Syntheses of a 6-(2-Pyrrolyl)-2,2′-bipyridine Derivative and Its Ruthenium Complex

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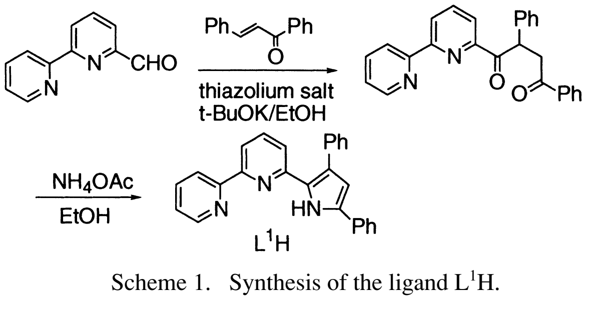
Syntheses of a new planar terdentate ligand, 6-(3,5-diphenyl-2-pyrrolyl)-2,2′-bipyridine (L^{1}H) and its ruthenium(II) complex ([Ru(L^1)$_2$]) are reported. The X-ray structure of [Ru(L^1)$_2$] showed the distorted octahedral Ru(II) center similar to the structures of terpyridine complexes. The cyclic voltammograms revealed that [Ru(L^1)$_2$] was more easily oxidized than [Ru(terpy)$_2$]$^{2+}$ by 1.10 V.

Metal complexes of pyrroles[1] are gathering interest as an activator of the pyrrole ring,[2] an intermediate for synthesizing pyrrole derivatives,[3] and as a component of conducting polymers.[4] On the other hand, considering the rich chemistry of polypyridine metal complexes, one can easily replace one or two pyridine rings in polypyridines with pyrrole rings to develop a different series of useful ligands.[5,6]

In this article we report the syntheses of 6-(3,5-diphenyl-2-pyrrolyl)-2,2′-bipyridine (L^{1}H) and its ruthenium complex [Ru(L^1)$_2$]. The compound L^{1}H is the first example of the "teraryl" ligand that has one pyrrole and two pyridine rings in this order,[9] and it will be a useful substitute for 2,2′:6′,2″-terpyridine (terpy) when more electron-donating character is desirable.

The synthesis of L^{1}H is shown in Scheme 1. The Stetter condensation[7] of 2,2′-bipyridine-6-carbaldehyde[8] with chalcone was utilized, followed by ring closure of the 1,4-diketone with an ammonium salt (67% yield). By use of pyridine-2,6-dicarbaldehyde as a starting material, the compound L^{2}H$_2$, 2,6-bis(3,5-diphenyl-2-pyrrolyl)pyridine, was also obtained (69% yield).



Scheme 1. Synthesis of the ligand L^{1}H.

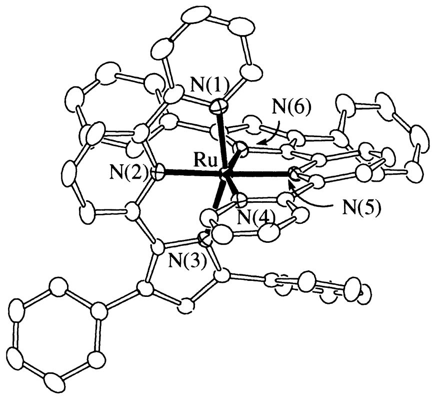


Fig. 1. ORTEP view (50% probability ellipsoids) of the complex [Ru(L^1)$_2$]. Selected bond lengths (Å): Ru–N(1), 2.052(3); Ru–N(2), 1.989(3); Ru–N(3), 2.076(3); Ru–N(4), 2.052(3); Ru–N(5), 1.994(3); Ru–N(6), 2.121(3). Selected bond angles (°): N(1)–Ru–N(2), 79.2(1); N(2)–Ru–N(3), 78.7(1); N(4)–Ru–N(5), 79.2(1); N(5)–Ru–N(6), 78.6(1), N(1)–Ru–N(4), 93.5(1); N(1)–Ru–N(6), 90.5(1); N(3)–Ru–N(4), 91.7(1); N(3)–Ru–N(6), 93.0(1).

The ORTEP drawing of the complex [Ru(L^1)$_2$] is shown in Fig. 1. The coordination geometry around the Ru(II) center is similar to that of [Ru(terpy)$_2$]X$_2$.[9] However, the six pyridine/pyrrole rings are not exactly coplanar; the dihedral angles between the neighboring rings are 8.5–19.4°.

The ^{1}H NMR spectrum of [Ru(L^1)$_2$] in (CD$_3$)$_2$SO revealed all signals in the diamagnetic region (5.7–8.5 ppm), which is consistent with the formulation of Ru(II) and two monoanionic ligands. The ESI (electrospray ionization) mass spectrum in acetone showed a cluster of peaks around *m*/*z* = 846 which matched the calculated isotopic pattern for [Ru(L^1)$_2$]$^+$; this apparently contradictory presence of Ru(III) species is attributed either to aerial oxidation of the sample solution or to a redox process inside the ionization chamber of the ESI-MS.

The cyclic voltammograms of [Ru(L^1)$_2$] and [Ru(terpy)$_2$](ClO$_4$)$_2$ are shown in Fig. 2. The Ru(III)/Ru(II) couple appeared at −0.29 V (versus ferrocene/ferrocenium couple) in [Ru(L^1)$_2$], which was 1.10 V more negative than in [Ru(terpy)$_2$](ClO$_4$), consistent with the strong donor character of the L^1 ligand. The first reduction wave (reduction of the ligand) was also negatively shifted by 0.51 V. At higher potential range (+0.5–0.7 V), [Ru(L^1)$_2$] showed irreversible waves suggesting the oxidative degradation of the complex. Apparently the oxidation of the pyrrole rings led to the degradation of the ligand and/or the decomplexation of the metal ion. Introduction of a substituent such as alkyl or aryl to the 3-position of the pyrrole ring may increase the stability under oxidative conditions; this will be our next project for improving this type of ligand.

Experimental

General. All reagents and solvents were of commercial reagent grade and were used without further purification. Elemental analyses were performed on a Yanaco MT-3 analyzer. ^{1}H NMR spectra were measured on a JEOL Lambda-500 (500 MHz) spec-

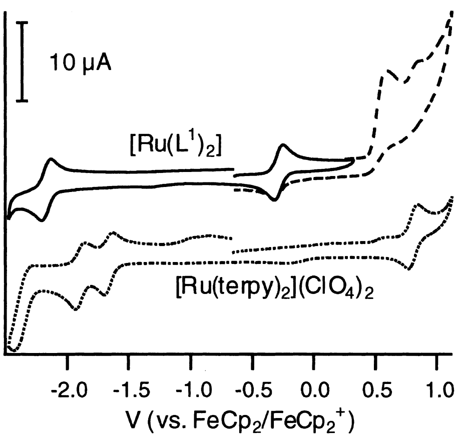


Fig. 2. The cyclic voltammograms of $[Ru(L^1)_2]$ and $[Ru(terpy)_2](ClO_4)_2$; glassy carbon electrode (0.3 mm diameter), 5.0×10^{-3} mol dm^{-3} solutions in DMF with 0.1 mol dm^{-3} Et_4NClO_4.

trometer and chemical shifts are reported in the δ scale relative to Me_4Si in ppm. Cyclic voltammetry was performed with an ALS Model 660 electrochemical analyzer. Mass spectra were obtained either on a JEOL JMS-GCMate-II spectrometer (for FAB) or on a Shimadzu LCMS-2010 spectrometer (for ESI).

6-(3,5-Diphenyl-2-pyrrolyl)-2,2′-bipyridine (L^1H). 2,2′-Bipyridine-6-carboxaldehyde (368 mg, 2.0 mmol), 1,3-diphenyl-2-propene-1-one (chalcone, 416 mg, 2.0 mmol), and 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (54 mg, 0.2 mmol) were mixed in a 30-mL flask. Ethanol (5 mL) was added, followed by a solution of sodium *t*-butoxide (19 mg, 0.2 mmol) in ethanol (2 mL). The flask was heated under argon stream to 90 °C for 20 h. The pale brown mixture was poured into water and extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4, and evaporated. The resulting orange-red oil (6-(1,4-dioxo-2,4-diphenylbutyl)-2,2′-bipyridine) was mixed with ammonium acetate (0.77 g, 10 mmol) in ethanol (5 mL), and the mixture was heated under argon to 90 °C for 42 h. Water (15 mL) was added, and the mixture was extracted with $CHCl_3$, washed with water, dried over Na_2SO_4, and evaporated. The residue was purified by medium-pressure column chromatography (Wakogel C-200, 20 × 150 mm, CH_2Cl_2, then CH_2Cl_2/MeOH = 100/2 (v/v)). The yellow main fraction was collected and evaporated. Yellow amorphous solid, yield 504 mg (1.35 mmol, 67%). Mp 76–80 °C. ^{1}H NMR ($CDCl_3$) δ pyrrole, 9.93 (1H, br), 6.61 (1H, d); pyridine, 8.69 (1H, dd), 8.45 (1H, d), 8.10 (1H, d), 7.88 (1H, td), 7.53 (1H, t), 7.35 (1H, d), 7.28 (1H, d); phenyl, 7.64 (2H, d), 7.52 (2H, d), 7.43 (2H, t), 7.41 (2H, t), 7.32 (1H, t), 7.27 (1H, t). HRMS (FAB, glycerol). Found: *m*/*z* 374.1507. Calcd for $C_{26}H_{20}N_3$ ($M + H^+$): *m*/*z* 374.1657.

2,6-Bis(3,5-diphenyl-2-pyrrolyl)pyridine (L^2H_2). The ligand L^2H_2 was prepared from 2,6-pyridinedicarboxaldehyde using a similar method to that for L^1H. Pale yellow powder, yield 705 mg (1.37 mmol, 69%). Mp (CH_2Cl_2/EtOH) 221–223 °C. ^{1}H NMR ($CDCl_3$) δ pyrrole, 9.54 (2H, br), 6.64 (2H, d); pyridine, 7.19 (1H, t), 7.01 (2H, d); phenyl, 7.58 (4H, d), 7.50 (4H, d), 7.41 (4H, t), 7.38 (4H, t), 7.29 (2H, t), 7.27 (2H, t). Anal. Found: C, 86.29; H, 5.31; N, 8.01%. Calcd for $C_{37}H_{27}N_3$: C, 86.52; H, 5.30; N, 8.18%.

$[Ru(L^1)_2]$. The ligand L^1H (55.2 mg, 148 μmol), $RuCl_3 \cdot xH_2O$ (19.4 mg, 74 μmol) and triethylamine (29.7 mg, 296 μmol) were mixed with EtOH (3.5 mL), and the mixture was heated to 100 °C with vigorous stirring for 17 h. After the mixture was cooled to room temperature, the deep-green precipitate was collected by filtration and washed with EtOH. Yield 49.4 mg (58.4 μmol, 79%). Mp (CH_2Cl_2/EtOH) > 300 °C. ^{1}H NMR ($(CD_3)_2SO$) δ 8.21 (1H, d), 7.80 (1H, br), 7.46 (7H, m), 7.28 (1H, t), 7.11 (1H, br), 6.88 (1H, br), 6.28 (3H, m), 6.70 (2H, d), 5.70 (1H, br). ESI-MS (in acetone) *m*/*z* 846 (M^+). Anal. Found: C, 73.28; H, 4.32; N, 9.82%. Calcd for $C_{53}H_{39}N_6O_{0.5}Ru$ ($[Ru(L^1)_2] \cdot 1/2EtOH$): C, 73.25; H, 4.52; N, 9.67%. Single crystals for X-ray studies were obtained by slow evaporation of the CH_2Cl_2/hexane solution.

X-ray Structure Determination. Cell constants and intensity data were collected at 193 K on a Rigaku Mercury diffractometer equipped with a Mo sealed tube operating at 50 kV 25 mA, a graphite monochromator, and a CCD detector. The data were collected to a maximum 2θ value of 55.0°. The structure were solved by direct methods[10] and refined on F by full-matrix least-squares techniques. All calculations were performed by the CrystalStructure[11] software package. Selected crystallographic parameters are as follows: $C_{52}H_{36}N_6Ru$, Fw 845.97, monoclinic, $P2_1/n$, $a = 9.444(3)$ Å, $b = 28.143(8)$ Å, $c = 15.297(5)$ Å, $\beta = 110.082(3)$°, $V = 3818(1)$ Å^3, $Z = 4$, $D_{calc} = 1.472$ g cm^{-3}, $R = 6.6\%$, $R_w = 9.1\%$.

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