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Controlled Specific Ligand Substitution and Chiroptical Properties of Ruthenium Bis(bipyridine) Nitrosoarene Complexes

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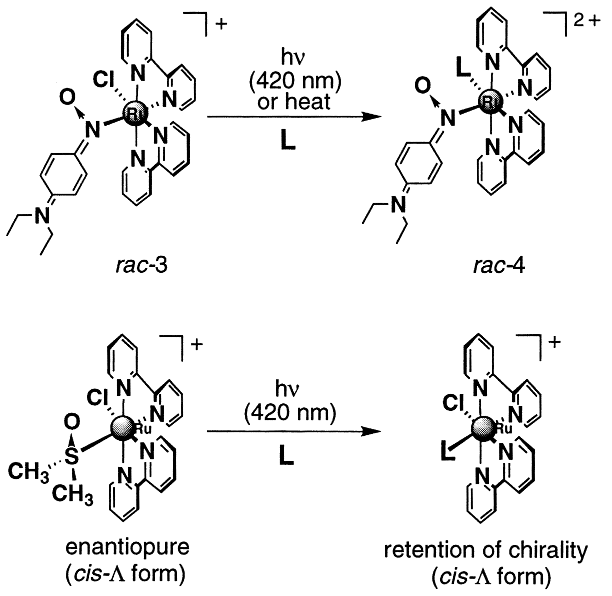
Reaction of *rac*-*cis*-Ru(Cl)$_2$(bpy)$_2$ with *N*,*N*-diethyl-4-nitrosoaniline (**2**) yields the compound *rac*-*cis*-[Ru(Cl)(bpy)$_2$(**2**)]Cl in 90–95% yield. Irradiation at 420 nm results in the novel specific substitution of the equatorial chloride ligand for MeCN, leaving the nitrosoarene ligand unaffected. X-ray analysis shows that the nitrosoarene ligand does not participate in an intramolecular π–π interaction with a bipyridine; molecular modelling confirms the relative instability of such a conformation. High thermal stability allows the Δ and Λ enantiomers to be separated and the circular dichroism spectra to be obtained; the anisotropy, or *g*, factors that are subsequently derived are found to be unexpectedly large.

The extensive and novel coordination, photo/electrochemical and chirality properties exhibited by ruthenium bipyridine compounds have resulted in extensive research being carried out in numerous areas including asymmetric catalysis,[1] chiropto/optoelectronics,[2] molecular/nanotechnology[3] and biomimetic systems.[4] Recently we have been interested in understanding and developing the photochemical, chiral and chiroptical properties of *cis*-RuCl(bpy)$_2$X type compounds. In these studies we have utilized two types of chiral/achiral X ligand, namely, S-coordinated sulfoxides[5] and P-coordinated phosphonite ligands.[6] For the S-coordinated species, it was recently demonstrated for the first time that irradiation could induce ligand-specific substitution of the sulfoxide group for a new ligand in an enantiopure sample with complete retention of the Δ/Λ configuration at the metal center, Scheme 1.[7] On the other hand, irradiation of the P-coordinated species resulted in the unprecedented generation of photochromically induced atropisomers, via ligand rotation around the Ru–P bond.[6] In relation to these ruthenium species, the compounds formed between nitrosoarene ligands (ArNO) and ruthenium have diverse redox properties, and are promising candidates for numerous catalytic reactions.[8] Herein we describe the synthetic, chiral and photochemical characteristics, along with potential applications of the N-coordinated nitrosoarene homologue *N*,*N*-diethyl-4-nitrosoaniline.

Experimental

Circular dichroism spectroscopy was performed on a JASCO J-720WI spectropolarimeter at 25 °C in acetonitrile, or in the HPLC eluent (0.1 M NaPF$_6$ (aq)/CH$_3$CN-mixed solvent, 60:40). The concentrations of the solutions were determined by UV/vis measurements. Optical resolution was performed on the preparative scale using a recycling liquid chromatograph JAI LC-908 equipped with a preparative chiral column, Daicel Chiralcel OD-R (20 mm × 250 mm). A CH$_3$CN:0.1 M NaPF$_6$ (aq) eluent, with a flow rate of 3 mL min^{-1}, was used. Monitoring the products of the synthetic reactions and the optical purity of the separated fractions was performed using an analytical HPLC system (JASCO GULLIVER series) equipped with an analytical chiral column, Daicel Chiralcel OD-R (4.6 mm × 250 mm), an HPLC pump PU-980, a 3-line Degasser DG-980-50, a UV/vis detector UV-970, and a column oven 860-CO. The eluent (CH$_3$CN:0.1 M NaPF$_6$ (aq)) flow rate was 0.4 mL min^{-1}, and the chromatograph was monitored at 290 nm and recorded with a JASCO integrator 807-IT. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 400 spectrometer, operating at 399.65 and 100.40 MHz, respectively. Unless indicated, NMR spectra were recorded in acetonitrile-d_3 or acetone-d_6 solutions.



Scheme 1. Photoprocesses of *cis*-Ru(bpy)$_2$(X)(Cl) compounds for X = S and N derivatives.

Irradiation Conditions. Photoirradiation experiments were carried out with a solution of **3**·Cl in CH$_3$CN (*c* = 0.02 M solution) in a Pyrex reactor equipped with an external cooling system and an argon bubbling system. An USHIO 500-W xenon lamp was employed as the light source and a glass filter was used to cut off light with a wavelength below 420 nm; alternatively a Xe lamp (0.5 mW cm^{-2}) fitted with a monochromator was used to give wavelengths of 600 nm (±5 nm) ($c = 5 \times 10^{-6}$ M in CH_3CN). Photoirradiation was carried out at 25 °C for 12 h and the progress of reaction was followed by HPLC analysis. The reaction proceeded with 100% conversion of the starting material (as revealed by UV-vis spectroscopy and HPLC analysis). After irradiation, organic solvent was removed, the products were redissolved in water and *rac*-**4** of the Cl^- was converted to the corresponding PF_6^- salts by addition of saturated $NaPF_6$. The precipitate was filtered off and resolved into pure enantiomers by preparative HPLC.

Synthesis. The synthesis of these products is relatively straightforward; to a 0.5 g (0.1 mmol) solution of *rac-cis*-$Ru(bpy)_2(Cl)_2$ (**1**) in EtOH was added 0.18 g (0.1 mmol) of the $Et_2NC_6H_4NO$ nitrosoarene ligand (**2**); the resulting solution was refluxed for 4 h under nitrogen resulting in the synthesis of *rac-cis*-[RuCl$(bpy)_2$(**2**)]Cl (**3**-Cl) in 90–95% yield. Selected data for **3**·Cl; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 6H), 3.41 (q, 4H), 6.43 (d, 2H), 7.18 (t, 1H), 7.25 (t, 1H), 7.35 (d, 1H), 7.47 (d, 1H), 7.59 (q, 2H), 7.90 (m, 2), 8.12 (t, 1H), 8.20 (t, 1H), 8.40 (d, 2H), 8.56 (d, 1H), 8.64 (m, 2H), 8.79 (d, 1H), 8.98 (d, 1H), 9.89 (d, 1H). ^{13}C NMR ($CDCl_3$) δ 12.5, 45.4, 109.8, 123.4, 123.8, 124.1, 124.6, 125.9, 126.0, 126.2, 126.3, 128.2, 137.4, 138.0, 138.4, 138.7, 150.0, 151.1, 153.0, 153.2, 154.0, 156.3, 157.3, 158.2, 163.2. Anal. Calcd for $C_{30}H_{30}Cl_2N_6ORu$ (662.5) Calcd: C, 49.54; H, 4.62; N, 11.22%; Found: C, 54.38; H, 4.56; N, 12.68%. MS (Acc. FAB$^+$) *m*/*z* 627 (M − Cl^-).

X-ray. Data were collected on a Rigaku AFC7R 4-circle diffractometer with filtered MoKα radiation and a rotating anode generator using the ω scan technique and the structure was solved using direct methods. Crystal structure determination of complex **4** $C_{32}H_{33}F_{12}N_7OP_2Ru$, $M_r = 922.66$, triclinic space group P-1; $a = 13.458(1)$, $b = 13.957(2)$, $c = 10.662(3)$ Å, $\alpha = 110.32(2)$, $\beta = 98.76(1)$, $\gamma = 84.303(9)$, $U = 1846.8(6)$ Å^3, $T = 293(2)$ K, space group P-1, $Z = 2$, 8932 reflections measured, 8476 unique ($R_{int} = 0.0176$), $R = 0.037$, $Rw = 0.032$ for 6468 observed data. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157351. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk). The details of structures have been deposited as Document No. 75007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Although the specific photo-induced mono-ligand substitution of the sulfoxide, over the chloride, has been achieved[5] (Scheme 1), the specific substitution of the chloride ligand over the adjacent equatorial ligand has hitherto remained elusive. However, by either irradiating (420 nm) or heating a solution of the nitrosoarene derivative *rac*-**3** in the presence of a new ligand (e.g. MeCN) the chloride can be quantitatively replaced whilst leaving the nitrosoarene group unaffected to give the compound *rac-cis*-[$Ru(bpy)_2$(MeCN)(**2**)]$^{2+}$ (**4**) (Scheme 1), as confirmed by X-ray analysis (Fig. 1). This shows the high degree of substitution control possible for these compounds via photochemical means, revealing a new methodology for the rational, controlled assembly of complex ruthenium centred species. The structure of this compound was confirmed by X-ray analysis of the acetonitrile coordinated derivative *rac-cis*-[$Ru(bpy)_2$(MeCN)(**2**)]$(PF_6)_2$ (**4**) as shown in Fig. 1. Unlike compounds found for the sulfoxide and phosphonite derivatives this compound does not display an intramolecular π–π interaction, with the nitrosoarene aromatic group directed away from the bipyridine ligands having a N(71)–Ru–N(51)–O(52) torsion angle of 221.1°. Additionally the N=O group is coplanar with the phenyl ring (O(52)–N(51)–C(53)–C(58) = −2.8°), and there is a stabilizing interaction between O(52) and the H of C(14) of 2.31 Å. As the (C(54)–C(55) and C(57)–C(58) bonds at 1.369(4) and 1.369(4) Å, respectively, are shorter than the other four bonds in the ring (1.399(4)–1.427(4) Å) it can be seen that the nitrosoarene moiety is in the quinoic form rather than the delocalised π-system form, which could conceivably contribute to the lack of any π–π interacting conformation.

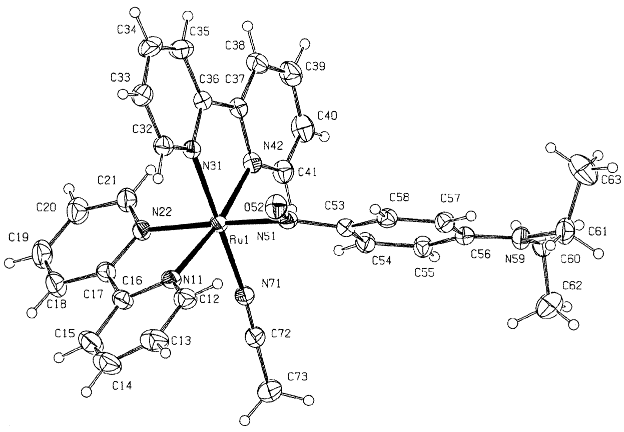


Fig. 1. X-ray structure (Ortep) of *rac-cis*-[$Ru(bpy)_2$(MeCN)(**2**)]$(PF_6)_2$ (**4**) with thermal ellipsoids at 50% probability.

As the phosphonite homologues *rac-cis*-[RuCl$(bpy)_2${PPh(OH)(OEt)}(Cl)]PF_6 and *rac-cis*-[RuCl$(bpy)_2${PPh$(OMe)_2$}(Cl)]PF_6 had been shown to photochromically generate atropisomers,[6] whether these nitrosoarene homologues could also exhibit this phenomenon was investigated, anticipating the possible generation of an intramolecular π–π interacting atropisomer. However, irradiation at either the LC (ca. 280 nm) or MLCT (ca. 580 nm) regions did not result in any sign of intramolecular rotation of the nitrosoarene moiety. As discussed previously, the varied, ligand dependent, photo-physical properties of these $Ru(bpy)_2$ systems hint at powerful and varied potential applications; thus it is important to understand the underlying rationale for the different activity of each ligand group (N, S and P coordinated). To this end we performed molecular mechanics (MM) calculations using the Universal force field[9] within the Cerius2 package,[10] a procedure which has been shown to accurately predict the different conformations established for the phosphites,[6] and we evaluated the potential energy surface of **3** for the rotation of the nitrosoarene moiety (**2**) around the Ru–N bond, Fig. 2.

The results shown in Fig. 2 show the changes in energy for different conformations of the nitroso moiety as characterised

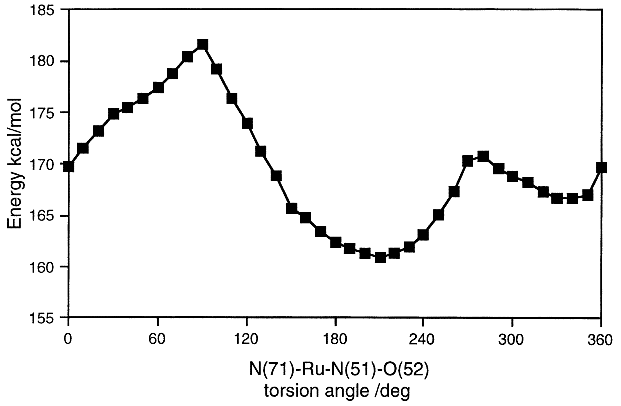


Fig. 2. Variation in the potential energy surface of **3** on rotation of the nitrosoarene moiety around the Ru–N bond.

by the N(71)–Ru–N(51)–O(52) torsion angle, which was varied between 0 and 360° in steps of 10°. There are two minima in the energy profile. The lowest has an energy minimum at a torsion angle (210°) close to that found in the crystal structure at 221.1°. There is however a second subsidiary minimum at 340°. This conformation is interesting as it does contain some π–π overlap, but in order to reduce the steric interactions, the nitroso group is no longer in the plane of the phenyl ring, as exemplified by an O(52)–N(51)–C(53)–C(58) torsion angle of 45°, thus reducing the degree of favorable conjugation, in comparison to that available in the quinoic form. This result indicates that the nitroso ligand, unlike the phosphonite ligand, does not have sufficient flexibility to take up different stable conformations and it therefore does not seem surprising that we were unable to generate photochemically other atropisomeric conformations, as was possible for the phosphite ligand. It should be noted in addition that the nitroso ligand is closer to the metal center than the phosphite ligand and this also adds to its rigidity (Ru–N 2.033(2) vs Ru–P 2.25 Å).

The thermal conformational flexibility often observed for ligands in these systems frequently contributes to making it difficult, or impossible, to separate racemic ruthenium bis(bipyridine) compounds into their respective Δ and Λ enantiomers; in this case, however, because of the relative conformational rigidity (as revealed by the MM calculation) we were able to separate the enantiomers of **3** by chiral HPLC (the MeCN (**4**) but not the chloride derivative is isolated due to reaction with the MeCN eluent, as a result of the high reactivity of the Ru–Cl bond compared with that of the Ru–N bond). The CD spectra of the enantiomers of **4** (Fig. 3a) show multiple bisignate Cotton effects which are particularly intense in the LC region around 300 nm. These interactions observed by CD spectroscopy are attributed to exciton coupling between the aromatic chromophores of the bipyridine and/or nitrosoarene moiety. By consideration of Exciton Coupling Theory we deduce that the order and signs of the Cotton effects confirm the identity of each enantiomer. For the solid line, the negative Cotton effect at ca. 300 nm corresponding to an anticlockwise orientation of the two bipyridine transitions, and the first negative and second positive Cotton effects in the MLCT region[11] (440–640 nm) both confirm the solid line as the Δ enantiomer. The opposite is true for the Λ enantiomer (dotted line).

As a consequence of the varied and versatile photochemical properties of these chiral ruthenium bipyridine compounds, they are prominent targets for "photo-active" chiral molecules in areas such as asymmetric catalysts and chiroptic/optoelectronic molecular systems. The key to the efficiency of these processes is the anisotropy, or *g* factor, of the molecule. Determination of the wavelength-dependent *g* factor profile reveals that **4** has a remarkably high anisotropy for these compounds, with a maximum of 0.0014 at 330 nm (Fig. 3b), in comparison to *cis*-$[\mathrm{Ru(Cl)(bpy)_2\{P(O^{\mathit{i}}Pr)_3\}]PF_6}$ (maximum *g* factor of 2×10^{-4} at 295 nm) which possesses the much more flexible $\mathrm{P(O^{\mathit{i}}Pr)_3}$ ligand in place of the nitrosoarene ligand of **4**. Whilst the interaction energy between the major coupling transitions is of primary importance in the magnitude of the *g* factors, the conformational stability of **4** (as revealed by the MM calculations) relative to *cis*-$[\mathrm{Ru(Cl)(bpy)_2\{P(O^{\mathit{i}}Pr)_3\}]PF_6}$ contributes to its larger *g* factor. The determination of the *g* factor profile, in principle, allows a more rational approach to the application of such organometallic complexes as asymmetric photoactive

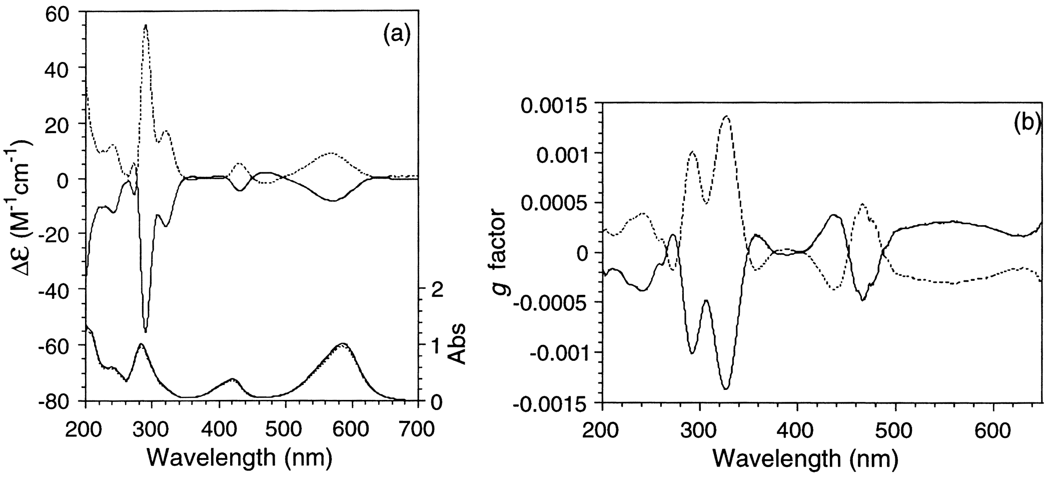


Fig. 3. (a) The CD and UV-vis spectra of the Δ (solid line) and Λ (dotted line) enantiomers of **4**, (b) *g* factors of the Δ (solid line) and Λ (dotted line) enantiomers of **4**.

catalysts, providing crucial information on the available ee's, irradiation wavelengths and conditions.

Additional host-guest binding studies were carried out with native γ-cyclodextrin (γ-CD), as the successful formation of such asymmetric supramolecular complexes is crucial to any enantiodiscriminating catalytic activity. Recently, in order to bind such ruthenium bipyridine anions it had been thought essential to modify the cyclodextrin rim to produce an anion so to increase Coulombic interactions with the ruthenium bipyridine cation.[12] In this case the ^{1}H NMR spectra of the *rac*-**4**-Cl : γ-CD complex showed distinct splitting of the guest signals into two sets, demonstrating the unusual encapsulation, and enantiodiscriminating recognition of the cationic guest molecule by the chiral cavity of the neutral γ-CD host.

These results show the degree of equatorial substitution control, conformational stability, and chiroptical activity. Considering the associated literature,[7] we conclude that these ruthenium nitrosoarene compounds show great potential to function as stereoselective photoactive catalysts, an issue which is currently been investigated.

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