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Preparative Routes to Luminescent Mixed-Ligand Rhenium(I) Dicarbonyl Complexes

Joanna L. Smithback, Jeffrey B. Helms, Erick Schutte, Stephen M. Woessner, and B. Patrick Sullivan*

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

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A series of mixed-ligand 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) rhenium(I) dicarbonyl complexes that are emissive in fluid solution has been prepared, which includes a new class of the type cis-[Re(CO)₂(P–P)(N–N)]⁺ (where P–P is a chelating diphosphine and N–N is a chelating polypyridine ligand). The four synthetic routes that have been developed rely on either reactive triflate displacement or abstraction of labile chloro ligands, followed by the use of the strong trans-labilizing effect of P donors or direct use of the trans effect of P donors. The spectroscopic, photophysical, and electrochemical properties of these new complexes systematically vary with the net donor ability of the ligands in the coordination sphere, as shown by correlations with Lever's E_L parameters. Lifetimes and quantum yields of the bipyridine complexes encompass a broad range, 25–1147 ns and ca. 0.002–0.11, respectively.

Introduction

Due to their favorable photophysical properties, such as room-temperature luminescence¹ from low-lying, tunable metal—ligand charge transfer (MLCT) ($d\pi$ (M) to π^* (L)) excited states, Re(I) diimine tricarbonyls have been applied in solar-energy conversion schemes², sensor development³, and biological labeling.⁴ Their excited-state lifetimes are largely controlled by the nonradiative rate-constant values (k_{nr}) due to "energy-gap law" behavior.^{5,6} Spectral fitting⁵ and excited-state resonance Raman spectroscopy⁶ have suggested that a high-frequency CO stretching mode may be involved in the radiationless decay process as an accepting mode. This suggests that the removal of a carbonyl to form a dicarbonyl species could result in more-favorable photophysical properties, such as increased quantum yields and lifetimes.

* Author to whom correspondence should be addressed. E-mail: bpat@uwyo.edu.

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This paper deals with our quest to prepare novel mixedligand rhenium(I) dicarbonyls, which indeed possess longlived excited states. The four synthetic routes that we have developed rely on a combination of triflate or chloride labilization and the trans effect of phosphine ligands. For example, trans-labilization of carbonyls yields a new class of complex, cis-[Re(CO)₂(P-P)(N-N)]⁺ (where P-P is a chelating phosphine and N-N is a chelating polypyridine ligand). For comparison purposes, we have included several preparations of phosphonite and phosphite complexes of the type *cis-trans*- $[Re(CO)_2(P)_2(N-N)]^+$ (where P is a monodentate phosphine, phosphonite, or phosphite and N-N is a chelating polypyridine ligand). Some complexes presented in this paper were previously communicated,⁷ and some related Re(I) dicarbonyl complexes have been published by Ishitani et al.8

Experimental Section

General Procedures. Infrared spectra were obtained on a Perkin-Elmer 1600 series FTIR. The solution spectra were taken in

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methylene chloride using a 1-mm length KCl flow cell. Electronic absorption spectra were acquired on a Hewlett-Packard 8452A diode array spectrophotometer, scanning the 190-820 nm spectral region. The samples were contained in 1.00-cm quartz cuvettes and referenced against a solvent blank. Molar extinction coefficients were averaged from absorbance measurements obtained at two or three different concentrations. ¹H and ³¹P{¹H} NMR spectra were recorded in acetonitrile on a Brüker GSX400 spectrometer. ¹H NMR spectra were internally referenced to the solvent, whereas ³¹P NMR spectra were externally referenced to 85% H₃PO₄. Electrochemical measurements were acquired using cyclic voltammetry on a Princeton Applied Research model 273A poteniostat/galvanostat attached to a PC operating Princeton Applied Research model 270/ 259 Research Electrochemistry Software. All measurements were recorded with a Pt disk working electrode using a Ag/AgCl reference electrode. Tetrabutylammonium hexafluorophosphate (ca. 0.1 M) was used as the supporting electrolyte, and each sample was deoxygenated under N2 for 10 min prior to scanning. Emission and excitation spectra were obtained in N₂-purged CH₂Cl₂ on a SLM 8000C photon-counting spectrofluorimeter with a 450 W ozone-free arc-lamp excitation source equipped with a cooled Hamamatsu R928 photomultiplier tube (PMT). Manufacturersupplied computer software carried out corrections for instrument response. Emission quantum yields (Φ_{em}) were measured relative to $[Ru(bpy)_3]^{2+}$ ($\phi_{em} = 0.062$ in N₂-purged CH₃CN) or fac- $[\text{Re}(\text{CO})_3(\text{bpy})\text{py}](\text{CF}_3\text{SO}_3)$ ($\phi_{\text{em}} = 0.012$ in air-saturated H₂O; average atmospheric pressure 585 mmHg in Laramie, WY). Excited-state lifetime measurements (τ) were acquired on either (1) an Edinburg LP900S1 time-resolved absorption/emission spectrophotometer equipped with a Continuum Minilite Nd:YAG laser or (2) an ISS K2 multifrequency phase and modulation spectrofluorimeter equipped with a dual-line (325 and 442 nm) continuouswave He-Cd laser. Samples were sealed in a 1-cm quartz fluorescence cuvette and purged with N_2 for 15 min prior to data acquisition. Lifetimes reported are the average for three runs over a frequency range of $1/\tau$. Lifetime measurements were referenced to a glycogen scattering standard. X-ray crystallographic data were collected at room temperature on a Siemens P4 diffractometer containing a molybdenum tube ($\lambda = 0.71073$ Å) and a graphite monochromator. The data were corrected for Lorentz-polarization effects and absorption. The structure was solved by Patterson methods and refined by least-squares technique effects using the SHELXTL program (Sheldrick, 1997). Elemental analyses were provided by Atlantic Microlabs, Inc., Norcross, GA.

Materials. All chemicals were purchased commercially and used as received unless otherwise noted. Re(CO)5Cl, bis(diphenylphosphino)methane (dppm), and cis-1,2-bis(diphenylphosphino)ethylene (c-dppene) were obtained from Strem Chemical Co. or Sigma-Aldrich. 1,2-Bis(diphenylphosphino)ethane (diphos) was obtained from Alfa-Aesar. Triphenylphosphine (PPh₃), triphenyl phosphite (P(OPh)₃), trimethyl phosphite (P(OCH₃)₃), methyldiphenylphosphinite (P(OCH₃)(Ph)₂), and dimethylphenylphosphonite (P(OCH₃)₂(Ph)) were obtained from Sigma-Aldrich. 4,7-Diphenyl-1,10-phenanthroline (Ph2phen)was obtained from Lancaster. 2,2'-Bipyridine (bpy), 1,10-phenanthroline (phen), o-dichlorobenzene (spectroscopic grade) (ODB), and all other reagent-grade solvents were obtained from Sigma-Aldrich. Tetrabutylammonium hexafluorophosphate (TBAH) was purchased from Sigma-Aldrich, recrystallized from CH₃CN/Et₂O, and dried in vacuo prior to use. Acidic alumina was purchased from Fisher and Sigma-Aldrich. Acetonitrile-d₃ (CD₃CN) was purchased from Cambridge Isotope Laboratories. Acetonitrile (spectroscopic grade) was obtained from Spectrum or Sigma-Aldrich and was dried over 4 Å molecular

sieves prior to use. All other spectroscopic-grade solvents were obtained from Spectrum Chemical Company.

Synthetic Procedures. Complexes of the type fac-Re(CO)₃ (N–N)L and fac-Re(CO)₃(P–P)L (where N–N is a chelating polypyridine ligand, L is Cl⁻ or CF₃SO₃⁻, and P–P is a chelating phosphine) were prepared according to literature.^{7,9} The previously reported *cis-trans*-[Re(CO)₂(PPh₃)₂(bpy)]PF₆⁻¹⁰ was synthesized by a new method.⁷ *mer*-Re(CO)₃(PPh₃)₂Cl was prepared by literature procedures,¹¹ except that the reaction time was 16–24 h in toluene and the product was recrystallized from mixtures of CH₂Cl₂/CH₃OH.

Method I: Synthesis from *fac*-Re(CO)₃(N-N)(CF₃SO₃). cis-[Re(CO)₂(bpy)(dppm)](CF₃SO₃) (1a). fac-Re(CO)₃(bpy)(CF₃-SO₃) (0.244 g (0.389 mmol)) and dppm (0.182 g (0.473 mmol)) were placed in a round-bottom flask with ca. 8 mL of odicholorobenzene (ODB). The resulting cloudy solution was purged with N_2 for 20 min. The reaction was stirred at reflux under N_2 for 3-5 h. During this time, the reaction changed from a cloudy-yellow to clear-yellow solution, finally resulting in a clear-orange solution. After the reaction had cooled to room temperature, hexanes were added to precipitate the yellow-orange product. The product was collected by suction filtration and washed with hexanes and diethyl ether before allowing to air-dry. The product was purified by column chromatography on acidic alumina, starting with a 90:10 ratio of CH2Cl2/CH3CN and gradually increasing the amount of CH₃CN in the eluant. The product was reprecipitated from CH₂Cl₂ into stirring diethyl ether. Yield: 283 mg (78%). Elemental Anal. Calcd for C₃₈H₃₀N₂O₅P₂F₃SRe: C, 48.98; H, 3.25; N 3.01. Found: C, 48.84; H, 3.34; N, 2.97. ¹H NMR (δ/ppm, CD₃CN): 9.60 (d, 1H, J = 5.5 Hz), 8.30 (d, 1H, J = 8.1 Hz), 8.13 (m, 2H), 7.97 (d, 1H, J = 5.5 Hz), 7.87 [7.92–7.80] (m, 3H), 7.53 (m, 14H), 7.18 (dt, 1H, J = 1.5, 7.6 Hz), 6.95 [7.00-6.90] (m, 3H), 6.51 [6.55-6.47] (m, 2H), 5.37 (dt, 1H, J = 16.6, 9.6 Hz), 5.18 (dt, 1H, J = 16.6, 9.6 Hz). ³¹P{¹H} NMR (δ/ppm, CD₃CN): -15.5 (s), -27.5 (d, J = 5 Hz). UV-visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 282 (21900), 302 (sh, 15700), 346 (3730), 438 (3270). IR (CH₂-Cl₂) (ν (CO), cm⁻¹): 1950, 1884.

cis-[Re(CO)2(phen)(dppm)](CF3SO3) (1b). Synthesis and purification were the same as for 1a except that 0.208 g (0.346 mmol) of fac-Re(CO)₃(phen)(CF₃SO₃) and 0.157 g (0.408 mmol) of dppm were used. Yield: 245 mg (74%). Elemental Anal. Calcd for C₄₀H₃₀N₂O₅P₂F₃SRe: C, 50.26; H, 3.16; N 2.93. Found: C, 50.31; H, 3.20; N, 3.03. ¹H NMR (δ /ppm, CD₃CN): 9.97 (d, 1H, J = 5.0Hz), 8.70 (d, 1H, J = 8.1 Hz), 8.36 (d, 1H, J = 8.6 Hz), 8.29 (d, 1H, J = 5.0 Hz), 8.08 (d, 1H, J = 8.6 Hz), 8.00 [8.04–7.96] (m, 3H), 7.91 (d, 1H, J = 8.6 Hz), 7.53 [7.74–7.35] (m, 13H), 7.30 (dd, 1H, J = 4.0, 5.5 Hz), 6.89 (dt, 1H, J = 1.5, 7.6 Hz), 6.58 (dt, 2H, J = 1.0, 7.6 Hz), 6.07 (dd, 2H, J = 5.5, 8.1 Hz), 5.34 (dt, 1H, J = 16.6, 10.1 Hz, 5.02 (dt, 1H, J = 16.6, 10.1 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): -15.9 (d, J = 5 Hz), -27.3 (d, J = 5Hz). UV-visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹cm⁻¹): 262 (sh, 30300), 270 (33400), 292 (sh, 16600), 336 (sh, 4140), 384 (4380), 426 (4380). IR (CH₂Cl₂) (v(CO), cm⁻¹): 1950, 1885.

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[*cis*-**Re**(**CO**)₂(**bpy**)(*c*-**dppene**)](**CF**₃**SO**₃) (**1c**). Synthesis and purification were the same as for **1a** except that 0.305 g (0.529 mmol) of *fac*-Re(CO)₃(bpy)(CF₃SO₃) and 0.237 g (0.598 mmol) of *c*-dppene were used. Yield: 402 mg (80%). Elemental Anal. Calcd for C₃₉H₃₀N₂O₅P₂F₃SRe: C, 49.63; H, 3.20; N 2.97. Found: C, 49.74; H, 3.17; N, 3.05. ¹H NMR (δ /ppm, CD₃CN): 9.59 (d, 1H, *J* = 5.5 Hz), 8.54 (dt, 1H, *J* = 49.4, 8.6 Hz), 8.13 (m, 2.5H), 8.00 (m, 2.5H), 7.81 (d, 1H, *J* = 8.1 Hz), 7.65 [7.71–7.59] (m, 7H), 7.50 [7.54–7.46] (m, 4H), 7.38 [7.44–7.33] (m, 5H), 7.10 (m, 1H), 6.83 (m, 3H), 6.18 (m, 2H). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 52.2 (d, *J* = 19 Hz), 42.2 (d, *J* = 19 Hz). UV–visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 272 (21400), 390 (3440). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1959, 1888.

cis-[**Re**(**CO**)₂(**phen**)(*c*-**dppene**)](**CF**₃**SO**₃) (**1d**). Synthesis and purification were the same as for **1a** except 0.362 g (0.603 mmol) of *fac*-Re(CO)₃(phen)(CF₃SO₃) and 0.278 g (0.701 mmol) of *c*-dppene were used. Yield: 584 mg (81%). Elemental Anal. Calcd for C₄₁H₃₀N₂O₅P₂F₃SRe: C, 50.88; H, 3.12; N 2.89. Found: C, 50.86; H, 3.06; N, 2.99. ¹H NMR (δ /ppm, CD₃CN): 9.97 (d, 1H, *J* = 5.5 Hz), 8.69 (d, 1H, *J* = 8.1 Hz), 8.58 (dt, 1H, *J* = 49.4, 9.1 Hz), 8.23 (d, 1H, *J* = 8.6 Hz), 8.01 [8.16–7.90] (m, 5H), 7.86 (d, 1H, *J* = 5.0 Hz), 7.77 (d, 1H, *J* = 9.1 Hz), 7.65 [7.69–7.61] (m, 5H), 7.44 [7.54–7.35] (m, 8H), 7.21 (dd, 1H, *J* = 5.0, 4.0 Hz), 6.73 (dt, 1H, *J* = 7.1, 1.5 Hz), 6.39 (dt, 2H, *J* = 7.6, 1.5 Hz), 5.73 (dt, 2H, *J* = 10.1, 2.5 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 53.2 (d, *J* = 19 Hz), 43.2 (d, *J* = 19 Hz). UV−visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 266 (32700), 298 (sh, 12400), 344 (4570), 376 (5050), 420 (sh, 3960). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1959, 1889.

cis-[**Re**(**CO**)₂(**bpy**)(**diphos**)](**CF**₃**SO**₃) (**1e**). Synthesis and purification were the same as for **1a** except that 0.182 g (0.316 mmol) of *fac*-Re(CO)₃(bpy)(CF₃SO₃) and 0.131 g (0.329 mmol) of diphos were used with reaction times not exceeding 3 h. Yield: 215 mg (72%). Elemental Anal. Calcd for C₃₉H₃₂N₂O₅P₂F₃SRe: C, 49.52; H, 3.41; N 2.96. Found: C, 49.31; H, 3.42; N, 2.84. ¹H NMR (δ / ppm, CD₃CN): 9.64 (d, 1H, *J* = 5.5 Hz), 8.12 (m, 2H), 7.91 [7.96–7.85] (m, 3H), 7.73 (t, 1H, *J* = 8.1 Hz), 7.64 [7.68–7.60] (m, 5H), 7.57 (m, 4H), 7.46 [7.52–7.41] (m, 5H), 7.37 [7.41–7.74] (m, 1H), 7.09 (t, 1H, *J* = 7.6 Hz), 6.82 [6.87–6.77] (m, 3H), 6.19 (t, 2H, *J* = 10.1 Hz), 3.31 (m, 2H), 2.81 (m, 2H). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 44.5 (d, *J* = 4 Hz), 35.7 (d, *J* = 5 Hz). UV–visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 278 (21200), 344 (sh, 3430), 392 (3210), 430 (sh, 2790). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1952, 1881.

cis-[Re(CO)₂(Ph₂phen)(dppm)](CF₃SO₃) (1f). Synthesis and purification were the same as for 1a except that 0.274 g (0.364 mmol) of fac-Re(CO)₃(Ph₂phen)(CF₃SO₃) and 0.165 g (0.429 mmol) of dppm were used. Purification was done by column chromatography, followed by repeated reprecipitation from CH₃CN into stirring diethyl ether. Yield: 194 mg (65%). Elemental Anal. Calcd for C₅₂H₃₈N₂O₅P₂F₃SRe: C, 56.36; H, 3.46; N 2.53. Found: C, 56.56; H, 3.54; N, 2.58. ¹H NMR (δ/ppm, CD₃CN): 10.03 (d, 1H, J = 5.5 Hz), 8.38 (d, 1H, J = 5.5 Hz), 8.07 (dd, 2H, J = 5.5, 7.1 Hz), 7.97 (m, 2H), 7.80 (d, 1H, J = 9.6 Hz), 7.64 [7.73–7.56] (m, 15H), 7.44 [7.53–7.36] (m, 8H), 7.27 (d, 1H, J = 5.5 Hz), 6.95 (t, 1H, J = 7.1 Hz), 6.66 (dt, 2H, J = 1.5, 7.6 Hz), 6.23 (dd, 2H, J = 6.0, 8.1 Hz), 5.38 (dt, 1H, J = 16.1, 10.1 Hz), 5.02 (dt, 1H, J = 16.1, 10.1 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): -16.3 (d, J = 5 Hz), -27.3 (d, J = 5 Hz). UV-visible (λ (nm), CH₂Cl₂) $(\epsilon \text{ in } M^{-1} \text{ cm}^{-1})$: 286 (43700), 316 (sh, 17700), 350 (7910), 394 (7790), 426 (7690). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1949, 1883.

cis-[Re(CO)₂(Ph₂phen)(*c*-dppene)](CF₃SO₃) (1g). Synthesis and purification were the same as for 1a except that 0.200 g (0.266 mmol) of *fac*-Re(CO)₃(Ph₂phen)(CF₃SO₃) and 0.114 g (0.288 mmol) of *c*-dppene were used. Purification was done by column

chromatography, followed by reprecipitation from hot toluene. Yield: 194 mg (65%). Elemental Anal. Calcd for $C_{53}H_{38}N_2O_5P_2F_3$ -SRe: C, 56.83; H, 3.42; N 2.50. Found: C, 56.63; H, 3.46; N, 2.45. ¹H NMR (δ /ppm, CD₃CN): 10.03 (d, 1H, J = 5.5 Hz), 8.61 (dt, 1H, J = 49.4, 8.6 Hz), 8.14 [8.20–8.08] (m, 2.5H), 7.98 [8.03–7.91] (m, 3.5H), 7.68 [7.75–7.62] (m, 11H), 7.59 [7.62–7.56] (m, 3H), 7.46 [7.55–7.36] (m, 10H), 7.18 (d, 1H, J = 5.5 Hz), 6.83 (t, 1H, J = 7.1 Hz), 6.52 (dt, 2H, J = 2.0, 8.1 Hz), 5.94 (t, 2H, J = 8.6 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 53.2 (d, J = 19 Hz), 42.6 (d, J = 19 Hz). UV–visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 278 (37900), 286 (38500), 318 (sh, 15400), 352 (9200), 380 (9680), 428 (sh, 7310). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1958, 1889.

cis-trans-[Re(CO)2(PPh3)2(bpy)](CF3SO3) (1h). fac-Re(CO)3-(bpy)(CF₃SO₃) (0.150 g (0.260 mmol)) and triphenylphosphine (PPh₃) (0.504 g (1.92 mmol)) were placed in a round-bottom flask with ca. 10-15 mL of ODB. The resulting solution was purged with N₂ for 20 min. The reaction was stirred at reflux under N₂ for 8 h. After the reaction had cooled to room temperature, 50 mL of a 1:1 solution of diethyl ether/hexanes was added, precipitating a greenish-yellow solid. The solid was collected via suction filtration and washed with hot toluene and then diethyl ether to remove any residual triphenylphosphine. The product was reprecipitated from methylene chloride into a 4:1 mixture of diethyl ether/hexanes. The product was collected on a fritted funnel and dried in vacuo overnight. Purification was achieved by column chromatography on acidic alumina, eluting with methylene chloride first the increasing the polarity by gradual introduction of acetone. The solvent was removed, leaving an oily yellow residue that was reprecipitated again from methylene chloride in a 4:1 mixture of diethyl ether/ hexanes, resulting in a greenish-yellow product. Yield: 240 mg (86%). Elemental Anal. Calcd for C₄₉H₃₈N₂O₅P₂F₃SRe: C, 54.90; H, 3.57; N 2.61. Found: C, 53.70; H, 3.64; N, 2.27. ¹H NMR (δ / ppm, CD₃CN): 8.33 (d, 2H, J = 8.5 Hz), 8.04 (d, 2H, J = 5.2Hz), 7.91 (t, 2H, J = 7.7 Hz), 7.30 [7.35-7.26] (m, 30H), 6.96 (t, 2H, J = 6.4 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 24.6. UVvisible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 298 (15700), 306 (13300), 422 (24500). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1938, 1868.

cis-trans-[**Re**(**CO**)₂(**P**(**OPh**)₃)₂(**bpy**)](**CF**₃**SO**₃) (**1i**). Synthesis and purification were the same as for **1h** except that 0.215 g (0.374 mmol) of *fac*-Re(CO)₃(bpy)(CF₃SO₃) and 2 mL (7.63 mmol) of triphenyl phosphite (P(OPh)₃) were used. The product was greenish yellow. Yield: 401 mg (92%) Elemental Anal. Calcd for $C_{49}H_{38}N_2O_{11}P_2F_3SRe: C, 50.39; H, 3.28; N, 2.40.$ Found: C, 50.51; H, 3.34; N, 2.38. ¹H NMR (δ /ppm, CD₃CN): 8.20 (t, 2H, *J* = 7.7 Hz), 7.72 (d, 2H, *J* = 5.9 Hz), 7.62 (d, 2H, *J* = 3.2 Hz), 7.45 (t, 2H, *J* = 6.3 Hz), 7.22 (t, 12H, *J* = 7.8 Hz), 7.13 (t, 6H, *J* = 7.4 Hz), 6.85 (d, 12H, *J* = 8.0 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 104.2. UV-visible (λ (nm), CH₂Cl₂) (ν (CO), cm⁻¹): 1985, 1914.

cis-trans-[**Re**(**CO**)₂(**P**(**OPh**)₃)₂(**phen**)](**CF**₃**SO**₃) (**1j**). Synthesis and purification were the same as for **1h** except that 0.175 g (0.292 mmol) of *fac*-Re(CO)₃(phen)(CF₃SO₃) and 2 mL (7.63 mmol) of triphenyl phosphite (P(OPh)₃) were used. The product was greenish yellow. Yield: 320 mg (92%) Elemental Anal. Calcd for C₅₁H₃₈N₂O₁₁P₂F₃SRe: C, 51.39; H, 3.21; N, 2.35. Found: C, 51.52; H, 3.27; N, 2.41. ¹H NMR (δ /ppm, CD₃CN): 8.62 (d, 2H, *J* = 7.2 Hz), 8.13 (t, 2H, *J* = 3.0 Hz), 7.92 (d, 2H, *J* = 5.6 Hz), 7.74 (d, 2H, *J* = 5.9 Hz), 7.52 (t, 12H, *J* = 8.2 Hz), 7.42 (t, 6H, *J* = 8.6 Hz), 6.98 (d, 12H, *J* = 9.1 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 103.9. UV-visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 302 (17700), 338 (35600), 378 (31400). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1984, 1914.

cis-trans-[Re(CO)₂(P(OCH₃)₃)₂(bpy)](CF₃SO₃) (1k). Synthesis and purification were the same as for 1h except that 0.215 g (0.374

mmol) of *fac*-Re(CO)₃(bpy)(CF₃SO₃) and 2 mL (17 mmol) of trimethyl phosphite (P(OPh)₃) were used. The product was light yellow. Yield: 226 mg (76%) Elemental Anal. Calcd for C₁₉H₂₆N₂O₁₁P₂F₃-SRe: C, 26.68; H, 3.29; N, 3.52. Found: C, 28.06; H, 3.32; N, 3.44. ¹H NMR (δ /ppm, CD₃CN): 10.22 (d, 2H, *J* = 4.6 Hz), 9.79 (d, 2H, *J* = 10.2 Hz), 9.43 (t, 2H, *J* = 8.3 Hz), 8.87 (t, 2H, *J* = 6.7 Hz), 2.62 (t, 18 H, *J* = 22.3 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 122.4. UV-visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 282 (13100), 294 (13000), 318 (sh), 374 (39300). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1961, 1888.

cis-trans-[**Re**(**CO**)₂(**P**(**OCH**₃)(**Ph**)₂)₂(**bpy**)](**CF**₃**SO**₃) (11). Synthesis and purification were the same as for **1h** except that 0.115 g (0.200 mmol) of *fac*-Re(CO)₃(bpy)(CF₃**SO**₃) and 2 mL (9.97 mmol) of methyldiphenylphosphinite (P(OCH₃)(Ph)₂) were used. The product was light yellow. Yield: 176 mg (90%) Elemental Anal. Calcd for C₃₉H₃₄N₂O₇P₂F₃SRe: C, 47.80; H, 3.50; N, 2.86. Found: C, 47.91; H, 3.54; N, 2.79. ¹H NMR (δ /ppm, CD₃CN): 8.54 (d, 2H, *J* = 5.7 Hz), 8.28 (d, 2H, *J* = 7.8 Hz), 8.03 (t, 2H, *J* = 4.1 Hz), 7.35 (t, 4H, *J* = 12.0 Hz), 7.22 (t, 2H, *J* = 2.8 Hz), 7.16 (t, 8H, *J* = 21.3 Hz), 6.68 (d, 8H, *J* = 17.2 Hz), 3.61 (t, 6H, *J* = 8.6 Hz). ³¹P{¹H} NMR (δ /ppm, CD₃CN): 119.7. UV-visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 298 (15100), 406 (32700). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1949, 1879.

cis-trans-[**Re**(**CO**)₂(**P**(**OCH**₃)₂(**Ph**))₂(**bpy**)](**CF**₃**SO**₃) (**1m**). Synthesis and purification were the same as for **1h** except that 0.148 g (0.257 mmol) of *fac*-Re(CO)₃(bpy)(CF₃SO₃) and 2 mL (12.6 mmol) of dimethylphenylphosphonite (P(OCH₃)₂(Ph)) were used. The product was light yellow. Yield: 228 mg (90%) Elemental Anal. Calcd for C₂₉H₃₀N₂O₉P₂F₃SRe: C, 39.24; H, 3.41; N, 3.16. Found: C, 39.29; H, 3.44; N, 3.14. ¹H NMR (δ /ppm, CD₃CN): 8.54 (d, 2H, *J* = 6.8 Hz), 8.18 (d, 2H, *J* = 8.9 Hz), 8.03 (t, 2H, *J* = 6.9 Hz), 7.33 [7.46–7.20] (m, 22H), 2.69 (t, 2H, *J* = 18.0 Hz). ³¹P{¹H</sup>} NMR (δ /ppm, CD₃CN): 149.2. UV–visible (λ (nm), CH₂-Cl₂) (ϵ in M⁻¹ cm⁻¹): 294 (14100), 324 (sh), 394 (32700). IR (CH₂-Cl₂) (ν (CO), cm⁻¹): 1957, 1866.

Method II: Synthesis from *fac*-Re(CO)₃(P-P)Cl. cis-[Re(CO)₂(dppm)(bpy)](PF₆) (2a). fac-Re(CO)₃(dppm)Cl (0.100 g (0.145 mmol)), TIPF₆ (0.053 g (0.15 mmol)), and bpy (0.025 g (0.16 mmol)) were combined with ca. 5 mL of ODB in a roundbottom flask covered with aluminum foil. The solution was refluxed for 7 h under N₂, undergoing a color change from white to yelloworange. A 15-mL scintered glass funnel was filled with a slurry of diatomaceous earth in methylene chloride. The cooled reaction mixture was passed through this slurry to remove the TlCl precipitate. The filtrate was transferred to a round-bottom flask, and the solvent was reduced to 15 mL via rotary evaporation. Diethyl ether was added to precipitate the yellow-orange product, which was isolated by suction filtration and washed with ether. The product was dried in vacuo for 24 h. Yield: 113 mg (84%). Spectroscopic data are the same as those for **1a**. Elemental Anal. Calcd for C₃₇H₃₀ N₂O₂P₃ F₆Re: C, 47.90; H, 3.26; N, 3.02. Found: C, 47.94; H, 3.23; N, 3.05.

cis-[Re(CO)₂(dppm)(phen)](PF₆) (2b). Synthesis and purification were the same as for **2a** except that 0.100 g (0.142 mmol) of *fac*-Re(CO)₃(dppm)Cl, 0.054 g (0.16 mmol) of TlPF₆, and 0.029 g (0.161 mmol) of phen were used. Yield: 118 mg (86%). Spectroscopic data are the same as those for **1b**. Elemental Anal. Calcd for $C_{39}H_{30}$ N₂O₂P₃ F₆Re: C, 49.22; H, 3.18; N, 2.94. Found: C, 48.08; H, 3.22; N, 2.85.

cis-[**Re**(**CO**)₂(*c*-**dppene**)(**bpy**)](**PF**₆) (**2c**). Synthesis and purification were the same as for **2a** except that 0.100 g (0.142 mmol) of *fac*-**Re**(**CO**)₃(*c*-**dppene**)**C**1, 0.053 g (0.15 mmol) of TIPF₆, and 0.024 g (0.15 mmol) of bpy were used. Yield: 177 mg (88%).

Spectroscopic data are the same as those for **1c**. Elemental Anal. Calcd for $C_{38}H_{30}$ N₂O₂P₃ F₆Re: C, 48.57; H, 3.22; N, 2.98. Found: C, 48.33; H, 3.21; N, 3.01.

cis-[**Re**(**CO**)₂(*c*-**dppene**)(**phen**)](**PF**₆) (**2d**). Synthesis and purification were the same as for **2a** except that 0.100 g (0.142 mmol) of *fac*-Re(CO)₃(*c*-dppene)Cl, 0.054 g (0.16 mmol) of TlPF₆, and 0.028 g (0.16 mmol) of phen were used. Yield: 125 mg (91%). Spectroscopic data are the same as those for **1d**. Elemental Anal. Calcd for $C_{40}H_{30}N_2O_2P_3$ F₆Re: C, 49.90; H, 3.14; N, 2.91. Found: C, 49.93; H, 3.15; N, 2.83.

Method III: Synthesis from mer-Re(CO)₃(PPh₃)₂Cl via Phosphine Displacement. *cis*-Re(CO)₂(PPh₃)(*c*-dppene)Cl (3a). mer-Re(CO)₃(PPh₃)₂Cl (0.101 g (0.122 mmol)) and c-dppene (0.050 g (0.126 mmol)) were added to a round-bottom flask with ca. 20 mL of toluene. The solution was refluxed under N₂ for 24 h, causing the cloudy solution to become clear and pale yellow. After the reaction cooled, the solvent was removed and the product was redissolved in a minimal amount of CH₂Cl₂. Approximately 10 mL of methanol was added to the solution, and the methylene chloride was slowly removed by rotary evaporation. The off-white precipitate was collected by suction filtration and washed with methanol before being allowed to air-dry. Yield: 102 mg (90%). Elemental Anal. Calcd for C₄₆H₃₇O₂P₃ClRe: C, 59.00; H, 3.98. Found: C, 57.63; H, 4.15. ¹H NMR (δ/ppm, CDCl₃): 7.34 [7.80–6.89] (m, 35H), 3.51 (t, 2H, J = 2.08 Hz). ³¹P{¹H} NMR (δ /ppm, CDCl₃): 49.6 (dd, J= 186.5, 9.40 Hz), 29.8 (dd, J = 21.01, 10.28 Hz), 12.1 (dd, J =186.7, 21.38 Hz). UV-visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 282 (51400), 290 (45500). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1948, 1866.

cis-Re(CO)₂(PPh₃)(c-dppene)(CF₃SO₃) (3b). cis-Re(CO)₂(PPh₃)-(c-dppene)Cl (0.103 g (0.110 mmol)) and AgSO₃CF₃ (0.034 g (0.13 mmol)) were added to a round-bottom flask with ca. 20 mL of CH₂Cl₂. The solution was stirred for less than an hour before a white precipitate, AgCl, was observed. The reaction was allowed to proceed for 4 h. The AgCl was removed via gravity filtration through diatomaceous earth. Solvent was removed via rotary evaporation. The product was precipitated from CH2Cl2 with hexanes, collected by suction filtration, and washed with CH₃OH and hexanes. Yield: 98 mg (82%). Elemental Anal. Calcd for C₄₇H₃₇O₅P₃F₃SRe: C, 53.71; H, 3.55. Found: C, 53.86; H, 3.99. ¹H NMR (δ/ppm, CDCl₃): 7.00 [7.70–6.30] (m, 35H), 1.26 (s, 2H). ³¹P{¹H} NMR (δ /ppm, CDCl₃): 49.4 (d, J = 649.1 Hz), 37.6 (d, J = 693.2 Hz), 18.0 (d, J = 26.1 Hz). UV-visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 270 (68570), 276 (50790). IR (CH₂Cl₂) $(\nu(CO), cm^{-1})$: 1981, 1922.

cis-[**Re**(**CO**)₂(*c*-**dppene**)(**bpy**)](**CF**₃**SO**₃) (3c). *cis*-Re(CO)₂-(PPh₃)(*c*-dppene)(SO₃CF₃) (0.053 g (0.050 mmol)) was stirred in 25 mL of acetonitrile with gentle heating for 36 h. Solvent was removed, resulting in an oily residue (IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1971, 1904). The resulting [Re(CO)₂(PPh₃)(*c*-dppene)(CH₃CN)]-(SO₃CF₃) was combined with 10.3 mg (0.066 mmol) of 2,2'-bipyridine in ca. 10 mL of toluene. The solution was purged with N₂ and refluxed for 4 h. Once the reaction cooled, the solvent was removed by rotary evaporation. The orange-yellow solid was redissolved in a minimal amount of methylene chloride. The product was reprecipitated by slowly adding the CH₂Cl₂ solution to cold, stirring diethyl ether. The orange-yellow product was collected by suction filtration and washed with several 10-mL aliquots of diethyl ether. Yield: 40 mg (83%). Spectroscopic data are the same as those for 1c.

cis-[Re(CO)₂(*c*-dppene)(phen)](CF₃SO₃) (3d). Synthesis and purification were the same as for 3c except that 0.057 g (0.054 mmol) of *cis*-[Re(CO)₂(PPh₃)(*c*-dppene)(CH₃CN)]SO₃CF₃ and 12.8 g (0.071 mmol) of 1,10-phenanthroline were used and the resulting

product was orange. Yield: 46 mg (87%). Spectroscopic data are the same as those for 1d.

"Melt Method". Method IV: The cis-[Re(CO)₂(bpy)₂](CF₃SO₃) (4a). fac-Re(bpy)(CO)₃(CF₃SO₃) (0.320 g (0.555 mmol)) and a large excess of bpy were placed in a 14 in. \times 0.75 in. tube. The tube was capped with a septum and purged with N₂. The mixture was magnetically stirred and heated until reflux. The reaction was continued for approximately 4 h, when a red solid appeared. The product was cooled and then dissolved in CH2Cl2 and transferred from the tube. Purification was achieved by column chromatography on acidic alumina with CH2-Cl₂/CH₃CN mixtures. Reprecipitation was accomplished from the addition of methylene chloride into stirring diethyl ether. Yield: 317 mg (81%). Elemental Anal. Calcd for C₂₃H₁₆N₄O₅F₃SRe: C, 39.26; H, 2.29; N, 7.96. Found: C, 39.43; H, 2.32; N, 7.91. ¹H NMR (δ /ppm, CD₃CN): 9.45 (d, 2H, J = 5.0 Hz), 8.48 (d, 2H, J= 8.6 Hz), 8.40 (d, 2H, J = 8.6 Hz), 8.15 (dt, 2H, J = 1.5, 8.1 Hz), 8.02 (dt, 2H, J = 1.5, 8.1 Hz), 7.63 (m, 2H), 7.41 (dd, 2H, J = 1.0, 5.5 Hz), 7.34 (m, 2H). UV-visible (λ (nm), CH₂Cl₂) (ϵ in $M^{-1} \text{ cm}^{-1}$): 288 (47400), 364 (6100), 400 (6590), 492 (5320), 564 (sh, 3660). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1922, 1852. FAB-MS⁺: 555.08.

cis-[**Re**(**CO**)₂(**phen**)₂](**CF**₃**SO**₃) (**4b**). Synthesis and purification were the same as for **4a** except that 0.256 g (0.427 mmol) of *fac*-Re(phen)(CO)₃(CF₃SO₃) and an excess of phen were used and the reaction time was reduced to 15 min. Continued heating resulted in a product that was insoluble in common solvents. Yield: 276 mg (86%). Elemental Anal. Calcd for C₂₇H₁₆N₄O₃F₃SRe•1/2H₂O: C, 42.13; H, 2.36; N, 7.28. Found: C, 42.17; H, 2.31; N, 7.31. ¹H NMR (δ /ppm, CD₃CN): 9.93 (dd, 2H, *J* = 5.5, 1.0 Hz), 8.76 (dd, 2H, *J* = 8.1, 1.5 Hz), 8.49 (dd, 2H, *J* = 8.6, 1.5 Hz), 8.22 (d, 2H, *J* = 8.6 Hz), 8.10 (d, 2H, *J* = 8.6 Hz), 8.03 (dd, 2H, *J* = 8.6, 5.0 Hz), 7.58 (dd, 2H, *J* = 5.0, 1.5 Hz), 7.46 (dd, 2H, *J* = 8.1, 5.0 Hz). UV-visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 266 (70600), 294 (sh, 20500), 358 (sh, 4930), 412 (8650), 476 (7030), 540 (5050). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1922, 1853.

cis-[**Re**(**CO**)₂(**Ph**₂**phen**)₂](**CF**₃**SO**₃) (**4c**). Synthesis and purification were the same as for **4a** except that 0.172 g (0.229 mmol) of *fac*-Re(Ph₂phen)(CO)₃(CF₃SO₃) and an excess of Ph₂phen were used and the reaction time was reduced to 15 min. Continued heating resulted in a product which was insoluble in common solvents. Yield: 176 mg (73%). Elemental Anal. Calcd for C₅₁H₃₂N₄O₅F₃-SRe•1/2H₂O: C, 58.00; H, 3.05; N, 5.30. Found: C, 58.23; H, 3.23; N, 5.33. ¹H NMR (δ /ppm, CD₃CN): 10.00 (d, 2H, *J* = 5.5 Hz), 8.17 (d, 2H, *J* = 9.6 Hz), 8.04 (d, 2H, *J* = 9.1 Hz), 7.98 (d, 2H, *J* = 5.5 Hz), 7.82 (d, 2H, *J* = 5.0 Hz), 7.44 (m, 3H). UV−visible (λ (nm), CH₂Cl₂) (ϵ in M⁻¹ cm⁻¹): 280 (83100), 298 (sh, 56300), 320 (sh, 24500), 368 (sh, 9190), 422 (13200), 498 (sh, 10690), 568 (sh, 7060). IR (CH₂Cl₂) (ν (CO), cm⁻¹): 1917, 1850.

Results and Discussion

Synthetic Methods. Earlier preparations of Re(I) with polypyridine acceptors appear in the literature. Complexes of the type *cis-trans*-[Re(CO)₂(N–N)(PR₃)₃]⁺ (where N–N is bpy or phen and R is Ph or OR) have been prepared by thermal or photochemical means,^{9b} and *cis*-[Re(CO)₂(bpy)₂]⁺ has been prepared in low yield by reaction of *fac*-Re(CO)₃-(bpy)Cl with excess bpy in refluxing ethylene glycol.¹⁰ Two similar, straightforward approaches to these and the new class of complex, *cis*-[Re(CO)₂(P–P)(N–N)]⁺, are shown in Scheme 1.

Method I relies on the displacement of a labile triflate and CO ligand by a phosphine donor, either monodentate (IA) or bidentate (IB). Method II reverses the order of binding, allowing the phosphine to bind first, followed by the use of its trans-labilizing ability to bind a bpy or phen ligand. Reaction conditions were generally mild, and column chromatography on alumina using methylene chloride and acetonitrile easily yielded pure materials. Yields were typically 70–90% after chromatography.

For chelating diphosphine ligands with a weak net donor effect, it is possible to displace the phosphine with a polypyridine group. In this case, fac-Re(CO)₂(P-P)L (where L is Cl^- or $CF_3SO_3^-$) was isolated, but further reaction with polypyridines resulted in fac-Re(CO)₃(N–N)L (where L is Cl^{-} or $CF_3SO_3^{-}$). It has also been observed that, once the polypyridine group is bound, these weakly coordinating ligands will not bind in the same manner as described above. In this case, fac-Re(CO)₃(N–N)L (where L is Cl⁻ or $CF_3SO_3^{-}$) was isolated, but further reaction with a chelating phosphine resulted in no reaction. These attempts, under various solvents (DCE, mesitylene, ODB, toluene, etc.) and thermal conditions, resulted in the same product, fac-Re- $(CO)_3(N-N)L$ (where L is Cl⁻ or CF₃SO₃⁻), each time. This led to a new approach for making complexes of the type cis-[Re(CO)₂(P-P)(N-N)]⁺. The combination of the complex mer-trans-Re(CO)₃(PPh₃)₂Cl and a strongly binding polypyridine ligand as an entering group, leads to the synthetic route shown in Scheme 2 that allows "customization" of the trans-labilizing effect. By starting with a mertricarbonyl species, it is easy to displace a CO due to the trans-labilizing effect of the other CO. One of the PPh₃'s is also easily displaced due to the trans-labilizing effect of the phosphine. This allows a chelating phosphine to bind easily, forming *cis*-Re(CO)₂(P–P)(PPh₃)Cl. The chealting phosphine then creates a trans-labilizing effect on the remaining PPh₃ ligand. Finally, labilization of the Cl via triflate metathesis followed by CH₃CN displacement yields two additional binding sites on the complex. This enables the polypyridine ligand to enter the coordination sphere without displacement of the chelating phosphine.

Here, the mer conformation of the carbonyls allows simultaneous phosphine and carbonyl displacement for binding the chelating phosphine. Removal of the chloride ligand in CH₃CN gives a complex that is susceptible to polypyridine reaction via dissociation of the remaining PPh₃ and CH₃CN ligands to give products of the formulation *cis*- $[\text{Re}(\text{CO})_2(\text{P-P})(\text{N-N})]^+$. Products are usually isolated on the basis of solubility and recrystallization, but in some cases, they need to be purified by column chromatography on alumina. Yields are typically 60–80%.

A reaction driven by harsh conditions is seen in Scheme 3 (Method IV), which utilizes a "melt" of a tricarbonyldiimine with excess diimine to produce complexes containing two polypyridine ligands. This reaction proceeds efficiently by heating the pure ligand (e.g., bpy) in a round-bottom flask under nitrogen or, more conveniently, in a test tube in a microwave oven open to the atmosphere. Reaction yields Scheme 1. Direct Synthesis of Phosphine-Diimine Dicarbonyls of Rhenium(I) Complexes^a



^{*a*} Two synthetic routes are shown (Method IA,B and Method II). The first is the addition of the chelating polypyridine ligand and labilization of the ancillary ligand, followed by phosphine addition. The second method involves chelating the phosphine, followed by the addition of the polypyridine ligand.

are approximately 75-85% after the products have been purified by chromatography on an alumina support.

Characterization. Characterization of the complexes was achieved by a combination of elemental analysis, IR spectroscopy, ³¹P NMR spectroscopy, and ¹H NMR spectroscopy. Two intense IR bands in the 1870–1890 and 1940–1960 cm⁻¹ regions and the appropriate number of ³¹P NMR spectral peaks are consistent with a mutually *cis*-CO geometry for all of the compounds. As shown in Table 1, by changing the chelate ligand, a relative assignment of the ligand donor ability can be made for isostructural complexes. The apparent trend is Ph₂phen > bpy, phen > dppm > diphos > *c*-dppene, corresponding to both CO modes increasing in energy (see later section on substituent effects).

The ³¹P NMR patterns and shifts of the complexes tend to be very simple and reflect the presence of a plane or the absence of symmetry at the metal. In some cases, the cis assignment can be made by through-bond *J*-coupling effects. Figure 1 shows the ³¹P NMR of Re(CO)₂(PPh₃)(*c*-dppene)-(Cl). The analysis of its *J*-coupling, described below, can be used to identify the cis assignment. Each of the peaks is a doublet of doublets, corresponding to three inequivalent phosphines in the molecule. The peaks at 12.1 and 49.6 ppm have a large *J*-coupling of 186 Hz. This corresponds to a phosphine trans to a CO and mutually cis to the other phosphines in the system. On the basis of the peak position of bound PPh₃ (10.04 ppm) in the precursor molecule, *mer*-Re(CO)₃(PPh₃)₂Cl, the smallest splitting (J = 9 Hz) on the peaks at 29.8 and 49.6 ppm is caused by the PPh₃. The peaks at 12.1 and 29.8 ppm experience a coupling constant of 20 Hz, corresponding to the end of *c*-dppene that is trans to the PPh₃. The intraligand *J*-coupling for the *c*-dppene is too small to be resolved.

Crystal Structure Data. X-ray crystallographic data for cis-Re(CO)₂(phen)₂(CF₃SO₃)·1/2CH₃CN is also consistent with the structural assignments of these compounds as cis-dicarbonyls. The crystal structure data of cis-[Re(CO)₂(phen)₂](CF₃SO₃), cis-[Re(CO)₂(c-dppene)(phen)](PF₆), and cis-trans-[Re(CO)₂(P(Ph)₂(OCH₃))₂(bpy)](CF₃SO₃), an example from each of three of the classes of compounds, can be found in Figure 2. There are several structural trans effects consistent within these types of compounds. It is observed that the Re–C(O) bonds trans to a polypyridine ligand, ranging from 1.887(10) Å in cis-[Re(CO)₂(c-dppene)(phen)]-(PF₆) (Figure 2ii), tend to be shorter than those trans to a phosphine, which range from 1.910(5) Å in cis-trans-[Re(CO)₂(P(Ph)₂(OCH₃))₂(bpy)](CF₃SO₃) (Figure 2iii) to

Luminescent Rhenium(I) Dicarbonyl Complexes

Scheme 2. Synthesis of Phosphine–Diimine Dicarbonyls of Rhenium(I) Complexes via Phosphine Displacement⁴



^{*a*} Method III is an indirect route that can be used to bind poorly chelating phosphines. This route utilizes the built-in trans effect of two mutually *trans*-triphenylphosphine ligands to bind the polypyridine ligand without interfering with the chelation of the entering diphosphine.

Scheme 3. Synthesis of cis-Re(CO)₂(N-N)₂⁺ Complexes via the "Melt Method"^{*a*}



^{*a*} Method IV uses harsh conditions to bind a second polypyridine ligand using *fac*-Re(CO)₃(N–N)OTf as the precursor complex.

1.931(5) Å in *cis*-[Re(CO)₂(*c*-dppene)(phen)](PF₆). An exception to this is found in the dppm complex, where Re– CO(N) = 1.888(14) Å and Re–CO(P) = 1.900(13) Å. Also, Re–N(diimine) bonds trans to a diphosphine, 2.115(8) Å in *cis*-[Re(CO)₂(phen)₂](CF₃SO₃) and 2.150(4) Å in *cis*-[Re(CO)₂-(*c*-dppene)(phen)](PF₆), are shorter than those trans to a CO, 2.190(7) and 2.210(4) Å, respectively. Re–P bonds trans to another phosphine, 2.4574(67) and 2.3852(60) Å in *cis*-Re(CO)₂(PPh₃)(*c*-dppene)Cl, are similar to those trans to a CO (2.4578(13) Å in *cis*-[Re(CO)₂(*c*-dppene)(phen)](PF₆) and 2.3868(11) Å in cis-[Re(CO)₂(P(Ph)₂(OCH₃))₂(bpy)](CF₃- SO_3)). Last, when both are trans to a CO, Re-P(phosphine) bonds, 2.4578(13) Å in cis-[Re(CO)₂(c-dppene)(phen)](PF₆) and 2.3868(11) Å in *cis-trans*-[Re(CO)₂(P(Ph)₂(OCH₃))₂(bpy)] (CF₃SO₃), are shorter than Re–N(diimine) bonds, 2.210(4) and 2.166(4) Å, respectively. It is also noted that CO bonds trans to a Cl are distinctly shorter (0.877(22) Å in cis-Re(CO)₂(PPh₃)(c-dppene)Cl) than other CO bonds, due to a large back-bonding effect. A better net donor trans to a CO would be expected to cause a weakening in the bond and an increased bond length due to increased electron density into the CO π^* orbitals; however, the C–O bond lengths appear to be the same, ranging from 1.145(6) to 1.168(6) Å, regardless of the trans ligand. In addition, bonds of a similar nature are of equal length across the series of complexes. Re-C(O)bonds trans to a polypyridine are typically 1.89 Å, whereas those trans to a phosphine range from 1.91 to 1.93 Å. Re-P bonds trans to a CO range from 2.39 to 2.46 Å, and those trans to a polypyridine range from 2.36 to 2.41 Å. Re-P bonds trans to another P range from 2.39 to 2.46 Å. Re-N bonds trans to a phosphine range from 2.12 to 2.17 Å, whereas the Re-N bonds trans to a CO range from 2.17 to 2.21 Å.

All bond angles support a distorted octahedron geometry. The N1–Re–N2 bond angles formed by the diimine are less than 90°, ranging from 74.2(2)° in *cis-trans*-[Re(CO)₂(P(Ph)₂-(OCH₃))₂(bpy)](CF₃SO₃) to 76.1(3)° in *cis*-[Re(CO)₂(phen)₂]-(CF₃SO₃), as required by the bite angle of the chelating diimine. The dihedral angles between the COs are consistently lower than 90°: 88.8(2)° in *cis-trans*-[Re(CO)₂(P(Ph)₂-

Tab	e 1	. 1	IR Spectral	Bands	and ³	¹ P NMR	Shifts	for the	Bis(diimine)	and	Phosphine-	-Diimine	Complexes ^{<i>a</i>}
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			³¹ P NMR	
compound	$\nu_{\rm CO}^b ({\rm cm}^{-1})$	δ (ppm)	$\Delta\delta^c$ (ppm)	$\Delta \delta_{\mathrm{av}^c}$ (ppm)
cis-[Re(CO) ₂ (bpy) ₂] ⁺	1922, 1852	-	-	_
cis-[Re(CO) ₂ (phen) ₂] ⁺	1922, 1853	_	_	-
cis-[Re(CO) ₂ (Ph ₂ phen) ₂] ⁺	1917, 1850	_	_	-
cis-[Re(CO) ₂ (bpy)(dppm)] ⁺	1950, 1884	-15.5, -27.5	5.0, -7.0	-1.0
cis-[Re(CO) ₂ (phen)(dppm)] ⁺	1950, 1885	-15.9, -27.3	4.6, -6.8	-1.1
<i>cis</i> -[Re(CO) ₂ (bpy)(<i>c</i> -dppene)] ⁺	1959, 1888	52.2, 42.2	73.2, 63.2	68.2
<i>cis</i> -[Re(CO) ₂ (phen)(<i>c</i> -dppene)] ⁺	1959, 1889	53.2, 43.2	64.2, 54.2	59.2
cis-[Re(CO) ₂ (bpy)(diphos)] ⁺	1952, 1881	44.5, 35.7	55.5, 46.7	51.1
<i>cis</i> -[Re(CO) ₂ (Ph ₂ phen)(dppm)] ⁺	1949, 1883	-16.3, -27.3	4.2, -6.8	-1.3
<i>cis</i> -[Re(CO) ₂ (Ph ₂ phen)(<i>c</i> -dppene)] ⁺	1958, 1889	53.2, 42.6	74.2, 63.6	68.9
cis-trans-[Re(CO) ₂ (PPh ₃) ₂ (bpy)] ⁺	1938, 1868	24.6	28.2	28.2
cis-trans-[Re(CO) ₂ (P(OPh) ₃) ₂ (bpy)] ⁺	1985, 1914	104.2	-25.4	-25.4
cis-trans-[Re(CO) ₂ (P(OPh) ₃) ₂ (phen)] ⁺	1984, 1914	103.9	-25.7	-25.7
cis-trans-[Re(CO) ₂ (P(OCH ₃) ₃) ₂ (bpy)] ⁺	1961, 1888	122.4	-19.4	-19.4
cis-trans-[Re(CO) ₂ (P(OCH ₃)(Ph) ₂) ₂ (bpy)] ⁺	1949, 1879	119.7	3.5	3.5
cis-trans-[Re(CO) ₂ (P(OCH ₃) ₂ (Ph)(bpy)] ⁺	1957, 1886	149.2	-12.6	-12.6
cis-Re(CO) ₂ (PPh ₃)(c-dppene)Cl ^d	1948, 1866	[12.8], [29.8, 49.6]	[16.4], [50.8, 70.6]	[16.4], [60.7]
cis-Re(CO) ₂ (PPh ₃)(c-dppene)OTf ^d	1981, 1922	[17.3], [37.6, 49.4]	[20.9], [58.6, 70.4]	[20.9], [64.5]

^{*a*} All complexes are the triflate salt unless otherwise noted. ^{*b*} IR data taken in methylene chloride. ^{*c*} $\Delta\delta$ is the coordination shift, $\Delta\delta_{av}$ is the average coordination shift. $\Delta\delta = \delta$ (coordinated phosphine) – δ (free ligand). Free ligand ³¹P NMR shifts in CD₃CN versus 85% H₃PO₄ as external standard: dppm (-20.5 ppm); *c*-dppene (-21.0 ppm); diphos (-11.0 ppm); PPh₃ (-3.6 ppm); P(OPh)₃ (129.6 ppm); P(OCH₃)₃ (141.8 ppm); P(OCH₃)₂(Ph) (161.8 ppm). ^{*d*} ³¹P NMR taken in CDCl₃.



Figure 1. ³¹P NMR of Re(CO)₂(PPh₃)(*c*-dppene)Cl showing how through-bond *J*-coupling effects can be used for the determination of structural conformation. This spectrum was taken in CDCl₃ with an 85% H₃PO₄ external standard. Phenyl omitted for clarity.

 $(OCH_3)_2(bpy)](CF_3SO_3)$, 86.9(6)° in *cis*-[Re(CO)₂(*c*-dppene)-(phen)](PF₆), and 85.6(2)° in *cis*-[Re(CO)₂(phen)₂](CF₃SO₃). The trans groupings are less than 180°, also consistent with distortion of the octahedral. In *cis*-[Re(CO)₂(phen)₂](CF₃-SO₃), the N1-Re-N1A angle is 165.5(4)°, and the N2-Re-C1A angle is 171.7(3)°. In *cis*-[Re(CO)₂(*c*-dppene)-(phen)](PF₆), the C1-Re-N2 angle is 172.0(2)°, the C1-Re-P1 angle is 173.71(14)°, and the N1-Re-P2 angle is 172.10(11)°. In *cis*-trans-[Re(CO)₂(P(Ph)₂(OCH₃))₂(bpy)](CF₃-

SO₃), the C–Re–N angles are 172.3(2) and 173.0(2)°. The Re–C–O bond angles are also somewhat distorted from a perfectly linear system, ranging from 174.6(4)° in *cis*-[Re(CO)₂-(*c*-dppene)(phen)](PF₆) to 189.9(6)° in *cis*-trans-[Re(CO)₂-(P(Ph)₂(OCH₃))₂(bpy)](CF₃SO₃). It appears that the smaller the bite angle of the chelating ligand, the larger the deviation from a perfect octahedron. For example, bpy has a smaller bite angle (74.2(2)°) than phen (75.78(14)°), causing the *cis*-COs in *cis*-trans-[Re(CO)₂(P(Ph)₂(OCH₃))₂(bpy)](CF₃SO₃)



Figure 2. Crystal structures of (i) cis-[Re(CO)₂(phen)₂](CF₃SO₃), (ii) cis-[Re(CO)₂(c-dppene)(bpy)](PF₆), and (iii) cis-trans-[Re(CO)₂-(P(Ph)₂(OCH₃))₂(bpy)](CF₃SO₃). Counterions and hydrogens have been omitted for clarity.

to be less distorted, $88.8(2)^\circ$, from 90° than in *cis*-[Re(CO)₂-(*c*-dppene)(phen)](PF₆), $85.6(2)^\circ$.

A crystal structure for *cis*-Re(CO)₂(PPh₃)(*c*-dppene)Cl was obtained, and although the overall refinement is very poor, it confirms the structural assignment made from the ³¹P NMR spectrum. A single molecule of acetonitrile also appears in the structure.

Electrochemical Studies. Cyclic voltammetry was performed in CH₃CN solution with tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte using a Pt button working electrode. In all cases, the potentials were calculated versus a Ag/AgCl reference electrode. As shown in Table 2, the general trend for the cis-[Re(CO)₂(P-P)(N-N)]⁺ and cis-[Re(CO)₂(P)₂(N-N)]⁺ complexes is to exhibit a single ligand-centered reduction wave and a metal-centered oxidation wave (Re^{II/I}), both of which are chemically and electrochemically reversible for the majority of the cases. For cis-[Re(CO)₂(bpy)₂]⁺ and related complexes, two reduction waves and one oxidation wave can be seen. When phen is the diimine ligand, the reductive branch of the cylic voltammogram is complicated by what appears to be adsorption phenomena.¹² Figure 3 shows cyclic voltammograms for three complexes: (a) cis- $[Re(CO)_2(Ph_2phen)_2](CF_3SO_3), (b) cis-[Re(CO)_2(Ph_2phen)-$ (dppm)](CF₃SO₃), and (c) cis-[Re(CO)₂(Ph₂phen)(c-dppene)]-(CF₃SO₃). Figure 3a shows two reversible reduction waves and a quasi-reversible oxidation, whereas Figure 3b demonstates a reversible first reduction and a partially reversible second reduction with irreversible oxidation showing some evidence of product formation. Figure 3c exhibits both reductive and oxidative reversibility.

The potential of the oxidation wave in the reversible cases can be explained by the relative donating/withdrawing nature of the chelate, as predicted by the Lever parameters, $E_{\rm L}$.¹³ Lever and colleagues developed this parameter, which can be used to describe the electrochemical potentials of certain transition metal complexes based on their coordinating behavior.14 This calculation invokes the summation of determined values for the ligands, followed by substitution into the equation: $E_{obs} = S_M[\Sigma E_L(L)] + I_M$. In the case of the Re(II)/Re(I) couple, $S_{\rm M} = 0.76$ and $I_{\rm M} = -0.95$. For our systems, when the reversible oxidations are plotted alongside calculated values, the result is a line described by the equation: y = 0.3503x + 0.8851 ($R^2 = 0.9426$). This can be used to tune the electrochemical potential based on the ligand sphere. Predicted electrochemical frequencies can also be compared to other directly measured properties, such as IR stretching frequencies. These relationships are shown in Figure 4 (calculated values for electrochemical potentials are found in Table 3). On the basis of the experimental values of $\nu(CO)$ and the correlation to Lever parameters, it is also possible to back-calculate the $E_{\rm L}$ value of Ph₂phen, which is found to be 0.23(1). This is to be expected on the basis of the electronic similarity with slightly more π donation than bpy and phen ($E_{\rm L} = 0.259$ and 0.26, respectively).

UV–Visible Spectroscopic and Photophysical Data. The complexes exhibit yellow-orange to red coloration in the solid and in solution due to MLCT transitions in the range of 380–560 nm. The corresponding luminescence occurs in the 600–700 nm range. Higher energy absorption features in the UV portion of the spectrum are assigned to intraligand (IL, $\pi - \pi^*$) absorptions of the diimine groups and phenyl groups on the phosphorus donors on the basis of the properties of similar

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Table 2. Electrochemical Data^{*a*} vs SCE Obtained by Cyclic Voltammetry with Ferrocene Internal Standard^{*b*}

complex	$E_{1/2}^{ m ox}({ m V})$	$E_{ m obs}{}^c$	$E_{1/2}^{\rm red}$ (V)
cis-[Re(CO) ₂ (bpy) ₂] ⁺	0.91 (r)	1.189	-1.30 (r), -1.51 (r)
cis-[Re(CO) ₂ (phen) ₂] ⁺	0.91 (r)	1.191	-1.32 (i), -1.52 (i)
cis-[Re(CO) ₂ (Ph ₂ phen) ₂]+	0.88 (q)	-	-1.26 (i), -1.42 (i)
<i>cis</i> -[Re(CO) ₂ (bpy)(dppm)] ⁺	1.26 (i), 1.42 (r)	1.319	-1.33 (r), -1.63 (i)
<i>cis</i> -[Re(CO) ₂ (phen)(dppm)] ⁺	1.24 (i), 1.42 (r)	1.320	-1.35 (i), -1.69 (i)
<i>cis</i> -[Re(CO) ₂ (bpy)(<i>c</i> -dppene)] ⁺	1.37 (r)	1.365	-1.35(r)
cis-[Re(CO) ₂ (phen)(c-dppene)] ⁺	1.37 (r)	1.366	-1.38 (i)
<i>cis</i> -[Re(CO) ₂ (bpy)(diphos)] ⁺	1.32 (r)	1.342	-1.35(r)
cis-[Re(CO) ₂ (Ph ₂ phen)(dppm)] ⁺	1.22 (i), 1.39 (r)	N/A	-1.29 (r), -1.57 (i)
<i>cis</i> -[Re(CO) ₂ (Ph ₂ phen)(<i>c</i> -dppene)] ⁺	1.35 (r)	N/A	-1.30(r)
cis-trans-[Re(CO) ₂ (PPh ₃) ₂ (bpy)] ⁺	1.40 (q)	-	-1.31 (r)
cis-trans-[Re(CO) ₂ (P(OPh) ₃) ₂ (bpy)] ⁺	1.19 (i)	-	-1.25(r)
cis-trans-[Re(CO) ₂ (P(OPh) ₃) ₂ (phen)] ⁺	1.19 (i)	-	-1.23 (r)
cis-trans-[Re(CO) ₂ (P(OCH ₃) ₃) ₂ (bpy)] ⁺	1.46 (q)	-	-1.28(r)
cis-trans-[Re(CO) ₂ (P(OCH ₃)(Ph) ₂) ₂ (bpy)] ⁺	1.42 (i)	-	-1.33 (r)
cis-trans-[Re(CO) ₂ (P(OCH ₃) ₂ (Ph)(bpy)] ⁺	1.52 (i)	-	-1.32 (r)
cis-Re(CO) ₂ (PPh ₃)(c -dppene)Cl ^d	1.02 (r)	1.282	_
cis-Re(CO) ₂ (PPh ₃)(c-dppene)OTf ^d	0.800 (q)	-	_

^{*a*} All complexes are the triflate salt unless otherwise noted; (r) = reversible, (i) = irreversible, (q) = quasireversible. ^{*b*} Scans (20 mV/s) were taken in CH₃CN with TBAH as the supporting electrolyte against a Ag/AgCl reference electrode. A Pt button was the working electrode, and a Pt wire was the counter electrode. Peak splitting for ferrocene under these conditions ranged from 0.28 to 0.21 V. ^{*c*} Calculated oxidation values versus SCE for reversible waves from Lever parameters. Ph₂phen value is not given in ref 14. ^{*d*} Taken in CH₂Cl₂. All other conditions were the same.



Figure 3. Typical cyclic voltammograms for the dicarbonyls for (a) *cis*- $[Re(CO)_2(Ph_2phen)_2](OTf)$, (b) *cis*- $[Re(CO)_2(Ph_2phen)(dppm)](OTf)$, and (c) *cis*- $[Re(CO)_2(Ph_2phen)(c-dppene)](OTf)$. Scans were taken at 20 mV/s in CH₃CN with a ca. 0.1 M TBAH supporting electrolyte. Pt button was used as the working electrode with a Ag/AgCl reference electrode.

d⁶ polypyridine complexes.¹⁴ This is further supported by their insensitivity to ligand sphere composition. Lowerenergy UV bands are assigned to metal–ligand charge transfer (MLCT) transitions on the basis of their similarity to MLCT transitions in other complexes.¹⁴ This is supported by their sensitivity to changes in composition of the



Figure 4. Calculated electrochemical oxidation potentials from E_L parameters vs (a) observed oxidation potentials and (b) IR stretching frequencies for Re(I) dicarbonyl complexes. Cyclic voltammetry data was taken at 20 mV/s in CH₃CN with a ca. 0.1 M TBAH supporting electrolyte. Pt button was used as the working electrode with a Ag/AgCl reference electrode. IR spectral data was taken in CH₂Cl₂.

coordination sphere. The overall red-shift in MLCT maxima of dicarbonyls compared to that of tricarbonyls can be attributed to the reduction in ligand field strength by destabilization of the $d\pi$ orbital set attained through CO removal. Because the MLCT is $d\pi - \pi^*$ in nature, destabilization of the $d\pi$ orbitals by replacement of an accepting

Table 3.	Bond Lengths an	nd Angles c	of Interest	for Different	Classes o	f Rhenium(I)	Dicarbonyl S	pecies
	0	0					2	

			cis-trans-[Re(CO) ₂ (P(Ph) ₂ (OCH ₃)) ₂ (bpy)]
	cis-[Re(CO) ₂ (phen) ₂](CF ₃ SO ₃)	cis-[Re(CO) ₂ (c -dppene)(phen)](PF ₆)	(CF_3SO_3)
		Lengths (Å)	
Re-C1(N)	1.887(10)	1.895(5)	1.893(5)
Re-C1(Cl)	N/A	N/A	N/A
Re-C2(P)	N/A	1.931(5)	1.910(5)
Re-P(CO)	N/A	2.4578(13)	2.3868(11)
Re-P2(N)	N/A	2.3647(13)	2.4077(11)
Re-P1(P3)	N/A	N/A	N/A
Re-P3(P1)	N/A	N/A	N/A
Re-N1(P)	2.115(8)	2.150(4)	2.172(4)
Re-N2(CO)	2.190(7)	2.210(4)	2.166(4)
C1-O1(N)	1.164(12)	1.163(5)	1.168(6)
C1-O1(Cl)	N/A	N/A	N/A
C2-O2(P2)	N/A	1.160(6)	1.145(6)
		Angles (deg)	
C1-Re-C2	86.9(6)	85.6(2)	88.8(2)
N1-Re-N2	76.1(3)	75.78(14)	74.2(2)
P1-Re-P2	N/A	82.06(4)	173.89(4)
Re-C1-O1	176.7(8)	175.7(4)	179.5(4)
Re-C2-O2	N/A	174.6(4)	179.9(6)
N1-Re-N1A	165.5(4)	N/A	N/A
C1A-Re-N2	171.7(3)	N/A	N/A
C1-Re-N2	N/A	172.0(2)	_
C2-Re-P1	N/A	173.71(14)	_
N1-Re-P2	N/A	172.10(11)	_
C2-Re-N2	_	_	172.3(2)
C1-Re-N1	—	_	173.0(2)

Table 4.	UV-Visible	Spectral	Data o	f Dicarbony	yls Obtained	in CH ₂ Cl ₂	
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	$\lambda_{\max} (nm) (\epsilon \times 10^{-3}, M^{-1} cm^{-1})$				
$\operatorname{complex}^{a}$	$\pi-\pi^*$	MLCT $(d\pi - \pi^*)$			
cis-[Re(CO) ₂ (bpy) ₂] ⁺	288 (47.4)	364 (6.11), 400 (6.59), 492 (5.32), 564 (sh)			
cis-[Re(CO) ₂ (phen) ₂] ⁺	266 (70.6), 294 (sh)	476 (7.03), 540 (5.05)			
cis-[Re(CO) ₂ (Ph ₂ phen) ₂]+	280 (83.1), 298 (sh), 320 (sh)	368 (sh), 422 (13.2), 498 (sh), 568 (sh)			
<i>cis</i> -[Re(CO) ₂ (bpy)(dppm)] ⁺	282 (21.9), 302 (sh)	346 (3.73), 438 (3.27)			
<i>cis</i> -[Re(CO) ₂ (phen)(dppm)] ⁺	262 (sh), 270 (33.4), 292 (sh)	336 (sh), 384 (4.38), 426 (sh)			
cis-[Re(CO) ₂ (bpy)(c -dppene)] ⁺	272 (21.4)	390 (3.44)			
cis-[Re(CO) ₂ (phen)(c -dppene)] ⁺	266 (32.7), 298 (sh)	344 (4.57), 376 (5.05), 420 (sh)			
<i>cis</i> -[Re(CO) ₂ (bpy)(diphos)] ⁺	278 (21.2)	344 (sh), 392 (3.21), 430 (sh)			
cis-[Re(CO) ₂ (Ph ₂ phen)(dppm)] ⁺	286 (43.7), 316 (sh)	350 (7.91), 394 (7.79), 426 (7.69)			
cis-[Re(CO) ₂ (Ph ₂ phen)(c-dppene)] ⁺	278 (37.9), 286 (38.5), 318 (sh)	352 (9.20), 380 (9.68), 428 (sh)			
<i>cis-trans</i> -[Re(CO) ₂ (PPh ₃) ₂ (bpy)] ⁺	298 (15.7), 306 (13.3)	422 (2.45)			
<i>cis-trans</i> -[Re(CO) ₂ (P(OPh) ₃) ₂ (bpy)] ⁺	286 (10.9), 320 (7.03)	372 (3.14)			
<i>cis-trans</i> -[Re(CO) ₂ (P(OPh) ₃) ₂ (phen)] ⁺	302 (17.7)	338 (3.56), 378 (3.14)			
cis-trans-[Re(CO) ₂ (P(OCH ₃) ₃) ₂ (bpy)] ⁺	282 (13.1), 294 (13.0), 318 (sh)	374 (3.93)			
cis-trans-[Re(CO) ₂ (P(OCH ₃)(Ph) ₂) ₂ (bpy)] ⁺	298 (15.1)	406 (3.27)			
cis-trans-[Re(CO) ₂ (P(OCH ₃) ₂ (Ph)(bpy)] ⁺	294 (14.1), 324 (sh)	394 (3.27)			

^{*a*} All complexes are the triflate salt.

group with a more net-donating ligand results in a red-shift in the absorption manifold (see Table 4).

For the *cis*-[Re(CO)₂(P–P)(N–N)]⁺ and *cis*-[Re(CO)₂(N–N)₂]⁺ complexes, lifetimes and quantum yields vary from 25 to 3840 ns and ca. 0.002 to 0.12, respectively. Inspection of the data in Table 5 reveals a variation of k_r over an order of magnitude, whereas k_{nr} varies over ca. 2.5 orders of magnitude. On the basis of previous preparative and photophysical studies of Meyer et al.,^{10,15} it is predicted that the absence of a high-frequency (>2000 cm⁻¹) CO stretching mode could result in less rapid nonradiative decay from the lowest-lying MLCT excited state manifold. Indeed, the new dicarbonyl complexes display relatively long lifetimes when compared to those of similar energy-gap behavior;¹⁵ i.e., a dicarbonyl complex of the same energy gap as that of a tricarbonyl complex has a longer lifetime. An energy-gap law plot (Figure 5) provides a visual comparison between

these classes of complexes. The plot shows the relationship between the change in $k_{\rm nr}$ (as $\ln(k_{\rm nr})$) and the excited-state energy (as $E_{\rm em}$). Table 5 provides the data used for this plot.

The Re(I) dicarbonyls slope (-1.209 eV^{-1}) is less steep than that of the Re(I) tricarbonyls (-1.458 eV^{-1}) . This difference is probably due to decreased vibrational overlap between excited- and ground-state surfaces, resulting from the loss of a high-frequency CO stretching mode, and thus the corresponding changes to the Franck–Condon factors relative to the tricarbonyl species. The *y*-intercept is also markedly smaller (34.46 for dicarbonyls vs 40.16 for tricarbonyls). This implies a decrease in the vibrationally induced electronic coupling between the excited state and ground state. Both of these considerations lead to longer lifetimes by a comparatively slower radiationless decay.

By comparison, energy-gap law plots for $Ru(II)^{16}$ and $Os(II)^{17}$ bipyridine complexes show similar results. For these

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Table 5. Luminescence Properties for Phosphine–Diimine or Diphosphine–Diimine Complexes of $Re(I)^a$

complex	$\lambda_{\rm em}{}^b$ (nm)	$\Phi_{\mathrm{em}}{}^b$	τ^{b} (ns)	$k_{\rm r}^{c} \times 10^4 ({ m s}^{-1})$	$k_{\rm nr}{}^c \times 10^6 ({\rm s}^{-1})$	ln k _{nr}
<i>cis</i> -[Re(CO) ₂ (bpy) ₂] ⁺	704	0.0017	25	6.80	39.9	17.5026
cis-[Re(CO) ₂ (phen) ₂] ⁺	712	0.0032	126	7.91	7.91	15.8838
cis-[Re(CO) ₂ (bpy)(dppm)] ⁺	642	0.020	768	2.60	1.28	14.0592
cis-[Re(CO) ₂ (phen)(dppm)] ⁺	644	0.031	2900	1.07	0.334	12.7193
<i>cis</i> -[Re(CO) ₂ (bpy)(<i>c</i> -dppene)] ⁺	612	0.033	378	8.73	2.56	14.7547
cis-[Re(CO) ₂ (phen)(c-dppene)] ⁺	603	0.12	3840	3.20	0.228	12.3389
cis-[Re(CO) ₂ (bpy)(diphos)] ⁺	624	0.027	325	8.31	2.99	14.9121
cis-trans-[Re(CO) ₂ (PPh ₃) ₂ (bpy)] ⁺	620	0.039	775	5.03	1.24	14.0306
<i>cis-trans</i> -[Re(CO) ₂ (P(OPh) ₃) ₂ (bpy)] ⁺	568	0.11	1147	9.59	0.776	13.5619
<i>cis-trans</i> -[Re(CO) ₂ (P(OPh) ₃) ₂ (phen)] ⁺	556	0.24	9700	2.47	0.0784	11.2696
cis-trans-[Re(CO) ₂ (P(OCH ₃) ₃) ₂ (bpy)] ⁺	614	0.017	375	4.53	2.62	14.7787
cis-trans-[Re(CO) ₂ (P(OCH ₃)(Ph) ₂) ₂ (bpy)] ⁺	618	0.037	447	8.28	2.15	14.5810
cis-trans-[Re(CO) ₂ (P(OCH ₃) ₂ (Ph)(bpy)] ⁺	610	0.035	547	6.40	1.76	14.3808
<i>cis-trans</i> -[Re(CO) ₂ (<i>t</i> -dppene) ₂ (bpy)] ^{+d}	637	0.014	191	7.33	5.16	15.4569
cis-trans-[Re(CO) ₂ (dppm) ₂ (bpy)] ^{+d}	634	0.014	199	7.04	4.96	15.4159

^{*a*} All complexes are the triflate salt. Spectra obtained in dearated CH₂Cl₂ at room temperature. ^{*b*} λ_{em} is the wavelength of maximum emission, Φ_{em} is the emission quantum yield, and τ is the excited-state lifetime. ^{*c*} k_r and k_{nr} are the radiative and nonradiative rate constants for excited-state decay, respectively. ^{*d*} Data from ref 7b. *t*-Dppene is *trans*-1,2-bis(diphenylphosphino)ethylene.



Figure 5. Energy-gap law plot for Re(I) diimine dicarbonyl complexes (solid line) and Re(I) diimine tricarbonyl complexes (dashed line). (\diamond) *cis*-*trans*-[Re(CO)₂(PPh₃)₂(bpy)]⁺ and (\triangle) *cis*-[Re(CO)₂(dppm)(bpy)]⁺, which were omitted from the best-fit line. Data for the dicarbonyls can be seen in Table 5. Data for the tricarbonyls were taken from ref 15.

complexes having emissive MLCT excited states, slopes are found to be -7.49 and -7.54 eV^{-1} and intercepts are 28.05 and 29.17, respectively, when measured in CH₃CN. In fact, the photophysical properties for the lowest MLCT excited state of *cis*-[Re(CO)₂(c-dppene)(bpy)]⁺ in CH₂Cl₂ are similar to those of [Ru(bpy)₃]²⁺ ($\lambda_{em} = 606 \text{ nm}, \tau = 488 \text{ ns}, \phi =$ 0.029)¹⁸ in CH₂Cl₂, and the photophysical properties of *cis*-[Re(CO)₂(Ph₂phen)₂]⁺ in CH₂Cl₂ are similar to those of [Os(bpy)₃]²⁺ in CH₃CN ($\lambda_{em} = 746 \text{ nm}, \phi = 0.00462$).¹⁷

(17) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. J. Am. Chem. Soc. 1982, 104, 630–632. Complexes of both Ru(II) and Os(II) are widely studied for practical use as molecular probes, sensors, and photosensitizers for solar energy conversion.¹⁷ This suggests that similar applications are available for Re(I) dicarbonyl complexes.

Conclusion

A series of Re(I) dicarbonyls was synthesized and studied, showing promising results to photochemical applications due to their long-lived excited-state lifetimes and high quantum yields. Four synthetic routes were developed to provide flexibility in the synthesis of other dicarbonyl species with mixed-ligand coordination spheres. The correlation to Lever parameters acts as a predictor of electrochemical and spectral properties of these systems and can be used to interpret the properties of the individual ligands.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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