DALTON COMMUNICATION

Chiral induction upon coordination to form an enantiomeric bis-chelate ruthenium(II)–tris(3-methyl-2-pyridylmethyl)amine complex

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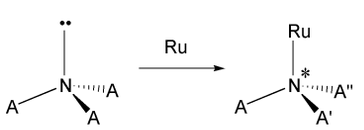
Chiral induction to a C_3-symmetric and non-prochiral tris(3-methyl-2-pyridylmethyl)amine was achieved upon coordination to a ruthenium(II) center by forming a stable *fac–cis* bis-chelate complex selectively and ^{1}H NMR spectroscopy showed that the chirality is maintained even in solution.

Chiral induction is currently one of the most exciting fields to study, for example, asymmetric catalysis[1] and absolute asymmetric synthesis[2] of organic compounds. In the solid state chiral crystallization, which is discriminated from spontaneous resolution, has been known to afford chiral crystals of achiral and non-prochiral compounds even in the absence of chiral environments such as benzophenone and triphenylbromomethane in chiral space groups.[3] Such compounds, however, do not usually show optical activity in solution. It would be very interesting if we could induce chirality toward achiral and non-prochiral compounds which were stable in solution. In order to generate chirality, a molecule or an intermediate should involve some information such as non-covalent weak interactions, electronic effects, steric hindrance and so on.

In the course of our investigation on the synthesis and characterization of a series of ruthenium–TPA complexes [TPA = tris(2-pyridylmethyl)amine],[4] the fundamentals of the stability of these complexes has been shown to lie in the cooperation of the σ-donation of the tertiary amino group of TPA and π-back bonding from the dπ orbitals of the ruthenium center to the pyridine π* orbitals.[4b] This differentiation in the electronic character of the binding sites of TPA would facilitate selective formation of certain geometries and configurations of the Ru–TPA complexes. In this paper, we describe the selective formation and characterization of an unprecedented bis-chelate TPA mononuclear complex of ruthenium as enantiomers due to chiral tertiary amino groups, by virtue of the introduction of a methyl group at the 3-position of the pyridine ring of TPA (Scheme 1).



Scheme 1

3-Me_3-TPA [3-Me_3TPA = tris(3-methyl-2-pyridylmethyl)-amine] showed interesting behavior in its ^{1}H NMR spectrum. In contrast to 5- or 6-Me_3-TPA for which a singlet assigned to the methyl group has been observed at 2.27 and 2.54 ppm in CD_3CN, respectively,[4b] the singlet for 3-Me_3-TPA was observed at 1.60 ppm which was shifted upfield probably due to shielding by neighboring pyridine rings, however the molecule was shown to be C_3-symmetric in solution as observed in 5- or 6-Me_3-TPA. The reaction of 3-Me_3-TPA with $RuCl_3$ in methanol in the presence of NEt_3 under N_2, in sharp contrast to the cases of TPA and 5-Me_3-TPA,[4b] did not give a bis-μ-chloro Ru(II) dinuclear complex but gave a novel bis-chelate Ru(II) mononuclear complex of 3-Me_3-TPA, $[Ru(3\text{-}Me_3\text{-}TPA)_2](PF_6)_2$ (**1**) in a moderate yield.† The stoichiometry did not affect the formation of **1** and we could not observe mono-chelate complexes under our conditions.

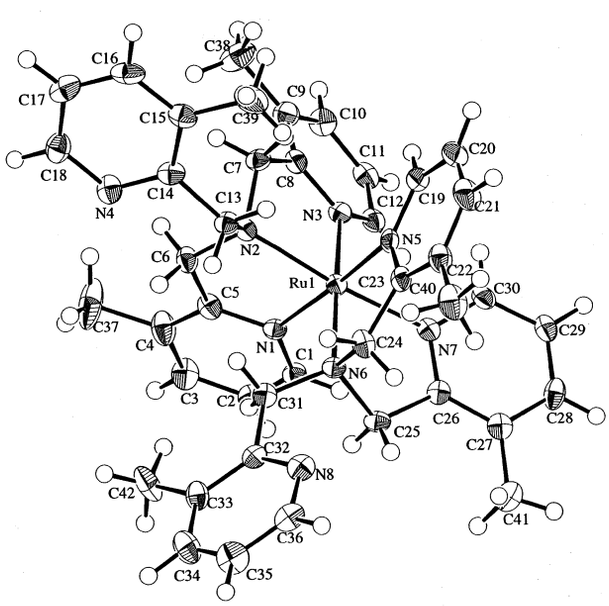


Fig. 1 An ORTEP drawing of the (*S*,*S*) isomer of **1** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and bond angles (°): Ru(1)–N(1), 2.067(3); Ru(1)–N(2), 2.164(3); Ru(1)–N(3), 2.070(3); Ru(1)–N(5), 2.048(4); Ru(1)–N(6), 2.160(3); Ru(1)–N(7), 2.068(3); N(1)–Ru(1)–N(2), 82.5(1); N(1)–Ru(1)–N(3), 81.0(1); N(1)–Ru(1)–N(5), 174.5(1); N(2)–Ru(1)–N(3), 78.9(1); N(2)–Ru(1)–N(7), 174.4(1); N(3)–Ru(1)–N(6), 174.5(1); N(5)–Ru(1)–N(6), 82.6(1); N(6)–Ru(1)–N(7), 78.5(1).

The crystal structure of **1** was determined unambiguously by X-ray crystallography.‡ An ORTEP[5] drawing of an (*S*,*S*) isomer of its cation moiety is given in Fig. 1 with the numbering scheme used. Selected bond lengths and angles are listed in the figure caption. The complex was revealed to be C_2-symmetric and chiral due to the asymmetric tertiary nitrogens and a unit cell contains two (*R*,*R*) and two (*S*,*S*) isomers to form a racemic crystal (see Fig. 2). As can be seen in Fig. 1, two 3-Me_3-TPA ligands bind to a Ru(II) center as tridentate ligands in a *fac* fashion. There are two possible stereoisomers for 3-Me_3-TPA coordination in the *fac* configuration as shown in Scheme 2. The isolated isomer turned out to be a *cis* isomer as shown in Fig. 1. The selective formation of the *cis* isomer can be rationalized by the following reasoning: a pyridine bound to a Ru(II) center can act as a π-acceptor and a tertiary amino group as a σ-donor, therefore, the tertiary amino group favors a position *trans* to the pyridine moieties to end up with the *cis* configuration rather than the *trans* one. This argument

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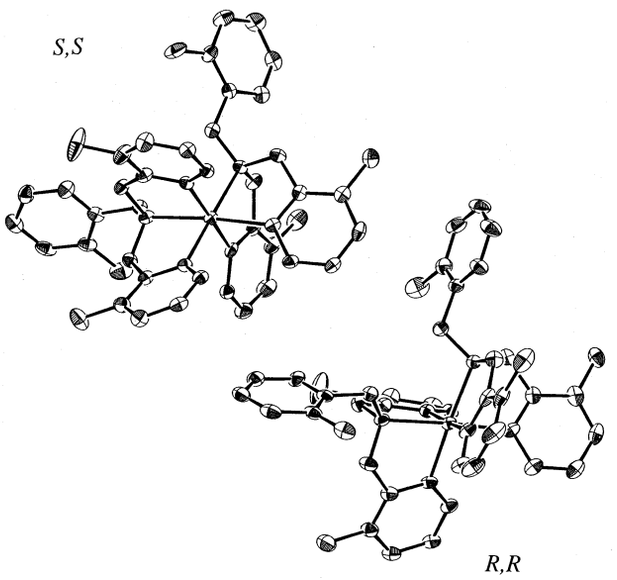
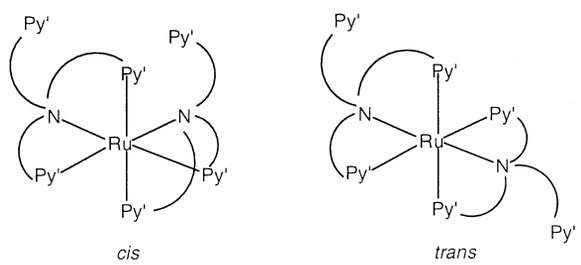


Fig. 2 An ORTEP drawing of an enantiomeric pair in an asymmetric unit of **1**.



Scheme 2

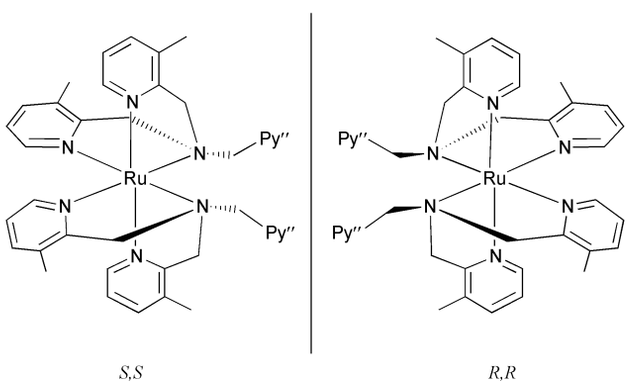


Fig. 3 A mirror image of the enantiomers of **1**.

also provides a rationale for the selective formation of the *fac* configuration of the tridentate 3-Me_3-TPA ligand; if the ligand binds to the ruthenium center in a *mer* configuration, the tertiary amino groups would be in an unfavorable *trans* arrangement to one another. Also, in the *mer* configuration, the two pyridine arms must be pulled toward the tertiary amino group creating an N(py)–Ru–N(py) angle in the range of 160–166° for Ru(II)–TPA complexes reported so far[4] and this strain can cause steric repulsion between the 3-methyl groups and the methylene hydrogens. In addition, this requirement for the *fac* geometry enforces the chiral configuration at the tertiary amino groups to give not a *meso* form but the *rac* forms (Fig. 3, *vide supra*).

In complex **1**, the ruthenium ion is surrounded by six nitrogen atoms from two tertiary amino groups and four pyridine nitrogens. The geometry around the Ru(II) ion is essentially octahedral and less distorted than for Ru–TPA complexes with tetradentate TPA ligands, since the two pyridines of the same molecule are not *trans* to each other. The bond lengths of Ru–N(py) range from 2.048(4) Å for Ru(1)–N(5) to 2.070(3) Å for Ru(1)–N(3) and those of Ru–N(amine) are 2.164(3) Å for Ru(1)–N(2) and 2.160(3) Å for Ru(1)–N(6) which are the longest bond distances found in Ru–TPA complexes. Those of the (*R*,*R*) isomer were almost the same. The separation between the uncoordinated pyridine nitrogens is 6.933(5) Å for the (*S*,*S*) isomer [N(4)···N(8)] and 6.836(5) Å for the (*R*,*R*) isomer [N(12)···N(16), figure not shown]. Between the two enantiomers in the asymmetric unit, a hydrophobic π–π interaction is operating (3.528(7)–3.609(6) Å).

In the ^{1}H NMR spectrum of **1** in DMSO-d_6 at room temperature, four AX doublets were observed ($\Delta\delta/J > 10$) at 5.74 and 4.66 ppm ($J_{AX} = 20$ Hz), 5.02 and 4.17 ppm ($J_{AX} = 15$ Hz), and one AB quartet ($\Delta\delta/J = 4.6$) at 4.07 and 4.58 ppm ($J_{AB} = 15$ Hz) due to the three methylene protons. As for the methyl groups, three singlets were observed at 1.87, 2.23, and 2.25 ppm. These observations indicate that the three pyridine arms are all inequivalent and retain an asymmetric configuration. At elevated temperatures (40–80 °C), a slight spectral change was observed, however, the chiral structure was found to be essentially maintained.

It has been reported that 3-Me_3-TPA forms a μ-oxo Fe(III) dimeric complex in which the ligand coordinates to the iron center in an η^4-fashion.[6] The η^3-coordination of TPA ligands with one uncoordinated pyridine arm has been reported in $[Cu(TPA)(PPh_3)]PF_6$ (tetrahedral) by Karlin and co-workers,[7] $[Re(O)(ethylene\ glycolato)(TPA)]PF_6$ and related complexes by Sugimoto and Sasaki,[8] and $[Cu(NO_2)_2(Htppa)]$ [Htppa = tris(6-pivaloylamino-2-pyridylmethyl)amine] (trigonal bipyramidal) by Masuda and co-workers.[9] On the other hand, bis-chelate TPA complexes have been reported on $[Mn(TPA)_2](ClO_4)_2$ by Gultneh and co-workers,[10] and $[Fe(TPA)_2]X_2$ (X = BPh_4 and OTf) by Diebold and Hagen.[11] In the case of $[Fe(TPA)_2](OTf)_2$, its structure has been demonstrated to bear the *fac–cis* configuration as observed in **1**, however, the structure does not remain the same in solution, one of the TPA ligands dissociates to give a mixture of mono- and bis-TPA complexes. In sharp contrast to the case of $[Fe(TPA)_2](OTf)_2$ which consists of a labile Fe(II) ion, a substitution-inert Ru(II) center allows complex **1** to retain the chiral bis-chelate structure with high stability even in solution. This is a significant advantage of ruthenium complexes toward application of the chirality induced by the Ru(II) ion and a TPA environment.

In summary, we have prepared the first stable chiral bis-chelate TPA complex of ruthenium as a metal center. The most striking feature of the reaction of 3-Me_3-TPA with ruthenium is chiral induction upon coordination even though 3-Me_3-TPA is achiral and non-prochiral and this phenomenon relies on the character of ruthenium and the ligand. This chiral induction can be applied to construct other chiral supramolecular assemblies based on Ru–pyridylamine complexes.

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Notes and references

† $[Ru(3\text{-}Me_3\text{-}TPA)_2](PF_6)_2$ (**1**) was synthesized as follows. To a solution of $RuCl_3 \cdot 3H_2O$ (1 mmol) in methanol (15 ml), was added a solution of 3-Me_3-TPA (1 mmol) and NEt_3 (10 mmol) in methanol (10 ml) *via* a cannula under N_2. The mixture was refluxed for 48 h and was filtered through a Celite pad. The red solution was concentrated to a small volume and $NaPF_6$ in methanol was added to form a yellow precipitate which was washed with methanol and diethyl ether and then dried (72% yield). Calc. for $C_{42}H_{48}N_8RuP_2F_{12}$: C, 47.78; H, 4.58; N, 10.61. Found: C, 47.67; H, 4.62; N, 10.53%. λ_{max}/nm (CH_3CN): 255, 358.

‡ A single crystal of **1**·2MeOH was obtained by recrystallization from methanol. Crystal data: $C_{88}H_{112}N_{16}Ru_2P_4F_{24}O_4$, $M = 2239.95$, yellow prism (0.30 × 0.10 × 0.50 mm), monoclinic, space group $P2_1/n$, $a = 19.9883(4)$, $b = 19.4365(5)$, $c = 24.5289(6)$ Å, $\beta = 91.8028(5)°$, $V = 9524.8(4)$ Å^3, $Z = 4$, $D_c = 1.562$ g cm^{-3}, μ(Mo-Kα) = 4.91 cm^{-1},

$R = 0.054$ for 11997 [$I > 2\sigma(I)$] reflections and $Rw = 0.155$ for all data. Structural refinements and calculations were carried out using the teXsan crystallographic software package.[12] The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included but not refined. Disorder was observed for one PF_6^-. CCDC reference number 151835. See http://www.rsc.org/suppdata/dt/b1/b100095k/ for crystallographic data in CIF or other electronic format.

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