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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 luminescence[1] from low-lying, tunable metal−ligand charge transfer (MLCT) ($d\pi(M)$ to $\pi^*(L)$) excited states, Re(I) diimine tricarbonyls have been applied in solar-energy conversion schemes[2], sensor development[3], 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 fitting[5] and excited-state resonance Raman spectroscopy[6] 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.

This paper deals with our quest to prepare novel mixed-ligand rhenium(I) dicarbonyls, which indeed possess long-lived 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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* Author to whom correspondence should be addressed. E-mail: bpat@uwyo.edu.

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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 $^{31}P\{^1H\}$ NMR spectra were recorded in acetonitrile on a Brüker GSX400 spectrometer. ^1H NMR spectra were internally referenced to the solvent, whereas ^{31}P NMR spectra were externally referenced to 85% H_3PO_4. 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 N_2 for 10 min prior to scanning. Emission and excitation spectra were obtained in N_2-purged CH_2Cl_2 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). Manufacturer-supplied 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 N_2-purged CH_3CN) or *fac*-$[Re(CO)_3(bpy)py](CF_3SO_3)$ ($\phi_{em} = 0.012$ in air-saturated H_2O; 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) continuous-wave 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 (PPh_3), triphenyl phosphite ($P(OPh)_3$), trimethyl phosphite ($P(OCH_3)_3$), methyldiphenylphosphinite ($P(OCH_3)(Ph)_2$), and dimethylphenylphosphonite ($P(OCH_3)_2(Ph)$) were obtained from Sigma-Aldrich. 4,7-Diphenyl-1,10-phenanthroline (Ph_2phen)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 CH_3CN/Et_2O, and dried in vacuo prior to use. Acidic alumina was purchased from Fisher and Sigma-Aldrich. Acetonitrile-d_3 (CD_3CN) 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 $CF_3SO_3^-$, and P−P is a chelating phosphine) were prepared according to literature.[7,9] The previously reported *cis-trans*-$[Re(CO)_2(PPh_3)_2(bpy)]PF_6$[10] was synthesized by a new method.[7] *mer*-$Re(CO)_3(PPh_3)_2Cl$ 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 CH_2Cl_2/CH_3OH.

Method I: Synthesis from *fac*-Re(CO)$_3$(N−N)(CF$_3$SO$_3$). *cis*-[Re(CO)$_2$(bpy)(dppm)](CF$_3$SO$_3$) (1a). *fac*-$Re(CO)_3(bpy)(CF_3SO_3)$ (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 *o*-dicholorobenzene (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 CH_2Cl_2/CH_3CN and gradually increasing the amount of CH_3CN in the eluant. The product was reprecipitated from CH_2Cl_2 into stirring diethyl ether. Yield: 283 mg (78%). Elemental Anal. Calcd for $C_{38}H_{30}N_2O_5P_2F_3SRe$: C, 48.98; H, 3.25; N 3.01. Found: C, 48.84; H, 3.34; N, 2.97. ^1H NMR (δ/ppm, CD_3CN): 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). $^{31}P\{^1H\}$ NMR (δ/ppm, CD_3CN): −15.5 (s), −27.5 (d, $J = 5$ Hz). UV−visible (λ (nm), CH_2Cl_2) (ϵ in M^{-1} cm^{-1}): 282 (21900), 302 (sh, 15700), 346 (3730), 438 (3270). IR (CH_2Cl_2) (ν(CO), cm^{-1}): 1950, 1884.

***cis*-[Re(CO)$_2$(phen)(dppm)](CF$_3$SO$_3$) (1b).** Synthesis and purification were the same as for **1a** except that 0.208 g (0.346 mmol) of *fac*-$Re(CO)_3(phen)(CF_3SO_3)$ and 0.157 g (0.408 mmol) of dppm were used. Yield: 245 mg (74%). Elemental Anal. Calcd for $C_{40}H_{30}N_2O_5P_2F_3SRe$: C, 50.26; H, 3.16; N 2.93. Found: C, 50.31; H, 3.20; N, 3.03. ^1H NMR (δ/ppm, CD_3CN): 9.97 (d, 1H, $J = 5.0$ Hz), 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). $^{31}P\{^1H\}$ NMR (δ/ppm, CD_3CN): −15.9 (d, $J = 5$ Hz), −27.3 (d, $J = 5$ Hz). UV−visible (λ (nm), CH_2Cl_2) (ϵ in $M^{-1}cm^{-1}$): 262 (sh, 30300), 270 (33400), 292 (sh, 16600), 336 (sh, 4140), 384 (4380), 426 (4380). IR (CH_2Cl_2) (ν(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)(CF$_3$SO$_3$) and 0.237 g (0.598 mmol) of *c*-dppene were used. Yield: 402 mg (80%). Elemental Anal. Calcd for $C_{39}H_{30}N_2O_5P_2F_3SRe$: C, 49.63; H, 3.20; N 2.97. Found: C, 49.74; H, 3.17; N, 3.05. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 52.2 (d, $J = 19$ Hz), 42.2 (d, $J = 19$ Hz). UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 272 (21400), 390 (3440). IR (CH$_2$Cl$_2$) (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)(CF$_3$SO$_3$) and 0.278 g (0.701 mmol) of *c*-dppene were used. Yield: 584 mg (81%). Elemental Anal. Calcd for $C_{41}H_{30}N_2O_5P_2F_3SRe$: C, 50.88; H, 3.12; N 2.89. Found: C, 50.86; H, 3.06; N, 2.99. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 53.2 (d, $J = 19$ Hz), 43.2 (d, $J = 19$ Hz). UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 266 (32700), 298 (sh, 12400), 344 (4570), 376 (5050), 420 (sh, 3960). IR (CH$_2$Cl$_2$) (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)(CF$_3$SO$_3$) 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 $C_{39}H_{32}N_2O_5P_2F_3SRe$: C, 49.52; H, 3.41; N 2.96. Found: C, 49.31; H, 3.42; N, 2.84. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 44.5 (d, $J = 4$ Hz), 35.7 (d, $J = 5$ Hz). UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 278 (21200), 344 (sh, 3430), 392 (3210), 430 (sh, 2790). IR (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1952, 1881.

***cis*-[Re(CO)$_2$(Ph$_2$phen)(dppm)](CF$_3$SO$_3$) (1f).** Synthesis and purification were the same as for **1a** except that 0.274 g (0.364 mmol) of *fac*-Re(CO)$_3$(Ph$_2$phen)(CF$_3$SO$_3$) and 0.165 g (0.429 mmol) of dppm were used. Purification was done by column chromatography, followed by repeated reprecipitation from CH$_3$CN into stirring diethyl ether. Yield: 194 mg (65%). Elemental Anal. Calcd for $C_{52}H_{38}N_2O_5P_2F_3SRe$: C, 56.36; H, 3.46; N 2.53. Found: C, 56.56; H, 3.54; N, 2.58. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): −16.3 (d, $J = 5$ Hz), −27.3 (d, $J = 5$ Hz). UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 286 (43700), 316 (sh, 17700), 350 (7910), 394 (7790), 426 (7690). IR (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1949, 1883.

***cis*-[Re(CO)$_2$(Ph$_2$phen)(*c*-dppene)](CF$_3$SO$_3$) (1g).** Synthesis and purification were the same as for **1a** except that 0.200 g (0.266 mmol) of *fac*-Re(CO)$_3$(Ph$_2$phen)(CF$_3$SO$_3$) 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 $C_{53}H_{38}N_2O_5P_2F_3SRe$: C, 56.83; H, 3.42; N 2.50. Found: C, 56.63; H, 3.46; N, 2.45. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 53.2 (d, $J = 19$ Hz), 42.6 (d, $J = 19$ Hz). UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 278 (37900), 286 (38500), 318 (sh, 15400), 352 (9200), 380 (9680), 428 (sh, 7310). IR (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1958, 1889.

***cis-trans*-[Re(CO)$_2$(PPh$_3$)$_2$(bpy)](CF$_3$SO$_3$) (1h).** *fac*-Re(CO)$_3$(bpy)(CF$_3$SO$_3$) (0.150 g (0.260 mmol)) and triphenylphosphine (PPh$_3$) (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 N$_2$ for 20 min. The reaction was stirred at reflux under N$_2$ 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 $C_{49}H_{38}N_2O_5P_2F_3SRe$: C, 54.90; H, 3.57; N 2.61. Found: C, 53.70; H, 3.64; N, 2.27. ^{1}H NMR (δ/ppm, CD$_3$CN): 8.33 (d, 2H, $J = 8.5$ Hz), 8.04 (d, 2H, $J = 5.2$ Hz), 7.91 (t, 2H, $J = 7.7$ Hz), 7.30 [7.35−7.26] (m, 30H), 6.96 (t, 2H, $J = 6.4$ Hz). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 24.6. UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 298 (15700), 306 (13300), 422 (24500). IR (CH$_2$Cl$_2$) (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)(CF$_3$SO$_3$) 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. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 104.2. UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 286 (10900), 320 (70300), 372 (31400). IR (CH$_2$Cl$_2$) (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)(CF$_3$SO$_3$) 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 $C_{51}H_{38}N_2O_{11}P_2F_3SRe$: C, 51.39; H, 3.21; N, 2.35. Found: C, 51.52; H, 3.27; N, 2.41. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 103.9. UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 302 (17700), 338 (35600), 378 (31400). IR (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1984, 1914.

***cis-trans*-[Re(CO)$_2$(P(OCH$_3$)$_3$)$_2$(bpy)](CF$_3$SO$_3$) (1k).** Synthesis and purification were the same as for **1h** except that 0.215 g (0.374

mmol) of *fac*-Re(CO)$_3$(bpy)(CF$_3$SO$_3$) 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 $C_{19}H_{26}N_2O_{11}P_2F_3SRe$: C, 26.68; H, 3.29; N, 3.52. Found: C, 28.06; H, 3.32; N, 3.44. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 122.4. UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 282 (13100), 294 (13000), 318 (sh), 374 (39300). IR (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1961, 1888.

***cis-trans*-[Re(CO)$_2$(P(OCH$_3$)(Ph)$_2$)$_2$(bpy)](CF$_3$SO$_3$) (1l).** Synthesis and purification were the same as for **1h** except that 0.115 g (0.200 mmol) of *fac*-Re(CO)$_3$(bpy)(CF$_3$SO$_3$) and 2 mL (9.97 mmol) of methyldiphenylphosphinite (P(OCH$_3$)(Ph)$_2$) were used. The product was light yellow. Yield: 176 mg (90%) Elemental Anal. Calcd for $C_{39}H_{34}N_2O_7P_2F_3SRe$: C, 47.80; H, 3.50; N, 2.86. Found: C, 47.91; H, 3.54; N, 2.79. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 119.7. UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 298 (15100), 406 (32700). IR (CH$_2$Cl$_2$) (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)(CF$_3$SO$_3$) and 2 mL (12.6 mmol) of dimethylphenylphosphonite (P(OCH$_3$)$_2$(Ph)) were used. The product was light yellow. Yield: 228 mg (90%) Elemental Anal. Calcd for $C_{29}H_{30}N_2O_9P_2F_3SRe$: C, 39.24; H, 3.41; N, 3.16. Found: C, 39.29; H, 3.44; N, 3.14. ^{1}H NMR (δ/ppm, CD$_3$CN): 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). ^{31}P{^{1}H} NMR (δ/ppm, CD$_3$CN): 149.2. UV−visible (λ (nm), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 294 (14100), 324 (sh), 394 (32700). IR (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1957, 1866.

Method II: Synthesis from *fac*-Re(CO)$_3$(P−P)Cl. *cis*-[Re(CO)$_2$(dppm)(bpy)](PF$_6$) (2a). *fac*-Re(CO)$_3$(dppm)Cl (0.100 g (0.145 mmol)), TlPF$_6$ (0.053 g (0.15 mmol)), and bpy (0.025 g (0.16 mmol)) were combined with ca. 5 mL of ODB in a round-bottom flask covered with aluminum foil. The solution was refluxed for 7 h under N$_2$, undergoing a color change from white to yellow-orange. 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 $C_{37}H_{30}$ $N_2O_2P_3$ F_6Re: 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)](PF$_6$) (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 TlPF$_6$, 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 $C_{39}H_{30}$ $N_2O_2P_3$ F_6Re: 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)Cl, 0.053 g (0.15 mmol) of TlPF$_6$, 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 $C_{38}H_{30}$ $N_2O_2P_3$ F_6Re: 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 TlPF$_6$, 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 $C_{40}H_{30}N_2O_2P_3$ F_6Re: 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)$_3$(PPh$_3$)$_2$Cl via Phosphine Displacement. *cis*-Re(CO)$_2$(PPh$_3$)(*c*-dppene)Cl (3a). *mer*-Re(CO)$_3$(PPh$_3$)$_2$Cl **(**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 N$_2$ 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 CH$_2$Cl$_2$. 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 $C_{46}H_{37}O_2P_3ClRe$: C, 59.00; H, 3.98. Found: C, 57.63; H, 4.15. ^{1}H NMR (δ/ppm, CDCl$_3$): 7.34 [7.80−6.89] (m, 35H), 3.51 (t, 2H, $J = 2.08$ Hz). ^{31}P{^{1}H} NMR (δ/ppm, CDCl$_3$): 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), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 282 (51400), 290 (45500). IR (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1948, 1866.

***cis*-Re(CO)$_2$(PPh$_3$)(*c*-dppene)(CF$_3$SO$_3$) (3b).** *cis*-Re(CO)$_2$(PPh$_3$)(*c*-dppene)Cl (0.103 g (0.110 mmol)) and AgSO$_3$CF$_3$ (0.034 g (0.13 mmol)) were added to a round-bottom flask with ca. 20 mL of CH$_2$Cl$_2$. 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 CH$_2$Cl$_2$ with hexanes, collected by suction filtration, and washed with CH$_3$OH and hexanes. Yield: 98 mg (82%). Elemental Anal. Calcd for $C_{47}H_{37}O_5P_3F_3SRe$: C, 53.71; H, 3.55. Found: C, 53.86; H, 3.99. ^{1}H NMR (δ/ppm, CDCl$_3$): 7.00 [7.70−6.30] (m, 35H), 1.26 (s, 2H). ^{31}P{^{1}H} NMR (δ/ppm, CDCl$_3$): 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), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 270 (68570), 276 (50790). IR (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1981, 1922.

***cis*-[Re(CO)$_2$(*c*-dppene)(bpy)](CF$_3$SO$_3$) (3c).** *cis*-Re(CO)$_2$(PPh$_3$)(*c*-dppene)(SO$_3$CF$_3$) (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 (CH$_2$Cl$_2$) (ν(CO), cm^{-1}): 1971, 1904). The resulting [Re(CO)$_2$(PPh$_3$)(*c*-dppene)(CH$_3$CN)](SO$_3$CF$_3$) was combined with 10.3 mg (0.066 mmol) of 2,2′-bipyridine in ca. 10 mL of toluene. The solution was purged with N$_2$ 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 CH$_2$Cl$_2$ 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)](CF$_3$SO$_3$) (3d).** Synthesis and purification were the same as for **3c** except that 0.057 g (0.054 mmol) of *cis*-[Re(CO)$_2$(PPh$_3$)(*c*-dppene)(CH$_3$CN)]SO$_3$CF$_3$ 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**.

Method IV: The "Melt Method". *cis*-[Re(CO)$_2$(bpy)$_2$](CF$_3$SO$_3$) (4a). *fac*-Re(bpy)(CO)$_3$(CF$_3$SO$_3$) (0.320 g (0.555 mmol)) and a large excess of bpy were placed in a 14 in. × 0.75 in. tube. The tube was capped with a septum and purged with N$_2$. 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 CH$_2$Cl$_2$ and transferred from the tube. Purification was achieved by column chromatography on acidic alumina with CH$_2$Cl$_2$/CH$_3$CN mixtures. Reprecipitation was accomplished from the addition of methylene chloride into stirring diethyl ether. Yield: 317 mg (81%). Elemental Anal. Calcd for C$_{23}$H$_{16}$N$_4$O$_5$F$_3$SRe: C, 39.26; H, 2.29; N, 7.96. Found: C, 39.43; H, 2.32; N, 7.91. ^{1}H NMR (δ/ppm, CD$_3$CN): 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), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 288 (47400), 364 (6100), 400 (6590), 492 (5320), 564 (sh, 3660). IR (CH$_2$Cl$_2$) (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)$_3$(CF$_3$SO$_3$) 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 C$_{27}$H$_{16}$N$_4$O$_5$F$_3$SRe·1/2H$_2$O: C, 42.13; H, 2.36; N, 7.28. Found: C, 42.17; H, 2.31; N, 7.31. ^{1}H NMR (δ/ppm, CD$_3$CN): 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), CH$_2$Cl$_2$) (ϵ in M^{-1} cm^{-1}): 266 (70600), 294 (sh, 20500), 358 (sh, 4930), 412 (8650), 476 (7030), 540 (5050). IR (CH$_2$Cl$_2$) (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(Ph$_2$phen)(CO)$_3$(CF$_3$SO$_3$) and an excess of Ph$_2$phen 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 C$_{51}$H$_{32}$N$_4$O$_5$F$_3$SRe·1/2H$_2$O: C, 58.00; H, 3.05; N, 5.30. Found: C, 58.23; H, 3.23; N, 5.33. ^{1}H NMR (δ/ppm, CD$_3$CN): 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 = 5.5 Hz), 7.75 (m, 4H), 7.68 (m, 6H), 7.53 (m, 6H), 7.48 (d, 3H, J = 5.0 Hz), 7.44 (m, 3H). UV−visible (λ (nm), CH$_2$Cl$_2$) (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 (CH$_2$Cl$_2$) (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)(PR$_3$)$_3$]$^+$ (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.

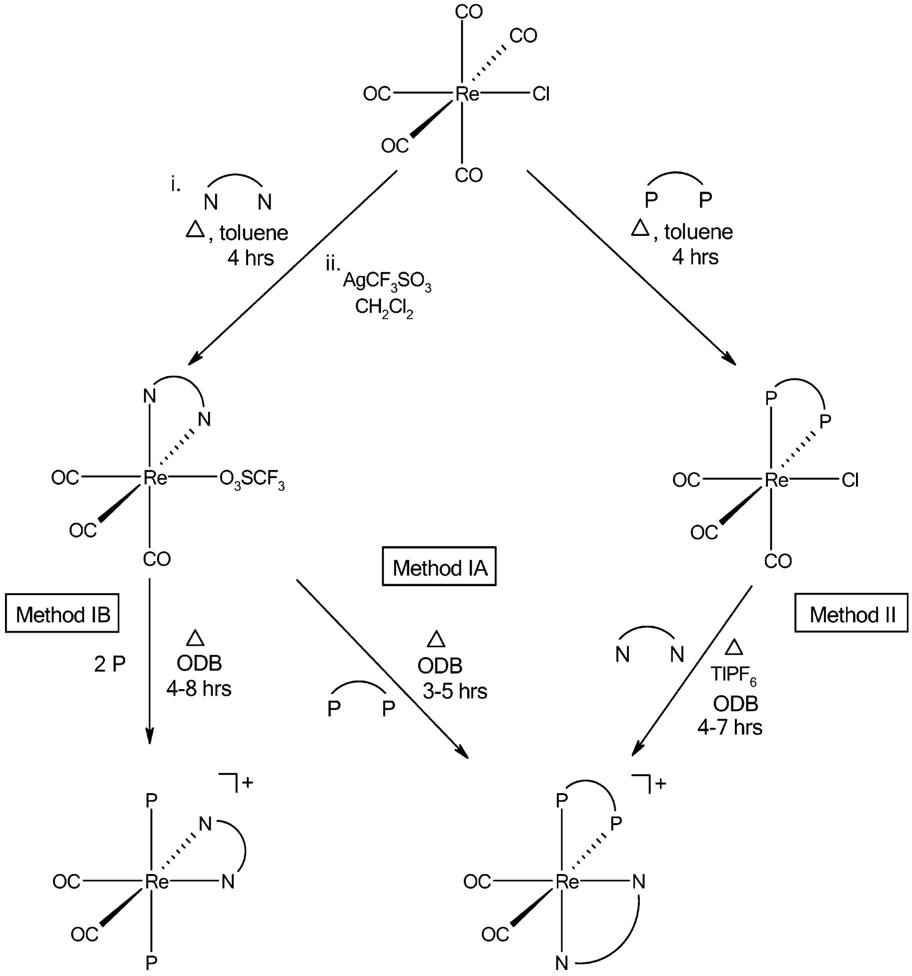
Method I relies on the displacement of a labile triflate and CO ligand by a phosphine donor, either monodentate (IA) or bidentate (IB). Method II reverses the order of binding, allowing the phosphine to bind first, followed by the use of its trans-labilizing ability to bind a bpy or phen ligand. Reaction 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$_3$SO$_3$$^-$) was isolated, but further reaction with polypyridines resulted in *fac*-Re(CO)$_3$(N−N)L (where L is Cl$^-$ or CF$_3$SO$_3$$^-$). It has also been observed that, once the polypyridine group is bound, these weakly coordinating ligands will not bind in the same manner as described above. In this case, *fac*-Re(CO)$_3$(N−N)L (where L is Cl$^-$ or CF$_3$SO$_3$$^-$) was isolated, but further reaction with a chelating phosphine resulted in no reaction. These attempts, under various solvents (DCE, mesitylene, ODB, toluene, etc.) and thermal conditions, resulted in the same product, *fac*-Re(CO)$_3$(N−N)L (where L is Cl$^-$ or CF$_3$SO$_3$$^-$), each time. This led to a new approach for making complexes of the type *cis*-[Re(CO)$_2$(P−P)(N−N)]$^+$. The combination of the complex *mer-trans*-Re(CO)$_3$(PPh$_3$)$_2$Cl and a strongly binding polypyridine ligand as an entering group, leads to the synthetic route shown in Scheme 2 that allows "customization" of the trans-labilizing effect. By starting with a *mer*-tricarbonyl species, it is easy to displace a CO due to the trans-labilizing effect of the other CO. One of the PPh$_3$'s is also easily displaced due to the trans-labilizing effect of the phosphine. This allows a chelating phosphine to bind easily, forming *cis*-Re(CO)$_2$(P−P)(PPh$_3$)Cl. The chealting phosphine then creates a trans-labilizing effect on the remaining PPh$_3$ ligand. Finally, labilization of the Cl via triflate metathesis followed by CH$_3$CN 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 CH$_3$CN gives a complex that is susceptible to polypyridine reaction via dissociation of the remaining PPh$_3$ and CH$_3$CN ligands to give products of the formulation *cis*-[Re(CO)$_2$(P−P)(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 tricarbonyl−diimine 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.

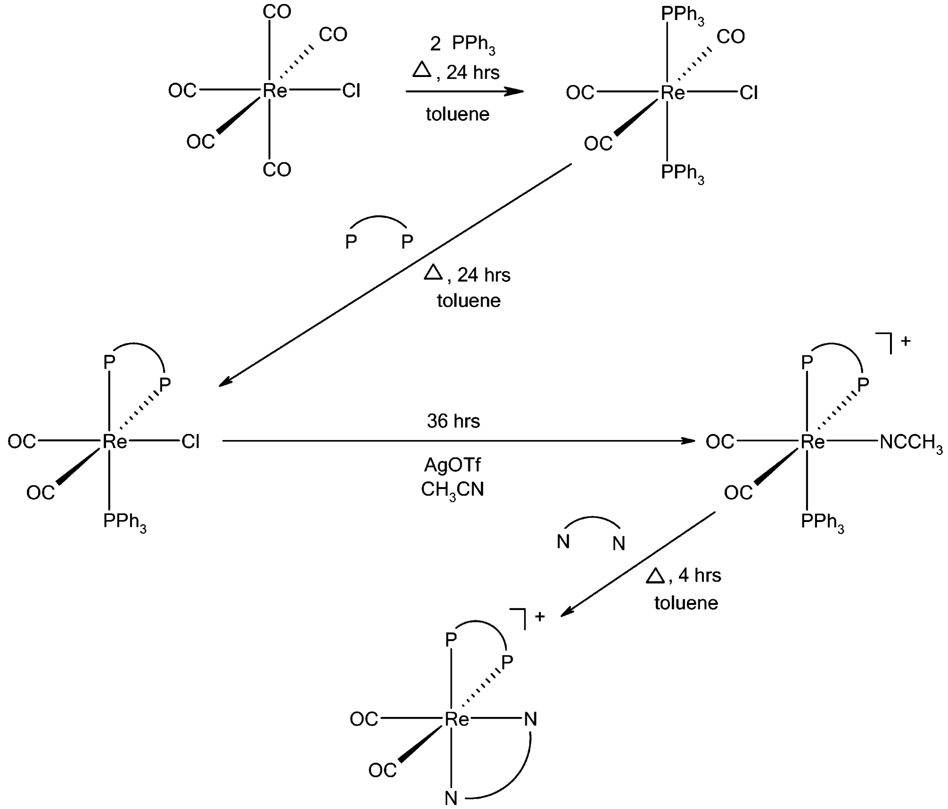
are approximately 75−85% after the products have been purified by chromatography on an alumina support.

Characterization. Characterization of the complexes was achieved by a combination of elemental analysis, IR spectroscopy, ^{31}P NMR spectroscopy, and ^{1}H NMR spectroscopy. Two intense IR bands in the 1870−1890 and 1940−1960 cm^{-1} regions and the appropriate number of ^{31}P 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 Ph_2phen > bpy, phen > dppm > diphos > *c*-dppene, corresponding to both CO modes increasing in energy (see later section on substituent effects).

The ^{31}P 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 ^{31}P NMR of $Re(CO)_2(PPh_3)$(*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 PPh_3 (10.04 ppm) in the precursor molecule, *mer*-$Re(CO)_3(PPh_3)_2Cl$, the smallest splitting ($J = 9$ Hz) on the peaks at 29.8 and 49.6 ppm is caused by the PPh_3. 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 PPh_3. The intraligand *J*-coupling for the *c*-dppene is too small to be resolved.

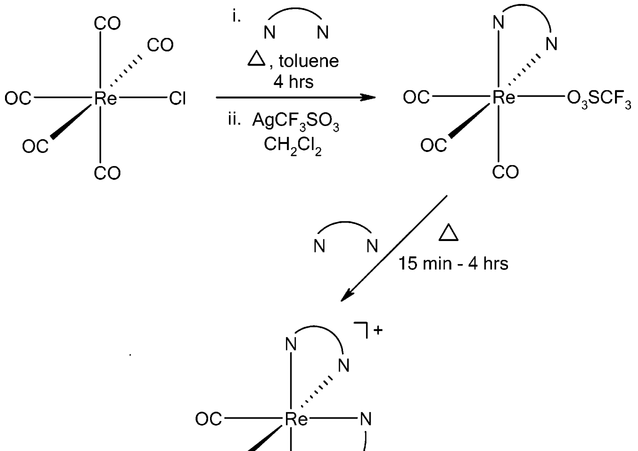
Crystal Structure Data. X-ray crystallographic data for *cis*-$Re(CO)_2(phen)_2(CF_3SO_3)\cdot 1/2CH_3CN$ is also consistent with the structural assignments of these compounds as *cis*-dicarbonyls. The crystal structure data of *cis*-$[Re(CO)_2(phen)_2](CF_3SO_3)$, *cis*-$[Re(CO)_2$(*c*-dppene)(phen)]$(PF_6)$, and *cis*-*trans*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)](CF_3SO_3)$, 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*-$[Re(CO)_2(phen)_2](CF_3SO_3)$ (Figure 2i) to 1.895(5) Å in *cis*-$[Re(CO)_2$(*c*-dppene)(phen)](PF_6) (Figure 2ii), tend to be shorter than those trans to a phosphine, which range from 1.910(5) Å in *cis*-*trans*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)](CF_3SO_3)$ (Figure 2iii) to

Scheme 2. Synthesis of Phosphine−Diimine Dicarbonyls of Rhenium(I) Complexes via Phosphine Displacement[a]



[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)](PF_6). 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*-$[Re(CO)_2(phen)_2](CF_3SO_3)$ and 2.150(4) Å in *cis*-$[Re(CO)_2$(*c*-dppene)(phen)](PF_6), 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*-$Re(CO)_2(PPh_3)$(*c*-dppene)Cl, are similar to those trans to a CO (2.4578(13) Å in *cis*-$[Re(CO)_2$(*c*-dppene)(phen)](PF_6) and 2.3868(11) Å in *cis*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)](CF_3SO_3)$). Last, when both are trans to a CO, Re−P(phosphine) bonds, 2.4578(13) Å in *cis*-$[Re(CO)_2$(*c*-dppene)(phen)](PF_6) and 2.3868(11) Å in *cis-trans*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)]$ (CF_3SO_3), 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*-$Re(CO)_2(PPh_3)$(*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*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)](CF_3SO_3)$ to 76.1(3)° in *cis*-$[Re(CO)_2(phen)_2](CF_3SO_3)$, 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*-$[Re(CO)_2(P(Ph)_2$-

Table 1. IR Spectral Bands and ^{31}P NMR Shifts for the Bis(diimine) and Phosphine−Diimine Complexes[a]

		^{31}P NMR		
compound	$\nu_{CO}{}^{b}$ (cm^{-1})	δ (ppm)	$\Delta\delta^{c}$ (ppm)	$\Delta\delta_{av}{}^{c}$ (ppm)
cis-$[Re(CO)_2(bpy)_2]^+$	1922, 1852	−	−	−
cis-$[Re(CO)_2(phen)_2]^+$	1922, 1853	−	−	−
cis-$[Re(CO)_2(Ph_2phen)_2]^+$	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
cis-$[Re(CO)_2(bpy)(c\text{-dppene})]^+$	1959, 1888	52.2, 42.2	73.2, 63.2	68.2
cis-$[Re(CO)_2(phen)(c\text{-dppene})]^+$	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
cis-$[Re(CO)_2(Ph_2phen)(dppm)]^+$	1949, 1883	−16.3, −27.3	4.2, −6.8	−1.3
cis-$[Re(CO)_2(Ph_2phen)(c\text{-dppene})]^+$	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-$Re(CO)_2(PPh_3)(c\text{-dppene})Cl^{d}$	1948, 1866	[12.8], [29.8, 49.6]	[16.4], [50.8, 70.6]	[16.4], [60.7]
cis-$Re(CO)_2(PPh_3)(c\text{-dppene})OTf^{d}$	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 ^{31}P NMR shifts in CD_3CN versus 85% H_3PO_4 as external standard: dppm (−20.5 ppm); *c*-dppene (−21.0 ppm); diphos (−11.0 ppm); PPh_3 (−3.6 ppm); $P(OPh)_3$ (129.6 ppm); $P(OCH_3)_3$ (141.8 ppm); $P(OCH_3)(Ph)_2$ (116.2 ppm); $P(OCH_3)_2(Ph)$ (161.8 ppm). [d] ^{31}P NMR taken in $CDCl_3$.

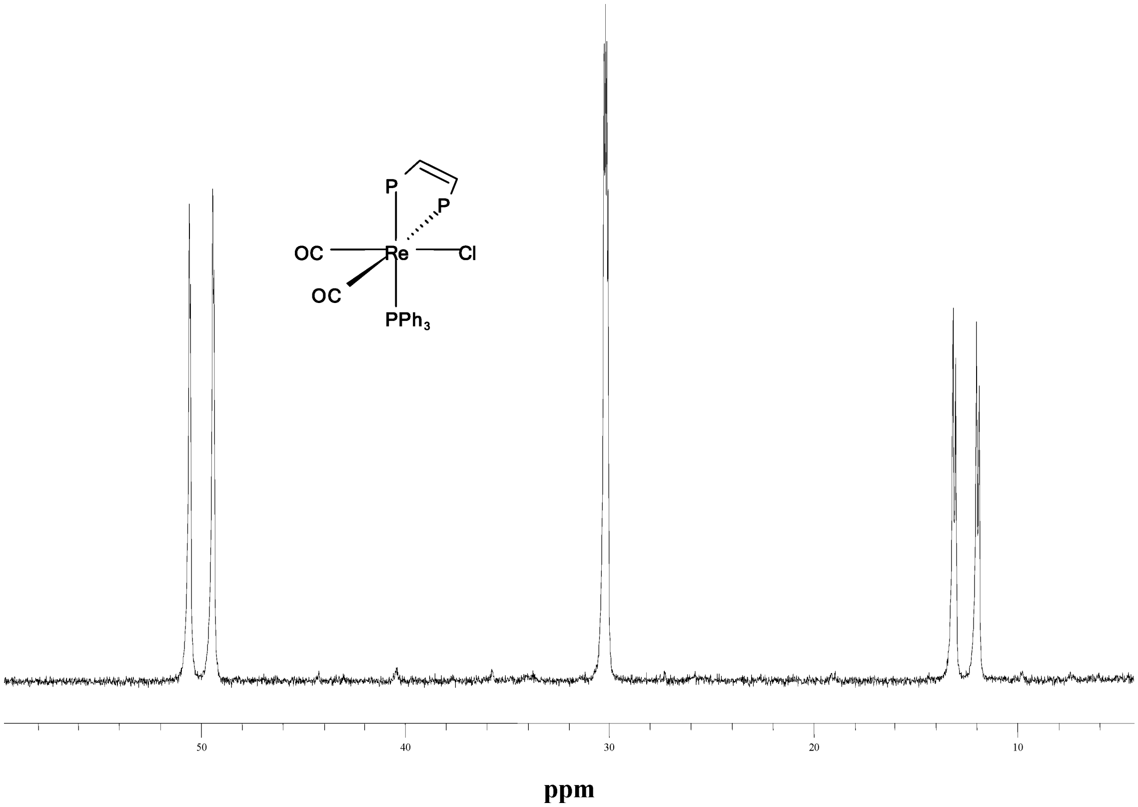


Figure 1. ^{31}P NMR of $Re(CO)_2(PPh_3)(c\text{-dppene})Cl$ showing how through-bond *J*-coupling effects can be used for the determination of structural conformation. This spectrum was taken in $CDCl_3$ with an 85% H_3PO_4 external standard. Phenyl omitted for clarity.

$(OCH_3))_2(bpy)](CF_3SO_3)$, 86.9(6)° in *cis*-$[Re(CO)_2(c\text{-dppene})(phen)](PF_6)$, and 85.6(2)° in *cis*-$[Re(CO)_2(phen)_2](CF_3SO_3)$. The trans groupings are less than 180°, also consistent with distortion of the octahedral. In *cis*-$[Re(CO)_2(phen)_2](CF_3SO_3)$, the N1−Re−N1A angle is 165.5(4)°, and the N2−Re−C1A angle is 171.7(3)°. In *cis*-$[Re(CO)_2(c\text{-dppene})(phen)](PF_6)$, 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*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)](CF_3SO_3)$, 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*-$[Re(CO)_2(c\text{-dppene})(phen)](PF_6)$ to 189.9(6)° in *cis-trans*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)](CF_3SO_3)$. 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*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)](CF_3SO_3)$

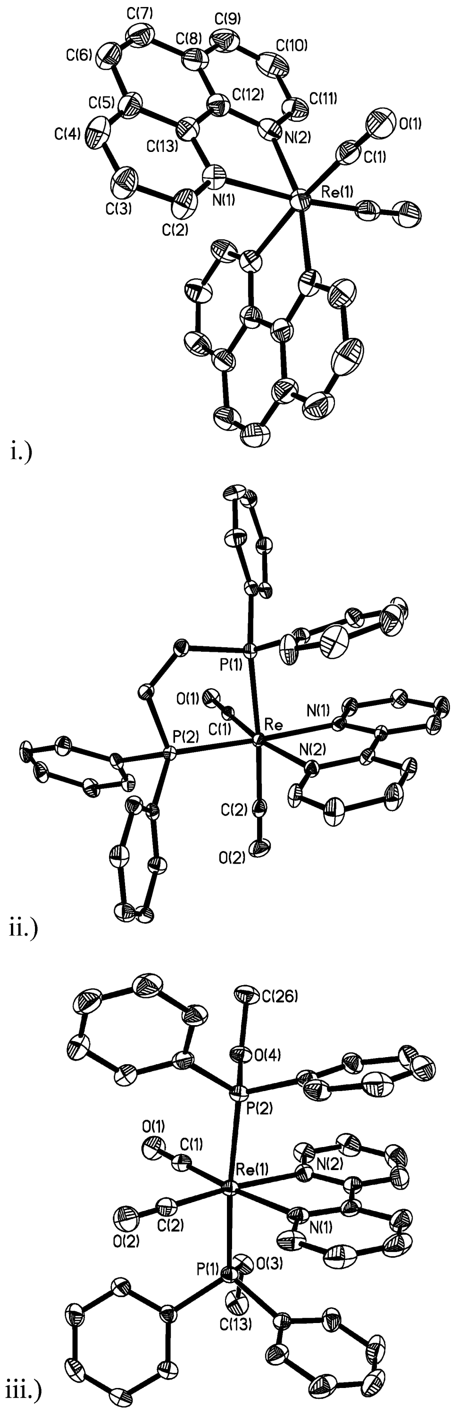


Figure 2. Crystal structures of (i) *cis*-$[Re(CO)_2(phen)_2](CF_3SO_3)$, (ii) *cis*-$[Re(CO)_2($*c*-dppene$)(bpy)](PF_6)$, and (iii) *cis*-*trans*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)](CF_3SO_3)$. Counterions and hydrogens have been omitted for clarity.

to be less distorted, 88.8(2)°, from 90° than in *cis*-$[Re(CO)_2($*c*-dppene$)(phen)](PF_6)$, 85.6(2)°.

A crystal structure for *cis*-$Re(CO)_2(PPh_3)($*c*-dppene$)Cl$ was obtained, and although the overall refinement is very poor, it confirms the structural assignment made from the ^{31}P NMR spectrum. A single molecule of acetonitrile also appears in the structure.

Electrochemical Studies. Cyclic voltammetry was performed in CH_3CN 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*-$[Re(CO)_2(Ph_2phen)(dppm)](CF_3SO_3)$, and (c) *cis*-$[Re(CO)_2(Ph_2phen)($*c*-dppene$)](CF_3SO_3)$. 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_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: $E_{obs} = S_M[\sum E_L(L)] + I_M$. In the case of the Re(II)/Re(I) couple, $S_M = 0.76$ and $I_M = -0.95$. 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 ν(CO) and the correlation to Lever parameters, it is also possible to back-calculate the E_L value of Ph_2phen, 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 ($E_L = 0.259$ 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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(12) (a) Chen, P.; Curry, M.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 2271–2280. (b) Yam, V. W.-W.; Lo, K. K.-W.; Cheung, K.-K.; Kong, R. Y.-C. *J. Chem. Soc., Chem. Commun.* **1995**, 1191–1193.

(13) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271–1285.

(14) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992.

Table 2. Electrochemical Data[a] vs SCE Obtained by Cyclic Voltammetry with Ferrocene Internal Standard[b]

complex	$E_{1/2}^{ox}$ (V)	E_{obs}[c]	$E_{1/2}^{red}$ (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-$[Re(CO)_2(Ph_2phen)_2]+$	0.88 (q)	–	−1.26 (i), −1.42 (i)
cis-$[Re(CO)_2(bpy)(dppm)]^+$	1.26 (i), 1.42 (r)	1.319	−1.33 (r), −1.63 (i)
cis-$[Re(CO)_2(phen)(dppm)]^+$	1.24 (i), 1.42 (r)	1.320	−1.35 (i), −1.69 (i)
cis-$[Re(CO)_2(bpy)(c\text{-dppene})]^+$	1.37 (r)	1.365	−1.35 (r)
cis-$[Re(CO)_2(phen)(c\text{-dppene})]^+$	1.37 (r)	1.366	−1.38 (i)
cis-$[Re(CO)_2(bpy)(diphos)]^+$	1.32 (r)	1.342	−1.35 (r)
cis-$[Re(CO)_2(Ph_2phen)(dppm)]^+$	1.22 (i), 1.39 (r)	N/A	−1.29 (r), −1.57 (i)
cis-$[Re(CO)_2(Ph_2phen)(c\text{-dppene})]^+$	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-$Re(CO)_2(PPh_3)(c\text{-dppene})Cl$[d]	1.02 (r)	1.282	–
cis-$Re(CO)_2(PPh_3)(c\text{-dppene})OTf$[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 CH_3CN 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. Ph_2phen value is not given in ref 14. [d] Taken in CH_2Cl_2. All other conditions were the same.

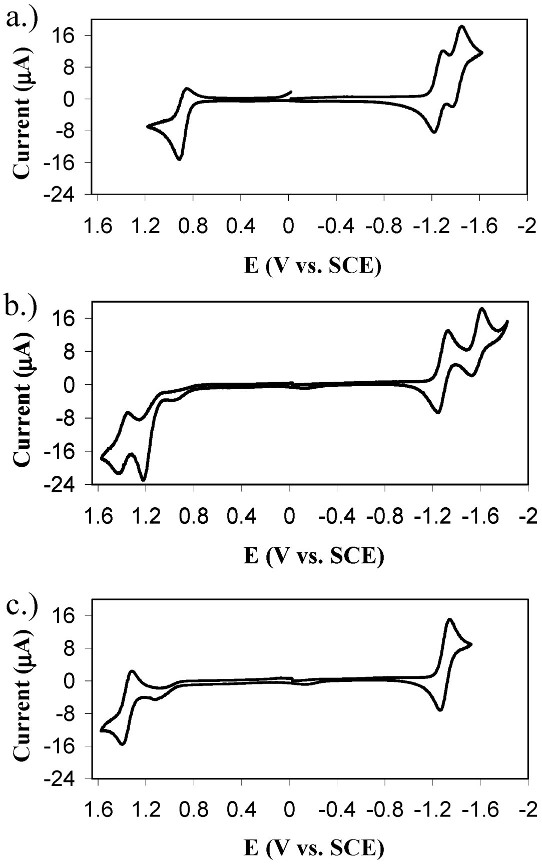

Figure 3. Typical cyclic voltammograms for the dicarbonyls for (a) *cis*-$[Re(CO)_2(Ph_2phen)_2](OTf)$, (b) *cis*-$[Re(CO)_2(Ph_2phen)(dppm)](OTf)$, and (c) *cis*-$[Re(CO)_2(Ph_2phen)(c\text{-dppene})](OTf)$. Scans were taken at 20 mV/s in CH_3CN with a ca. 0.1 M TBAH supporting electrolyte. Pt button was used as the working electrode with a Ag/AgCl reference electrode.

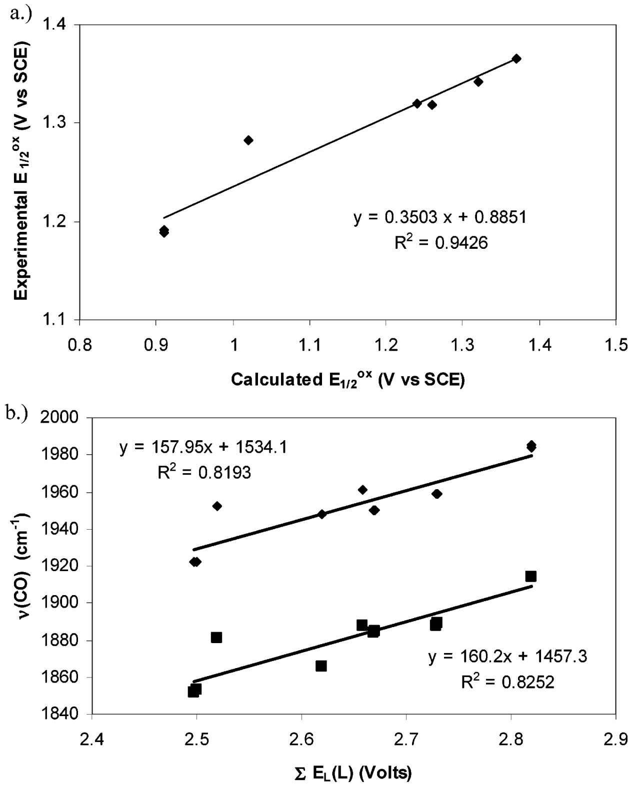

Figure 4. Calculated electrochemical oxidation potentials from E_L parameters vs (a) observed oxidation potentials and (b) IR stretching frequencies for Re(I) dicarbonyl complexes. Cyclic voltammetry data was taken at 20 mV/s in CH_3CN with a ca. 0.1 M TBAH supporting electrolyte. Pt button was used as the working electrode with a Ag/AgCl reference electrode. IR spectral data was taken in CH_2Cl_2.

d^6 polypyridine complexes.[14] This is further supported by their insensitivity to ligand sphere composition. Lower-energy 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 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 and Angles of Interest for Different Classes of Rhenium(I) Dicarbonyl Species

	cis-$[Re(CO)_2(phen)_2](CF_3SO_3)$	*cis*-$[Re(CO)_2$(*c*-dppene)(phen)](PF_6)	*cis-trans*-$[Re(CO)_2(P(Ph)_2(OCH_3))_2(bpy)]$ (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 of Dicarbonyls Obtained in CH_2Cl_2

	λ_{max} (nm) ($\epsilon \times 10^{-3}$, $M^{-1}\,cm^{-1}$)	
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-$[Re(CO)_2(Ph_2phen)_2]^+$	280 (83.1), 298 (sh), 320 (sh)	368 (sh), 422 (13.2), 498 (sh), 568 (sh)
cis-$[Re(CO)_2(bpy)(dppm)]^+$	282 (21.9), 302 (sh)	346 (3.73), 438 (3.27)
cis-$[Re(CO)_2(phen)(dppm)]^+$	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)
cis-$[Re(CO)_2(bpy)(diphos)]^+$	278 (21.2)	344 (sh), 392 (3.21), 430 (sh)
cis-$[Re(CO)_2(Ph_2phen)(dppm)]^+$	286 (43.7), 316 (sh)	350 (7.91), 394 (7.79), 426 (7.69)
cis-$[Re(CO)_2(Ph_2phen)$(*c*-dppene)$]^+$	278 (37.9), 286 (38.5), 318 (sh)	352 (9.20), 380 (9.68), 428 (sh)
cis-trans-$[Re(CO)_2(PPh_3)_2(bpy)]^+$	298 (15.7), 306 (13.3)	422 (2.45)
cis-trans-$[Re(CO)_2(P(OPh)_3)_2(bpy)]^+$	286 (10.9), 320 (7.03)	372 (3.14)
cis-trans-$[Re(CO)_2(P(OPh)_3)_2(phen)]^+$	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_{nr} (as $\ln(k_{nr})$) and the excited-state energy (as E_{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

Table 5. Luminescence Properties for Phosphine−Diimine or Diphosphine−Diimine Complexes of Re(I)[a]

complex	$\lambda_{em}{}^{b}$ (nm)	$\Phi_{em}{}^{b}$	τ^{b} (ns)	$k_r{}^{c} \times 10^4$ (s^{-1})	$k_{nr}{}^{c} \times 10^6$ (s^{-1})	ln k_{nr}
cis-$[Re(CO)_2(bpy)_2]^+$	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
cis-[Re(CO)$_2$(bpy)(*c*-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
cis-trans-$[Re(CO)_2(P(OPh)_3)_2(bpy)]^+$	568	0.11	1147	9.59	0.776	13.5619
cis-trans-$[Re(CO)_2(P(OPh)_3)_2(phen)]^+$	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
cis-trans-[Re(CO)$_2$(*t*-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 CH_2Cl_2 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.

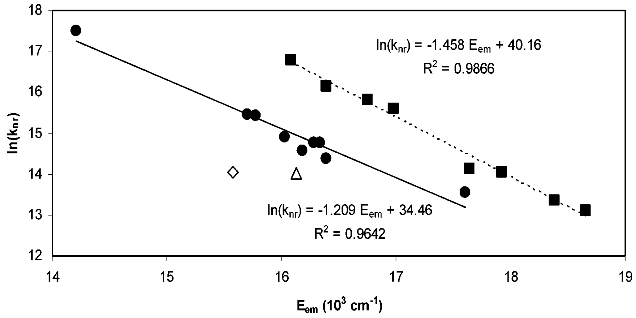

Figure 5. Energy-gap law plot for Re(I) diimine dicarbonyl complexes (solid line) and Re(I) diimine tricarbonyl complexes (dashed line). (◇) *cis-trans*-$[Re(CO)_2(PPh_3)_2(bpy)]^+$ and (△) *cis*-$[Re(CO)_2(dppm)(bpy)]^+$, which were omitted from the best-fit line. Data for the dicarbonyls can be seen 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 CH_3CN. In fact, the photophysical properties for the lowest MLCT excited state of *cis*-[Re(CO)$_2$(c-dppene)(bpy)]$^+$ in CH_2Cl_2 are similar to those of $[Ru(bpy)_3]^{2+}$ ($\lambda_{em} = 606$ nm, $\tau = 488$ ns, $\phi = 0.029$)[18] in CH_2Cl_2, and the photophysical properties of *cis*-$[Re(CO)_2(Ph_2phen)_2]^+$ in CH_2Cl_2 are similar to those of $[Os(bpy)_3]^{2+}$ in CH_3CN ($\lambda_{em} = 746$ nm, $\phi = 0.00462$).[17] 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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