Kinetics and Mechanism of the Facile Diastereomeric Isomerization of a Tris(bidentate)ruthenium(II) Complex Bearing a Misdirected Bipyridyl Ligand: Δ/Λ-(δ/λ-1,1'-Biisoquinoline)bis(2,2'-bipyridine)ruthenium(II)

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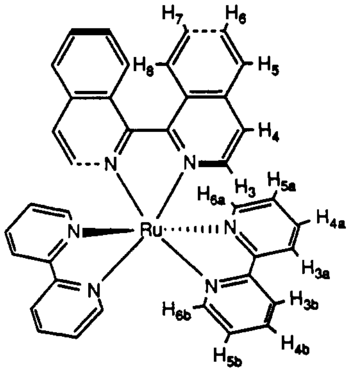
The geometric[1] and stereochemical[2] isomers of octahedral coordination complexes and the mechanisms[3] by which they interconvert have been of interest to chemists for more than a century. Complexes of the general formula $[Ru(L\text{-}L)_3]^{2+}$, where L-L is a neutral bidentate ligand, have been found to be stereochemically rigid. For example, $[Ru(bipy)_3]^{2+}$, which can be resolved into its Δ and Λ forms, only slowly racemizes at elevated temperatures[4] or upon irradiation.[5]

We have synthesized $[Ru^{II}(bipy)_2(1,1'\text{-biiq})]^{2+}$ (**1**),[6] which we believe is the first example of a metal complex in which the ligand 1,1'-biisoquinoline binds in a η^2 fashion.[6,7] The 1,1'-biiq ligand is expected to be nonplanar because of unfavorable transannular steric interactions between H_8 and $H_{8'}$. Consequently, **1** is chiral at the metal center and the 1,1'-biiq ligand and therefore should exist in two diastereomeric forms. Indeed, the ^1H NMR spectrum of **1** reveals an ~3:1 mixture of the two diastereomers in acetone solutions at 25 °C. A single-crystal X-ray structure determination of **1** was undertaken. Surprisingly, only one of the two diastereomers was found to crystallize from acetonitrile/ether (quantitative yield based on total Ru). The latter result implies that the two diastereomers of **1** are in equilibrium on the time scale of the crystallization (1 week). Compound **1** crystallizes in a centrosymmetric space group as pairs of enantiomers; the conformation of the five-membered chelate ring is λ when the configuration at the metal is Λ. Remarkably, the ^1H NMR spectrum obtained a few minutes after the single crystal used in the X-ray study was dissolved in acetone at 25 °C again revealed an ~3:1 mixture of the diastereomers. A second single crystal, which proved to have the same cell dimensions as the crystal used in the X-ray study, was dissolved in acetone at −80 °C; the resulting ^1H NMR spectrum was that of the major diastereomer.



1 = $Ru^{II}(bipy)_2(1,1'\text{-biiq})]^{2+}$

Two fundamentally distinct pathways exist for interconversion of the diastereomers of **1**: isomerization about the metal center or isomerization about the ligand. The latter would be facile if the 1,1'-biiq ligand dissociated completely from the metal; however, steric repulsion of the H_8 and $H_{8'}$ atoms should prohibit them from passing one another when the ligand is bound to the metal in a bidentate fashion and rotation about the 1,1' bond upon cleavage of just one of the ruthenium–isoquinoline bonds appears hindered. Mechanisms for intramolecular isomerization of octahedral metal complexes that do not involve the rupturing of metal–ligand bonds have been proposed by Bailar (trigonal twist)[8] and by Râ̂y and Dutt (rhombic twist).[9] The stereochemical and geometric factors that govern the latter two mechanisms have been thoroughly reviewed.[10,11] Considering the fact that the doubly-unsaturated five-membered heterometallacyclic ring formed by the 1,1'-biiq ligand is highly strained, the possibility of dissociation of just one of the isoquinoline donors and subsequent isomerization of the resulting five-coordinate intermediate should also be considered a viable mechanism. Common mechanisms for the isomerization of five-coordinate species include the Berry and turnstile pseudorotations.[12]

We have investigated the dynamic behavior of **1** using spin saturation transfer (SST),[13] spin inversion transfer (SIT),[14] and 2D EXSY[15] spectroscopy. In order to assign the ^1H NMR spectrum of the diastereomeric mixture of **1** and facilitate the dynamic NMR experiments, we synthesized the derivative of **1** containing bipy-d_8 ligands.[16] The ^1H NMR spectrum of **1-d$_{16}$** (Figure 1), the COSY NMR spectrum of **1**, and the results of the X-ray analysis of (Δ,δ/Λ,λ)-**1** taken together have enabled us to assign the ^1H NMR spectrum of **1**.[17] Interconversion of (Δ,δ/Λ,λ)-**1** and (Δ,λ/Λ,δ)-**1** is not taking place via complete dissociation of the 1,1'-biiq ligand since we do not observe the capture of $[Ru^{II}(bipy)_2]^{2+}$ by added bipy to give the inert $[Ru^{II}(bipy)_3]^{2+}$ and spin-labeled free 1,1'-biiq and bipy do not exchange with **1** on the time scale of isomerization. The interconversion is therefore intramolecular. SIT and EXSY experiments demonstrate the C_2 symmetry of **1** and the *cis*/*trans* relationship of the bipy ligands are maintained during the interconversion of the diastereomers (Figure 2): $K = 2.88$, $k(3_{maj} \rightarrow 3_{min}) = 12.8(8)\ s^{-1}$,

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(1) Jørgensen, C. K. *J. Prakt. Chem.* **1889**, *39*, 16; **1890**, *41*, 449.

(2) Werner, A. *Justus Liebigs Ann. Chem.* **1912**, *386*, 1; *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 1228, 3061.

(3) (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; John Wiley: New York, 1968. (b) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; VCH: Weinheim, Germany, 1991.

(4) Dwyer, F. P.; Gyarfas, E. C. *J. Proc. R. Soc. N.S.W.* **1949**, *83*, 174.

(5) Porter, G. B.; Sparks, R. H. *J. Photochem.* **1980**, *13*, 123.

(6) For an example of a complex that bears a bridging 1,1'-biiq ligand see: Dai, L.; Zhu, Z.; Zhang, Y.; Ni, C.; Zhang, Z.; Zhou, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1760.

(7) Compound **1** completes the series $[Ru(bipy)_2(L\text{-}L)]^{2+}$, where L-L are symmetric benzannelated bipy ligands, i.e. 1,1'-biisoquinoline, 3,3'-biisoquinoline (Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; Zelewsky, A. *Inorg. Chem.* **1985**, *24*, 202) and 2,2'-biquinoline (Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675). Previous reports of L-L = "2,2'-biisoquinoline" actually involved 3,3'-biisoquinoline (Balzani, V. Personal communication).

(8) Bailar, J. C., Jr. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165.

(9) Râ̂y, P. C.; Dutt, N. K. *J. Indian Chem. Soc.* **1943**, *20*, 81.

(10) Kepert, D. L. *Prog. Inorg. Chem.* **1977**, *23*, 1.

(11) (a) Rodger, A.; Johnson, B. F. G. *Inorg. Chem.* **1988**, *27*, 3061. (b) Rodger, A.; Schipper, P. E. *Inorg. Chem.* **1988**, *27*, 458.

(12) (a) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (b) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70. (c) Mislow, K. *Acc. Chem. Res.* **1970**, *3*, 321. (d) Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288. (e) Gillespie, P.; Hoffman, P.; Klusacek, H.; Marquarding, D.; Pfohl, S.; Ramirez, F.; Tsolis, E. A.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 687.

(13) (a) Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211. (b) Green, M. L. H.; Sella, A.; Wong, L.-L. *Organometallics* **1992**, *11*, 2650.

(14) (a) Alger, J. R.; Prestegard, J. H. *J. Magn. Reson.* **1977**, *27*, 137. (b) Kuchel, R. W.; Chapman, B. E. *J. Theor. Biol.* **1983**, *105*, 569. (c) Robinson, G.; Kuchel, P. W.; Chapman, B. E. *J. Magn. Reson.* **1985**, *63*, 314. (d) Bellon, S. F.; Chen, D.; Johnston, E. R. *J. Magn. Reson.* **1987**, *73*, 168.

(15) Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Sik, V.; Stephenson, D. *J. Magn. Reson.* **1986**, *70*, 34.

(16) Chirayil, S.; Thummel, R. P. *Inorg. Chem.* **1989**, *28*, 812.

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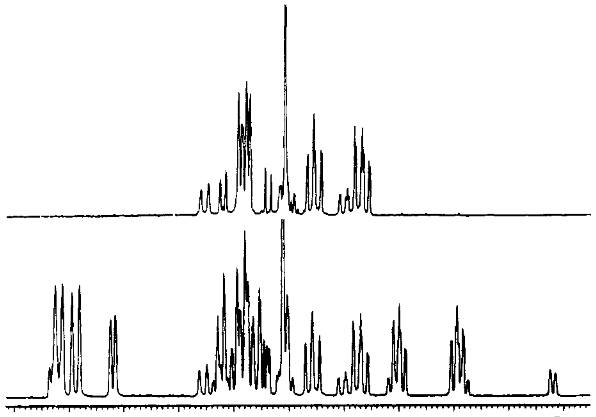

Figure 1. ^{1}H NMR spectra of **1** and **1-d$_{16}$** at 300 MHz and 25 °C.

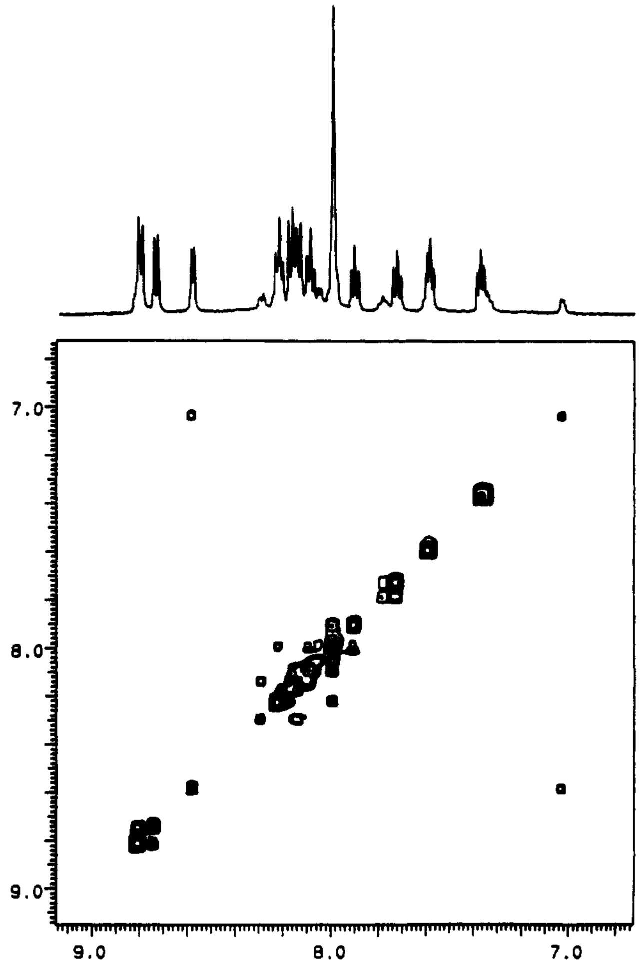

Figure 2. 2D EXSY spectrum at 500 MHz and 80 °C revealing the interconversion of $(\Delta,\delta/\Lambda,\lambda)$-**1** and $(\Delta,\lambda/\Lambda,\delta)$-**1**.

$k(6a_{maj} \rightarrow 6a_{min}) = 12.7(3)$ s^{-1}, and $k(6b_{maj} \rightarrow 6a_{min}) \approx 0$ s^{-1} at 80 °C. These experiments rule out regular mechanisms that involve twisting the ligands in a way that preserves the C_2 axial symmetry of the molecule but interchange the *cis/trans* relationship of the bipy ligands with respect to the 1,1′-biiq ligand (e.g. Bailar or Râу–Dutt twist). Also, interconversion of the diastereomers of **1** through an irregular mechanism that involves dissociation of one of the isoquinoline donors of 1,1′-biiq to give a five-coordinate intermediate that subsequently rotates one or both of the bidentate ligands in a way that destroys the C_2 relationship between the ligands (e.g. productive Berry and some turnstile pseudorotations) is not possible. There remain two plausible mechanisms that involve dissociation of one end of the 1,1′-biisoquinoline that are consistent with the available experimental data: (1) ~360° rotation about the 1,1′ bond of the η^1-biisoquinoline ligand[18] or (2) turnstile rotation of the five-coordinate metal center in a way that preserves the C_2 symmetry and *cis/trans* relationship of the bipy ligands.[19,20] A third mechanism, one that does not involve bond breaking, has also not been ruled out: (3) isomerization of the ligand via a planar η^2-1,1′-biiq.[21] However, to the best of our knowledge, such an isomerization involving a 1,1′-binaphthyl skeleton is without precedent.[22] An answer to the fundamental question of whether isomerization is taking place at the metal or the ligand awaits further study.

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Supplementary Material Available: Text for an experimental section describing the synthesis and crystal structure determination of the $(\Delta,\delta/\Lambda,\lambda)$-**1** (major) diastereomer, an ORTEP diagram of (Λ,λ)-**1**, a COSY spectrum of **1**, and a nonlinear least-squares fit of the spin inversion transfer data used to calculate $k(6a_{maj} \rightarrow 6a_{min})$ (Figures S1–S3), and crystallographic data, atomic coordinates, and anisotropic thermal parameters of the non-hydrogen atoms (Tables S1–S3) (11 pages). Ordering information is given on any current masthead page.

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(17) The following assignments are based upon the assumption that most of the resonances that correspond to the bipy ligands exhibit nearly the same chemical shifts. The one exception is H_{6a}, which is significantly shielded by the aromatic ring of the 1,1′-biiq ligand in the minor isomer (Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1021). $(\Delta,\delta/\Lambda,\lambda)$-**1** (major) diastereomer: ^{1}H NMR (acetone-d_6, 25 °C, 500 MHz) δ 8.85 (d, bipy H_{3b}, $J = 8.0$ Hz), 8.79 (d, bipy H_{3a}, $J = 8.0$ Hz), **8.65 (d, bipy H_{6a}, $J = 7.0$ Hz)**, 8.25 (dt, bipy H_{4b}, $J = 7.0, 8.0$ Hz), 8.18 (d, biiq H_5, $J = 8.0$ Hz), 8.17 (d, biiq H_8, $J = 8.0$ Hz), 8.12 (dt, bipy H_{4a}, $J = 7.0, 8.0$ Hz), 8.03 (s, biiq $H_{3,4}$), 8.02 (t, bipy H_{6b}, $J = 7.0$ Hz), 7.93 (t, biiq H_7, $J = 8.0$ Hz), 7.75 (t, biiq H_6, $J = 8.0$ Hz), 7.61 (dt, bipy H_{5b}, $J = 7.0, 8.0$ Hz), 7.40 (dt, bipy H_{5a}, $J = 7.0, 8.0$ Hz). $(\Delta,\lambda/\Lambda,\delta)$-**1** (minor) diastereomer: ^{1}H NMR (acetone-d_6, 25 °C, 500 MHz) δ 8.87 (d, bipy H_{3b}, $J = 8.0$ Hz), 8.79 (d, bipy H_{3a}, $J = 8.0$ Hz), 8.41 (d, biiq H_8, $J = 8.0$ Hz), 8.25 (dt, bipy H_{4b}, $J = 7.0$ 8.0 Hz), 8.24, 8.09 (d, biiq $H_{3,4}$, $J = 7.0$ Hz), 8.17 (d, biiq H_5, $J = 8.0$ Hz), 8.13 (dt, bipy H_{4a}, $J = 7.0, 8.0$ Hz), 8.10 (t, bipy H_{6b}, $J = 7.0$ Hz), 8.01 (t, biiq H_6, $J = 8.0$ Hz), 7.80 (t, biiq H_7, $J = 8.0$ Hz), 7.62 (dt, bipy H_{5b}, $J = 7.0, 8.0$ Hz), 7.39 (dt, bipy H_{5a}, $J = 7.0, 8.0$ Hz), **7.05 (d, bipy H_{6a}, $J = 7.0$ Hz)**.

(18) The isomerization of 1,1′-binaphthyl, which involves bringing H_2 and $H_{8'}$ in close proximity, has a half-life of ~10 h at 25 °C in several solvents: (a) Cooke, A. S.; Harris, M. M. *J. Chem. Soc. B* **1963**, 2365. (b) Colter, A. K.; Clements, L. M. *J. Phys. Chem.* **1964**, *68*, 651. (c) Kress, R. B.; Duesler, E. N.; Etter, M. C.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1980**, *102*, 7709 and references therein. No rate data are available for isomerization of free 1,1′-biiq; however, it is expected to be rapid since the 2 position is unsubstituted. Since Ru(bipy)$_2$ is substantially larger than a hydrogen atom, one might expect the barrier to rotation about the 1,1′ bond of the intermediate $[\mathrm{Ru^{II}(bipy)_2}(\eta^1\text{-}1,1'\text{-biiq})]^{2+}$ to be greater than that for 1,1′-binaphthyl.

(19) This mechanism would involve the uncommon pentagonal planar geometry: Hoskins, B. F.; Pannan, C. D. *J. Chem. Soc., Chem. Commun.* **1975**, 408.

(20) The unlikely possibility that one end of a bipy ligand is dissociating, followed by isomerization at the metal center, could be addressed by using a less flexible ligand such as 1,10-phenanthroline: Basolo, F.; Hayes, J. C.; Neumann, H. M. *J. Am. Chem. Soc.* **1954**, *76*, 3807.

(21) A planar transition state is likely for the isomerization of related nonplanar bipy ligands: Thummel, R. P.; Lefoulon, F.; Korp, J. D. *Inorg. Chem.* **1987**, *26*, 2370.

(22) It is noteworthy that in its ground-state structure the donor orbitals of the twisted 1,1′-biiq ligand are "misdirected" with respect to the σ-acceptor orbitals at the metal (Ashby, M. T.; Lichtenberger, D. L. *Inorg. Chem.* **1985**, *24*, 636). A planar 1,1′-biiq would redirect the ligand's donor orbitals (Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L.; Ortega, R. B. *Inorg. Chem.* **1986**, *25*, 3154), which could help overcome the energy required to bend the 1,1′ bond sufficiently to allow H_8 and $H_{8'}$ to pass one another.