Solvent-Free Synthesis of Bis(2,2′:6′,2″-terpyridin-4′-yl)amine and Its Metal Complexes

Reza-Ali Fallahpour*

Institute of Organic Chemistry, University of Zurich UZH, Winterthurerstrasse 190, 8057 Zurich, Switzerland
Fax +41(61)3639869; E-mail: Reza.Fallahpour@oci.uzh.ch

Received 6 January 2008; revised 13 February 2008

Abstract: The key compound bis(2,2′:6′,2″-terpyridin-4′-yl)amine was prepared in one step starting from 4′-amino-2,2′:6′,2″-terpyridine and 4′-bromo-2,2′:6′,2″-terpyridine in quantitative yield. In addition, we have established an easy and efficient route for the synthesis of the bromoterpyridine compound. Using the novel ligand, two ruthenium complexes were also prepared.

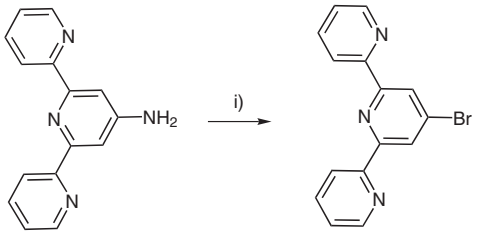
Key words: aminoterpyridine, bromoterpyridine, amino-bridged terpyridine, metallodendrimers

Dendrimers, in principal, and in particular metallodendrimers, belong to a rapidly growing field within supramolecular chemistry.[1] The metal centers are incorporated into the dendrimers for electron transfer[2] or as a chromophore.[3] Although 2,2′:6′,2″-terpyridine (tpy) ligands do not exhibit the desired photochemical properties with transition metals, e.g., with ruthenium(II); the geometric and stereochemical advantages of the tpy ligand make it an interesting molecule. 2,2′:6′,2″-Terpyridine seems to be among the most versatile ligands for complex formation with transition metals. Most work in this field has been concerned with attaching functional groups directly to C4′ of the 2,2′:6′,2″-terpyridine.[4] We have also been involved in the functionalization of oligopyridines and have developed methods to achieve this goal.[5] In addition, we have also reported the preparation of 2,2′:6′,2″-terpyridine 1′-oxides.[6] We now wish to report the synthesis of an amine-bridged tpy ligand **3** and its ruthenium(II) complexes.

In the series of amino-substituted terpyridine ligands only two compounds, 4′-amino-2,2′:6′,2″-terpyridine (tpy-NH_2, **1**)[5c] and 4′-(dimethylamino)-2,2′:6′,2″-terpyridine[5c] have been reported previously; both tpy ligands have been incorporated into metal-bonded complexes.

4′-Amino-2,2′:6′,2″-terpyridine (**1**) was converted into 4′-bromo-2,2′:6′,2″-terpyridine (tpy-Br, **2**) using standard methodology (Scheme 1).[6] This method allows also the preparation of halogen-substituted symmetric and asymmetric terpyridine ligands.

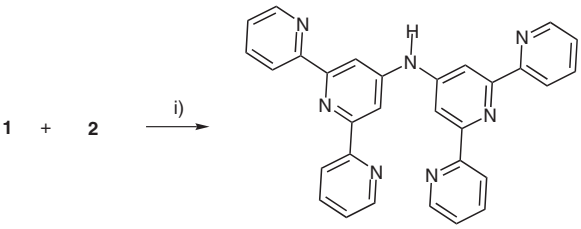
We became interested in the amine-bridged tpy ligand **3**, firstly, due to the possibility of functionalization of the amine nitrogen atom to form a trisubstituted amine as a core for dendrimers.



1 2

Scheme 1 *Reagents and conditions*: (i) 48% HBr, Br_2, $NaNO_2$, 0 °C, 30 min, 59%.

When we reacted **1** and **2** to prepare our desired ligand **3** in acetonitrile or dimethyl sulfoxide in the presence of a base, even in the form of a metal complex, the reaction failed. However, when **1** and **2** were reacted in a melt at 240 °C, compound **3** only was formed, the remainder of the product mixture was unreacted starting materials. Hence, this is a clean reaction and the yield is quantitative with respect to the reacted compounds. The turnover of the reaction is more than 98%, but it is not dependant on the reaction time or the ratio of the starting materials. The reaction of **1** and **2** in the ratio of 1:1 gave only compound **3**; when two or more equivalents of **2** were reacted with **1**, product **3** was again isolated in quantitative yield (Scheme 2).

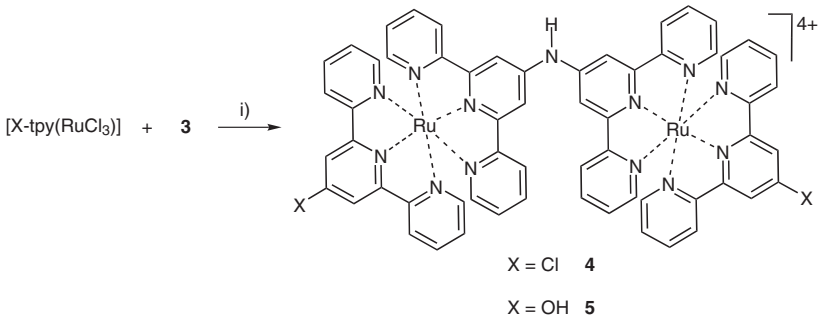


3

Scheme 2 *Reagents and conditions*: (i) neat, 240 °C, 16 h, 100%.

Due to the symmetry of the molecule, only five signals would be expected (and are observed) in the ^{1}H NMR spectrum of bis(2,2′:6′,2″-terpyridin-4′-yl)amine (**3**). Compound **3** was compared with 4′-amino-2,2′:6′,2″-terpyridine (**1**). In deuterochloroform solution H3′ was shifted to low field and was observed as a singlet at δ = 8.33 ($\Delta\delta$ = 0.59) while H6 (δ = 8.68, $\Delta\delta$ = 0.06) and H3 (δ = 8.65, $\Delta\delta$ = 0.07) were slightly shifted to low field, respectively. In the Maldi-TOF mass spectrum of **1**, parent

SYNTHESIS 2008, No. 10, pp 1514–1516
Advanced online publication: 07.04.2008
DOI: 10.1055/s-2008-1072574; Art ID: Z00408SS



Scheme 3 *Reagents and conditions*: (i) [$RuCl_3$(Cl-tpy)], *N*-ethylmorpholine, MeOH, 64 °C, 1 h, **4** (61%); [$RuCl_3$(HO-tpy)], *N*-ethylmorpholine, MeOH, 64 °C, 1 h, **5** (54%).

ion peaks were observed at *m*/*z* = 479. All the analytical and spectroscopic data are in accord with the proposed formulation and structure.

Two ruthenium complexes of this ligand were prepared by standard methods, to exemplify its reactivity and properties (Scheme 3). Compound **3** was reacted with trichloro(4′-hydroxy-2,2′:6′,2″-terpyridine)ruthenium [$RuCl_3$(HO-tpy)][5c] and trichloro(4′-chloro-2,2′:6′,2″-terpyridine)ruthenium [$RuCl_3$(Cl-tpy)][5c] in methanol to obtain the complexes **4** and **5** in 61% and 54% yield, respectively. Both complexes **4** and **5** are symmetric and exhibit ten signals in the ^{1}H NMR spectra, each five for **4** and 4′-hydroxy-2,2′:6′,2″-terpyridine or 4′-chloro-2,2′:6′,2″-terpyridine. In complex **5**, H3‴ of 4′-hydroxy-2,2′:6′,2″-terpyridine was observed at δ = 8.23 while in complex **4** it was observed at δ = 8.87, which is consistent with the electron-releasing and -withdrawing groups; H3′ of the 4′-aminoterpyridine was observed at δ = 8.85 for **4** and at δ = 8.69 for **5**.

Ruthenium(II) complexes **4** and **5** are electrochemically active in acetonitrile solution, each exhibiting a wave corresponding to the ruthenium(II)/ruthenium(III) process. The potential of the ruthenium(II) complexes **4** and **5** (vs ferrocene-ferrocenium internal reference) are 0.93 and 0.89 V, respectively, which are comparable with other ruthenium complexes of tpy ligands.

In conclusion, we have shown an easy and efficient solvent-free synthesis of 4′-bromo-2,2′:6′,2″-terpyridine (**2**) and bis(2,2′:6′,2″-terpyridin-4′-yl)amine (**3**) and metal complexes **4** and **5** of **3**. Both compounds are interesting starting materials in coordination and dendrimer chemistry.

All reagents were used as supplied. Silica gel (0.060–0.200 mm) was supplied from Merck and aluminum oxide (type 507 C neutral; 100–125 mesh) from Fluka. Melting points were measured on Büchi 535 and are not corrected. IR spectra were recorded on a Mattson Genesis Fourier-transform spectrophotometer with samples in compressed KBr discs. UV spectra were measured on Perkin-Elmer lambda 19. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 250 spectrometer and referenced against TMS. TOF (Maldi) spectra were recorded using a PerPespective Biosystems Voyagers-RP Biospectrometry Workstation. Electrochemical measurements were performed with an Ecochemie Autolab PGSTAT 20 potentiostat.

All of the starting oligopyridines and the novel amine bridged **3** and catalysts are currently available from HetCat, Switzerland (www.hetcat.com).

4′-Bromo-2,2′:6′,2″-terpyridine (2)

4′-Amino-2,2′:6′,2″-terpyridine (**1**, 500 mg, 2.01 mmol) was dissolved in 48% HBr (10 mL). Br_2 (0.4 mL) was added at 0 °C followed by $NaNO_2$ (500 mg) in H_2O (2 mL) and the mixture was stirred for 30 min. The soln was neutralized by adding NaOH (2.0 g) in H_2O (5 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried ($MgSO_4$) and solvent was removed. Compound **2** was purified by chromatography (silica gel, CH_2Cl_2–hexane, 1:1); yield: 0.37 g (59%); mp 135 °C.

^{1}H NMR ($CDCl_3$): δ = 8.71 (m, 2 H, H6), 8.64 (s, 2 H, H3′), 8.57 (d, *J* = 7.80 Hz, 2 H, H3), 7.86 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 2 H, H4), 7.35 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 2 H, H5).

^{13}C NMR ($CDCl_3$): δ = 156.47, 154.93, 149.20, 136.93, 135.06, 124.23, 124.20, 121.40.

MS (Maldi-TOF): *m*/*z* = 312.

Anal. Calcd for $C_{15}H_{10}BrN_3$: C, 57.72; H, 3.23; N, 13.46. Found: C, 57.61; H, 3.35; N, 13.22.

Bis(2,2′:6′,2″-terpyridin-4′-yl)amine (3)

A mixture of 4′-bromo-2,2′:6′,2″-terpyridine (**2**, 100 mg, 0.32 mmol) and 4′-amino-2,2′:6′,2″-terpyridine (**1**, 100 mg, 0.40 mmol) was heated at 240 °C in a closed glass ampoule for 20 h. After cooling to r.t. the black residue was dissolved in MeOH (50 mL). The organic solvent was removed. Chromatographic separation (alumina, CH_2Cl_2–hexane, 1:1) gave the first fraction, compound **2**, followed by compound **3**. As a last fraction compound **1** was collected. The separation was made easy, since compound **3** reacts with iron(II) to give a blue complex while **1** and **2** give purple complexes. Compound **3** was recrystallized (EtOH) to give a yellow microcrystalline solid; yield: 150 mg (100%, with respect to reacted **2**); mp 195–196 °C.

IR (KBr): 3423 (m), 1607 (m), 1578 (s), 1528 (s), 1430 (m), 1342 (m), 1293 (m), 1231 (m), 999 (m), 786 cm^{-1} (m).

^{1}H NMR ($CDCl_3$): δ = 8.68 (d, *J* = 7.80 Hz, 4 H, H6), 8.65 (d, *J* = 8.30 Hz, 4 H, H3), 8.33 (s, 4 H, H3′), 7.87 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 4 H, H4), 7.34 (ddd, *J* = 8.30, 7.80, 1.95, 4 H, H5), 6.68 (br s, 1 H, NH).

^{1}H NMR (CD_3OD): δ = 8.62 (d, *J* = 7.80 Hz, 4 H, H6), 8.57 (d, *J* = 8.30 Hz, 4 H, H3), 8.24 (s, 4 H, H3′), 7.97 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 4 H, H4), 7.44 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 4 H, H5).

^{13}C NMR ($CDCl_3$): δ = 156.93, 156.12, 154.48, 149.06, 136.75, 123.78, 121.35, 109.58.

MS (EI): *m*/*z* (%) = 479 (54, M), 401 (100, M – pyridine), 374 (12), 297 (5), 240 (19), 200 (12), 78 (9, pyridine).

Anal. Calcd for $C_{30}H_{21}N_7 \cdot H_2O$: C, 72.42; H, 4.66; N, 19.71. Found: C, 72.17; H, 4.62; N, 19.34.

Synthesis of Ruthenium(II) Complexes 4 and 5; General Procedure

Terpyridine **3** (20 mg) and *N*-ethylmorpholine (0.1 mL) were added to a suspension of [$RuCl_3$(Cl-tpy)] or [$RuCl_3$(HO-tpy)] (1 mol equiv) in MeOH (20 mL) and the mixture was heated for 1 h. The resulting soln was filtered through Celite, and then excess NH_4PF_6 was added to the filtrate. This was collected by filtration and washed with ice-cold MeOH (5 mL), H_2O (5 mL), and Et_2O (5 mL) and air dried. Purification was performed by chromatography (silica gel, MeCN–NH_3, 30:1). Both complexes were further purified by recrystallization (diffusion of Et_2O into the MeCN soln).

Ruthenium Complex 4.

Yield: 45 mg (61%).

^{1}H NMR (CD_3CN): δ = 8.87 (s, 4 H, H3‴), 8.85 (s, 4 H, H3′), 8.56 (d, *J* = 7.80 Hz, 4 H, H3″), 8.53 (d, *J* = 7.80 Hz, 4 H, H3), 7.99 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 4 H, H4″), 7.93 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 4 H, H4), 7.67 (d, *J* = 5.35 Hz, 4 H, H6″), 7.40 (d, *J* = 5.35 Hz, 4 H, H6), 7.30 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 4 H, , H5″), 7.18 (ddd, *J* = 8.30, 7.80, 1.95 Hz, 4 H, H5).

MS (Maldi-TOF): *m*/*z* = 1506 [M + 2 PF_6], 1361 [M + PF_6], 1216 [M], 1181 [M – Cl], 949 [M – tpyCl], 848 [M – Ru(tpy-Cl)].

UV (MeCN): λ_{max} = 275, 305, 350, 507 nm; λ_{min} = 280, 347, 394 nm.

Anal. Calcd for $C_{60}H_{41}Cl_2F_{24}N_{13}P_4Ru_2 \cdot 2\ H_2O$ (1833.04): C, 40.53; H, 2.55; N, 10.24. Found: C, 40.01; H, 3.01; N, 9.68.

CV: E^o = 0.93 V.

Ruthenium Complex 5

Yield: 40 mg (54%).

^{1}H NMR (CD_3CN): δ = 8.69 (s, 4 H, H3′), 8.54 (d, *J* = 7.80 Hz, 4 H, H3), 8.45 (d, *J* = 7.80 Hz, 4 H, H$^{3''}$), 8.23 (s, 4 H, H3‴), 7.94 (m, 8 H, H4, H4″), 7.56 (d, *J* = 5.35 Hz, 4 H, H6), 7.50 (d, *J* = 5.35 Hz, 4 H, H6″), 7.23 (m, H4, H4″, 8 H).

MS (Maldi-TOF): *m*/*z* = 1759 [M + 4 PF_6], 1469 [M + 2 PF_6], 1179 [M], 930 [M – tpyOH], 829 [M – Ru(tpy-OH)].

UV (MeCN): λ_{max} = 272, 303, 352, 509 nm; λ_{min} 277, 347, 400 nm.

Anal. Calcd for $C_{60}H_{43}F_{24}N_{13}O_2P_4Ru_2 \cdot H_2O$ (1778.13): C, 40.53; H, 2.55; N, 10.24. Found: C, 39.88; H, 2.99; N, 10.81.

CV: E^o = 0.89 V.

Acknowledgment

I would like to thank Professor J. S. Siegel and the University of Zurich.

References

(1) (a) *Topics in Current Chemistry*, Vol. 197; Vögtle, F., Ed.; Springer Verlag: Berlin, **1998**. (b) *Topics in Current Chemistry*, Vol. 210; Vögtle, F., Ed.; Springer Verlag: Berlin, **2000**. (c) *Topics in Current Chemistry*, Vol. 212; Vögtle, F., Ed.; Springer Verlag: Berlin, **2001**.

(2) Chow, H.-F.; Mong, T. K.-K.; Nongrum, M. F.; Wan, C.-W. *Tetrahedron* **1998**, *54*, 8543.

(3) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

(4) (a) Potts, K. *Bull. Soc. Chim. Belg.* **1990**, *99*, 741. (b) Ziessel, R. *Synthesis* **1999**, 1839. (c) Constable, E. C. *Chem. Commun.* **1997**, 1073. (d) Grosshenny, V.; Ziessel, R. *J. Organomet. Chem.* **1993**, *C19-C22*, 453. (e) Pabst, G. R.; Sauer, J. *Tetrahedron* **1999**, *55*, 5067. (f) Càrdenas, D. J.; Sauvage, J.-P. *Synlett* **1996**, 916.

(5) (a) Fallahpour, R.-A.; Constable, E. C. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2263. (b) Fallahpour, R.-A.; Neuburger, M.; Zehnder, M. *Polyhedron* **1999**, *18*, 2445. (c) Fallahpour, R.-A. *Eur. J. Inorg. Chem.* **1998**, 1205. (d) Fallahpour, R.-A.; Neuburger, M.; Zehnder, M. *New J. Chem.* **1999**, *23*, 53. (e) Fallahpour, R.-A.; Neuburger, M.; Zehnder, M. *Synthesis* **1999**, 1051. (f) Fallahpour, R.-A. *Synthesis* **2000**, 1138. (g) Fallahpour, R.-A. *Synthesis* **2000**, 1665. (h) Fallahpour, R.-A. *Helv. Chim. Acta* **2000**, *83*, 384. (i) Fallahpour, R.-A.; Neuburger, M. *Helv. Chim. Acta* **2001**, *84*, 710. (j) Fallahpour, R.-A. *Synthesis* **2003**, 153.

(6) Fallahpour, R.-A.; Neuburger, M. *Eur. J. Org. Chem.* **2001**, 1853.