

New Synthetic Routes to Biscarbonylbipyridinerhenium(I) Complexes *cis,trans*-[Re(X₂bpy)(CO)₂(PR₃)(Y)]ⁿ⁺ (X₂bpy = 4,4'-X₂-2,2'-bipyridine) via Photochemical Ligand Substitution Reactions, and Their Photophysical and Electrochemical Properties

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Photochemical ligand substitution of *fac*-[Re(X₂bpy)(CO)₃(PR₃)]⁺ (X₂bpy = 4,4'-X₂-2,2'-bipyridine; X = Me, H, CF₃; R = OEt, Ph) with acetonitrile quantitatively gave a new class of biscarbonyl complexes, *cis,trans*-[Re(X₂bpy)(CO)₂(PR₃)(MeCN)]⁺, coordinated with four different kinds of ligands. Similarly, other biscarbonylrhenium complexes, *cis,trans*-[Re(X₂bpy)(CO)₂(PR₃)(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(Me₂bpy)(CO)₂{P(OEt)₃}(PPh₃)](PF₆) was determined by X-ray analysis. Crystal data: C₃₈H₄₂N₂O₅F₆P₃Re, monoclinic, *P*2₁/*a*, *a* = 11.592(1) Å, *b* = 30.953(4) Å, *c* = 11.799(2) Å, *V* = 4221.6(1) Å³, *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(X₂bpy)(CO)₂(PR₃)(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)₂(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 CO₂, (3) thermal and photo-

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(1) Stufkens, D. J. *Comments Inorg. Chem.* **1992**, *13*, 359–385.

(2) (a) Koike, K.; Hori, H.; Westwell, J. R.; Ishizuka, M.; Takeuchi, K.; Ibusuki, T.; Enjouji, K.; Konno, H.; Sakamoto, K.; Ishitani, O. *Organometallics* **1997**, *16*, 5724–5729. (b) Hori, H.; Johnson, F. P. A.; Koike, K.; Ishitani, O.; Ibusuki, T. *J. Photochem. Photobiol., A* **1996**, *96*, 171–174. (c) Hori, H.; Johnson, F. P. A.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *J. Chem. Soc., Dalton Trans.* **1997**, 1019–1023.

(3) Kalyanasundaram, K. *Photochemistry of polypyridine and porphyrin complexes*; Academic Press Ltd.: London, 1992.

(4) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759–833.

(5) Schanze, K. S.; Walters, K. A. In *Photoinduced electron transfer in metal-organic dyads*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1998; Vol. 2, pp 75–127.

(6) Schanze, K. S.; MacQueen, D. B.; Perkins, T. A.; Cabana, L. A. *Coord. Chem. Rev.* **1993**, *122*, 63–89.

(7) (a) Slone, R. V.; Hupp, J. T. *Inorg. Chem.* **1997**, *36*, 5422. (b) Slone, R. V.; Yoon, D. I.; Calhoun, R. M.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 7, 11813–11814.

(8) Although the biscarbonyl complexes [Re(LL)(CO)₂(PR₃)₂]⁺ were spectroscopically detected following the electrochemical reduction of [Re(LL)(CO)₃(PR₃)]⁺ in the presence of excess PR₃, 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)₃Cl 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.

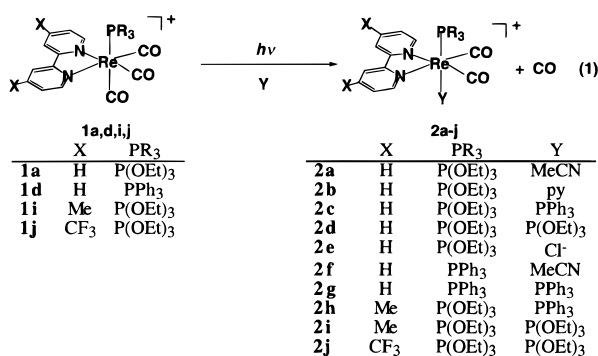
(10) Ishitani, O.; George, M. W.; Ibusuki, T.; Johnson, F. P. A.; Koike, K.; Nozaki, K.; Pac, C.; Turner, J. J.; Westwell, J. R. *Inorg. Chem.* **1994**, *33*, 4712–4717.

(11) (a) Casper, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104–2109. (b) Schutte, E.; Helms, J. B.; Woessner, S. M.; Bowen, J.; Sullivan, B. P. *Inorg. Chem.* **1998**, *37*, 2618–2619.

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) C_{2v} symmetry, which simplifies the interpretation of the $\nu(\text{CO})$ region of the IR spectra compared to those of the tricarbonyl complexes.^{10,11b} In addition, the biscarbonyl complexes may potentially work as building blocks for "linear-shaped" supramolecules such as photoactive molecular-scale wires. In contrast, tricarbonyl complex(es) [*fac*-Re(LL)(CO)₃(L')]ⁿ⁺ could be used only as building blocks for "L-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 biscarbonyl diimine complexes have been reported:⁸ (1) thermal substitution of the tricarbonyl complex ClRe(bpy)(CO)₃ with a phosphine ligand such as PPh₃ in solution at high temperature to give *cis,trans*- or *cis,cis*-[Re(bpy)(CO)₂(PR₃)₂]⁺ and (2) the photochemical substitution of ClRe(bpy)(CO)₃ by P(OEt)₃ in the presence of an electron donor to yield *cis,trans*-[Re(bpy)(CO)₂{P(OEt)₃}₂]⁺.⁹ Unfortunately, these methods have serious limitations as general synthesis routes for biscarbonyl diimine complexes because the effective substitution can occur only with two identical phosphorus ligands.

We report here the first example of the photochemical substitution of the axial CO ligand in a tricarbonylbipyridine-rhenium(I) complex, which may open up a novel general synthetic route for a new class of biscarbonyl complexes, *cis,trans*-[Re(X₂bpy)(CO)₂(PR₃)(Y)]⁺, coordinated with four different kinds of ligands (eq 1). Their structures, spectroscopy, and electrochemistry are also reported.



Experimental Section

General Procedures. UV/vis spectra were recorded using a Hitachi 330 spectrophotometer or an Otsuka-Denshi Photal-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 solution (0.5 M H₂SO₄) of quinine bisulfate was used as the standard ($\phi_{\text{em}} = 0.546$),¹² after applying a correction for differing refractive indices of the solvents. IR spectra were recorded in acetonitrile with a JEOL JIR-6500 FTIR spectrophotometer using 1 cm⁻¹ resolution. Proton NMR was measured on a Bruker AC300P system (300 MHz) or a JEOL JNM-LA 500FT system (500 MHz). Emission lifetime measurements were carried out as described elsewhere.¹¹ The redox potentials of the complexes were measured in an acetonitrile solution containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as the supporting electrolyte by cyclic voltammetric techniques using an ALS/CHI CHI-620 electrochemical analyzer, with a glassy-carbon disk working electrode (3 mm diameter), a Ag/AgNO₃ (0.1 M) reference electrode, and a Pt counter electrode. The supporting electrolyte was dried in vacuo at 100 °C for 1 day prior to use.

(12) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.

Materials. Acetonitrile and CH₂Cl₂ were dried over CaH₂. Tetrahydrofuran (THF) was distilled from Na/benzophenone just before use. Ligands bpy and Me₂bpy (Tokyo Kasei Kogyo Co.) were used as received. 2-Chloro-4-trifluoromethylpyridine was kindly supplied from Ishihara Sangyo Co. and used for the preparation of (CF₃)₂bpy.¹³ ClRe(bpy)(CO)₃¹⁴ was synthesized according to the literature, and a similar method was used for the synthesis of ClRe(Me₂bpy)(CO)₃ and ClRe{(CF₃)₂bpy}(CO)₃ using Me₂bpy and (CF₃)₂bpy as the chelating ligands, respectively.

Synthetic Procedures. While the synthesis of the SbF₆⁻ salt of [Re(bpy)(CO)₃(PR₃)₂]⁺ (R = OEt or Ph) was reported as a two-step synthesis,¹⁵ the PF₆⁻ salt of [Re(X₂bpy)(CO)₃{P(OEt)₃}₂]⁺ (X = H, Me, CF₃) can be prepared in a single step in reasonable yields as follows.

[Re(bpy)(CO)₃{P(OEt)₃}₂]⁺PF₆⁻ (1a**).** A THF solution (100 mL) containing 104 mg (0.23 mmol) of ClRe(bpy)(CO)₃ and 65 mg (0.25 mmol) of silver trifluoromethanesulfonate was refluxed under an argon atmosphere for 3 h. After removal of the AgCl precipitate by filtration, P(OEt)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 NH₄⁺PF₆⁻ 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 ¹H NMR spectrum and the IR bands for CO stretching are essentially identical to those reported for the SbF₆⁻ salt.¹⁵

[Re(bpy)(CO)₃(PPh₃)₂]⁺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.¹⁵

[Re(Me₂bpy)(CO)₃{P(OEt)₃}₂]⁺PF₆⁻ (1i**) and [Re{(CF₃)₂bpy}(CO)₃{P(OEt)₃}₂]⁺PF₆⁻ (**1j**)** were synthesized in a manner similar to that of **1a** using ClRe(Me₂bpy)(CO)₃ and ClRe{(CF₃)₂bpy}(CO)₃ instead of ClRe(bpy)(CO)₃.

Data for 1i. Yield: 93%. Anal. Calcd for C₂₂H₂₇N₂O₉F₃PR₂S: C, 34.33; H, 3.54; N, 3.64. Found: C, 34.11; H, 3.32; N, 3.65. ¹H NMR (δ , 300 MHz, CDCl₃): 8.84 (s, bpy-3,3'), 8.65 (d, $J = 5.7$, bpy-6,6'), 7.38 (d, $J = 5.7$ Hz, bpy-5,5'), 3.78 (quintet, $J_{\text{HP}} = J = 7.0$ Hz, POCH₂), 2.68 (s, CH₃-bpy), 1.04 (t, $J = 7.0$ Hz, CH₃-[CH₂OP]). ¹³C 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', bpy-5,5'), 62.4 (d, $J_{\text{CP}} = 7.3$ Hz, CH₂OP), 21.4 (bpy-CH₃), 15.8 (d, $J_{\text{CP}} = 5.8$ Hz, CH₃-[CH₂OP]). IR (CH₃CN): $\nu(\text{CO})/\text{cm}^{-1} = 2045, 1958, 1926$. UV/vis (CH₃CN): $\lambda_{\text{max}}/\text{nm} (\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}) = 330$ (sh, 5.9), 315 (18.6), 304 (15.8).

Data for 1j. Yield: 85%. Anal. Calcd for C₂₁H₂₁N₂O₆F₁₂P₂Re: C, 28.87; H, 2.42; N, 3.21. Found: C, 28.85; H, 2.24; N, 2.99. ¹H 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, $J_{\text{HP}} = J = 7.0$ Hz, CH₂OP), 0.98 (t, $J = 7.0$ Hz, CH₃). ¹³C NMR (δ , 75.5 MHz, CDCl₃): 192.2, 192.0 (C=O), 156.3 (bpy-2,2'), 155.0 (bpy-6,6'), ~ 141 (m, bpy-4,4'), 124.2, 121.3 (bpy-3,3', bpy-5,5'), 62.8 (d, $J_{\text{CP}} = 7.5$ Hz, CH₂OP), 15.4 (d, $J_{\text{CP}} = 6.1$ Hz, CH₃-[CH₂OP]). IR (CH₃CN): $\nu(\text{CO})/\text{cm}^{-1} = 2053, 1971, 1935$. UV/vis (CH₃CN): $\lambda_{\text{max}}/\text{nm} (\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}) = 363$ (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. [Re(bpy)(CO)₂{P(OEt)₃}(MeCN)]⁺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

(13) Furue, M.; Maruyama, K.; Oguni, T.; Naiki, M.; Kamachi, M. *Inorg. Chem.* **1992**, *31*, 3792–3795.

(14) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

(15) Hori, H.; Koike, K.; Ishizuka, M.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *J. Organomet. Chem.* **1997**, *530*, 169–176.

Table 1. Yields and Elemental Analysis Data of **2**

	[Re(X ₂ bpy)(CO) ₂ (PR ₃)(Y)] ⁺			yield/% ^a		elemental anal./% ^b [found (calcd)]		
	X	PR ₃	Y	one-step method	two-step method ^c			
						C	N	H
2a	H	P(OEt) ₃	MeCN	87		32.31 (32.00)	5.52 (5.60)	3.40 (3.49)
2b	H	P(OEt) ₃	py	68		35.37 (35.03)	5.21 (5.33)	3.56 (3.58)
2c	H	P(OEt) ₃	PPh ₃	75 ^d	84	44.62 (44.49)	2.80 (2.88)	3.86 (3.94)
2c	H	PPh ₃	P(OEt) ₃	50 ^e				
2d ^f	H	P(OEt) ₃	P(OEt) ₃	76				
2e	H	P(OEt) ₃	Cl ⁻	65 ^g	90	36.02 (36.03)	4.60 (4.67)	3.90 (3.86)
2f	H	PPh ₃	MeCN	65		45.51 (45.39)	4.84 (4.96)	3.07 (3.10)
2g	H	PPh ₃	PPh ₃	84	70	53.73 (53.98)	2.54 (2.62)	3.50 (3.59)
2h	Me	P(OEt) ₃	PPh ₃	90		45.97 (45.65)	2.71 (2.80)	4.30 (4.23)
2i	Me	P(OEt) ₃	P(OEt) ₃	96		35.61 (35.68)	2.83 (3.08)	4.51 (4.66)
2j	CF ₃	P(OEt) ₃	P(OEt) ₃	55		30.07 (30.83)	2.68 (2.77)	3.44 (3.58)

^a Isolated yields of the PF₆⁻ salts except for the neutral complex **2e**. ^b For the PF₆⁻ salts except for **2e** (neutral complex) and **2i** (CF₃SO₃⁻ salt). ^c Based on **2a** or **2f** used. ^d The triethyl phosphite complex **1a** was used as the starting material, and **2g** was produced in 4% yield. ^e The triphenylphosphine complex **1d** was used as the starting material, and **2d** was produced in 25% yield. ^f The reported compound.⁹ ^g Accompanied by 6% recovery of the starting complex even after 34 h of irradiation.

Table 2. $\nu(\text{CO})$ Frequencies (cm⁻¹) and EFFF Force Constants (N m⁻¹) for **2** in CH₂Cl₂ Solution

complex	$\nu(\text{CO})$	k_{CO}^a	$k_{\text{CO,CO}}^b$
2a	1954, 1878	1483	58.8
2b	1945, 1871	1471	57.0
2c	1948, 1876	1477	55.6
2d	1956, 1881	1487	58.1
2e	1936, 1857	1453	60.5
2f	1944, 1872	1471	55.5
2g	1938, 1867	1463	54.6
2h	1946, 1873	1473	56.3
2h ^c	1944, 1865	1466	60.8
2i	1954, 1879	1484	58.1
2j	1963, 1891	1501	56.0

^a Principal force constants. ^b Interaction force constants. ^c In KBr disk.

was then evaporated under reduced pressure. The resulting dark yellow solid **2a** 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.

[Re(bpy)(CO)₂(P(OEt)₃)(py)]⁺PF₆⁻ (**2b**) was obtained by irradiation of a THF solution (50 mL) containing 200 mg of **1a** and 1 g of pyridine under an argon atmosphere for 12 h. The subsequent procedures are analogous to those used for **2a**.

[Re(bpy)(CO)₂(P(OEt)₃)₂]⁺PF₆⁻ (**2d**) was obtained by irradiation of an acetonitrile solution (150 mL) containing 500 mg of **1a** and 10 mL of P(OEt)₃ under an argon atmosphere for 12 h.

[Re(bpy)(CO)₂(PPh₃)(MeCN)]⁺PF₆⁻ (**2f**) was prepared by irradiation of an acetonitrile solution (50 mL) containing 200 mg of **1d** under an argon atmosphere for 4 h. Longer irradiation should be avoided, because decomposition of **2f** occurred to give green byproducts.

[Re(bpy)(CO)₂(PPh₃)₂]⁺PF₆⁻ (**2g**) was obtained by irradiation of an acetone solution (50 mL) containing 52 mg of **1a** and 0.31 g of PPh₃ under an argon atmosphere for 20 h.

[Re(Me₂bpy)(CO)₂(P(OEt)₃)₂]⁺PF₆⁻ (**2i**). An acetonitrile solution (150 mL) containing the CF₃SO₃⁻ salt of **1i** (513 mg) and 10 mL of P(OEt)₃ was irradiated under an argon atmosphere for 1 h. The solution was then evaporated to dryness under reduced pressure, and the resulting dark yellow solid was washed with ether. The product was recrystallized using ether-CH₂Cl₂ and dried in vacuo. The PF₆⁻ salt of the product **2i** was obtained using a procedure analogous to that for **1a**. Elemental analysis of the CF₃SO₃⁻ salt was carried out.

[Re{(CF₃)₂bpy}(CO)₂(P(OEt)₃)₂]⁺PF₆⁻ (**2j**). An acetonitrile solution (150 mL) containing 500 mg of **1j** and 10 mL of P(OEt)₃ was irradiated under an argon atmosphere for 8 h. The solution was evaporated under reduced pressure to give a brown oil, which contained mainly **2j** with a small amount of the starting complex **1j**. To a solution of the oil in 10 mL of methanol was added a saturated methanol solution

of NH₄PF₆ (1 mL) and then a small amount of water. The solution was kept in a refrigerator overnight. The resulting orange-red solid was washed with water. Alternatively, **2j** was successfully isolated by column chromatography on silica gel using CH₂Cl₂ eluent.

Two-Step Method. [Re(bpy)(CO)₂(P(OEt)₃)(PPh₃)]⁺PF₆⁻ (**2c**). The acetonitrile complex **2a** was photochemically synthesized using 190 mg of **1a** as described above. A solution of **2a** and 2 g of PPh₃ in 150 mL of acetone was refluxed for 12 h under an argon atmosphere, and then the solution was evaporated to dryness under reduced pressure. Excess PPh₃ was removed from the crude mixture by column chromatography on silica gel using CH₂Cl₂-ethyl acetate (90:10, v/v) as eluent. The yellow product **2c** was recrystallized using ether-CH₂Cl₂ and dried in vacuo.

[Re(bpy)(CO)₂(P(OEt)₃)Cl]⁺ (2e). A methylene chloride solution (80 mL) containing **2a** (190 mg) and NEt₄⁺Cl⁻ (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**.

[Re(bpy)(CO)₂(PPh₃)₂]⁺PF₆⁻ (**2g**). An acetone solution (60 mL) containing **2f** (100 mg) and PPh₃ (1.0 g) was refluxed under an Ar atmosphere for 12 h. After the solution was evaporated to dryness under reduced pressure, the residue was washed with 100 mL of ether and separated with column chromatography on silica gel using CH₂Cl₂-ethyl acetate as eluent. The yellow layer was collected and evaporated under reduced pressure, giving the product **2g** as a yellow solid, which was recrystallized using ether-CH₂Cl₂ and dried in vacuo.

Crystal Structure Determination of [Re(Me₂bpy)(CO)₂(P(OEt)₃)(PPh₃)]⁺PF₆⁻ (2h**).** All X-ray data were collected on a Mac Science MXC18K four-circle diffractometer using graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. The unit cell dimensions were determined from 22 reflections in the range $31^\circ < 2\theta < 35^\circ$. The crystallographic data are given in Table 3. A total of 9546 diffraction-intensity data were collected using the 2θ - θ scan over all the 2θ range (2.0 - 62.0°). Three standard reflections were measured at intervals of 100 reflections. The intensity data were corrected for Lorentz and polarization effects. The absorption correction was not applied. The crystal structure was solved by the direct method using the SIR92 program.¹⁶ All computations were carried out using the CRYSTAN-GM program system.¹⁷ Of the 7813 unique reflections ($R_{\text{int}} = 0.060$), over the index ranges $14 > h > 0$, $43 > k > 0$, and $15 > l > -15$, the 4349 reflections with criterion $I_0 > 1.5\sigma(I_0)$ were used in the full-matrix least-squares refinement based on minimization of the function $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was $w^{-1} = \sigma^2(F_o) + 0.0002|F_o|^2$. The atomic and anomalous scattering factors were taken from the literature.¹⁸

- (16) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.
 (17) Edwards, C.; Gilmore, C. J.; Mackey, S.; Stewart, N. *CRYSTAN-GM*, Ver. 6.3.3; Mac Science: Yokohama, Japan, 1996.

Table 3. Crystallographic Data for **2h**

empirical formula	C ₃₈ H ₄₂ N ₂ O ₅ F ₆ P ₃ Re	β /deg	94.312(7)	R^a	0.066
fw	999.90	$V/\text{\AA}^3$	4221.6(1)	R_w^b	0.058
cryst syst	monoclinic	Z	4	S^c	2.813
space group	$P2_1/a$ (no. 14)	T/K	295	Δ/σ	0.0005
$a/\text{\AA}$	11.592 (1)	$D_{\text{calcd}}/\text{g cm}^{-3}$	1.57	$\Delta\rho_{\text{max}}/\text{e \AA}^{-3}$	1.01
$b/\text{\AA}$	30.953 (4)	μ/cm^{-1}	30.951	$\Delta\rho_{\text{min}}/\text{e \AA}^{-3}$	-1.01
$c/\text{\AA}$	11.799 (2)	$F(000)$	1992		

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}. \quad ^c S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}.$$

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

Bond Lengths			
Re(1)–P(1)	2.448(5)	Re(1)–P(2)	2.349(7)
Re(1)–N(1)	2.179(15)	Re(1)–N(2)	2.145(17)
Re(1)–C(1)	1.84(3)	Re(1)–C(2)	1.88(3)
O(1)–C(1)	1.18(4)	O(2)–C(2)	1.17(3)
Bond Angles			
P(1)–Re(1)–N(1)	90.9(5)	P(1)–Re(1)–N(2)	89.3(5)
P(1)–Re(1)–C(1)	90.1(8)	P(1)–Re(1)–C(2)	91.2(7)
P(2)–Re(1)–C(1)	90.3(8)	P(2)–Re(1)–C(2)	91.2(7)
P(2)–Re(1)–N(1)	86.7(5)	P(2)–Re(1)–N(2)	89.9(5)
N(1)–Re(1)–N(2)	74.1(7)	N(1)–Re(1)–C(1)	95.9(8)
N(1)–Re(1)–C(2)	173.6(9)	N(2)–Re(1)–C(1)	170.0(8)
N(2)–Re(1)–C(2)	99.9(9)	C(1)–Re(1)–C(2)	90.1(10)
P(1)–Re(1)–P(2)	177.6(2)		

Table 5. Electronic Absorption and Emission Data for **2** at Room Temperature

complex ^a	absorption $\lambda_{\text{max}}/\text{nm}^b$		emission ^b		
	MLCT	$\pi-\pi^*$ (bpy)	$\pi-\pi^*$ (PPh ₃)	$\lambda_{\text{max}}/\text{nm}$	$\tau_{\text{em}}/\text{ns}$
2a	386 (4000)	294 (19 000)		639 <0.002	<i>d</i>
2b	397 (4100)	295 (23 000)		651 <0.002	12
2c	387 (3800)	291 (18 000)	269 (20 000)	620 0.031	350
2d	369 (4000)	289 (17 000)		618 ^c 0.017 ^c	250 ^c
2e	423 (2100)	300 (13 000)		nd ^e	
2f	401 (3800)	301 (20 000)	270 (17 000)	650 <0.002	<i>d</i>
2g	410 (2800)	295 (20 000)	270 (22 000)	619 0.037	640
2h	381 (3700)	290 (18 000)	267 (21 000)	612 0.040	560
2i	364 (5100)	283 (22 000)		609 ^c 0.026 ^c	340 ^c
2j	404 (4900)	297 (23 000)		668 ^c 0.005 ^c	20 ^c

^a All complexes are PF₆⁻ salts except for the neutral complex **2e**.

^b Data were obtained from DMF solutions except for the data denoted by the superscript *c*. ^c 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 $U_{\text{iso}} \approx 0.1$ –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) $k_{\text{CO,CO}}$.^{37–39} The biscarbonyl complexes **2** have two equivalent CO groups and hence only two force constants: k_{CO} and $k_{\text{CO,CO}}$. With only two observed $\nu(\text{CO})$ 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:

$$\lambda = K(\nu_{\text{sym}})^2 = \mu(k_{\text{CO}} + k_{\text{CO,CO}})$$

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

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

(18) Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

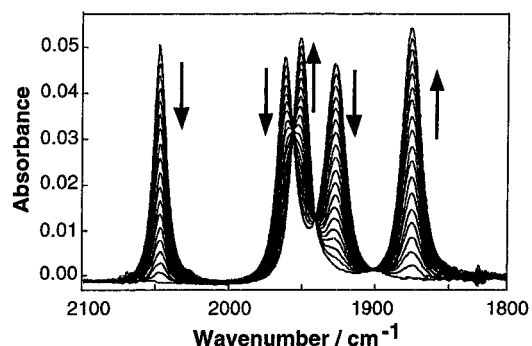


Figure 1. In situ FT-IR absorption spectra of an Ar-saturated acetonitrile solution containing **1a** (0.1 M) under irradiation with a 30 s monitoring interval. The cell path length was 2 mm.

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

$$k_{\text{CO}} = K(\mu^{-1})\{(\nu_{\text{sym}})^2 + (\nu_{\text{asym}})^2\}$$

$$k_{\text{CO,CO}} = K(\mu^{-1})\{(\nu_{\text{sym}})^2 - (\nu_{\text{asym}})^2\}$$

Results and Discussion

Photochemical Ligand Substitution Reaction of **1a.** An Ar-purged acetonitrile solution containing **1a** was irradiated to give biscarbonyl complex *cis,trans*-[Re(bpy)(CO)₂{P(OEt)₃}(MeCN)]⁺ (**2a**) in an 88% isolated yield (eq 1). The progress of this ligand substitution reaction was followed by in situ IR measurements in solution using a gastight optical cell of calcium fluoride, into which an Ar-purged acetonitrile solution had been introduced. This cell was placed in the optical chamber of an FT-IR spectrometer and then irradiated using an optical fiber through which 365 nm light was introduced from a Xe lamp with a band-pass filter placed outside the spectrometer. Figure 1 shows the IR spectral changes in the CO-stretching region following the irradiation; two new bands attributable to **2a** appear with isosbestic points as the three bands of **1a** decrease. This spectral change clearly demonstrates the quantitative photochemical conversion of **1a** to **2a**. The quantum yield of the photochemical reaction was 0.089 at 25 °C. The triphenylphosphine complex **1d** was also photochemically converted to the corresponding biscarbonyl complex **2f** in quantitative yield.

It is well-known that the complexes *fac*-[Re(LL)(CO)₃(Z)] (Z = alkyl or metal carbonyl moieties such as Me, Et, and M(CO)₅ (M = Re, Mn, etc.)) are photolabile enough to undergo facile homolytic fission of the Re–Z bond via a ³σπ* (and/or ³σσ*) excited state to give [Re⁰(LL)(CO)₃] and (Z•).^{1,19–22} In contrast to this well-known reaction type, the present photo-

(19) Rossenaar, B. D.; George, M. W.; Johnson, F. P. A.; Stufkens, D. J.; Turner, J. J.; Vlček, A. *J. Am. Chem. Soc.* **1995**, *117*, 11582–11583.

(20) Rossenaar, B. D.; Kleverlaan, C. J.; Vandeven, M. C. E.; Stufkens, D. J.; Vlček, A. *Chem. Eur. J.* **1996**, *2*, 228–237.

(21) Stufkens, D. J. *Coord. Chem. Rev.* **1990**, *104*, 39–112.

(22) Meyer, T. J.; Casper, J. V. *Chem. Rev.* **1985**, *85*, 187–218.

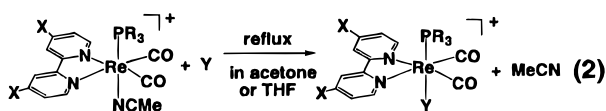
chemical ligand substitution is entirely different, providing the first example for the exclusive loss of the axial CO ligand from tricarbonyl complexes $fac\text{-[Re(LL)(CO)}_3\text{(L')]}^{n+}$. A notable structural feature of the reactions is that L' must be a phosphorus ligand.²³ This type of photochemical 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 $[fac\text{-Re(X}_2\text{bpy)(CO)}_3\text{(PR}_3)]^+$ and ligand L' , e.g., pyridine and phosphorus compounds at $>330\text{ nm}$ for 4–48 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 two 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 **2c** 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*- $[\text{Re}(\text{bpy})(\text{CO})_2(\text{PR}_3)(Y)]^{n+}$ ($Y = \text{the neutral ligand, } n = 1, \text{PF}_6^- \text{ salt; } Y = \text{Cl}^-, n = 0$) 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

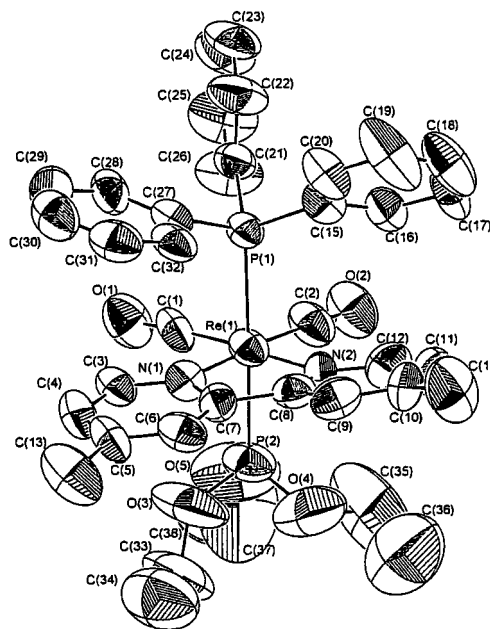


Figure 2. ORTEP drawing and labeling scheme for the atoms of the cation of **2h**. Thermal ellipsoids are at the 50% probability level.

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 $\nu(\text{CO})$ 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., $[\text{Re}(\text{X}_2\text{bpy})(\text{CO})_2(\text{PR}_3)(Y)]^{n+}$ ($n = 0, Y = \text{Cl}^-, n = 1, Y = \text{neutral ligands}$). In $^1\text{H NMR}$, only three or four sets of peaks appear for X_2bpy or bpy , clearly indicating that all the complexes **2** have C_{2v} 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 $[\text{Re}(\text{Me}_2\text{bpy})(\text{CO})_2\{\text{P(OEt)}_3\}(\text{PPh}_3)]^+$ 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 biscarbonyldiiminerhenium complexes, though more than 10 sets of crystal data have been reported for tricarbonyldiiminerhenium complexes.^{25–36a} The complex **2h** has a steric structure similar

(23) Recently, Rillema and co-workers reported photochemical ligand substitution reactions of tetracarbonyldiiminerhenium(I) complexes $[\text{Re}(\text{LL})(\text{CO})_4]^+(\text{CF}_3\text{SO}_3^-)$, giving the corresponding tricarbonyl complexes $[\text{Re}(\text{LL})(\text{CO})_3(\text{CF}_3\text{SO}_3)]$. Shaver, R. J.; Rillema, D. P. *Inorg. Chem.* **1992**, *31*, 4101–4107.

(24) Irradiation using 313 nm light instead of $>330\text{ nm}$ light caused a decrease in the yield of **2** accompanied by the formation of green complexes. The photochemistry of **2** is under investigation in our laboratory.

(25) Horn, E.; Show, M. R. *Aust. J. Chem.* **1980**, *33*, 2369–2376.
 (26) Yam, V. W. W.; Wong, K. M. C.; Cheung, K. K. *Chem. Commun.* **1998**, 135–136.
 (27) Gelling, A.; Orrell, K. G.; Osborne, A. G.; Sik, V.; Hursthouse, M. B.; Coles, S. J. *J. Chem. Soc., Dalton Trans.* **1996**, 203–209.
 (28) Guilhem, J.; Pascard, C.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1989**, 1449–1454.
 (29) Winslow, L. N.; Rillema, D. P.; Welch, J. H.; Singh, P. *Inorg. Chem.* **1989**, *28*, 1596–1599.
 (30) Yam, V. W. W.; Lau, V. C. Y.; Cheung, K. K. *Organometallics* **1996**, *15*, 1740–1744.
 (31) Civitello, E. R.; Dragovich, P. S.; Karpishin, T. B.; Novick, S. G.; Bierach, G.; Oconnell, J. F.; Westmoreland, T. D. *Inorg. Chem.* **1993**, *32*, 237–241.
 (32) Moya, S. A.; Schmidt, R.; Pastene, R.; Sartori, R.; Muller, U.; Frenzen, G. *Organometallics* **1996**, *15*, 3463–3465.
 (33) Wallace, L.; Woods, C.; Rillema, D. P. *Inorg. Chem.* **1995**, *34*, 2875–2882.
 (34) Shaver, R. J.; Perkovic, M. W.; Rillema, D. P.; Woods, C. *Inorg. Chem.* **1995**, *34*, 5446–5454.

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 bpy 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 constant(s) k_{CO} and the interaction force constant(s) $k_{\text{CO,CO}}$.^{37–39} The biscarbonyl complexes **2** have only two equivalent CO groups, thus allowing the complete analysis of the force fields.⁴⁰ 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 π -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 > PPh₃ > py > Cl[–] for Y and CF₃ > H > Me for X.

It has been reported that the C–O bond length r_{CO} ⁴¹ and the bond angle θ between the CO groups in metal carbonyls³⁸ can be estimated by the following equations:

$$r_{\text{CO}} = 1.647 - 0.184 \ln k_{\text{CO}} \quad (r_{\text{CO}}, \text{\AA}; k_{\text{CO}}, \text{mdyn/\AA})$$

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

where I is the intensity of relevant vibration modes. The calculated r_{CO} and θ 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 $r_{\text{CO}} = 1.18(4)$ and $1.17(3)$ 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 θ .

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 (X₂bpy) charge-transfer transition. This assignment is based on a considerable solvatochromic shift of the band and substantial

Table 6. Electrochemical Data for **2**^a

complex	$E_{1/2}^{\text{red}}/\text{V}^b$	$E_{\text{p}}^{\text{red}}/\text{V}^c$	$E_{1/2}^{\text{ox}}/\text{V}^b$	$E_{\text{p}}^{\text{ox}}/\text{V}^d$
2a	–1.69 (75)	–1.87	0.92 (68)	
2b		–1.64	0.89 (61)	
2c	–1.71 (65)	–2.26		1.09
2d	–1.71 (65)	–2.32	1.10 (77)	
2e		–1.87	0.47 (67)	1.13
2f	–1.70 (64)	–1.91	0.89 (69)	
2g	–1.71 (64)	–2.26		1.10
2h	–1.80 (65)	–2.33		1.05
2i	–1.80 (69)	–2.37	1.06 (82)	
2j	–1.26 (67)	–1.96	1.23 (86)	

^a The cyclic voltammograms of **2** were taken in MeCN solutions containing *n*-Bu₄NBF₄ (0.1 M) at a 200 mV/s scan rate using a glassy-carbon working electrode, a Pt counter electrode, and a Ag/AgNO₃ (0.1 M, an MeCN solution) reference electrode under an Ar atmosphere. All potentials are reported against a Ag/AgNO₃ 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.

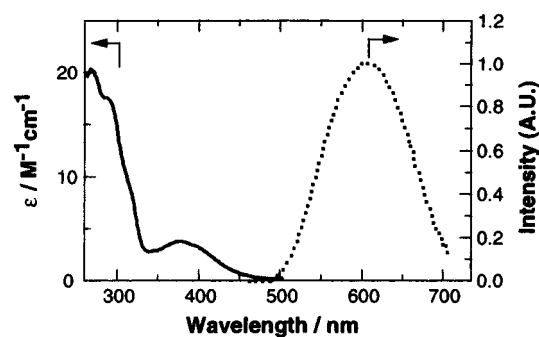


Figure 3. UV/vis absorption (solid line) and emission (dotted line) spectra of **2h** in a DMF solution at room temperature.

dependence of the band on the property of X in the X₂bpy ligands. A red shift of the band occurs by 10–15 nm upon changing the solvent from DMF to CH₂Cl₂. A further shift to the red occurs with an increase in the electron-withdrawing strength of X in the order CF₃ > H > Me. The shift is also dependent upon Y, shifting to the red in the order Cl[–] > py > PPh₃ > MeCN > P(OEt)₃ > CO. This change is attributable to changes in the electron density on the central metal, which is affected by the σ - and π -donating/accepting abilities of L and PR₃. 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 π – π^* transition localized on the bpy ligand, which shows relatively low sensitivity to both solvent polarity and electronic properties of the ligand L.⁴² The π – π^* transition band localized on the phenyl groups of the PPh₃ 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 O₂. 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

(35) Anderson, P. A.; Keene, F. R.; Horn, E.; Tiekink, E. R. T. *Appl. Organomet. Chem.* **1990**, *4*, 523–533.

(36) (a) Stor, G. J.; Hartl, F.; Vanoutersterp, J. W. M.; Stufkens, D. J. *Organometallics* **1995**, *14*, 1115–1131. (b) Johnson, F. P. A.; George, M. W.; Hartle, F.; Turner, J. J. *Organometallics* **1996**, *15*, 3374–3387. (c) Christensen, P.; Hamnett, A.; Muir, A. V. G.; Timney, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1455–1463. (d) Paolucci, F.; Marcaccio, M.; Paradisi, S.; Roffia, S.; Bignozzi, C. A.; Amatore, C. *J. Phys. Chem. B* **1998**, *102*, 4759–4769. (e) Klein, A.; Vogler, C.; Kaim, W. *Organometallics* **1996**, *15*, 236–244.

(37) Cotton, F. A.; Kraihazel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(38) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(39) Burdett, J. K.; Poliakoff, M.; Timmey, J. A.; Turner, J. J. *Inorg. 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 $\nu(\text{CO})$ frequencies, but possess four force constants. Gamelin, D. R.; George, M. W.; Glyn, P.; Grevels, F. W.; Johnson, F. P. A.; Klotzbucher, W.; Morrison, S. L.; Russell, G.; Schaffner, K.; Turner, J. J. *Inorg. Chem.* **1994**, *33*, 3246–3250.

(41) Morrison, S. L.; Turner, J. J. *J. Mol. Struct.* **1994**, *317*, 39.

(42) The absorption maxima of free bpy and PPh₃ were observed at 280 and 236 nm and 260 and 194 nm in MeCN solution, respectively.

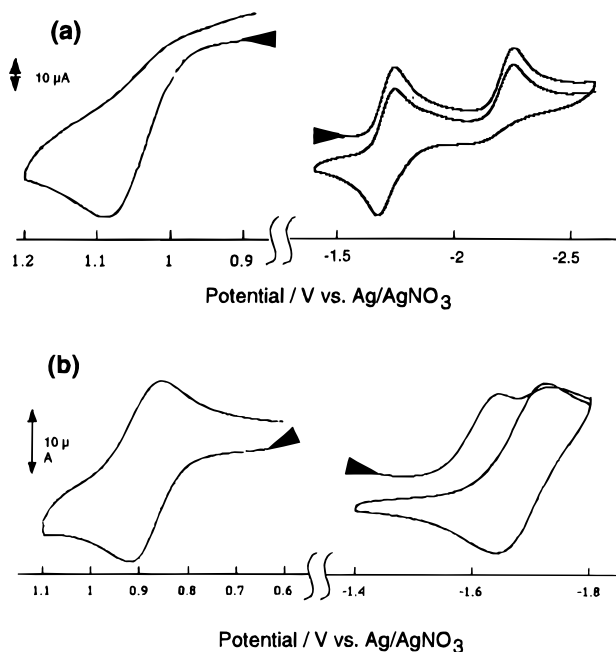


Figure 4. Cyclic voltammograms of 0.5 mM (a) **2c** and (b) **2b** in acetonitrile solutions containing 0.1 M *n*-Bu₄NBF₄ taken using a glassy-carbon working electrode, a Pt wire counter electrode, and a Ag/AgNO₃ reference electrode. The scan rate was 200 mV/s. The cathodic curves were obtained by scanning 1.5 times.

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 ³MLCT excited state and the lower emission quantum yield than the corresponding tricarbonyl complexes, such as [Re(bpy)(CO)₃{P(OEt)₃}]⁺ ($\tau_{em} = 1034$ ns, $\Phi_{em} = 0.088$, $\lambda_{max} = 522$ nm in MeCN), [Re(bpy)(CO)₃(py)]⁺ ($\tau_{em} = 669$ ns, $\Phi_{em} = 0.16$, $\lambda_{max} = 558$ nm in MeCN), and [Re(bpy)(CO)₃(MeCN)]⁺ ($\tau_{em} = 1201$ ns, $\Phi_{em} = 0.41$, $\lambda_{max} = 530$ nm in MeCN).^{15,45} One of the reasons should be the smaller energy gap of **2** between the ³MLCT excited state and the ground state than those of the tricarbonyl complexes. The energy gap low, however, does not interpret the “abnormally” lower emission quantum yields of **2a**, **2b**, and **2f**. Although, 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 [Re(X₂bpy)(CO)₃(L')]ⁿ⁺ (L' = halide, pyridine, MeCN, PR₃, 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.^{2,15,36,43} In a previous paper,¹⁰ we have reported that the first reversible reduction of **2d** yields [Re^I(bpy^{•-})(CO)₂{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

or Cl⁻ complexes (**2b**, **2e**) were irreversibly reduced as shown in Figure 4b, giving the solvento complex **2a**, the $E_{1/2}^{red}$ of which is -1.69 V, as the product (Table 6). It has been reported that the one-electron reduction of the tricarbonyl complexes with L' = Cl⁻ or pyridine causes dissociation of the L' ligand, while the one-electron-reduced species of [Re(bpy)(CO)₃{P(OEt)₃}]⁺ is much more stable because of the stronger π -acidic character of the P(OEt)₃ ligand.^{2a,b,36,43} The one-electron-reduced species of **2b** and **2e** should be unstable enough to undergo a facile ligand substitution reaction as shown in eqs 3 and 4.^{43,44}

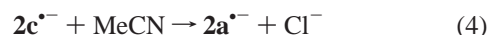
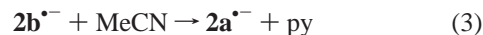


Table 6 summarizes the electrochemical properties of **2**. It is noteworthy that the first oxidation waves for the complexes with acetonitrile, pyridine, or Cl⁻ ligand (**2a**, **2b**, **2e**, **2f**) are reversible on a time scale of the cyclic voltammetric measurements (Figure 4b). This is in contrast to the irreversible anodic waves for most of the reported tricarbonyl diimine complexes.^{36c,d} 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 acetonitrile, 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., Re^I/Re^{II}. This is analogous to the behavior of Re(α -diimine)(CO)₃X (X = halide).⁴⁴

Conclusion

The present investigation has provided the first examples for the photochemical substitution of the axial CO ligand in tricarbonylbipyridinerhenium complexes with a phosphorus ligand. The photochemical ligand substitution reaction opens up synthetic routes for a new class of the biscarbonylbipyridinerhenium complexes *cis,trans*-[Re(X₂bpy)(CO)₂(PR₃)(Y)]ⁿ⁺. 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.

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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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(43) (a) Hori, H.; Ishihara, J.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *J. Photochem. Photobiol., A* **1999**, *5159*, 1–6. (b) Hori, H.; Johnson, F. P. A.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *J. Chem. Soc., Dalton Trans.* **1997**, 1019–1023.

(44) BreiKss, A. I.; Abruña, H. D. *J. Electroanal. Chem.* **1986**, 347–358.

(45) Casper, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *13*, 359.