

Photochemical Synthesis of *mer*-[Re(bpy)(CO)₃Cl]

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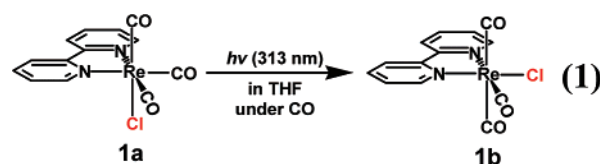
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The *mer* isomer of Re(bpy)(CO)₃Cl (bpy = 2,2'-bipyridine) has been synthesized photochemically and isolated for the first time. The *mer* complex is a useful starting material for the synthesis of *cis,cis*-[Re(bpy)(CO)₂(L)Cl]-type complexes.

There are two constitutional isomers, facial and meridional structures, in some groups of metal complexes, such as [M(L-L)(CO)₃X]ⁿ⁺ and [M(L-L')₃]ⁿ⁺ (L-L and L-L' = symmetrical and unsymmetrical bidentate ligands; X = monodentate ligand).^{1–3} It is interesting to consider how different their properties and reactivities are. The facial and meridional isomers of [Ir(ppy)₃] (ppy = 2-phenylpyridine) have recently been isolated, and their photophysical properties and reactivities are quite different.^{4,5}

The complex described in this paper, *fac*-[Re(bpy)(CO)₃Cl] (**1a**; bpy = 2,2'-bipyridine), is emissive at room temperature even in solution⁶ and has a unique photocatalytic property for CO₂ reduction.⁷ Although its photophysics and photo-reactivity have been studied in detail for more than 3 decades, the isomer *mer*-[Re(bpy)(CO)₃Cl] (**1b**) has not yet been

reported. We report here the first photochemical synthesis of **1b** (eq 1) and its spectroscopic properties and reactivity.



A tetrahydrofuran (THF) solution (400 mL) containing 101 mg (0.22 mmol) of **1a** was irradiated under a CO atmosphere by a high-pressure Hg lamp (500 W) with a K₂CrO₄ (3.3 × 10⁻³ mol dm⁻³) solution filter (1 cm, 305 nm < λ < 320, and 405 nm < λ), until **1a** had decreased to 90% (about 3 h of irradiation). During the irradiation, the reaction vessel was cooled with tap water. The solvent was evaporated under reduced pressure, leaving a deep-red oil, which was chromatographed on a silica column using a CH₂Cl₂ eluent. The first fraction contained **1b**, and the second contained starting complex **1a**. The brown-red solids **1b** were recrystallized with CH₂Cl₂/ether to give a yield of 33%. Even under an Ar atmosphere in the absence of CO, **1b** was also produced, but the yield fell to 20%. Irradiation using 366 nm instead of 313 nm light did not give any **1b**. We can determine the quantities of **1a** and **1b** by using high-performance liquid chromatography (HPLC) with an ODS column and a 1:1 (v/v) mixture eluent of MeOH and H₂O (Figure S1 in the Supporting Information). In the first stage of the photo-reaction, until 20% of **1a** had been converted, the yield of **1b** was greater than 90% based on the **1a** consumed, and the quantum yield of a decrease of **1a** was 4.8 × 10⁻³. Further irradiation caused decomposition of **1b**, so that the yield of **1b** decreased.^{8,9}

There are considerable differences in the spectral data between the facial and meridional isomers. In ¹H NMR spectra (Figure 1), eight aromatic proton signals are observed for **1b**,¹⁰ but only four are observed for **1a** because there is a mirror plane between the two pyridine rings of the bpy

- (8) At room temperature, **1b** was not stable even in solvents with low nucleophilicity, such as THF, acetone, and CH₂Cl₂. When **1b** had been dissolved in these solvents for several hours, black precipitates were formed that were insoluble in both water and organic solvents.
(9) Reverse isomerization from **1b** to **1a** did not occur either photochemically (313 nm irradiation) or thermally (reflux in THF).

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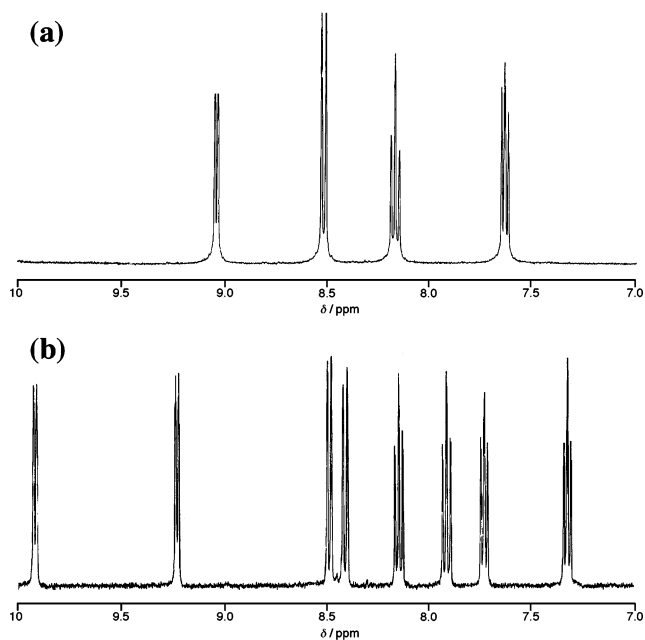


Figure 1. ^1H NMR aromatic proton signals of **1a** (a) and **1b** (b) measured in $\text{THF-}d_8$ solutions.

ligand. The proton signal attributed to the 6 position of the bpy ligand in **1b** is shifted 0.7 ppm to a lower magnetic field compared with **1a**.

Similar downfield shifts have been reported for $[\text{Ru}(\text{tpy})(\text{bpy})\text{Cl}]^+$ ($\text{tpy} = 2,2',6',2''\text{-terpyridine}$)¹¹ and $(OC-6-24)\text{-[Re}(\text{bpy})(\text{CO})_2(\text{MeCN})\text{Cl}]$,¹² which have the Cl ligand in the trans position to the bpy ligand. This phenomenon is probably caused by CH–n interaction (n refers to lone-pair electrons in Cl) between the Cl ligand and the H atom in the 6 position of the bpy ligand.

Figure 2 shows ^{13}C NMR spectra of **1a** and **1b** measured in CD_2Cl_2 at 223 K. There were 5 aromatic carbon signals for **1a** but 10 for **1b**. A further difference in the strength of the signals is attributed to the CO ligands. For these measurement conditions (1.1 s of acquisition time and 2.0 s of recycle decay with the ^1H NMR decoupling method), the height of the signal for carbon without protons is usually lower than that with a proton, as is observed in Figure 2a. However, the height of the signal at 189.5 ppm in Figure 2b, which is due to the equatorial CO ligand because of its similar chemical shift to that of **1b**, is similar to those of the aromatic carbons with one proton. These observations imply that the relaxation time for the carbon in the equatorial CO

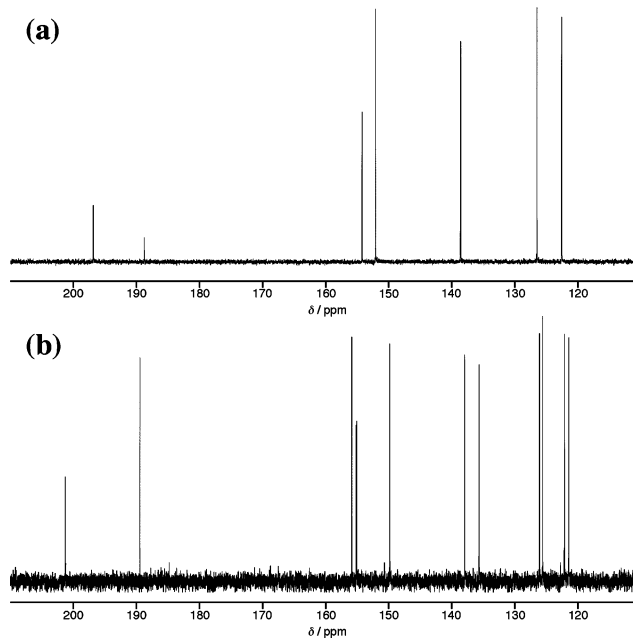


Figure 2. ^{13}C NMR spectra of **1a** (a) and **1b** (b) measured in CD_2Cl_2 at 223 K.

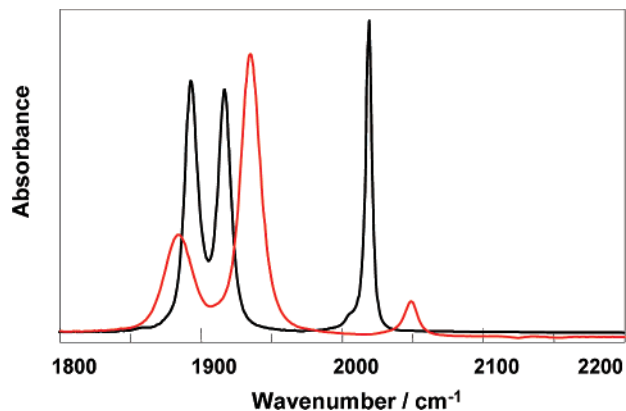


Figure 3. IR spectra of **1a** (black line) and **1b** (red line) measured in THF solutions.

ligand should be much shorter than that for the other CO ligands possibly because of the higher shielding anisotropy of **1b** than **1a**.

The CO stretching bands in the IR spectrum of **1b** have a pattern similar to that of $\text{mer-}[\text{Mn}(\text{H-DAB})(\text{CO})_3\text{Cl}]$ (H-DAB = 1,4-diaza-1,3-butadiene),¹ that is, three peaks with different strengths (Figure 3).¹³

Two broad absorption bands at 352 nm ($\lambda_{\text{max}} = 6500$) and 475 nm ($\lambda_{\text{max}} = 2800$) were observed in the UV/vis absorption spectrum of a CH_2Cl_2 solution containing **1b** (Figure 3), which were 25–30 nm blue-shifted in MeCN (Figure S2 in the Supporting Information). Therefore, both are attributable to metal-to-ligand charge-transfer (MLCT) absorption. On the other hand, sharper and stronger bands at 302 nm ($\lambda_{\text{max}} = 20\,000$) and 285 nm ($\lambda_{\text{max}} = 28\,000$) can be attributed to $\pi\text{-}\pi^*$ (bpy) absorption because of a much diminished effect of solvent polarity. The MLCT absorption bands are red-shifted by 50–100 nm compared with those of **1a** (Figure 4). The meridional isomer **1b** does not emit at

(10) The elemental analysis and the spectroscopic properties of **1b** are as follows. Anal. Calcd for $\text{C}_{13}\text{H}_8\text{ClN}_2\text{O}_3\text{Re}$: C, 33.81; H, 1.75; N, 6.07. Found: C, 33.75; H, 1.96; N, 5.83. ^1H NMR (δ/ppm , 400 MHz, CD_2Cl_2): 9.89 (d, $J = 5.6$ Hz, 1H, bpy-6'), 9.27 (d, $J = 5.6$ Hz, 1H, bpy-6), 8.23 (d, $J = 8.0$ Hz, 1H, bpy-3'), 8.15 (d, $J = 8.0$ Hz, 1H, bpy-3), 8.11 (dd, $J = 8.0$ and 7.2 Hz, 1H, bpy-4'), 7.87 (dd, $J = 8.0$ and 7.2 Hz, 1H, bpy-4), 7.70 (dd, $J = 7.2$ and 5.6 Hz, 1H, bpy-5'), 7.27 (dd, $J = 7.2$ and 5.6 Hz, 1H, bpy-5). ^{13}C NMR (δ/ppm , 125 MHz, CD_2Cl_2 , 223 K): 201.2, 189.5, 155.9, 155.2, 155.1, 149.8, 138.0, 135.7, 126.1, 125.6, 122.1, 121.5. FT-IR (CH_2Cl_2 , $\nu_{\text{CO}}/\text{cm}^{-1}$): 2048, 1935, 1884. ^{13}C NMR of *fac* isomer **1a** (δ/ppm , 125 MHz, CD_2Cl_2 , 223 K): 196.8, 188.7, 154.2, 152.0, 138.5, 126.4, 122.5.

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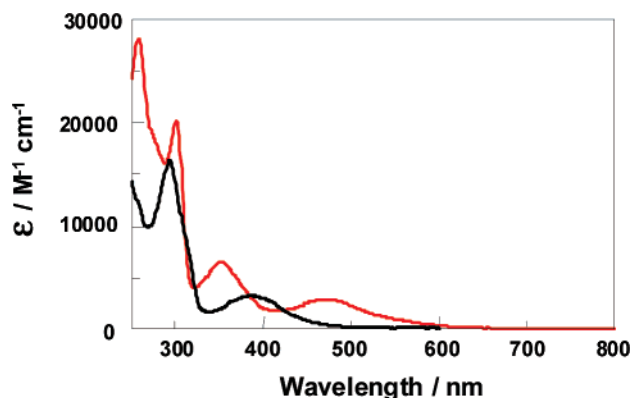
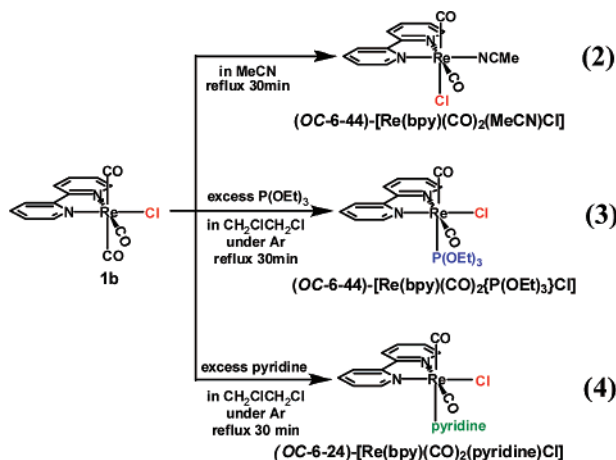


Figure 4. UV/vis absorption spectra of **1a** (black line) and **1b** (red line) measured in CH_2Cl_2 solutions.

room temperature in solution, whereas **1a** can emit in the same conditions with $\tau_{\text{em}} = 39$ ns in methyltetrahydrofuran¹⁴ probably because of the much lower excitation energy in the MLCT excited state of **1b**.

An acetonitrile solution containing **1b** was refluxed for 30 min, at which time the solvent had just evaporated, giving $(OC-6-44)-[\text{Re}(\text{bpy})(\text{CO})_2(\text{MeCN})\text{Cl}]$ (**2**; eq 2). Although we recently reported that **2** can also be made by photoreaction of **1a** in a MeCN solution using 313 nm light, a 1:1 mixture with another isomer, $(OC-6-42)-[\text{Re}(\text{bpy})(\text{CO})_2(\text{MeCN})\text{Cl}]$, was obtained; separation using column chromatography is necessary for isolation of **2**.¹² In the presence of excess $\text{P}(\text{OEt})_3$ or pyridine, a 1,2-dichloroethane solution of **1b** was refluxed for 30 min to give $(OC-6-44)-[\text{Re}(\text{bpy})(\text{CO})_2-$



$\{\text{P}(\text{OEt})_3\}\text{Cl}]$ or $(OC-6-24)-[\text{Re}(\text{bpy})(\text{CO})_2(\text{pyridine})\text{Cl}]$, in 75% and 51% isolated yields, respectively (eqs 3 and 4).¹⁵ No other methods for the synthesis of such complexes have been reported.¹⁶

In conclusion, we have found that the facial isomer **1a** photochemically isomerizes to the meridional isomer **1b** using a solvent with relatively low nucleophilicity and high-energy light. This is the first report concerning a meridional isomer of rhenium(I) diimine complexes. The spectroscopic properties of **1b** are very different from those of **1a**. The isolated complex **1b** is a useful starting material for the synthesis of *cis,cis*- $[\text{Re}(\text{bpy})(\text{CO})_2(\text{L})\text{Cl}]$ -type complexes.

Supporting Information Available: HPLC charts of photo-reaction products (Figure S1) and UV/vis absorption spectra of **1b** measured in MeCN and CH_2Cl_2 solutions (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Synthesis of $(OC-6-44)-[\text{Re}(\text{bpy})(\text{CO})_2\{\text{P}(\text{OEt})_3\}\text{Cl}]$ and $(OC-6-24)-[\text{Re}(\text{bpy})(\text{CO})_2(\text{pyridine})\text{Cl}]$: A 1,2-dichloroethane solution containing 15.0 mg of **1b** (0.032 mmol) and excess $\text{P}(\text{OEt})_3$ or pyridine was refluxed under an Ar atmosphere for 30 min. The solvent was evaporated under reduced pressure, giving a deep-purple oil, and the addition of pentane gave black precipitates. Purification was achieved by recrystallization using $\text{CH}_2\text{Cl}_2/\text{pentane}$. $(OC-6-44)-[\text{Re}(\text{bpy})(\text{CO})_2\{\text{P}(\text{OEt})_3\}\text{Cl}]$. Yield: 75%. Anal. Calcd for $\text{C}_{18}\text{H}_{23}\text{ClN}_2\text{O}_5\text{PRe}$: C, 36.03; H, 3.86; N, 4.67. Found: C, 36.06; H, 4.08; N, 4.73. ^1H NMR (δ/ppm , 400 MHz, $(\text{CD}_3)_2\text{CO}$): 9.87 (d, $J = 5.6$ Hz, 1H, bpy-6), 9.26 (d, $J = 5.6$ Hz, 1H, bpy-6'), 8.60 (d, $J = 8.1$ Hz, 1H, bpy-3), 8.46 (d, $J = 8.1$ Hz, 1H, bpy-3'), 8.22 (dd, $J = 8.1$ and 7.2 Hz, 1H, bpy-4), 7.87 (dd, $J = 8.1$ and 7.2 Hz, 1H, bpy-4'), 7.78 (dd, $J = 7.2$ and 5.6 Hz, 1H, bpy-5), 7.32 (dd, $J = 7.2$ and 5.6 Hz, 1H, bpy-5'), 3.80 (quint, $J = 7.0$ Hz, 6H, POCH_2), 0.96 (t, $J = 7.0$ Hz, 9H, OCH_2CH_3). ^{13}C NMR (δ/ppm , 125 MHz, $(\text{CD}_3)_2\text{CO}$): 197.7, 196.8, 158.0, 157.7, 157.0, 151.5, 138.8, 135.1, 127.1, 126.3, 124.1, 123.2, 61.3 (d, $^2J_{\text{C-P}} = 4.3$ Hz, OCH_2), 61.3 (d, $^3J_{\text{C-P}} = 5.8$ Hz, OCH_2CH_3). ^{31}P NMR (δ , 202 MHz, $(\text{CD}_3)_2\text{CO}$): 115.7. FT-IR (CH_2Cl_2 , $\nu_{\text{CO}}/\text{cm}^{-1}$): 1925, 1836. $(OC-6-24)-[\text{Re}(\text{bpy})(\text{CO})_2(\text{pyridine})\text{Cl}]$. Yield: 51%. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{ClN}_3\text{O}_2\text{Re}$: C, 39.80; H, 2.55; N, 8.19. Found: C, 39.80; H, 2.48; N, 7.95. ^1H NMR (δ/ppm , 400 MHz, CD_2Cl_2): 9.81 (d, $J = 5.6$ Hz, 1H, bpy-6), 9.47 (d, $J = 5.6$ Hz, 1H, bpy-6'), 8.38 (d, $J = 5.2$ Hz, 2H, py-2,6'), 8.06 (d, $J = 8.0$ Hz, 1H, bpy-3), 8.01 (t, $J = 8.0$ Hz, 1H, py-3,5), 7.93 (d, $J = 8.0$ Hz, 1H, bpy-3'), 7.71 (dd, $J = 8.0$ and 7.2 Hz, 1H, bpy-4), 7.66 (t, $J = 8.0$ and 5.0 Hz, 1H, py-4), 7.62 (t, $J = 8.0$ Hz, 1H, py-4), 7.21 (dd, $J = 8.0$ and 7.2 Hz, 1H, bpy-4'), 7.10 (dd, $J = 7.2$ and 5.6 Hz, 2H, bpy-5,5'). FT-IR (CH_2Cl_2 , $\nu_{\text{CO}}/\text{cm}^{-1}$): 1901, 1823. Because of the low solubility and instability of this complex, ^{13}C NMR could not be measured.

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