Efficient Stereospecific Syntheses of Chiral Ruthenium Dimers

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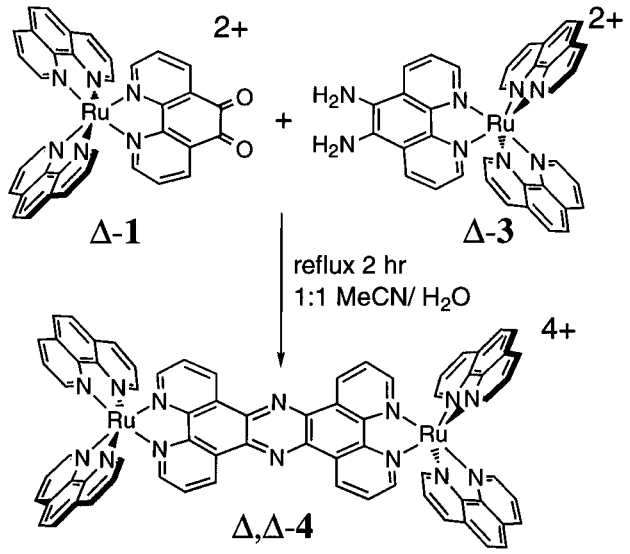
Oligonuclear Ru(II) complexes with polypyridine ligands are under intense study because of the rich photophysical and electrochemical properties of these systems and potential applications in various supramolecular structures as electronic and photomolecular devices.[1] Relatively little attention, however, has been paid to the absolute stereochemistry of these supermolecules in cases where substitutionally inert, octahedral tris chelate $[Ru(L\text{-}L)_3]^{z+}$ complexes are used as molecular building blocks. Supramolecular species, such as dimers,[2] trimers,[3] dendrimers,[4] and polymers,[5] constructed from these tris(bidentate) complexes are usually assembled via ligand displacement reactions with little direct control for the product stereochemistry. As a consequence of the chirality of these building blocks[6] (Δ or Λ), the products consist of complicated mixtures of enantiomers and diastereomers which are difficult, if not impossible, to further purify.[7] We have developed a synthetic strategy that will allow the efficient assembly of enantiomerically pure oligonuclear and dendrimeric ruthenium complexes from chiral precursors. This approach differs from other reported stereospecific syntheses using enantiopure precursors in that the resulting bridge between metal centers is formed irreversibly[8] and reaction does not involve ligand displacement reactions at the chiral center.[9,10] We employ a simple organic condensation reaction between coordinated functionalized 1,10-phenanthroline (phen) ligands to bridge monomers without disturbing the metal-complex stereochemistry. The success of this strategy is demonstrated here in the stereospecific synthesis of three isomeric dimers (Δ-Δ, Λ-Λ, Λ-Δ) based on octahedral Ru complexes.

Scheme 1



The condensation of Δ-$[Ru(phen)_2$(1,10-phenanthroline-5,6-dione)$]^{2+}$ (Δ-**1**)[11] with Δ-$[Ru(phen)_2$(1,10-phenanthroline-5,6-diamine)$]^{2+}$ (Δ-**3**) in refluxing 1:1 MeCN/H_2O (Scheme 1) yields the dinuclear complex, Δ,Δ-$[(phen)_2Ru$(tpphz)$Ru(phen)_2]^{4+}$ (Δ,Δ-**4**)[12] (where tpphz = tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2″,3″-*j*]phenazine). Formation of the phenazine ring has been optimized and occurs in nearly quantitative yield, which is essential for the practical synthesis of higher nuclearity species. Previously, various phenazine compounds formed via this type of condensation reaction were obtained in yields ranging from 30 to 94%, most commonly around 80%.[2ab,8,11ab,13] While all of these reactions were performed in nonaqueous solvents, we have found that aqueous or mixed aqueous solvents at reflux give isolated yields of 95−98% for the synthesis of **4**. The resulting aromatic bridge is symmetrical and rigid, is formed irreversibly, and provides an electronic conduit between redox centers. The tpphz ligand has been used previously to form

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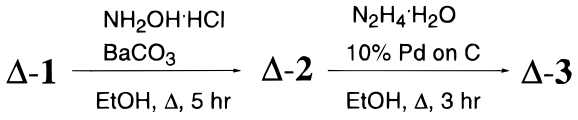
Scheme 2



structurally related dimers, such as $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ [2a,b] and ruthenium-based coordination polymers.[5a] Our work differs in that formation of the tpphz ligand occurs from the reaction of coordinated precursors, which is optimal for maintaining optical purity.

The enantiomers of (±)-**1**$(PF_6)_2$ are obtained on a large scale (>1 g) by the resolution of the corresponding chloride with sodium arsenyl-L-tartrate and subsequent metathesis of the individual diastereomers with ammonium hexafluorophosphate, as described in ref 11a. The enantiomers of (±)-**3** are formed directly from the resolved complexes, Δ-**1** and Λ-**1**, by initial conversion to $[Ru(phen)_2$(1,10-phenanthroline-5,6-dioxime$]^{2+}$ (**2**) and subsequent reduction with $N_2H_4 \cdot H_2O$ using a 10% Pd/C catalyst to give Δ-**3** and Λ-**3**, respectively (Scheme 2).[14] This synthetic route minimizes the number of optical resolutions required and ties the absolute stereochemistry of **3** to that of **1**.[15]

The other two dinuclear complexes, Λ,Λ-**4** and Λ,Δ-**4**, were obtained similarly by condensing appropriate dione and diamine species. ^1H and ^{13}C NMR spectra of the diastereomers Δ, Δ-**4** and Δ,Λ-**4** are indistinguishable,[16] probably because the large distance between Ru centers (∼12.7 Å);[2a] however, circular dichroism (CD) data clearly identify the diastereomers and enantiomers. The Δ,Λ-**4** meso diastereomer is not optically active[17] whereas the enantiomers, Δ,Δ-**4** and Λ,Λ-**4**, show equal but opposite molar ellipticities (shown in Figure 1), as expected. The overall magnitude of the molar ellipticity is approximately twice that of the starting materials, indicating an additive contribution of each metal center to the CD.

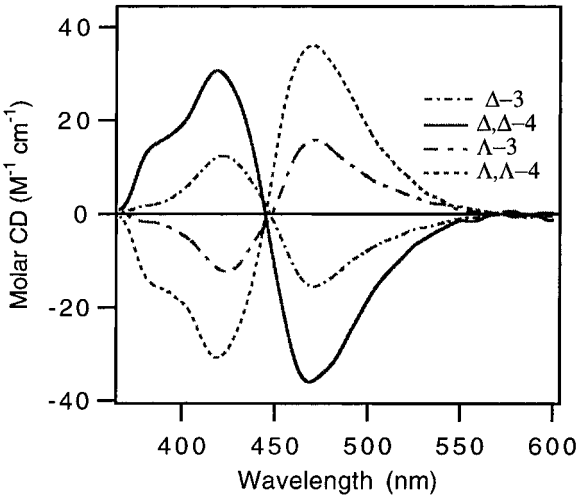


Figure 1. CD spectra of enantiomers of **3** and **4** in acetonitrile.

This work demonstrates the viability of using coupling reactions between coordinated ligands in chiral metal complexes as a completely modular approach to the stereospecific synthesis of dinuclear metal complexes. The phenazine coupling reaction on coordinated ligands has been optimized to occur in high yield with retention of optical activity to form an irreversible bridge between monomers. We are currently pursuing the extension of this reaction toward the synthesis of enantiopure multi-metal assemblies.

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(12) A solution of 148 mg (0.154 mmol) of Δ-**1**$(PF_6)_2$ and 153 mg (0.159 mmol) of Δ-**3**$(PF_6)_2$ in 20 mL of 1:1 MeCN/H_2O was refluxed under N_2 for 3 h. The solution was then concentrated to a small volume and the product precipitated by addition of an excess of NH_4PF_6 dissolved in 10 mL of H_2O. The precipitate was filtered off, washed with three 10 mL portions of water, and dried *in vacuo* at 60 °C for 12 h. Yield: 283 mg (96%). Δ,Δ-**4**$(PF_6)_4$ ^1H NMR (300 MHz, acetone-d_6), δ**:** phen 8.78 (d, J = 8.18 Hz, 8H), 8.56 (d, J = 5.21 Hz, 8H), 8.39 (s, 8H), 7.77 (dd, J_1 = 8.06 Hz, J_2 = 5.33 Hz, 8H); tpphz 10.08 (d, J = 8.30 Hz, 4H), 8.37 (d, J = 5.41 Hz, 4H), 7.98 (dd, J_1 = 8.08 Hz, J_2 = 5.42 Hz, 4H). Δ,Δ-**4**$(PF_6)_4$ ^{13}C NMR (75 MHz, acetone-d_6), δ**:** phen 155.91, 148.85, 138.00, 131.99, 129.10, 127.13; tpphz 154.42, 154.00, 151.99, 141.37, 130.99, 128.41. Anal. Calcd for **4**$(PF_6)_4 \cdot 2H_2O$**,** $C_{72}H_{48}N_{14}F_{24}O_2P_4Ru_2$: C, 44.97; H, 2.52; N, 10.20. Found: C, 44.22; H, 2.34; N, 9.77. Trace impurities can be removed by chromatography on neutral alumina (10 mg/mL NH_4PF_6 in acetone).

(13) Other examples of the phenazine condensation reaction include: (a) Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921. (b) Amouyal, E.; Homsi, A.; Chambron, J.-C.; Sauvage, J.-P. *J. Chem. Soc., Dalton Trans.* **1990**, 1841.

(14) Selected data for **2**$(PF_6)_2$ follow. Typical yield: 80%. Anal. Calcd for $C_{36}H_{24}N_8F_{12}O_2P_2Ru$: C, 43.60; H, 2.44; N, 11.30. Found: C, 43.55; H, 2.41; N, 10.91. Δ-**3**$(PF_6)_2$. Typical yield: 80%. ^1H NMR (300 MHz, DMSO-d_6), δ: phen 8.76 (d, J = 7.17 Hz, 4H), 8.37 (s, 4H), 8.06 (d, J = 4.69 Hz, 2H), 7.80 (d, J = 4.76 Hz, 2H), 7.74 (m, 4H); phen$(NH_2)_2$ 8.73 (d, J = 8.48 Hz, 2H), 7.68 (d, J = 4.75 Hz, 2H), 7.52.(dd, J_1 = 8.53, J_2 = 5.08 Hz, 2H), 5.99(s, 4H, $-NH_2$). Anal. Calcd for **3**$(PF_6)_2$, $C_{36}H_{26}N_8F_{12}P_2Ru$: C, 44.96; H, 2.73; N, 11.65. Found: C, 44.68; H, 2.55; N, 11.38.

(15) CD for Δ-**3**$(PF_6)_2$ in acetonitrile (λ_{extr} in nm ($\Delta\epsilon/M^{-1}$ cm^{-1})): 258 (+166), 270 (−230), 303 (−85), 422 (+12), 470 (−17).

(16) Selected NMR data are as follows. Λ,Λ-**4**$(PF_6)_4$ ^1H NMR (300 MHz, acetone-d_6)**,** δ**:** phen 8.78 (d, J = 8.05 Hz, 8H), 8.56 (d, J = 5.20 Hz, 8H), 8.39 (s, 8H), 7.79 (dd, J_1 = 8.20 Hz, J_2 = 5.13 Hz, 8H); tpphz 10.08 (d, J = 7.31 Hz, 4H), 8.37 (d, J = 5.21 Hz, 4H), 7.99 (dd, J_1 = 8.19 Hz, J_2 = 5.12 Hz, 4H). Δ,Λ-**4**$(PF_6)_4$ ^1H NMR (300 MHz, acetone-d_6)**,** δ**:** phen 8.02 (d, J = 8.05 Hz, 8H), 8.54 (d, J = 5.31 Hz, 8H), 8.43 (s, 8H), 7.83 (m, 8H); tpphz 10.11 (d, J = 8.37 Hz, 4H), 8.35 (d, J = 5.14 Hz, 4H), 8.03 (dd, J_1 = 8.39 Hz, J_2 = 5.47 Hz, 4H). **4**$(PF_6)_4$ (the product of racemic starting materials) ^1H NMR (300 MHz, acetone-d_6), δ**:** phen 8.78 (d, J = 8.32 Hz, 8H), 8.56 (d, J = 5.27 Hz, 8H), 8.39 (s, 8H), 7.78 (dd, J_1 = 8.32 Hz, J_2 = 5.32 Hz, 8H); tpphz 10.07 (d, J = 8.03 Hz, 4H), 8.37 (d, J = 5.41 Hz, 4H), 7.98 (dd, J_1 = 7.98 Hz, J_2 = 5.48 Hz, 4H). **4**$(PF_6)_4$ ^{13}C NMR (75 MHz, acetone-d_6), δ: phen 155.96, 148.84, 138.01, 132.08, 129.12, 127.16; tpphz 154.44, 154.01, 152.01, 141.40, 130.98, 128.43.

(17) The slight CD detected indicates a minor optical impurity in the starting materials. Possible racemization reactions during the coupling reaction were ruled out by control experiments which indicated no change in the optical activity of the reactants after refluxing in MeCN/H_2O for 8 h.