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Ruthenium(II)Cl_2-Bis(oxazolinyl)bipyridine Complex. Its Structure and Reactivity

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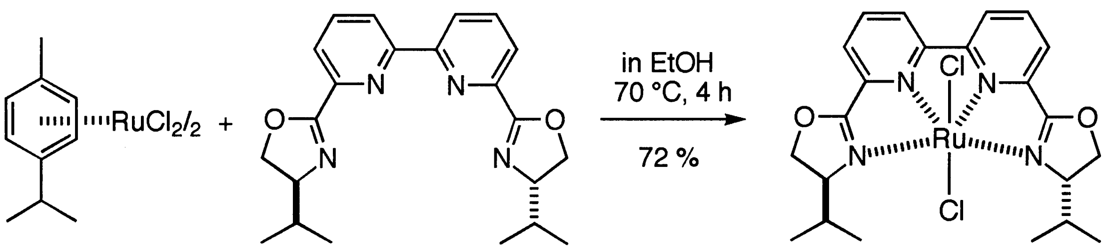
A mixture of $[Ru(II)Cl_2(p\text{-cymene})]_2$ and 6,6'-bis(oxazolinyl)-2,2'-bipyridine (Bipymox-ip) was heated in ethanol at 70 °C to produce $Ru(II)Cl_2$(Bipymox-ip), of which structure was clarified by X-ray analysis to show that Bipymox-ip binds as a tetradentate ligand. Its catalytic activities for transformations of diazoacetates in dimerization and cyclopropanation with styrene were examined and its spectroelectrochemistry 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 $RhCl_3$.$^{1)}$ Bipymox giving a C_2-symmetrical complex with $RhCl_3$ 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 C_2-symmetrical octahedral complex with $Ru(II)Cl_2$. Its chemical properties will also be described.

A mixture of $[Ru(II)Cl_2(p\text{-cymene})]_2$ (**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, $RuCl_2$(Bipymox-ip), (**3**) in 72% yield.$^{3)}$ The complex **3** proved to be C_2-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 $RuCl_2$ 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 monoixde at 70 °C gave only a mono-carbonyl complex, $RuCl_2(CO)$(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 $RuCl_2(CO)$ moiety.



1 **2** Bipymox-ip **3**

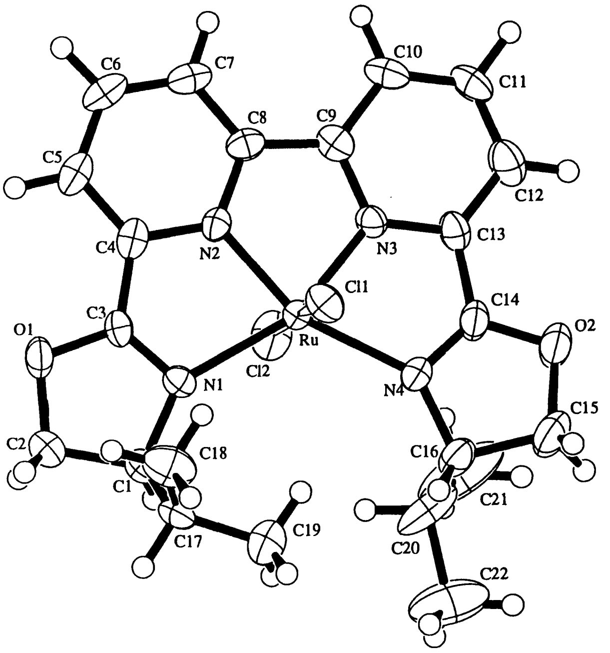
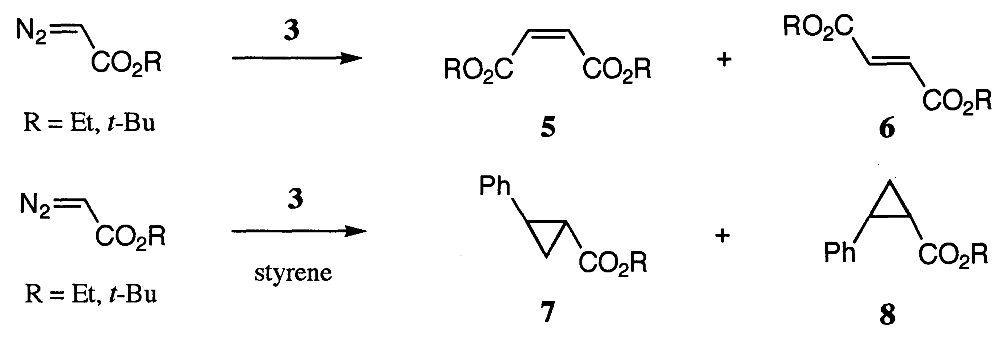
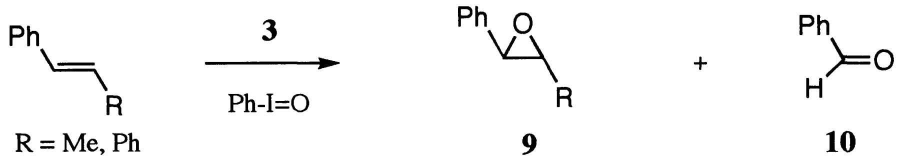


Fig. 1. Complex **3**. Thermal ellipsoids scaled at 50% probability level. Selected bond distances (Å) and angles (degree): Ru-N(1) 2.189(4), Ru-N(2) 1.938(4), Ru-N(3) 1.927(4), Ru-N(4) 2.151 (4), Ru-Cl(1) 2.389(2), Ru-Cl(2) 2.385(2); N(1)-Ru-N(2) 77.6(2), N(1)-Ru-N(3) 158.8(2), N(1)-Ru-N(4) 124.1(2), 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 (N_2CHCO_2R, R = Et and *t*-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 R = Et, 53% yield, **5**:**6** = 96:4; for R = *t*-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 R = Et, 54% yield, **7**:**8** = 72:28; for R = *t*-Bu, 53% yield, **7**:**8** = 67:33. Although we have recently observed highly enantioselective cyclopropanation with a similar bis(oxazolinyl)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**, R = 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 CH_3CN/ $[(C_4H_9)_4N]BF_4$ (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 CH_3CN, 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 CH_3CN. 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 $CH_3CN/[(C_4H_9)_4N]BF_4$ (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 pπ(Cl)-dπ(Ru(III)) ligand-to-metal charge-transfer (LMCT) transition.

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

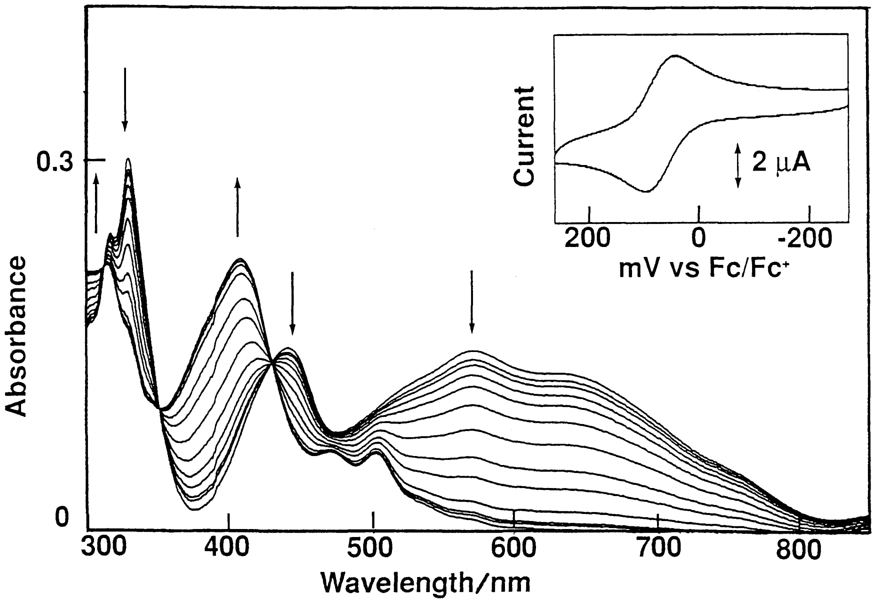


Fig. 2. UV/VIS spectral changes accompanying the electrochemical oxidation at +0.3 V vs Fc/Fc$^+$ of the complex **3** (5.66 x 10^{-4} M) in $CH_3CN/[(C_4H_9)_4N]BF_4$(0.1 M). (UV/VIS cell length = 0.05 cm) In the inset is shown a cyclic voltammogram of **3** (4.0 x 10^{-4} M) at a platinum disk electrode. Scan rate=100 mV s^{-1}.

References

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3) Synthesis of $RuCl_2$(Bipymox) **3**: A mixture of $[Ru(II)Cl_2(p\text{-cymene})]_2$ (**1**) (184 mg, 0.60 mmol) and 6,6'-bis(oxazolinyl)-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, CH_2Cl_2-MeOH) to give 237 mg (0.43 mmol, 72%) of **3** as dark red solids; mp >300 °C, ^1H NMR (270 MHz, $CDCl_3$, 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). ^{13}C NMR (67.8 MHz, $CDCl_3$, 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 $C_{22}H_{26}N_4O_2Cl_2Ru$: C, 48.00; H, 4.76; N, 10.18%.

4) Crystal data for **3**: $C_{22}H_{26}N_4O_2Cl_2Ru$, M = 550.45, orthorhombic cell, space group $P2_12_12_1$ (#19), a =13.004(3), b = 15.482(2), c = 11.5137 (8) Å, V = 2318.0 (7) $Å^3$, Z = 4, D_c = 1.577 g cm^{-3}, m = 9.33 cm^{-1}. The intensity data ($2\theta < 55°$) were collected on a Rigaku AFC-7R diffractometer with graphite monochromated Mo-Kα radiation (l = 0.71069 Å) and the structure was solved by heavy-atom Patterson methods (DIRDIF92PATTY). 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 ($I > 3\sigma(I)$) and 280 variable parameters and converged with R = 3.1% and R_w = 2.6%.

5) In the case of bis(oxazolinyl)pyridine-$RhCl_3$, 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, $CDCl_3$, 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). ^{13}C NMR (67.8 MHz, $CDCl_3$, 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 $C_{23}H_{26}N_4O_3Cl_2Ru(0.5CH_2Cl_2)$: C, 45.46; H, 4.38; N, 9.09%.

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