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SHORT COMMUNICATION

A CONVENIENT AND EFFICIENT ONE-STEP METHOD FOR THE SYNTHESIS OF DICOMPARTMENTAL LIGANDS WITH HEXA- AND TETRADENTATE COORDINATION SITES

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ABSTRACT. A convenient and more efficient method for the preparation of 1,6-bis(2-pyridyl)-2,5-bis(2-hydroxy-3-formyl-5-methyl benzyl)-2,5-diazahexane, L^1H_2 and 1,7-bis(2-pyridyl)-2,6-bis(2-hydroxy-3-formyl-5-methyl benzyl)-2,6-diazaheptane, L^2H_2 are described. The ligands were prepared by reaction of two moles of 3-(chloromethyl)-2-hydroxy-5-methyl benzaldehyde with a mole of N,N'-bis(2-pyridyl)dopamine in THF at ambient conditions in high yield (75-80%).

KEY WORDS: Dicompartmental ligand, Synthesis, Phenol-based ligand, Acyclic ligand

INTRODUCTION

The design and synthesis of dinucleating ligands containing two different compartments has received considerable attention during the past decade, due to their possibility of binding simultaneously two metal ions in close proximity to each other [1-3]. Since unsymmetrical dicompartmental ligands are important for providing discrete heterodinuclear core complexes, various types of dicompartmental ligands including the end-off, the side-off and the macrocyclic type have been developed [4-6]. They have the basic structures of type **I** where "B" is a donating atom (Scheme 1). An elegant development of unsymmetrical dicompartmental ligand type **II** was introduced by Bosnich and coworkers [7]. This type of ligand is interesting in several aspects such as: the hexadentate coordination site (N_4O_2) and the tetradentate coordination site (O_4) can accommodate different metal ions with different coordination numbers and geometrical environments [8-10]; the size of the compartment can be varied by extending the diamine moiety of the ligand [11, 12]. Labile metal ions like Zn^{2+} and Cu^{2+} in the six-dentate coordination site are substantially less labile than those in the tetradentate site of the ligand type **I** [13]. The two metal ions reside in close proximity and can communicate via the phenoxide bridging groups [14, 15]. The solubilities of these nonplanar complexes are also higher than those of the solubilities of compounds type **I** [16]. The metal ion at the four-dentate coordination site could act as a binding center, while the coordinatively saturated metal ion could participate in redox process via an outer-sphere mechanism [17]. The other aspect of interest with this system is that the monometallic acyclic ligand **II** can be cyclized with a di- or triamine compound to give corresponding macrocyclic complexes with ligands of type **III** [3, 9].

Although the Bosnich ligand **I** is very promising in many ways, as pointed out above, their study and possible applications are limited by their complicated synthetic procedure. The original method [9] requires nine consecutive steps to produce **I** with total yield of about 7% to obtain ligand **II**. In 1998 Busch and coworkers provided a simple route to the synthesis of ligand **II** by a Mannich reaction [16]. Although, this procedure was much simple the yield was

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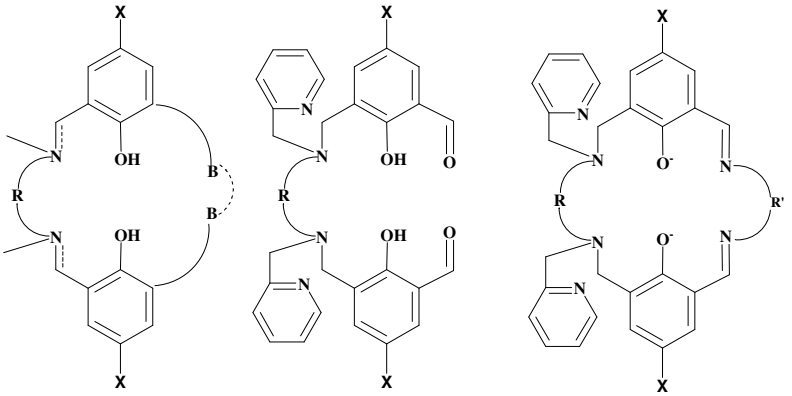
less than 25% and necessitated a cumbersome purification procedure and more importantly, it was limited to the preparation of ligands with a methylenediamine fragment.

Thus, a new and more efficient method for the preparation of **II** is needed if the promising potentialities of these compounds are to be more fully realized. We report here a new and more efficient procedure for the synthesis of compound **II**.



Scheme 1

EXPERIMENTAL

All the chemicals and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and used without further purification. N,N'-bis(2-pyridylmethyl)-1,2-diaminoethane, N,N'-bis(2-pyridylmethyl)-1,3-diaminopropane (**IV**) [18] and 3-(chloromethyl)-2-hydroxy-5-methylbenzaldehyde (**V**) were prepared according to published procedures [19]. Elemental analyses were performed by a LECO CHN-600 Elemental Analyzer (Germany). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 DRX Fourier Transform Spectrometer (Germany). Infrared spectra were recorded in a KBr mixture by a single beam Bruker VECTOR22 FTIR (Germany). Mass spectra were obtained on a VG 70E double focusing spectrometer (USA). All samples were dried to constant weight under high vacuum prior to analysis.

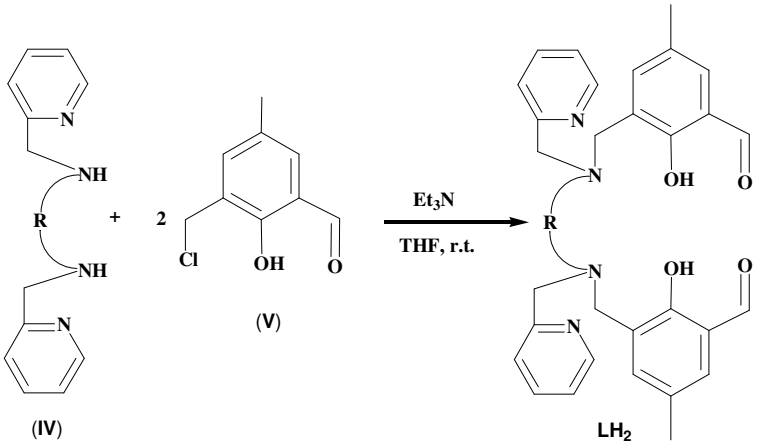
General method for the preparation of ligand, LH_2. To a solution of 3-(chloromethyl)-2-hydroxy-5-methylbenzaldehyde (0.363 g, 2 mmol) in THF (10 mL) was added Et_3N (0.5 mL, 6 mmol). To the resultant mixture was added dropwise a solution of N,N'-bis(2-pyridyl) diamine (**IV**) (1 mmol) in THF (20 mL) (see Scheme 2). The mixture was stirred overnight at room temperature and then the precipitate was filtered and washed with THF (2 × 10 mL). The solvent was removed from the filtrate under reduced pressure. To the resultant oily residue was added an aqueous solution of 32% HCl (5 mL) and the mixture was stirred for 10 min. The mixture was then extracted with methylene chloride (3 × 10 mL). The aqueous phase was made alkaline by addition of a saturated solution of $NaHCO_3$ and the resultant mixture was extracted with methylene chloride (3 × 10 mL). The combined CH_2Cl_2 fractions were dried over anhydrous Na_2SO_4. Filtration and concentration of the solution under reduced pressure gave the desired product as a brown oil.

Purification. To an ethanol solution (5 mL) of the crude compound was added Et_3N (0.2 mL, 2 mmol) and LiCl (0.04 g, 2 mmol) in ethanol (8 mL). A yellow solid precipitated almost immediately. The mixture was stirred for 1 h. The lithium salt of the desired ligand was collected, washed with ethanol (2 × 3 mL), Et_2O (2 × 3 mL) and pentane (2 × 3 mL) and dried under vacuum. Li_2L was obtained as a pure pale yellow solid. The Li_2L can be converted to pure LH_2 as follows: to a suspension of Li_2L in ethanol (10 mL) was added two equivalents of acetic acid and the mixture was stirred for 5 min before the ethanol was removed by distillation. The pale yellow residue was dissolved in CH_2Cl_2 (10 mL) and filtered through Celite and anhydrous Na_2SO_4. Concentration under reduced pressure gave LH_2 in quantitative yield (75-80% based on starting materials). Characterization of LH_2 and Li_2L by NMR, IR spectroscopies, mass spectrometry and elemental analysis were accordance with those reported in the literature [7, 15, 16]. Characterization data for Li_2L^1: ^{1}H NMR (300 MHz in $CDCl_3$) δ: 2.17 (s, 6H), 2.70, 2.80 (system AB, J_{AB} = 9.5 Hz, 4H), 3.24, 3.94 (system AB, J_{AB} = 11.2 Hz, 4H), 3.59, 3.82 (system AB, J_{AB} = 15.2 Hz, 4H), 6.91 (t, J = 9.2 Hz, 4H), 7.36 (t, d; J = 7.5, 1.6 Hz, 2H), 8.35 (d, J = 4.1 Hz, 2H), 9.40 (s, 2H). ^{13}C NMR (300 MHz in $CDCl_3$) δ: 20.3 (q), 57.1 (t), 59.2 (t), 61.6 (t), 119.2 (s), 121.7 (d), 122.6 (d), 123.4 (s), 129.8 (s), 136.1 (d), 136.5 (d), 139.3 (d), 149.2 (d), 159.3 (s), 171.0 (s) and 193.98 (d). UV-VIS: 262 nm (1.7 x 10^4 L mol^{-1} cm^{-1}), 342 nm (4.1 x 10^3 L mol^{-1} cm^{-1}). Anal. calcd for $C_{32}H_{32}N_4O_4Li_2$: C, 69.82; H, 5.86; N, 10.18. Found: C, 69.61, H, 5.93; N, 9.95.

Characterization data for Li_2L^2. ^{1}H NMR (300 MHz in $CDCl_3$) δ: 2.07 (m, 2H); 2.15 (s, br. 6H); 2.43 (s, br. 2H); 2.84 (s, 2H); 3.20 (s, br. 2H); 3.24 (s, br. 2H); 3.93 (d, J = 12.6 Hz, 2H); 4.29 (s, br. 2H); 6.44 (d, J = 7.7 Hz, 2H); 6.75 (s, 4H); 7.04 (s, 2H); 7.18 (t, J = 15.1 Hz, 2H); 8.47 (d, J = 4.3 Hz, 2H); 9.15 (s, 2H). ^{13}C NMR (300 MHz in $CDCl_3$) δ: 20.3 (q), 24.9 (t), 52.4 (t), 55.7 (t), 62.2 (t), 118.6 (s), 120.9 (d), 121.2 (d), 122.6 (s), 130.4 (s), 135.6 (d), 136.1 (d), 138.9 (d), 149.8 (d), 158.7 (s), 171.1 (s) and 193.3 (d). UV-VIS: 262 nm (1.5 x 10^4 L mol^{-1} cm^{-1}), 342 nm (5.6 x 10^3 L mol^{-1} cm^{-1}). Anal. calcd for $C_{33}H_{34}N_4O_4Li_2$: C, 70.20; H, 6.08; N, 9.93. Found: C, 70.02; H, 5.86; N, 10.15. Electrospray mass spectrometry was used to confirm the identities of the foregoing compounds.

RESULTS AND DISCUSSION

The reaction between N,N'-bis(2-pyridylmethyl)-diamine (**IV**) and 3-(chloromethyl)-2-hydroxy-5-methylbenzaldehyde (**V**) under ambient conditions provided the desired ligands as oil (Scheme 2). The reaction yield was high (more than 80%) and the product was sufficiently pure for further treatment. However, it can be further purified by addition a solution of LiCl and isolation of products as the solid lithium salt of the ligand, Li_2L with yield of 75-80% based on the starting materials used. Acidification was performed to recover the organic ligand, LH_2; however this is not always necessary because we have also been successful in directly using the Li_2L as starting materials in the preparations of the heterodimetallic complexes [20, 21]. Given the large number of different possible groups that can be substituted on the amines or on the phenolic rings, the approach taken here should provide considerable versatility in the development of a number of new compartmental ligands with different functional groups as well as their heterodimetallic compounds.



Scheme 2

It can be concluded that a simple, more efficient and one-step procedure has been successfully used for the preparation of dicompartmental multifunctional acyclic ligands of L^1H_2 and L^2H_2. The work up procedure is easy and the pure desired compounds can be isolated as lithium salt after a simple filtration. This method is quite general and it can be used with a variety of diamines. Using the ligand prepared as a precursor for synthesis of a vide variety of dicompartmental marcrocyclic ligands is another advantage of this procedure.

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REFERENCES

1. Gavrilova, A.L.; Bosnich, B. *Chem. Rev.* **2004**, 104, 349.
2. Vigato, P.A.; Tamburini, S. *Coord. Chem. Rev.* **2004**, 248, 1717.
3. McCollum, D.G.; Fraser, C.; Ostrande, R.; Rheingold, A.L.; Bosnich, B. *Inorg. Chem.* **1994**, 33, 2383.
4. Okawa, H.; Furutachi, H.; Fenton, D.E. *Coord .Chem. Rev.* **1998**, 174, 51.
5. Vigato, P.A.; Tamburini, S.; Fenton, D.E. *Coord. Chem. Rev.* **1990**, 106, 25.
6. Akilan, P.; Thirumavalavan, M.; Kandaswamy, M. *Polyhedron* **2003**, 22, 3483.
7. Fraser, C.; Johnston, L.; Rheingold, A.L.; Hagerty, B.S.; Williams, G.K.; Whelan, L., Bosnich, B. *Inorg. Chem.* **1992**, 31, 1835.
8. Rahnama, A.N.; Golchoubian, H.; Pritchard, R. *Bull. Chem. Soc. Jpn.* **2005**, 78, 1047.
9. Golchoubian, H.; Baktash, E.; Welter, R. *Inorg. Chem. Commun.* **2007**, 10, 120.
10. Bosnich, B. *Inorg. Chem.* **1999**, 38, 2554.

11. Fraser, C.; Ostrander, R.; Rheingold, A.L.; White, C.; Bosnich, B. *Inorg. Chem.* **1994**, 33, 324.
12. McCollum, D.G.; Hall, L.; White, C.; Ostrander, R.; Rheingold, A.L.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1994**, 33, 924.
13. Fraser. C.; Bosnich, B. *Inorg. Chem.* **1994**, 33, 338.
14. Golchoubian, H.; Waltz, W.L.; Quail, J.W. *Can. J. Chem.* **1999**, 37, 77.
15. McCollum, D.G.; Yap, G.P.A.; Rheingold, A.L.; Bosnich, B. *J. Am. Chem. Soc.* **1996**, 118, 1365.
16. Rybak-Akimova, E.V.; Alcock, N.W.; Busch, D.H. *Inorg. Chem.* **1998**, 37, 1536.
17. Incarvito, C.; Rheingold, A.L.; Gavrilova, A.L.; Qin, C.J.; Bosnich, B. *Inorg. Chem.* **2001**, 40, 4101.
18. Goodwin, H.A.; Lions, F. *J. Am. Chem. Soc.* **1960**, 82, 5013.
19. Guerriero, P.; Tamburini, S.; Vigato, P.A. *Coord. Chem. Rev.* **1995**, 139, 17.
20. Golchoubian, H.; Baktash, E.; Welter, R. *Inorg. Chem. Commun.* **2007**, 10, 1035.
21. McCollum, D.G.; Yap, G.P.A.; Liable-Sands, L.; Rheingold, A.L.; Bosnich, B. *Inorg. Chem.* **1997**, 36, 2230.