New Synthetic Routes to Biscarbonylbipyridinerhenium(I) Complexes
cis,trans-[Re(X$_2$ bpy)(CO)$_2$(PR$_3$)(Y)]$^{n+}$ (X$_2$ bpy = 4,4′-X$_2$-2,2′-bipyridine) via Photochemical Ligand Substitution Reactions, and Their Photophysical and Electrochemical Properties

Kazuhide Koike,† Junji Tanabe, Shigeki Toyama, Hideaki Tsubaki, Kazuhiko Sakamoto, Jeremy R. Westwell,∥ Frank P. A. Johnson,§ Hisao Hori,¶ Hideki Saitoh, and Osamu Ishitani*

Graduate School of Science and Engineering and Faculty of Science, Saitama University, 255 Shimo-Okubo, Urawa, Saitama 338-8570, Japan

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Photochemical ligand substitution of fac-[Re(X$_2$ bpy)(CO)$_2$(PR$_3$)]$^+$ (X$_2$ bpy = 4,4′-X$_2$-2,2′-bipyridine; X = Me, H, CF$_3$; R = OEt, Ph) with acetonitrile quantitatively gave a new class of biscarbonyl complexes, cis,trans-[Re(X$_2$ bpy)(CO)$_2$(PR$_3$)(MeCN)]$^{n+}$, coordinated with four different kinds of ligands. Similarly, other biscarbonylrhenium complexes, cis,trans-[Re(X$_2$ bpy)(CO)$_2$(PR$_3$)(Y)]$^{n+}$ (n = 0, Y = Cl$^-$; n = 1, Y = pyridine, PR$_3$), were synthesized in good yields via photochemical ligand substitution reactions. The structure of cis,trans-[Re(2Me-bpy)(CO)$_2$(P(OEt)$_3$)(PPh$_3$)](PF$_6$) was determined by X-ray analysis. Crystal data: Cs$_2$H$_2$N$_2$O$_2$F$_3$P$_3$Re, monoclinic, P2$_1$/a, a = 11.592(1) Å, b = 30.953(4) Å, c = 11.799(2) Å, V = 4221.6(1) Å$^3$, Z = 4, 7813 reflections, R = 0.066. The biscarbonyl complexes with two phosphorus ligands were strongly emissive from their 3MLCT state with lifetimes of 20–640 ns in fluid solutions at room temperature. Only weak or no emission was observed in the cases Y = Cl$^-$, MeCN, and pyridine. Electrochemical reduction of the biscarbonyl complexes with Y = Cl$^-$ and pyridine in MeCN resulted in efficient ligand substitution to give the solvento complexes cis,trans-[Re(X$_2$ bpy)(CO)$_2$(PR$_3$)(MeCN)]$^+$.

Introduction

Many kinds of tricarbonyldiiminerhenium complexes fac-[Re(LL)(CO)$_3$(L')]$^{n+}$ (LL = diimine ligand, L' = monodentate ligand, n = 0 or 1) have been synthesized, and their photophysical and photochemical properties have received a great deal of attention in the last two decades.1−3 Recently, they have been frequently used as building blocks for multifunctional bimetallic complexes and supramolecular systems because the photochemical and electrochemical properties of rhenium complexes can be widely changed by the relatively straightforward introduction of various kinds of mono- and bidentate ligands (L' and LL).4 For example, covalently linked donor−acceptor pairs containing the rhenium complex(es) have been utilized in many studies for intramolecular electron- and energy-transfer reactions,4−6 and macrocyclic tetrametallic assemblies, “molecular squares”, have been constructed using the rhenium complexes as corners.7

On the other hand, only a few biscarbonyl diimine complexes [Re(LL)(CO)$_3$(L')(Y)]$^{n+}$ have been reported due to the lack of a general synthetic method.8−11 From the few examples reported of the biscarbonyl complexes, several intriguing features are apparent: (1) relatively long-lived emissions in solution even at room temperature, (2) photocatalytic functions of some complexes for the reduction of CO$_2$, (3) thermal and photochemical ligand substitution reactions,4−6 and macrocyclic tetrametallic assemblies, “molecular squares”, have been constructed using the rhenium complexes as corners.7

(8) Although the biscarbonyl complexes [Re(LL)(CO)$_3$(PR)$_3$]$^{n+}$ were spectroscopically detected following the electrochemical reduction of [Re(LL)(CO)$_3$(PR)$_3$]$^{n+}$ in the presence of excess PR$_3$, the products have not been isolated, and consequently, the use of this electrochemical reaction as a synthetic method has not been established. See refs 36a,b in this paper.
(9) (a) It has been reported that this substitution reaction is initiated by electron transfer from an electron donor to the excited state of Re(bpy)(CO)$_3$Cl and, consequently, proceeds via a reaction mechanism different from the photochemical ligand substitution reactions reported in this paper. (b) Pac, C.; Kaseda, S.; Ishii, K.; Yanagida, S. J. Chem. Soc., Chem. Commun. 1991, 787.
chemical stability, (4) the appearance of the MLCT (metal-to-ligand charge-transfer) absorption band at longer wavelength by ~40 nm compared with those of the corresponding tricarbonyl complexes, and (5) C2v symmetry, which simplifies the interpretation of the v(CO) region of the IR spectra compared to those of the tricarbonyl complexes. In addition, the tricarbonyl complexes may potentially work as building blocks for “linear-shaped” supramolecules such as photoactive molecular-scale wires. In contrast, tricarbonyl complex(es) ([Re(X2 bpy)(CO)2(PR3)(Y)]+ for “linear-shaped” supramolecules because the substitutable ligands, i.e., LL, and L’, are in positions cis to one another.

Only two practical synthetic methods for the tricarbonyl diimine complexes have been reported: (1) a thermal substitution of the axial CO ligand in a tricarbonylbipyridine-rhenium(I) complex, which may open up a novel general synthesis route for biscarbonyl diimine complexes that have limitations as general synthesis routes for biscarbonyl diimine complexes. (2) The PF6− salt of [Re([bpy](CO)3)] instead of [Re(bpy)(CO)3]+ was synthesized in a manner similar to that of [Re[(CF3)2bpy](CO)3]− using Me2bpy and (CF3)2bpy as the chelating ligands, instead of C2Me5bpy, to yield 132 mg of solid. To the solution of the salt of [Re(bpy)(CO)3]−, a THF solution (100 mL) containing tetraethylammonium hexafluorophosphate (0.25 mmol) of silver trifluoromethanesulfonate was refluxed under an argon atmosphere for 3 h. After removal of the AgCl precipitate by filtration, [Re(bpy)(CO)3]+ (1.2 mL) was added to the filtrate. The solution was refluxed overnight under an Ar atmosphere. Evaporation under reduced pressure left a yellow solid, which was washed with ether and then recrystallized from CH2Cl2–ether to yield 132 mg of solid. To the solution of the solid in 5 mL of methanol was added dropwise a concentrated NH4PF6 methanolic solution. The precipitated PF6− salt of 1a was collected by filtration, washed with water, and then dried in vacuo. Yield: 133 mg, 80%. For the PF6− salt, it was confirmed that the H NMR spectrum and the IR bands for CO stretching are essentially identical to those reported for the SBF6− salt.

\[\text{[Re(bpy)(CO)3]}(\text{P(OR)3})\]\text{PF6−} (1a). A similar procedure for 1a was applied to the synthesis of 1d. Yield: 88%. The spectroscopic data of 1d have been reported elsewhere.

\[\text{[Re(Me2bpy)(CO)3]}(\text{P(OR)3})\]\text{PF6−} (1d). A similar procedure for 1a was applied to the synthesis of 1d. Yield: 88%. The spectroscopic data of 1d have been reported elsewhere.

\[\text{[Re(Me2bpy)(CO)3]}(\text{P(OEt)3})\]\text{PF6−} (1j) were synthesized in a manner similar to that of \[\text{[Re(Me}2\text{bpy)(CO)3]}(\text{P(OEt)3})\] instead of \[\text{[Re(bpy)(CO)3]}(\text{P(OEt)3})\].

\[\text{[Re(X2 bpy)(CO)3]}(\text{P(OEt)3})\]\text{PF6−} (1i) and \[\text{[Re[(CF3)2bpy](CO)3]}(\text{P(OEt)3})\]\text{PF6−} (1f) were synthesized in a manner similar to that of \[\text{[Re(X2 bpy)(CO)3]}(\text{P(OEt)3})\] instead of \[\text{[Re(bpy)(CO)3]}(\text{P(OEt)3})\].

Data for 1i. Yield: 93%. Anal. Caled for C22H27N2O9F3PReS: C, 34.33; H, 3.54; N, 3.64. Found: C, 34.11; H, 3.32; N, 3.65. ′H NMR (δ, 300 MHz, CDCl3): 8.84 (s, bpy-3′,3′), 8.65 (d, J = 5.7 Hz, bpy-6′,6′), 7.38 (d, J = 5.7 Hz, bpy-5′,5′), 3.78 (quintet, JQ = 13 Hz, CH2OP), 2.68 (s, CH2−bpy), 1.04 (t, J = 7.0 Hz, CH3−[CH2OP]). ′C NMR (δ, 75.5 MHz, CDCl3): 193.6, 193.4 (C=O), 156.0 (bpy-2′,2′), 154.1 (bpy-4′,4′), 152.1 (bpy-6′,6′), 128.4, 126.6 (bpy-3′,3′,5′,5′), 62.4 (d, JCF = 7.3 Hz, CH2OP), 21.4 (bpy−CH2), 15.8 (d, JCF = 5.8 Hz, CH2−[CH2OP]). IR (CH3CN): ν(CO)/cm−1 = 2045, 1958, 1926. UV/vis (CH3CN): λmax/nm (ε/10^3 M−1 cm−1) = 330 (5.9), 315 (18.0), 304 (15.8).

Data for 1j. Yield: 85%. Anal. Caled for C21H21N2O6F12P2Re: C, 34.28; H, 2.42; N, 3.21. Found: C, 34.85; H, 2.24; N, 3.29. ′H NMR (δ, 300 MHz, CDCl3): 9.15 (d, J = 5.8, bpy-6′,6′), 8.78 (s, bpy-3′,3′), 7.88 (d, J = 4.7 Hz, bpy-5′,5′), 3.78 (quintet, JQ = 5.5 Hz, CH2OP), 0.98 (t, J = 7.0 Hz, CH3). ′C NMR (δ, 75.5 MHz, CDCl3): 192.2, 192.0 (C=O), 156.3 (bpy-2′,2′), 155.0 (bpy-6′,6′), 141.4 (m, bpy-4′,4′), 122.1, 121.3 (bpy-3′,3′,5′,5′), 62.8 (d, JCF = 7.0 Hz, CH2OP), 15.4 (d, JCF = 5.8 Hz, CH2−[CH2OP]). IR (CH3CN): ν(CO)/cm−1 = 2053, 1971, 1935, UV/vis (CH3CN): λmax/nm (ε/10^3 M−1 cm−1) = 363 (3.7), 322 (9.5), 309 (9.6), 274 (15.8).

The complexes 2 were synthesized by two methods: a photochemical one-step method and/or a two-step method via thermal ligand substitution of the acetonitrile complexes 2a and 2f. The yields and elemental analysis, and IR data are summarized in Tables 1 and 2, respectively. Proton NMR data are given in the Supporting Information.

**One-Step Method.** \[\text{[Re(bpy)(CO)3]}(\text{P(OEt)3})\](MeCN)\text{PF6−} (2a). A vessel containing an acetonitrile solution (80 mL) of 200 mg (0.27 mmol) of 1a was immersed in a water bath maintained at ~25 °C and then irradiated under an argon atmosphere using a high-pressure mercury lamp with a uranyl glass filter (>330 nm) for 12 h. The solvent


**Experimental Section**

**General Procedures.** UV/vis spectra were recorded using a Hitachi 330 spectrophotometer or an Otsuka-Densi Photol-2000 multichannel spectrophotometer with a D2 (25 W)/I2 (25 W) mixed lamp. Emission spectra at 25 °C were measured with a Hitachi F-3000 fluorescence spectrophotometer. To determine the quantum yields for emission, a spectrophotometer. To determine the quantum yields for emission, a spectrophotometer. To determine the quantum yields for emission, a spectrophotometer. To determine the quantum yields for emission, a spectrophotometer.
was then evaporated under reduced pressure. The resulting dark yellow solid was washed with ether, recrystallized from ether–CH₂Cl₂, and dried in vacuo.

Procedures similar to those described above were adopted for the one-step preparation of 2b, d–f, g as shown below.

**Table 2.** ν(CO) Frequencies (cm⁻¹) and EFF Force Constants (N m⁻¹) for 2 in CH₂Cl₂ Solution

<table>
<thead>
<tr>
<th>complex</th>
<th>ν(CO)</th>
<th>k_CO</th>
<th>k_CO CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1954, 1878</td>
<td>1483</td>
<td>58.8</td>
</tr>
<tr>
<td>2b</td>
<td>1945, 1871</td>
<td>1471</td>
<td>57.0</td>
</tr>
<tr>
<td>2c</td>
<td>1948, 1876</td>
<td>1477</td>
<td>55.6</td>
</tr>
<tr>
<td>2d</td>
<td>1956, 1881</td>
<td>1487</td>
<td>58.1</td>
</tr>
<tr>
<td>2e</td>
<td>1936, 1857</td>
<td>1453</td>
<td>60.5</td>
</tr>
<tr>
<td>2f</td>
<td>1944, 1872</td>
<td>1471</td>
<td>55.5</td>
</tr>
<tr>
<td>2g</td>
<td>1938, 1867</td>
<td>1463</td>
<td>54.6</td>
</tr>
<tr>
<td>2h</td>
<td>1946, 1873</td>
<td>1473</td>
<td>56.3</td>
</tr>
<tr>
<td>2i</td>
<td>1944, 1865</td>
<td>1466</td>
<td>60.8</td>
</tr>
<tr>
<td>2j</td>
<td>1954, 1879</td>
<td>1484</td>
<td>58.1</td>
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**Table 1.** Yields and Elemental Analysis Data of 2

<table>
<thead>
<tr>
<th>[Re(X,bpy)(CO)₂(PR₃)]⁺</th>
<th>yield/%</th>
<th>elemental anal/% [found (calcd)]</th>
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<tbody>
<tr>
<td>X</td>
<td>Y</td>
<td>one-step method</td>
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<td>---</td>
<td>---</td>
<td>-----------------</td>
</tr>
<tr>
<td>2a</td>
<td>H</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2b</td>
<td>H</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2c</td>
<td>H</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2e</td>
<td>H</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2d</td>
<td>H</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2e</td>
<td>H</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2f</td>
<td>H</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2g</td>
<td>Me</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2h</td>
<td>Me</td>
<td>P(OEt)₃</td>
</tr>
<tr>
<td>2j</td>
<td>CF₃</td>
<td>P(OEt)₃</td>
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</tbody>
</table>

a Isolated yields of the PF₆⁻ salts except for the neutral complex 2e. b For the PF₆⁻ salts except for 2 (neutral complex) and 2i (CF₃SO₃⁻ salt).

Crystal Structure Determination of [Re(Mebp)(CO)₄(OEt)₃]⁺PF₆⁻ (2e). A methylene chloride solution (80 mL) containing 2a (190 mg) and NEt₃Cl (1.69 g) was refluxed under an Ar atmosphere for 8 h. After evaporation of the solution, the residue was dissolved in 100 mL of CH₂Cl₂, and then the solution was washed three times with water. The organic layer was dried on MgSO₄, and evaporated to dryness under reduced pressure to leave a yellow solid. Recrystallization from ether–CH₂Cl₂ gave 2e.

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[Re(bpy)(CO)₂(PPh₃)₂][PF₆] (2e).
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References:

(17) Edwards, C.; Gilmore, C. J.; Mackey, S.; Stewart, N. CRYSTAL- GM, Ver. 6.3.3; Mac Science: Yokohama, Japan, 1996.
Table 3. Crystallographic Data for 2h

<table>
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<tr>
<th>empirical formula</th>
<th>C_{64}H_{32}N_{16}O_{16}F_{8}P_{4}Re</th>
<th>β/deg</th>
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<tr>
<td>fw</td>
<td>999.90</td>
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<td>4221.6(1)</td>
</tr>
<tr>
<td>crystal syst</td>
<td>monoclinic</td>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>space group</td>
<td>P_2/1/a (no. 14)</td>
<td>D_{achi}/cm^{-3}</td>
<td>295</td>
</tr>
<tr>
<td>a/Å</td>
<td>11.592 (1)</td>
<td>1.57</td>
<td>0.0005</td>
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<tr>
<td>b/Å</td>
<td>30.953 (4)</td>
<td>30.951</td>
<td>1.01</td>
</tr>
<tr>
<td>c/Å</td>
<td>11.799 (2)</td>
<td>1992</td>
<td>0.0121</td>
</tr>
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α = \frac{\sum w(F_d) - \sum w(F)]/\sum w(F)]^1/2, \quad \beta = \sum w(F_d) - \sum [w(F)]^2/(m - n)]^1/2.

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for 2h**

<table>
<thead>
<tr>
<th>Bond Lengths</th>
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<tbody>
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<td>Re(1)–P(1)</td>
<td>2.448(5)</td>
<td>2.349(7)</td>
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<tr>
<td>Re(1)–N(1)</td>
<td>2.179(15)</td>
<td>2.145(17)</td>
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<tr>
<td>Re(1)–C(1)</td>
<td>1.84(3)</td>
<td>1.88(3)</td>
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</tr>
<tr>
<td>O(1)–C(1)</td>
<td>1.18(4)</td>
<td>1.17(3)</td>
<td></td>
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<tr>
<td>Bond Angles</td>
<td></td>
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</tr>
<tr>
<td>P(1)–Re(1)–N(1)</td>
<td>90.9(5)</td>
<td>89.3(5)</td>
<td></td>
</tr>
<tr>
<td>P(1)–Re(1)–C(1)</td>
<td>90.1(8)</td>
<td>91.2(7)</td>
<td></td>
</tr>
<tr>
<td>P(2)–Re(1)–C(1)</td>
<td>90.3(8)</td>
<td>91.2(7)</td>
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</tr>
<tr>
<td>P(2)–Re(1)–N(1)</td>
<td>86.7(5)</td>
<td>89.9(5)</td>
<td></td>
</tr>
<tr>
<td>N(1)–Re(1)–N(1)</td>
<td>74.7(1)</td>
<td>95.9(8)</td>
<td></td>
</tr>
<tr>
<td>N(1)–Re(1)–C(2)</td>
<td>173.6(9)</td>
<td>170.0(8)</td>
<td></td>
</tr>
<tr>
<td>N(2)–Re(1)–C(2)</td>
<td>99.9(9)</td>
<td>90.1(10)</td>
<td></td>
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<td>P(1)–Re(1)–P(2)</td>
<td>177.6(2)</td>
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**Table 5. Electronic Absorption and Emission Data for 2a at Room Temperature**

<table>
<thead>
<tr>
<th>complex</th>
<th>MLCT</th>
<th>π–π*</th>
<th>π–π*</th>
<th>λ_{max}/nm</th>
<th>φ_{em}</th>
<th>τ_{em}/ns</th>
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<tbody>
<tr>
<td>2a</td>
<td>386(4000)</td>
<td>294 (19 000)</td>
<td>639</td>
<td>&lt;0.002</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>397 (4100)</td>
<td>293 (20 000)</td>
<td>651</td>
<td>&lt;0.002</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>387 (3800)</td>
<td>291 (18 000)</td>
<td>620</td>
<td>0.031</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>369 (4000)</td>
<td>289 (17 000)</td>
<td>618</td>
<td>0.017</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>423 (2100)</td>
<td>300 (13 000)</td>
<td>650</td>
<td>&lt;0.002</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>2f</td>
<td>401 (3800)</td>
<td>301 (20 000)</td>
<td>270 (17 000)</td>
<td>619</td>
<td>0.037</td>
<td>350</td>
</tr>
<tr>
<td>2g</td>
<td>410 (2800)</td>
<td>295 (20 000)</td>
<td>270 (22 000)</td>
<td>612</td>
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<td>560</td>
</tr>
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<td>2h</td>
<td>381 (3700)</td>
<td>290 (18 000)</td>
<td>267 (21 000)</td>
<td>609</td>
<td>0.026</td>
<td>340</td>
</tr>
<tr>
<td>2i</td>
<td>364 (5100)</td>
<td>283 (22 000)</td>
<td>668</td>
<td>0.005</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>2j</td>
<td>404 (4900)</td>
<td>297 (23 000)</td>
<td>668</td>
<td>0.005</td>
<td>20</td>
<td></td>
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</table>

α All complexes are PF_6^- salts except for the neutral complex 2e.

β Data were obtained from DMP solutions except for the data denoted by the superscript c.

γ Data were obtained from MeCN solutions. d Not measured. e Not detected.

Most hydrogen atoms were assigned by calculation and their parameters restrained for C–H length 0.96 Å and fixed thermal parameters U_{iso} = 0.1–0.3. No secondary extinction corrections were applied. Table 4 shows selective bond lengths and angles of 2h.

Energy-Factored Force Field Calculations. Energy-factored force field (EFFF) theory, when applied to transition metal carbonyls, has been well demonstrated to determine both the principal force constant(s) k_{CO} and the interaction force constant(s) k_{CO,CO}.

The biscarbonyl complexes 2 have two equivalent CO groups and hence only two force constants: k_{CO} and k_{CO,CO}. With only two observed ν(CO) frequencies, and using the EFFF assumptions, it is possible to solve the force field for this compound exactly (Table 5). In theory, CO stretching frequencies (ν, cm^{-1}) are described by the following secular equations:

\[ \lambda = K(\nu_{\text{sym}}^2 - \mu k_{CO}) \]
\[ \lambda = K(\nu_{\text{asym}}^2 - \mu k_{CO} - k_{CO,CO}) \]

where \(\mu\) is the reduced mass (0.145 83) and \(K = 4.04 \times 10^{-4}\).

Results and Discussion

Photochemical Ligand Substitution Reaction of 1a. An Ar-saturated acetonitrile solution containing 1a (0.1 M) under irradiation with a 30 s monitoring interval. The cell path length was 2 mm.

Therefore, the principal and interaction force constants can be calculated using the following equations:

\[ k_{CO} = K(\nu_{\text{sym}}^2 + (\nu_{\text{asym}}^2) \]
\[ k_{CO,CO} = K(\nu_{\text{sym}}^2 - (\nu_{\text{asym}})^2) \]

References


chemical ligand substitution is entirely different, providing the first example for the exclusive loss of the axial CO ligand from tricarbonyl complexes \( \text{fac-}[\text{Re}(\text{L})(\text{CO})_3(L')]^{+} \). A notable structural feature of the reactions is that \( L' \) must be a phosphorus ligand.\(^{23}\) This type of photochemical ligand substitution reactions was not observed in the case of \( L' = \text{halides and pyridine derivatives.} \)

**New Synthesis Methods of 2.** We have developed two synthetic routes for 2, i.e., the one-step and two-step methods, by taking advantage of the photochemical ligand substitution reactions of 1 described above.

(1) Photochemical one-step synthesis: This procedure is straightforward and involves irradiation of a solution containing \( \text{fac-}[\text{Re}(\text{X}_2\text{bpy})(\text{CO})_3(\text{PR}_3)]^{+} \) and ligand \( L' \), e.g., pyridine and phosphorus compounds at \( >330 \text{ nm} \) for \( 4\sim48 \text{ h} \), followed by the usual workup.\(^{24}\) Isolated yields of 2 are synthetically reasonable (55–96%), as shown in Table 1. Although there are two possible structural isomers of 2, the cis,cis and cis,trans forms, only the cis,trans isomer is produced by this method.

The method is certainly suitable for high-yield synthesis of the biscarbonyl complexes which have the same phosphorus ligands or one phosphorus and another neutral ligand, i.e., 2a, 2b, 2d, 2f, 2g, 2i, and 2j. The one-step synthesis of 2c having different phosphorus ligands can be achieved in reasonable yield but is accompanied by the formation of the complex 2d or 2g having two identical ligands (P(OEt)\(_3\) or PPh\(_3\)) in 5–30% yields depending on the irradiation time. The two-step method described below is more suitable for the synthesis of this type of compound, because the isolation of 2e and 2h from the byproducts is not straightforward. In the case of the chloro complex 2e, the two-step method is more suitable because the one-step reaction is very slow; even after 34 h of irradiation, 6% of the starting complex still remained in the solution.

(2) Two-step method: This method utilizes the acetonitrile complexes 2a and 2f as the precursor compound which can be easily prepared in good isolated yields (eq 1 and Table 1) using the photochemical one-step method described above. An important point of this method is that the acetonitrile ligand is much more thermally labile than the other ligands (eq 2). This reaction efficiently proceeds just upon refluxing a solution containing the acetonitrile complex (2a or 2f) and ligand \( Y \) for several hours. The progress of the reaction can be easily followed by monitoring the CO-stretching bands using FT-IR spectroscopy so that the end point of the reaction may be detected. Removal of the solvent and the excess ligand from the reaction mixture gave cis,trans-[Re(bpy)(CO)\(_2\)(PR)\(_3\)](Y)\(^{+}\) (\( Y = \text{the neutral ligand, } n = 1, \text{PR}^+_n \text{ salt; } Y = \text{Cl}^- \), \( n = 0 \)) in good yields (Table 1). The cis,cis isomer was not detected during the reaction at all.

This method is especially suitable for the synthesis of the biscarbonyl complexes 2c and 2h, which have two different phosphorus ligands. The phosphorus ligands are not thermally substituted even under reflux in the presence of an excess of the ligand. The chloride complex 2e was also obtained by this method in a good yield.

**Characterization of 2 and the X-ray Crystal Structure of 2h.** All the complexes have two intense IR bands in the ν(CO) region, which are similar in intensity (Table 2). In addition, elemental analysis (Table 1) and electrospray-ionization mass spectroscopic data support the presence of two carbonyl ligands in 2, i.e., \([\text{Re}(\text{X}_2\text{bpy})(\text{CO})_3(\text{PR})_n(\text{Y})]^{+} (n = 0, Y = \text{Cl}^-, n = 1, Y = \text{neutral ligand})\). In \(^{1}H\) NMR, only three or four sets of peaks appear for X(bpy) or bpy, clearly indicating that all the complexes 2 have \( C\text{}_2\) symmetry, i.e., the trans configuration of PR\(_3\) and Y coordinating to the central rhenium atom (eqs 1 and 2).

X-ray crystallographic data confirmed the identity of 2h. The ORTEP drawing of the \([\text{Re}(\text{Me}_2\text{bpy})(\text{CO})_3(\text{P(OEt})_3)](\text{PPh}_3)]^{+}\) unit is shown in Figure 2. The two CO ligands are in cis positions; P(OEt)\(_3\) and PPh\(_3\) are, actually, in trans positions. This is the first example of X-ray crystallographic data for biscarbonyldiminerhenium complexes, though more than 10 sets of crystal data have been reported for tricarbonyldiminerhenium complexes.\(^{25–36}\) The complex 2h has a steric structure similar

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to that of the reported tricarbonyl bipyridine complexes; i.e.,
the octahedral coordination on the rhenium center is rather
distorted due to the chelating effect of the bipy ligand (Table 4).
Some interesting features can be seen for the X-ray structure
of 2h compared with those of tricarbonyl complexes: shorter
Re–CO bond distances (1.84(3) and 1.88 (3 )Å) but longer CO
bond distances for the carbonyl ligands (1.18(4) and 1.17(3)
Å) vs 1.90 –1.94 Å for Re–C; 1.10 –1.16 Å for equatorial CO
in most tricarbonyl complexes. The axis line P–Re–P is bent
(2.4°) toward the space between the carbonyl ligands.

EffF theory, when applied to transition metal carbonyls, has
been well demonstrated to determine both the principal force

\( k_{CO} \) and the interaction force constant(s) \( k_{CO,CO} \). These

The calculated force constants for 2 are shown in Table 2. In

principle, the force constants of the CO groups in metal

carbonyls should be affected by the electron density on the

central metal because of the \( \sigma \)-back-donation from the d-orbital

of the metal ion to the antibonding orbitals of the CO groups.

Therefore, the values of \( k_{CO} \) depend on the electron-withdrawing

strength of the ligands \( Y \) and the substituents \( X \), which are

in the order \( P(OEt)_3 > MeCN > PPh_3 > py > Cl^- \) for \( Y \) and

\( CF_3 > H > Me \) for \( X \).

It has been reported that the C–O bond length \( r_{CO} \) and the

bond angle \( \theta \) between the CO groups in metal carbonyls \( ^{38} \) can

be estimated by the following equations:

\[
r_{CO} = 1.647 - 0.184 \ln k_{CO} \quad (\text{r}_{CO}, \text{Å}; k_{CO}, \text{mdyn/Å})
\]

\[
\tan^2(\theta/2) = I(\text{antisym})/I(\text{sym})
\]

where \( I \) is the intensity of relevant vibration modes. The

calculated \( r_{CO} \) and \( \theta \) using the above equations and the observed

IR frequencies in a KBr disk (Table 2) are 1.153 Å and 99.8°.

The values obtained from the crystallographic data are \( r_{CO} =

1.18(4) and 1.17(3) \text{Å} and \( \theta = 91.2^\circ \) (Table 6). The differences

between the calculated and observed values are less than 3%

for \( r_{CO} \) but are relatively large (8.6%) for \( \theta \).

Spectroscopic and Electrochemical Properties of 2. Table

5 summarizes the UV/vis absorption and emission data for 2.

Figure 3 shows the UV/vis absorption and emission spectra for

2h as a typical example. For all the complexes, the lowest energy

absorption band is attributed to the metal-to-ligand (Xbpy)

charge-transfer transition. This assignment is based on a

considerable solvatochromic shift of the band and substantial

dependence of the band on the property of \( X \) in the Xbpy

ligands. A red shift of the band occurs by 10–15 nm upon

changing the solvent from DMF to CH_2Cl_2. A further shift to

the red occurs with an increase in the electron-withdrawing

strength of \( X \) in the order \( CF_3 > H > Me \). The shift is also

dependent upon \( Y \), shifting to the red in the order \( Cl^- > py > PPh_3 > MeCN > P(OEt)_3 > CO \). This change is attributable to

changes in the electron density on the central metal, which is

affected by the \( \sigma \)- and \( \pi \)-donating/accepting abilities of \( L \) and

\( PR_3 \). This order for the electron-donating properties of the

ligands is also supported by the IR spectroscopic results (vide

supra) and electrochemical data (vide infra).

The strong absorption band around 290 nm can be assigned to

the \( \pi-\pi^* \) transition localized on the bipy ligand, which shows

relatively low sensitivity to both solvent polarity and electronic

properties of the ligand \( L \). \( ^{42} \) The \( \pi-\pi^* \) transition band localized

on the phenyl groups of the PPh_3 ligand appears around 268

nm. \( ^{42} \)

The complexes which have two phosphorus ligands, except for

2j, emit around 620 nm with emission lifetimes of 250–

640 ns at room temperature. The emission was efficiently

quenched upon addition of O_2. We recently reported that the

emissive state of 2d is triplet MLCT, which is the lowest excited

state. \( ^{10} \) Since the emission properties of 2c, 2g, 2h, and 2i

are similar to those of 2d, their emissive states should also be

3MLCT. On the other hand, 2b and 2j emit with lower emission

quantum yields and shorter lifetimes compared with the

complexes described above (Table 5). In contrast, the complexes

Table 6. Electrochemical Data for 2

<table>
<thead>
<tr>
<th>complex</th>
<th>( E_{1/2}^{ox} )/V</th>
<th>( E_{1/2}^{red} )/V</th>
<th>( E_{1/2}^{ox} )/V</th>
<th>( E_{1/2}^{red} )/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1.69 (75)</td>
<td>1.87</td>
<td>0.92 (68)</td>
<td>0.89 (61)</td>
</tr>
<tr>
<td>2b</td>
<td>1.71 (65)</td>
<td>2.26</td>
<td>1.90</td>
<td>1.10 (77)</td>
</tr>
<tr>
<td>2c</td>
<td>1.71 (65)</td>
<td>2.32</td>
<td>1.87</td>
<td>0.47 (67)</td>
</tr>
<tr>
<td>2f</td>
<td>1.70 (64)</td>
<td>1.91</td>
<td>0.89 (69)</td>
<td>1.13</td>
</tr>
<tr>
<td>2g</td>
<td>1.71 (64)</td>
<td>2.26</td>
<td>1.10</td>
<td>1.05</td>
</tr>
<tr>
<td>2h</td>
<td>1.80 (65)</td>
<td>2.33</td>
<td>1.80 (69)</td>
<td>2.37</td>
</tr>
<tr>
<td>2j</td>
<td>1.26 (67)</td>
<td>1.96</td>
<td>1.23 (86)</td>
<td>1.06 (82)</td>
</tr>
</tbody>
</table>

(\( a \) The cyclic voltammograms of 2 were taken in MeCN solutions

containing n-Bu_4NBF_4 (0.1 M) at a 200 mV/s scan rate using a glassy-

carbon working electrode, a Pt counter electrode, and an Ag/AgNO_3

(0.1 M, an MeCN solution) reference electrode under an Ar atmosphere.

All potentials are reported against a Ag/AgNO_3 reference. \( b \) Redox

potential for the reversible or quasi-reversible process and peak potential
difference (mV) (in parentheses). \( c \) Peak potential for irreversible

reduction. \( d \) Peak potential for irreversible oxidation.

Figure 3. UV/vis absorption (solid line) and emission (dotted line) spectra of 2h in a DMF solution at room temperature.

by tedious experimentation, e.g., the use of 13 CO isotope labeling, or


(36) (a) Stor, G. J.; Hartl, F.; Vanouteren, J. W. M.; Stuifens, D. J.

Organometallics 1995, 14, 1115–1131. (b) Johnson, F. P. A.; George,


3387. (c) Christensen, P.; Hamnett, A.; Murray, A. V. G.; Timney, J. A.


Marcaccio, M.; Paradisi, C.; Roffia, S.; Bignozzi, C. A.; Amatore, C.


Kaim, W. Organometallics 1996, 15, 236–244.


(38) Braterman, P. S. Metal Carboxyl Spectra; Academic Press: London,

1975.


Chem. 1978, 17, 948.

(40) For tricarbonyl complexes, analysis of the force fields can be done

via tedious experimentation, e.g., the use of 13CO isotope labeling, or

using arbitrary approximations. This is necessary as these complexes

exhibit only three \( (\text{RC}) \) frequencies, but possess four force constants.

Ganclini, D. R.; George, M. W.; Glyn, P.; Grevels, F. W.; Johnson,

F. P. A.; Klotzbucher, W.; Morrison, S. L.; Russell, G.; Schaffner,


(42) The absorption maxima of free bipy and PPh_3 were observed at 280

and 236 nm and 260 and 194 nm in MeCN solution, respectively.
containing the Cl⁻ or MeCN ligand (2a, 2e, and 2f) reveal no or only weak emission at room temperature. Most of 2 show the shorter lifetime of the 1MLCT excited state and the lower emission quantum yield than the corresponding tricarbonyl complexes, such as 

\[[\text{Re}(\text{bpy})(\text{CO})_3(\text{P}(	ext{O})\text{Et})_3)]^+ \quad (\tau_{\text{em}} = 1034 \text{ ns}) \]

\[\Phi_{\text{em}} = 0.088, \lambda_{\text{max}} = 522 \text{ nm in MeCN}, \text{[Re(bpy)(CO)](py)}^+ \quad (\tau_{\text{em}} = 669 \text{ ns}) \]

\[\Phi_{\text{em}} = 0.16, \lambda_{\text{max}} = 558 \text{ nm in MeCN}, \text{[Re(bpy)(CO)](MeCN)}^+ \quad (\tau_{\text{em}} = 1201 \text{ ns}) \]

\[\Phi_{\text{em}} = 0.41, \lambda_{\text{max}} = 530 \text{ nm in MeCN}. \]

One of the reasons should be the smaller energy gap of 2 between the 1MLCT excited state and the ground state than those of the tricarbonyl complexes. The energy gap low, however, does not interpret the “abnormally” lower energy gap of 2d, 2i, and 2j. In this point, we do not know the reason, it is noteworthy that 2 h of irradiation to an acetonitrile solution containing 2b and P(OEt)₃ did not cause decomposition of the complex at all, and consequently, photolability of the complex is not the reason.

Figure 4a illustrates the cyclic voltammograms of 2c measured for an acetonitrile solution. In the cathodic scan, one reversible wave and another irreversible wave were observed, and similar cathodic waves were observed for the complexes which have two phosphorus ligands, i.e., 2c, 2d, and 2g–j. The electrochemical properties of the tricarbonyl bipyridine complexes 

\[[\text{Re}(\text{bpy})(\text{CO})_3(L')^{+}\text{ (L'} = \text{halide, pyridine, MeCN, PR}_3, \text{etc.}) \] have been well investigated, and it has been established that the one-electron reduction of these complexes is attributable to a bpy-based reduction. In a previous paper, we have reported that the first reversible reduction of 2d yields [Re(bpy)²(CO)](P(OEt)₃)₂] on the basis of spectroscopic data obtained by flow electrolysis. In an analogy, therefore, the reversible wave of the other complexes might also be attributable to a bpy-based reduction. In contrast, the pyridine 

\[2b^- + \text{MeCN} \rightarrow 2a^- + \text{py} \quad (3)\]

\[2c^- + \text{MeCN} \rightarrow 2a^- + \text{Cl}^- \quad (4)\]

Table 6 summarizes the electrochemical properties of 2. It is noteworthy that the first oxidation waves for the complexes with acetoinol, pyridine, or Cl⁻ ligand (2a, 2b, 2e, 2f) are reversible on a time scale of the cyclic voltametric measurements (Figure 4b). This is in contrast to the irreversible anodic waves for most of the reported tricarbonyl diimine complexes. The oxidized complexes of 2a, 2b, 2e, and 2f are stabilized to a greater degree than the oxidized tricarbonyl complexes, probably arising from much weaker π-acidities and the stronger σ-basicities of the acetoinol, pyridine, and Cl⁻ ligands, compared to the axial CO ligand of the latter. On the other hand, only quasi-reversible or irreversible oxidation waves were observed for the complexes with two phosphorus ligands, which are relatively strongly π-acidic (Figure 4a). Inspection of the data in Table 6 clearly indicates that the oxidation potentials are more strongly affected by the electronic properties of the ligand L than the reduction potentials (for example, 2a–g), while the substituents X on the bpy ligand give important effects on the reduction potentials (2d, 2i, 2j). These results suggest that the anodic waves of 2 are attributable to a metal-based oxidation, e.g., Re²⁺/Re³⁺. This is analogous to the behavior of Re(α-diimine)(CO)₃X (X = halide).42

**Conclusion**

The present investigation has provided the first examples for the photochemical substitution of the axial CO ligand in tricarbonylbipyridine-rhenium complexes with a phosphorus ligand. The photochemical ligand substitution reaction opens up synthetic routes for a new class of the biscarbonylbipyridine-rhenium complexes cis,trans-[Re(X₂bpy)(CO)₂(PR)₃(Y)]⁺. It has been found that they are relatively stable for the most part and, in some cases, are strongly emissive even in a fluid solution at room temperature. This may suggest their suitability for use as photocatalysts. There is potential for the synthetic methods to be applied to make a building block for “linear-shaped” (one-dimensional) supramolecules because the substitutable ligands, i.e., PR₃ and Y, are in positions trans to each other. These studies are underway in our laboratory.

**Acknowledgment.** We thank Dr. C. Pac (Kawamura Institute for Chemical Research) for his comments.

**Supporting Information Available:** An X-ray crystallographic file for 2h, in CIF format, and ¹H NMR chemical shift data for 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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