1,10-phenanthroline (phendiamine) is particularly important in that it can either directly bridge two metal centers or be condensed with a variety of ortho-quinones to form additional derivatives. For example, the useful bridging ligand, tetrapyrido[3,2-a:2',3",2"-h:2"',3"'-j]phenazine (tpphz), is readily formed upon condensation of phendiamine with 1,10-phenanthroline-5,6-dione (phendione).[3]

The synthesis of 5,6-diamino-1,10-phenanthroline was only recently reported by two independent groups.[3,4] The two procedures are similar and are comprised of two steps: i) amination of 5-nitrophenanthroline with hydroxylamine in strongly basic medium or with liquid ammonia in presence of strongly oxidizing agent $KMnO_4$ ii) subsequent reduction of 5-nitro-6-amino-1,10-phenanthroline. Overall yields are low, approximately 25% from 5-nitrophenanthroline or 22% from phen, largely due to the poor yields in the amination step. This report describes a new two step synthesis of phendiamine from phendione in which yields are approximately triple (typical yields are 79% based on phendione, 67% based on phen) those previously obtained. Furthermore, the reaction conditions are relatively mild, permitting conversion of N,N-coordinated phendione to the coordinated diamine in similar yields.

As shown in Scheme 1A, phendione[5] is converted to the dioxime by a modification of the procedure first reported by Inglett and Smith.[6] NMR data obtained in DMSO with added $ZnCl_2$ reveal the crude product to be approximately 95% pure, consisting of a mixture of the *syn* and *anti* - isomers in approximately a 1:2 ratio, respectively. Due to poor solubility, the dioxime is not purified further before conversion to the diamine. Catalytic reduction (10% Pd/C) of a slurry of the dioxime in EtOH with hydrazine hydrate cleanly yields the diamine as a tan solid. The coordinated diamine was prepared similarly (Scheme 1B) starting from $[(phen)_2Ru(phendione)]Cl_2$.[7] The stereochemistry about the ruthenium is unaffected as evidenced by the similarity of the sign and magnitude of the CD spectra of the product if resolved Δ (or Λ)-$[(phen)_2Ru(phendione)]Cl_2$ is used as starting material.[8] Such properly modified chiral complexes have been shown to be useful precursors for the synthesis of variety of optically pure dinuclear[8], tetranuclear[9] and dendrimeric metal complexes.

Scheme 1.



1,10-phenanthroline-5,6-dioxime: A mixture of 0.420g (2.00 mmol) phendione, 0.486g (7.00 mmol) of $NH_2OH \cdot HCl$, and 0.592g of (3.00 mmol) of $BaCO_3$ in 30 mL of ethanol were stirred and refluxed for 12 hr. After removal of the solvent, the residue was treated with 40 mL of 0.2 M HCl, stirred for 30 minutes and filtered. The light yellow solid was washed with succesively water, ethanol and ether and dried under vacuum at 80°C. Yield 0.464g (95%). m.p. 230°C (dec). Anal. Calcd for $C_{12}H_8N_4O_2 \bullet 0.25\ H_2O$: C, 58.89; H, 3.49; N, 22.89. Found: C, 58.74; H, 3.24; N, 22.47. EIMS (m/z) 240.0 (M^+).

5,6-diamino-1,10-phenanthroline: A slurry of 0.400g (1.63 mmol) of phendioxime and 0.40 g of Pd-C (10%) in 100 mL of dry ethanol were purged with N_2 and heated to reflux. To this mixture, a solution of 3.50 mL of $N_2H_4 \bullet H_2O$ and 15 mL of ethanol was added over a period of an hour and the resulting mixture refluxed for 12 hr. The mixture was filtered hot through a bed of Celite and the pad was washed four times with 20 mL each of boiling ethanol. The filtrate was taken to dryness under reduced pressure and the residue was triturated with 30 mL of water and left at 4°C overnight. The tan solid that separated was filtered and washed with cold water and dried. Yield 0.285 g (83%). m.p. >350°C. The compound is identical in all respects to that reported in refs 3 and 4.

Acknowledgments: Financial support of this work by Robert A. Welch Foundation (Grant Y-1301) and Petroleum Research Fund, administered by the American Chemical Society (PRF No. 29292-G3) is gratefully acknowledged. We also thank Johnson-Matthey for the generous loan of rutheniumtrichloride

References

1) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: New York, 1995.
2) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759-833.
3) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J.-P. *Inorg. Chem.* **1996**, *35*, 2937-2944.
4) Camren, H.; Chang, M.-Y.; Zhang, L.; McGuire, M. E. *Synth. Commun.* **1996**, *26*, 1247-1252.
5) Yamada, M.; Tanaka, Y.; Yoshimoto, Y.; Kuroda, S.; Shimao, I. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1006-1011.
6) Inglett, G. E.; Smith, G. F. *J. Am. Chem. Soc.* **1950**, *72*, 842-844.
7) Hiort, C.; Lincoln, P.; Nordén, B. *J. Am. Chem. Soc.* **1993**, *115*, 3448-3454.
8) MacDonnell, F. M.; Bodige, S. *Inorg. Chem.* **1996**, *35*, 5758-5759.
9) Bodige, S.; Torres, A. S.; Maloney, D. J.; Tate, D.; Walker, A.; Kinsel, G.; MacDonnell, F. M. *J. Am. Chem. Soc.* in press.

(*Received in USA* 19 *August* 1997; *revised* 17 *September* 1997; *accepted* 18 *September* 1997)