

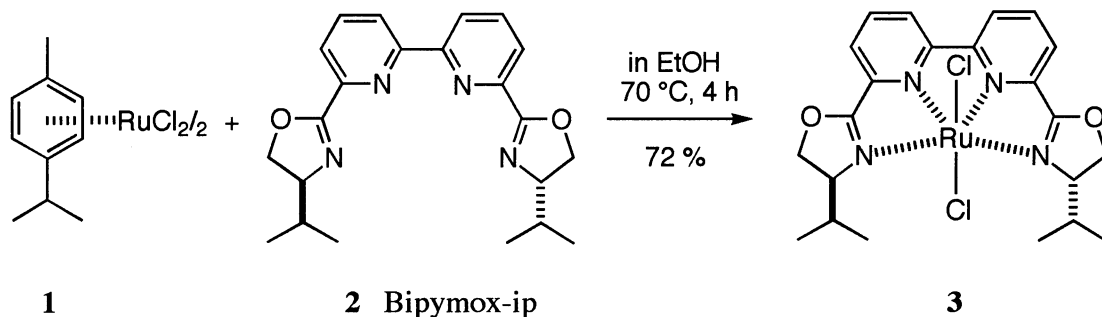
Ruthenium(II)Cl₂-Bis(oxazolinyl)bipyridine Complex. Its Structure and Reactivity

Hisao NISHIYAMA,* Soon-Bong PARK, Masa-aki HAGA,[†] Katsuyuki AOKI, and Kenji ITOH
 School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441
[†] Department of Chemistry, Faculty of Education, Mie University, 1515 Kamihama, Tsu, Mie 514

A mixture of [Ru(II)Cl₂(*p*-cymene)]₂ and 6,6'-bis(oxazolinyl)-2,2'-bipyridine (Bipymox-ip) was heated in ethanol at 70 °C to produce Ru(II)Cl₂(Bipymox-ip), of which structure was clarified by X-ray analysis to show that Bipymox-ip binds as a tetradentate ligand. Its catalytic activities for transformations of diazoacetates in dimerization and cyclopropanation with styrene were examined and its spectro-electrochemistry was studied.

Recently we have reported an optically active 6,6'-bis(oxazolinyl)-2,2'-bipyridine ligand (Bipymox-ip) as a chiral ligand for the asymmetric catalytic hydrosilylation with RhCl₃.¹⁾ Bipymox giving a C₂-symmetrical complex with RhCl₃ was thought to act as a bidentate ligand on the basis of NMR study. However, we report herein that Bipymox can bind as a tetradentate ligand, making a stable C₂-symmetrical octahedral complex with Ru(II)Cl₂. Its chemical properties will also be described.

A mixture of [Ru(II)Cl₂(*p*-cymene)]₂ (1)²⁾ and Bipymox-ip (2) in a solution of absolute ethanol was heated at 70 °C for 4 h to give an air stable complex, RuCl₂(Bipymox-ip), (3) in 72% yield.³⁾ The complex 3 proved to be C₂-symmetrical by NMR study and was crystallographically analyzed to show a distorted octahedral structure possessing a tetradentate Bipymox-ip (Fig. 1).⁴⁾ The bond angle of the N(1)-Ru-N(4) is 124.1°. The bond lengths of N(1)-Ru and N(4)-Ru (2.189 and 2.151 Å) are longer than those of N(2)-Ru and N(3)-Ru (1.927 and 1.938 Å).⁵⁾ Thus Bipymox can coordinate to the RuCl₂ skeleton by its four nitrogen sites but the oxazolines are loosely linking. Therefore it is reasonable that the treatment of the complex 3 under carbon monoxide at 70 °C gave only a mono-carbonyl complex, RuCl₂(CO)(Bipymox-ip) (4).⁶⁾ No further addition of carbon monoxide to 4 was observed to suggest a strong tridentate linkage of Bipymox-ip to the RuCl₂(CO) moiety.



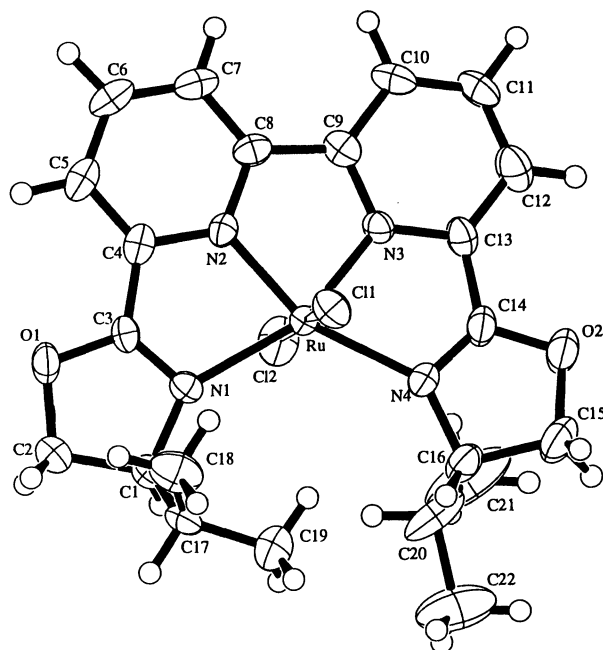
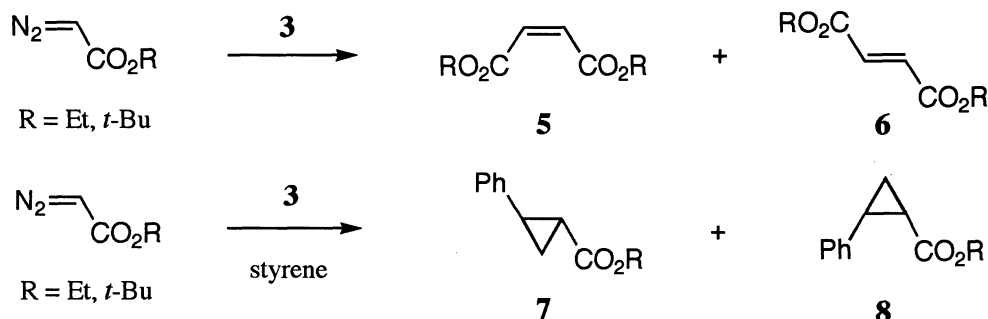


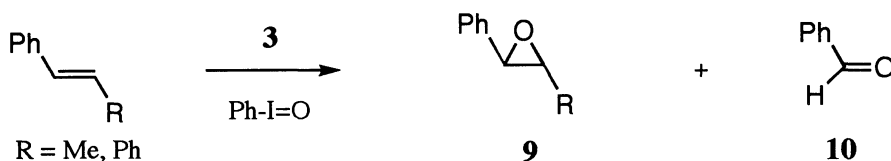
Fig. 1. Complex **3**. Thermal ellipsoids scaled at 50% probability level. Selected bond distances (Å) and angles (degree): Ru-N(1) 2.189(4), Ru-N(2) 1.938(4), Ru-N(3) 1.927(4), Ru-N(4) 2.151 (4), Ru-Cl(1) 2.389(2), Ru-Cl(2) 2.385(2); N(1)-Ru-N(2) 77.6(2), N(1)-Ru-N(3) 158.8(2), N(1)-Ru-N(4) 124.1(2), N(2)-Ru-N(3) 81.2(2), Cl(1)-Ru-Cl(2) 176.23(5).

Interestingly, the complex **3** (0.05 mmol) catalyzed the dimerization of diazoacetates ($\text{N}_2\text{CHCO}_2\text{R}$, $\text{R} = \text{Et}$ and $t\text{-Bu}$) (1.0 mmol) in 1,2-dichloroethane (2.0 ml) at 65 °C for 1 day to give the moderate yields and the extremely high ratios of the corresponding maleate (**5**) and the fumarate (**6**); for $\text{R} = \text{Et}$, 53% yield, **5**:**6** = 96:4; for $\text{R} = t\text{-Bu}$, 50% yield, **5**:**6** = 95:5. The predominant formation of the *cis*-olefins was also recently reported by the reaction with ruthenium- and osmium-porphyrin derivatives.⁷⁾ Moreover in the presence of styrene (5.0 mmol) under the same condition with **3** and the diazoacetates, the corresponding cyclopropanated products **7** and **8** were obtained in the moderate yields; for $\text{R} = \text{Et}$, 54% yield, **7**:**8** = 72:28; for $\text{R} = t\text{-Bu}$, 53% yield, **7**:**8** = 67:33. Although we have recently observed highly enantioselective cyclopropanation with a similar bis(oxazolynil)pyridine-ruthenium catalyst,⁸⁾ the asymmetric induction with **3** resulted in low for the products **7** and **8** (<10%).



The complex **3** (0.02 mmol) also showed a catalytic activity for oxidation of olefins (2.0 mmol) with iodosyl benzene (1.0 mmol) in 1,2-dichloroethane (2.0 ml) at 60 °C for 1 day to give the corresponding epoxide (**9**, $\text{R} = \text{Me}$) (0.28 mmol) and benzaldehyde (0.36 mmol) (**10**) for *trans*- β -methylstyrene, and the

corresponding epoxide (**9**, R = Ph) (0.03 mmol) and benzaldehyde (0.41 mmol) for *trans*-stilbene.⁹⁾ The selectivity for the epoxidation was not high. The asymmetric induction for the both epoxides was not observed.



We also examined the electrochemical property of the complex **3** to elucidate its catalytic activity above described. The cyclic voltammography of the complex **3** in CH₃CN/[(C₄H₉)₄N]BF₄ (0.1 M) at a platinum disk electrode exhibited a reversible one-electron Ru(II/III) oxidation process at -0.08 V vs Fc/Fc⁺ (Fig. 2). During the electrochemical experiments in CH₃CN, the oxidation-reduction cycle was repeated without decomposition of **3**. The complex has an absorption maxima at 573 (ε 4030), 441 (4100) nm, which can be assigned as a dπ-π*(Bipymox) metal-to-ligand charge-transfer (MLCT) transition in CH₃CN. The absorption bands at 331(8330) and 318(6630) nm correspond to an intraligand π-π*(Bipymox) transition. The electrochemical oxidation at +0.3 V vs Fc/Fc⁺ in CH₃CN/[(C₄H₉)₄N]BF₄ (0.1 M) leads to a complete loss of two MLCT bands and an appearance of new bands at 501 (ε 1340), 470 sh, 408 (5720) and 315 (5970) nm. The characteristic band at 408 nm can be assigned as a π(Cl)-dπ(Ru(III)) ligand-to-metal charge-transfer (LMCT) transition.

Thus we have developed the new ruthenium(II) system having tetradentate bis(oxazolonyl)bipyridine ligand as a non-porphyrin-metal system. We are now studying on its catalytic activity including asymmetric induction.

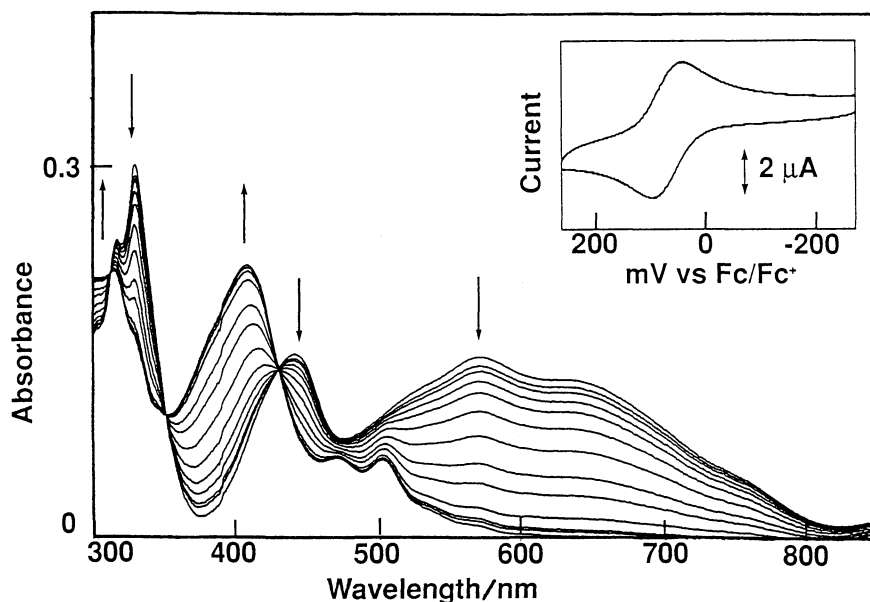


Fig. 2. UV/VIS spectral changes accompanying the electrochemical oxidation at +0.3 V vs Fc/Fc⁺ of the complex **3** (5.66×10^{-4} M) in CH₃CN/[(C₄H₉)₄N]BF₄ (0.1 M). (UV/VIS cell length = 0.05 cm) In the inset is shown a cyclic voltammogram of **3** (4.0×10^{-4} M) at a platinum disk electrode. Scan rate = 100 mV s⁻¹.

References

- 1) H. Nishiyama, S. Yamaguchi, S.-B. Park, and K. Itoh, *Tetrahedron: Asymmetry*, **4**, 143 (1993).
- 2) M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, **1974**, 233.
- 3) Synthesis of RuCl₂(Bipymox) **3**: A mixture of [Ru(II)Cl₂(*p*-cymene)]₂ (**1**) (184 mg, 0.60 mmol) and 6,6'-bis(oxazoliny)-2,2'-bipyridine (**2**) (227 mg, 0.60 mmol) in absolute ethanol (20 ml) was heated at 70 °C for 4 h. After concentration under reduced pressure, the residue was purified by column chromatography (silica-gel, CH₂Cl₂-MeOH) to give 237 mg (0.43 mmol, 72%) of **3** as dark red solids; mp >300 °C, ¹H NMR (270 MHz, CDCl₃, tms) δ 1.12 (d, *J* 6.84 Hz, 6 H), 1.25 (d, *J* 6.84 Hz, 6 H), 4.65 (m, 2H), 4.84 (t, *J* 8.5 Hz, 2 H), 4.91 (t, *J* 8.5 Hz, 2 H), 7.50 (t, *J* 7.8, 2 H), 7.84 (d, *J* 7.8 Hz, 2 H), 7.87 (d, *J* 7.8 Hz, 2 H). ¹³C NMR (67.8 MHz, CDCl₃, tms) δ 16.99, 19.38, 31.45, 70.32, 72.65, 120.8, 123.7, 128.4, 150.6, 161.1, 167.3. Found: C, 47.94; H, 4.77; N, 10.25%. Calcd for C₂₂H₂₆N₄O₂Cl₂Ru: C, 48.00; H, 4.76; N, 10.18%.
- 4) Crystal data for **3**: C₂₂H₂₆N₄O₂Cl₂Ru, *M* = 550.45, orthorhombic cell, space group P2₁2₁2₁ (#19), *a* = 13.004(3), *b* = 15.482(2), *c* = 11.5137 (8) Å, *V* = 2318.0 (7) Å³, *Z* = 4, *D_c* = 1.577 g cm⁻³, *m* = 9.33 cm⁻¹. The intensity data (2θ < 55°) were collected on a Rigaku AFC-7R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and the structure was solved by heavy-atom Patterson methods (DIRDIF92PATY). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. The final cycle of refinement was based on 2641 observed reflection (*I* > 3σ(*I*)) and 280 variable parameters and converged with *R* = 3.1% and *R_w* = 2.6%.
- 5) In the case of bis(oxazoliny)pyridine-RhCl₃, the bond length of the nitrogen(oxazoline)-ruthenium is 2.06-2.08 Å. H. Nishiyama, M. Kondo, T. Nakamura, and K. Itoh, *Organometallics*, **10**, 500 (1991).
- 6) Spectroscopic data for **4**: IR (KBr disk) 1970 cm⁻¹ (ν C=O). ¹H NMR (270 MHz, CDCl₃, tms) δ 1.05-1.20 (four doublets), 2.25 (m, 2 H), 4.23-4.45 (m, 4 H), 4.70-5.15 (m, 4 H), 7.97 (d, *J* = 7.8 Hz, 2 H), 8.37 (t, *J* = 7.8, 7.8 Hz, 2 H), 9.83 (d, *J* = 7.8 Hz, 2 H). ¹³C NMR (67.8 MHz, CDCl₃, tms) δ 15.73, 17.08, 18.66, 18.81, 30.50, 31.59, 68.67, 71.24, 72.91, 73.83, 126.2, 128.9, 140.6, 146.4, 146.5, 158.2, 158.4, 167.9, 168.2, 185.2. Deep orange, mp 161-165 °C (dec). Found: C, 45.15; H, 4.57; N, 9.09%. Calcd for C₂₃H₂₆N₄O₃Cl₂Ru(0.5CH₂Cl₂): C, 45.46; H, 4.38; N, 9.09%.
- 7) J. P. Collman, E. Rose, and G. D. Venburg, *J. Chem. Soc., Chem. Commun.*, **1993**, 934; D. A. Smith, D. N. Reynolds, and L. K. Woo, *J. Am. Chem. Soc.*, **115**, 2511 (1993); L. K. Woo and D. A. Smith, *Organometallics*, **11**, 2344 (1992).
- 8) H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, and K. Itoh, *J. Am. Chem. Soc.*, **116**, 2223 (1994).
- 9) For examples: G. Balavoine, C. Eskenazi, F. Meunier, and H. Riviere, *Tetrahedron Lett.*, **25**, 3187 (1984); J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, **107**, 5790 (1985); C. L. Bailey and R. S. Drago, *J. Chem. Soc., Chem. Commun.*, **1987**, 179; S. Perrier, T. C. Lau, and J. K. Kochi, *Inorg. Chem.*, **29**, 4190 (1990); T. Hikita, K. Tamaru, A. Yamagishi, and T. Iwamoto, *ibid.*, **28**, 2221 (1989); C. Ho, W.-H. Leung, and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, **1991**, 2933; M. M. T. Khan, D. Srinivas, R. I. Kureshy, and N. H. Khan, *Polyhedron*, **10**, 2559 (1991); H. Ohtake, T. Higuchi, and M. Hirobe, *Tetrahedron Lett.*, **33**, 2521 (1992); J. M. Fisher, A. Fulford, and P. S. Bennett, *J. Mol. Catal.*, **77**, 229 (1992) and references therein.

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