

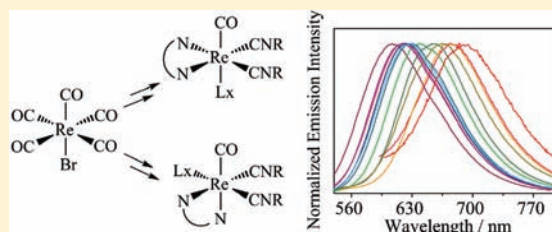
Synthesis, Functionalization, Characterization, and Photophysical Study of Carbonyl-Containing Isocyano Rhenium(I) Diimine Complexes

Apple Wai-Yi Cheung, Larry Tso-Lun Lo, Chi-Chiu Ko,* and Shek-Man Yiu

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

Supporting Information

ABSTRACT: New classes of tunable rhenium(I) diimine luminophores with formula of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ and $[\text{Re}(\text{CO})(\text{L}_x)(\text{CNC}_6\text{H}_4\text{Cl}-4)_2(1,10\text{-phenanthroline})]\text{PF}_6$, ($\text{R} = \text{C}_6\text{H}_5$, 4- BrC_6H_4 , 4- ClC_6H_4 , 4- MeOC_6H_4 , 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$; $\text{N}-\text{N} = 1,10\text{-phenanthroline}$, 5,6-dibromo-1,10-phenanthroline, 4,4'-di-*tert*-butyl-2,2'-bipyridine; $\text{L}_x = \text{MeCN}$, pyridine and PPh_3) have been synthesized. Different synthetic routes including photo-ligand substitution and thermal carbonyl ligand substitution through the oxidative decarbonylation with trimethyl amine N-oxide, for the facial and meridional isomeric forms of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ were investigated. On the basis of these synthetic strategies, different ligand modification and functionalization of the rhenium(I) diimine luminophores with tailored excited state properties could be readily achieved. The structures of both facial and meridional conformations of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ and the complex precursors *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_3^i\text{Pr}-2,6)_3]\text{OTf}$ were determined by X-ray crystallography. These complexes display an orange to red $^3\text{MLLCT} [\text{d}\pi(\text{Re}) \rightarrow \pi^*(\text{N}-\text{N})]$ phosphorescence at room temperature. Detailed photophysical investigations revealed that the physical, photophysical, electrochemical, and excited state properties can be fine-tuned and tailored through the modifications of the substituents on isocyanide or diimine ligands.



INTRODUCTION

After the first report on the visible-light metal-to-ligand charge-transfer (MLCT) transitions and the long-lived MLCT phosphorescence of Re(I) tricarbonyl diimine complexes¹ $[\text{Re}(\text{N}-\text{N})(\text{CO})_3\text{X}]$ ($\text{N}-\text{N} = \text{diimine}$), tremendous attention has been paid to the derivatization of both the diimine ligand or the axial coligand. With the rational design of the ligands, the characteristic MLCT excited state and its luminescence features can be utilized for a wide range of applications, such as the emissive layer for light-emitting devices,² photosensitizers,³ photocatalysts,⁴ and chemosensors.⁵ However, when these ligands were modified with functional moieties for different applications, further tuning of the physical and excited state properties is challenging as carbonyl ligands cannot be derivatized. To improve the tunability of the systems, we have successively developed tunable rhenium(I) diimine luminophores,⁶ $[\text{Re}(\text{CNR})_4(\text{N}-\text{N})]^{+6a}$ and $[\text{Re}(\text{CO})_2(\text{CNR})_2(\text{N}-\text{N})]^{+6b}$ by replacing the carbonyl ligands with readily tunable isoelectronic isocyanide ligands. With these luminophores, the photophysical and physical properties could be readily modified by changing the substituent on the N-atom of the isocyanide ligands.⁶ To improve the flexibility of functionalization, we have developed new synthetic strategies based on the photo-ligand substitution reactions and carbonyl ligand substitution reactions through the oxidative decarbonylation reaction to prepare the tri(isocyanato) analogue complexes

($[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]^{+}$) and to incorporate another type of coligand into these isocyano rhenium(I) diimine complexes.

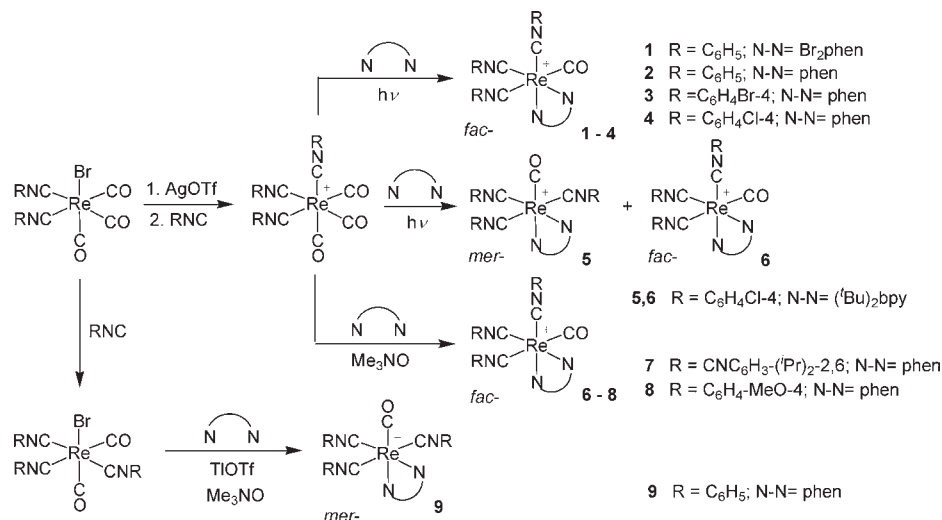
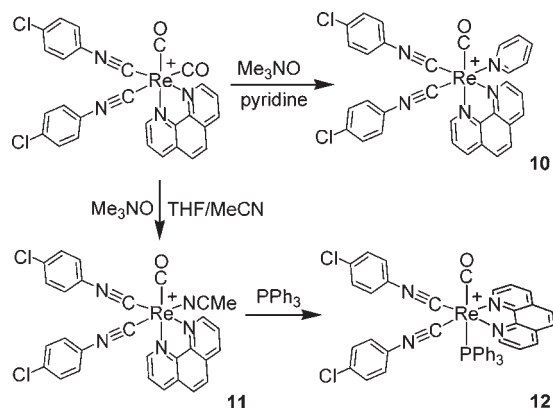
Since $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]^{+}$ can exist as two geometrical isomers, the facial tri(isocyanato) and the meridional tri(isocyanato) arrangements, selective synthetic routes to each of these isomers are also reported. As noted in the previous work on tris-cyclometalated Ir(III) complexes,⁷ pronounced differences in the metal-centered oxidation potential, emission energy, lifetime, and quantum yield between facial and meridional isomers with the same empirical formula have been observed. The different photophysical properties between the facial and the meridional isomers of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]^{+}$ are also discussed.

EXPERIMENTAL SECTION

Materials and Reagents. 1,10-Phenanthroline monohydrate (phen), 4,4'-di-*tert*-butyl-2,2'-bipyridine (*t*Bu₂bpy), triphenylphosphine (PPh_3), thallium trifluoromethanesulfonate (TlOTf), silver trifluoromethanesulfonate (AgOTf), and $[\text{Re}_2(\text{CO})_{10}]$ were purchased from Strem Chemical Company and used without further purification. Anilines, pyridine, formic acid, phosphorus oxychloride, and trimethyl amine N-oxide dihydrate ($\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$) were obtained from Aldrich Chemical Co. 5,6-Dibromo-1,10-phenanthroline (Br_2phen) was prepared

Received: December 5, 2010

Published: April 25, 2011

Scheme 1. Synthetic Routes for the *fac*- and *mer*-[Re(CO)(CNR)₃(N–N)]PF₆ (1–9)Scheme 2. Synthetic Routes for [Re(CO)(L_x)(CNR)₂(N–N)]PF₆ (10–12)

according to a previously published procedure.^{3c,f} Substituted phenyl isocyanide ligands, C₆H₅NC, 4-BrC₆H₄NC, 4-ClC₆H₄NC, 4-MeOC₆H₄NC, and 2,6-ⁱPr₂C₆H₃NC were prepared from the corresponding substituted anilines according to the synthetic methodology reported by Ugi and co-workers.⁸ Re(CO)₅Br was synthesized from the reaction between [Re₂(CO)₁₀] and bromine according to a literature procedure.⁹ *cis*-[Re(CO)₂(CNC₆H₄Cl-4)₂(phen)]PF₆ and the complex precursors with general formula of *fac*-[Re(CO)₃(CNR)₂Br] were prepared according to our previously reported procedures.^{6b} All solvents were of analytical reagent grade and were used without further purification.

The synthetic routes for target complexes are summarized in Schemes 1 and 2. Unless specified in the procedure, all the reactions were performed under anhydrous conditions and strictly inert argon atmosphere using the standard Schlenk technique.

General Synthetic Procedure for *fac*-[Re(CO)₃(CNR)₃]CF₃SO₃.

To a mixture of [Re(CO)₃(CNR)₂Br] (0.35 mmol) and AgOTf (107.9 mg, 0.42 mmol, 1.2 mol equiv.) in tetrahydrofuran (THF, 40 mL) were heated to reflux for 2 h. The resulting suspension was filtered to remove the precipitated AgBr. Thereafter, a slight excess of CNR (0.46 mmol, 1.3 mol equiv.) was added and stirred at 50 °C for 12 h. After removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane/acetone (3:1 v/v) as eluent.

fac-[Re(CO)₃(CNC₆H₅)₃]CF₃SO₃. Yield: 160 mg, 0.22 mmol; 63%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.48–7.53 (m, 9H, phenyl H's), 7.76–7.78 (m, 6H, phenyl H's). ESI-MS: *m/z* 580 [M]⁺. IR (KBr disk, ν/cm⁻¹) 1999, 2064 ν(C≡O); 2170, 2210 ν(N≡C). Elemental analyses, Calcd for [Re(CO)₃(CNC₆H₅)₃]CF₃SO₃ (found) %: C 41.21 (41.19), H 2.07 (2.15), N 5.77 (5.80).

fac-[Re(CO)₃(CNC₆H₄Br-4)₃]CF₃SO₃. Yield: 207 mg, 0.21 mmol; 61%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.60–7.63 (m, 6H, phenyl H's), 7.70–7.73 (m, 6H, phenyl H's). ESI-MS: *m/z* 817 [M]⁺. IR (KBr disk, ν/cm⁻¹) 2005, 2058 ν(C≡O); 2170, 2214 ν(N≡C). Elemental analyses, Calcd for [Re(CO)₃(CNC₆H₄Br-4)₃]CF₃SO₃ · 1/2CH₃COCH₃ (found) %: C 32.01 (32.25), H 1.52 (1.60), N 4.23 (4.46).

fac-[Re(CO)₃(CNC₆H₄Cl-4)₃]CF₃SO₃. Yield: 222 mg, 0.27 mmol; 76%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.44 (d, 6H, *J* = 7.5 Hz, phenyl H's), 7.78 (d, 6H, *J* = 7.5 Hz, phenyl H's). ESI-MS: *m/z* 682 [M]⁺. IR (KBr disk, ν/cm⁻¹) 2000, 2061 ν(C≡O); 2174, 2213 ν(N≡C). Elemental analyses, Calcd for [Re(CO)₃(CNC₆H₄Cl-4)₃]CF₃SO₃ (found) %: C 36.09 (36.21), H 1.45 (1.32), N 5.05 (4.93).

fac-[Re(CO)₃(CNC₆H₄OMe-4)₃]CF₃SO₃. Yield: 197 mg, 0.24 mmol; 69%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 3.85 (s, 9H, OMe H's), 7.00 (d, 6H, *J* = 9.0 Hz, phenyl H's), 7.66 (d, 6H, *J* = 9.0 Hz, phenyl H's). ESI-MS: *m/z* 670 [M]⁺. IR (KBr disk, ν/cm⁻¹) 1990, 2055 ν(C≡O); 2184, 2210 ν(N≡C). Elemental analyses, Calcd for [Re(CO)₃(CNC₆H₄OMe-4)₃]CF₃SO₃ (found) %: C 41.07 (41.12), H 2.59 (2.75), N 5.13 (5.18).

fac-[Re(CO)₃(CNC₆H₃ⁱPr₂-2,6)₃]CF₃SO₃. Yield: 254 mg, 0.26 mmol; 74%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.29 (d, 36H, *J* = 6.9 Hz, ⁱPr H's), 3.18 (septet, 6H, *J* = 6.9 Hz, ⁱPr H's), 7.30 (d, 6H, *J* = 7.8 Hz, phenyl H's), 7.52 (t, 3H, *J* = 7.8 Hz, phenyl H's). ESI-MS: *m/z* 832 [M]⁺. IR (KBr disk, ν/cm⁻¹) 2012, 2065 ν(C≡O); 2160, 2201 ν(N≡C). Elemental analyses, Calcd for [Re(CO)₃(CNC₆H₃ⁱPr₂-2,6)₃]CF₃SO₃ (found) %: C 52.64 (52.35), H 5.24 (5.35), N 4.28 (4.28).

mer-[Re(CO)₂(CNC₆H₅)₃Br]. To a solution of Re(CO)₅Br (203.1 mg, 0.5 mmol) and CNC₆H₅ (0.22 mL, 2.15 mmol, 4.3 mol equiv.) in a solvent mixture of THF and toluene (1:3 v/v, 60 mL) were strongly refluxed for 2 days. After removal of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane/acetone (4:1 v/v) as eluent to give the analytically pure complexes as off-white powder. Yield: 133 mg, 0.21 mmol; 42%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.30–7.46 (m, 15H, phenyl H's). ESI-MS: *m/z* 632

$[M+H]^+$. IR (KBr disk, ν/cm^{-1}) 1862, 1986 br $\nu(\text{C}\equiv\text{O})$; 2085 br $\nu(\text{N}\equiv\text{C})$. Elemental analyses, Calcd for $[\text{Re}(\text{CO})_2(\text{CNC}_6\text{H}_5)_3\text{Br}]$ (found) %: C 43.74 (43.50), H 2.39 (2.32), N 6.65 (6.56).

fac- $[\text{Re}(\text{CO})(\text{CNC}_6\text{H}_5)_3(\text{Br}_2\text{phen})]\text{PF}_6$ (**1**). *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{CF}_3\text{SO}_3$ (72.8 mg, 0.1 mmol) and Br_2phen (40.8 mg, 0.12 mmol, 1.2 mol equiv.) were mixed and dissolved in argon-degassed benzene (12 mL). The resulting solution was then irradiated with UV light ($\lambda = 254$ nm) for 2 h at room temperature using a Pen-Ray mercury lamp (11SC-1) in a water cooled quartz jacket, during which the solution gradually turned orange. After removal of solvent under reducing pressure, the residue was purified by column chromatography on silica gel using dichloromethane/acetone (3:1 v/v) as eluent. Subsequent metathesis reaction in methanol with a saturated methanolic solution of ammonium hexafluorophosphate gave the target complex as a PF_6^- salt. Analytically pure dark red crystals were obtained from slow diffusion of diethyl ether vapor into a concentrated acetone solution of the complexes. Yield: 40.3 mg, 0.040 mmol; 40%. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.29–7.47 (m, 15H, phenyl H's), 8.13 (dd, 2H, $J = 5.1$, 8.6 Hz, 3,8-phen H's), 9.04 (dd, 2H, $J = 1.2$, 8.6 Hz, 4,7-phen H's), 9.60 (dd, 2H, $J = 1.2$, 5.1 Hz, 2,9-phen H's). ESI-MS: m/z 862 $[\text{M}]^+$. IR (KBr disk, ν/cm^{-1}) 842 $\nu(\text{P}-\text{F})$; 1924 $\nu(\text{C}\equiv\text{O})$; 1999, 2082, 2148 $\nu(\text{N}\equiv\text{C})$. Elemental analyses, Calcd for $1 \cdot \text{CH}_3\text{COCH}_3$ (found) %: C 41.74 (41.55), H 2.56 (2.51), N 6.58 (6.65).

fac- $[\text{Re}(\text{CO})(\text{CNC}_6\text{H}_5)_3(\text{phen})]\text{PF}_6$ (**2**). The complex was synthesized according to a procedure similar to that used for **1**, except phen (23.8 mg, 0.12 mmol) was used instead of Br_2phen in the photosubstitution reaction. Orange solids were obtained by slowly diffusing diethyl ether vapor into a concentrated dichloromethane solution of **2**. Yield: 40 mg, 0.047 mmol; 47%. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.17–7.48 (m, 15H, phenyl H's) 8.03 (dd, 2H, $J = 5.1$, 8.3 Hz, 3,8-phen H's), 8.18 (s, 2H, 5,6-phen H's), 8.70 (d, 2H, $J = 8.3$ Hz, 4,7-phen H's), 9.60 (d, 2H, $J = 5.1$ Hz, 2,9-phen H's). ESI-MS: m/z 704 $[\text{M}]^+$. IR (KBr disk, ν/cm^{-1}) 840 $\nu(\text{P}-\text{F})$; 1924 $\nu(\text{C}\equiv\text{O})$; 1996, 2080, 2148 $\nu(\text{N}\equiv\text{C})$. Elemental analyses, Calcd for **2** (found) %: C 48.11 (48.09), H 2.73 (2.66), N 8.25 (8.31).

fac- $[\text{Re}(\text{CO})(\text{CNC}_6\text{H}_4\text{Br}-4)_3(\text{phen})]\text{PF}_6$ (**3**). The complex was synthesized according to a procedure similar to that used for **1**, except *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_4\text{Br}-4)_3]\text{CF}_3\text{SO}_3$ (96.8 mg, 0.1 mmol) and phen (23.8 mg, 0.12 mmol) were used in place of *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{CF}_3\text{SO}_3$ and Br_2phen in the photosubstitution reaction. Analytically pure orange crystals were obtained from slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of **3**. Yield: 50 mg, 0.046 mmol; 46%. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.12 (d, 2H, $J = 8.8$ Hz, phenyl H's), 7.33 (d, 4H, $J = 8.8$ Hz, phenyl H's), 7.43 (d, 2H, $J = 8.8$ Hz, phenyl H's), 7.6 (d, 4H, $J = 8.8$ Hz, phenyl H's), 8.04 (dd, 2H, $J = 5.1$, 8.2 Hz, 3,8-phen H's), 8.13 (s, 2H, 5,6-phen H's), 8.65 (dd, 2H, $J = 1.4$, 8.2 Hz, 4,7-phen H's), 9.60 (dd, 2H, $J = 1.4$, 5.1 Hz, 2,9-phen H's). ESI-MS: m/z 942 $[\text{M}]^+$. IR (KBr disk, ν/cm^{-1}) 842 $\nu(\text{P}-\text{F})$; 1932 $\nu(\text{C}\equiv\text{O})$; 1998, 2076, 2146 $\nu(\text{N}\equiv\text{C})$. Elemental analyses, Calcd for **3** (found) %: C 37.62 (37.99), H 1.86 (1.85), N 6.45 (6.45).

fac- $[\text{Re}(\text{CO})(\text{CNC}_6\text{H}_4\text{Cl}-4)_3(\text{phen})]\text{PF}_6$ (**4**). The complex was synthesized according to a procedure similar to that used for **1**, except *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_4\text{Cl}-4)_3]\text{CF}_3\text{SO}_3$ (83 mg, 0.1 mmol) and phen (23.8 mg, 0.12 mmol) were used in place of *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{CF}_3\text{SO}_3$ and Br_2phen in the photosubstitution reaction. Orange crystals were obtained by slowly diffusing diethyl ether vapor into a concentrated dichloromethane solution of **4**. Yield: 47.5 mg, 0.050 mmol; 50%. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.18 (d, 2H, $J = 8.8$ Hz, phenyl H's), 7.24 (d, 2H, $J = 8.8$ Hz, phenyl H's), 7.38 (d, 4H, $J = 8.8$ Hz, phenyl H's), 7.43 (d, 4H, $J = 8.8$ Hz, phenyl H's), 8.03 (dd, 2H, $J = 5.1$, 8.2 Hz, 3,8-phen H's), 8.12 (s, 2H, 5,6-phen H's), 8.64 (dd, 2H, $J = 1.3$, 8.2 Hz, 4,7-phen H's), 9.60 (dd, 2H, $J = 1.3$, 5.1 Hz, 2,9-phen

H's). ESI-MS: m/z 806 $[\text{M}]^+$. IR (KBr disk, ν/cm^{-1}) 843 $\nu(\text{P}-\text{F})$; 1906 $\nu(\text{C}\equiv\text{O})$; 2007, 2076, 2146 $\nu(\text{N}\equiv\text{C})$. Elemental analyses, Calcd for **4** (found) %: C 42.89 (42.92), H 2.12 (2.30), N 7.36 (7.31).

mer- $[\text{Re}(\text{CO})(\text{CNC}_6\text{H}_4\text{Cl}-4)_3(^t\text{Bu}_2\text{bpy})]\text{PF}_6$ (**5**). The complex was synthesized according to a procedure similar to that used for **1**, except *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_4\text{Cl}-4)_3]\text{CF}_3\text{SO}_3$ (124.5 mg, 0.15 mmol) and $^t\text{Bu}_2\text{bpy}$ (48 mg, 0.18 mmol) were used in place of *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{CF}_3\text{SO}_3$ and Br_2phen in the photosubstitution reaction. Recrystallization by slow diffusion of diethyl ether vapor into a concentrated acetone solution of the complex gave the analytically pure **5** as yellow crystals. Yield: 66 mg, 0.064 mmol; 42%. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 1.48 (s, 18H, ^tBu H's), 7.14 (d, 4H, $J = 8.9$ Hz, phenyl H's), 7.29 (d, 4H, $J = 8.9$ Hz, phenyl H's), 7.36 (d, 2H, $J = 8.9$ Hz, phenyl H's), 7.41 (d, 2H, $J = 8.9$ Hz, phenyl H's), 7.48 (dd, 1H, $J = 1.9$, 5.9 Hz, 5-bpy H's), 7.78 (dd, 1H, $J = 1.9$, 5.9 Hz, 5'-bpy H's), 8.30 (d, 2H, $J = 1.9$ Hz, 3,3'-bpy H's), 9.04 (d, 1H, $J = 5.9$ Hz, 6-bpy H's), 9.08 (d, 1H, $J = 5.9$ Hz, 6'-bpy H's). ESI-MS: m/z 894 $[\text{M}]^+$. IR (KBr disk, ν/cm^{-1}) 844 $\nu(\text{P}-\text{F})$; 1897 $\nu(\text{C}\equiv\text{O})$; 2008, 2075, 2146 $\nu(\text{N}\equiv\text{C})$. Elemental analyses, Calcd for $5 \cdot \text{CH}_3\text{COCH}_3$ (found) %: C 47.02 (46.92), H 3.85 (3.97), N 6.38 (6.52).

fac- $[\text{Re}(\text{CO})(\text{CNC}_6\text{H}_4\text{Cl}-4)_3(^t\text{Bu}_2\text{bpy})]\text{PF}_6$ (**6**). A mixture of *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_4\text{Cl}-4)_3]\text{CF}_3\text{SO}_3$ (124.5 mg, 0.15 mmol) and $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ (40 mg, 0.36 mmol, 2.4 mol equiv.) in THF/MeCN (10:1 v/v, 200 mL) was heated to 50 °C and stirred at this temperature overnight. The crude intermediate *fac*- $[\text{Re}(\text{CO})(\text{MeCN})_2(\text{CNC}_6\text{H}_4\text{Cl}-4)_3]\text{CF}_3\text{SO}_3$ was purified by column chromatography on silica gel using dichloromethane/acetone (3:1 v/v) as eluent. Thereafter, the orange red residue of *fac*- $[\text{Re}(\text{CO})(\text{MeCN})_2(\text{CNC}_6\text{H}_4\text{Cl}-4)_3]\text{CF}_3\text{SO}_3$ was mixed with $^t\text{Bu}_2\text{bpy}$ (48 mg, 0.18 mmol, 1.2 mol equiv.) in THF/MeCN (110 mL, 10:1 v/v) and stirred at 50–60 °C for 12 h. It was then purified by column chromatography on silica gel using dichloromethane/acetone (3:1 v/v) as eluent. Subsequent metathesis reaction with ammonium hexafluorophosphate in minimum amount of methanol gave the target complex as PF_6^- salt. Orange crystals were obtained by slowly diffusing diethyl ether vapor into a concentrated dichloromethane solution of **6**. Yield: 72 mg, 0.069 mmol; 46%. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 1.49 (s, 18H, ^tBu H's), 7.29–7.31 (m, 8H, phenyl H's), 7.39 (d, 2H, $J = 8.8$ Hz, phenyl H's), 7.41 (d, 2H, $J = 8.8$ Hz, phenyl H's), 7.61 (dd, 2H, $J = 1.8$, 5.9 Hz, 5,5'-bpy H's), 8.28 (d, 2H, $J = 1.8$ Hz, 3,3'-bpy H's), 9.07 (d, 2H, $J = 5.9$ Hz, 6,6'-bpy H's). ESI-MS: m/z 894 $[\text{M}]^+$. IR (KBr disk, ν/cm^{-1}) 844 $\nu(\text{P}-\text{F})$; 1930 $\nu(\text{C}\equiv\text{O})$; 1993, 2076, 2150 $\nu(\text{N}\equiv\text{C})$. Elemental analyses, Calcd for **6** (found) %: C 46.18 (45.93), H 3.49 (3.35), N 6.73 (6.82).

fac- $[\text{Re}(\text{CO})(\text{CNC}_6\text{H}_3^i\text{Pr}_2-2,6)_3(\text{phen})]\text{PF}_6$ (**7**). The complex was synthesized according to a procedure similar to that used for **6**, except $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_3^i\text{Pr}_2-2,6)_3]\text{CF}_3\text{SO}_3$ (147.2 mg, 0.15 mmol) and phen (35.6 mg, 0.18 mmol) were used in place of *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_4\text{Cl}-4)_3]\text{CF}_3\text{SO}_3$ and $^t\text{Bu}_2\text{bpy}$. Subsequent metathesis reaction with ammonium hexafluorophosphate in a minimum amount of methanol gave the target complex as PF_6^- salt. Red powdery solid was obtained by slowly diffusing diethyl ether vapor into a concentrated dichloromethane solution of **7**. Yield: 91 mg, 0.083 mmol; 55%. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.76 (d, 12H, $J = 6.9$ Hz, ^iPr H's), 1.31 (dd, 24H, $J = 1.9$, 6.9 Hz, ^iPr H's) 2.45 (septet, 2H, $J = 6.9$ Hz, ^iPr H's), 3.50 (septet, 4H, $J = 6.9$ Hz, ^iPr H's), 6.98 (d, 2H, $J = 7.8$ Hz, phenyl H's), 7.19–7.30 (m, 7H, phenyl H's), 8.03 (dd, 2H, $J = 5.1$, 8.2 Hz, 3,8-phen H's), 8.30 (s, 2H, 5,6-phen H's), 8.86 (dd, 2H, $J = 1.3$, 8.2 Hz, 4,7-phen H's), 9.58 (dd, 2H, $J = 1.3$, 5.1 Hz, 2,9-phen H's). ESI-MS: m/z 957 $[\text{M}]^+$. IR (KBr disk, ν/cm^{-1}) 845 $\nu(\text{P}-\text{F})$; 1928 $\nu(\text{C}\equiv\text{O})$; 2020, 2076, 2144 $\nu(\text{N}\equiv\text{C})$. Elemental analyses, Calcd for **7** (found) %: C 56.71 (56.45), H 5.40 (5.52), N 6.36 (6.28).

fac- $[\text{Re}(\text{CO})(\text{CNC}_6\text{H}_4\text{OMe}-4)_3(\text{phen})]\text{PF}_6$ (**8**). The complex was synthesized according to a procedure similar to that used for **6**, except

fac-[Re(CO)₃(CNC₆H₄OMe-4)₃]CF₃SO₃ (123 mg, 0.15 mmol) and phen (35.6 mg, 0.18 mmol) were used in place of *fac*-[Re(CO)₃(CNC₆H₄Cl-4)₃]CF₃SO₃ and ^tBu₂bpy. Subsequent recrystallization by slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of **8** afforded the analytically pure complex as red crystals. Yield: 50 mg, 0.05 mmol; 35%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 3.86 (s, 9H, OMe H's), 6.76 (d, 2H, *J* = 9.1 Hz, phenyl H's), 6.96 (d, 4H, *J* = 9.1 Hz, phenyl H's), 7.06 (d, 2H, *J* = 9.1 Hz, phenyl H's), 7.36 (d, 4H, *J* = 9.1 Hz, phenyl H's), 8.02 (dd, 2H, *J* = 5.3, 8.2 Hz, 3,8-phen H's), 8.19 (s, 2H, 5,6-phen H's), 8.72 (dd, 2H, *J* = 1.4, 8.2 Hz, 4,7-phen H's), 9.60 (dd, 2H, *J* = 1.4, 5.3 Hz, 2,9-phen H's). ESI-MS: *m/z* 794 [M]⁺. IR (KBr disk, ν/cm⁻¹) 844 ν(P–F); 1917 ν(C≡O); 2015, 2085, 2150 ν(N≡C). Elemental analyses, Calcd for **8** (found) %: C 47.34 (47.32), H 3.11 (3.13), N 7.46 (7.51).

mer-[Re(CO)(CNC₆H₅)₃(phen)]PF₆ (**9**). A mixture of *mer*-[Re(CO)₂(CNC₆H₅)₃Br] (90 mg, 0.14 mmol), phen (84.7 mg, 0.43 mmol, 3 mol equiv.) and TlOTf (54 mg, 0.154 mmol, 1.1 mol equiv.) in argon-degassed THF (90 mL) was heated to 60 °C and stirred overnight. Thereafter, Me₃NO·2H₂O (17 mg, 0.154 mmol, 1.1 mol equiv.) was added, and the reaction mixture was stirred at 55 °C for 4 days. After purification by column chromatography on silica gel using dichloromethane/acetone (3:1 v/v) as eluent and subsequent metathesis reaction with ammonium hexafluorophosphate, the target complex was obtained as PF₆⁻ salt. Analytically pure orange crystals were obtained from the slow diffusion of diethyl ether vapor into a dichloromethane/methanol solution (10:1 v/v) of **9**. Yield: 40 mg, 0.041 mmol; 41%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.05–7.08 (m, 5H, phenyl H's), 7.26–7.35 (m, 5H, phenyl H's), 7.48 (d, 5H, *J* = 4.4 Hz, phenyl H's), 7.91 (dd, 1H, *J* = 5.2, 8.2 Hz, 3-phen H's), 8.16 (dd, 1H, *J* = 5.2, 8.2 Hz, 8-phen H's), 8.18 (s, 1H, 6-phen H's), 8.22 (s, 1H, 5-phen H's), 8.66 (dd, 1H, *J* = 1.2, 8.2 Hz, 4-phen H's), 8.79 (dd, 1H, *J* = 1.2, 8.2 Hz, 7-phen H's), 9.58 (d, 2H, *J* = 5.2 Hz, 2,9-phen H's). ESI-MS: *m/z* 704 [M]⁺. IR (KBr disk, ν/cm⁻¹) 842 ν(P–F); 1888 ν(C≡O); 1999, 2077, 2147 ν(N≡C). Elemental analyses, Calcd for **9**·CH₃OH (found) %: C 47.73 (47.66), H 3.09 (2.94), N 7.95 (8.09).

cis,cis-[Re(CO)(py)(CNC₆H₄Cl-4)₂(phen)]PF₆ (**10**). A solution of *cis,cis*-[Re(CO)₂(CNC₆H₄Cl-4)₂(phen)]PF₆ (100 mg, 0.12 mmol) and Me₃NO·2H₂O (16 mg, 0.144 mmol, 1.2 mol equiv.) in degassed pyridine (40 mL) was warmed and stirred overnight at 40 °C. Thereafter, dichloromethane (50 mL) was added and then washed with diluted hydrochloric acid (0.1 M, 50 mL × 2) and copious amount of water. The organic layer was collected and purified by column chromatography on silica gel with acetone/dichloromethane (4:1 v/v) as eluent. A dark brown crystalline solid was obtained from the slow diffusion of diethyl ether vapor into a concentrated acetone solution of **10**. Yield: 62 mg, 0.062 mmol; 52%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 6.85 (d, 2H, *J* = 8.9 Hz, phenyl H's), 7.17–7.20 (m, 4H, 2 pyridyl H's and 2 phenyl H's), 7.41 (s, 4H, phenyl H's), 7.56–7.61 (m, 1H, pyridyl H's), 7.96 (dd, 1H, *J* = 5.1, 8.3 Hz, 3-phen H's), 8.04 (d, 1H, *J* = 8.3 Hz, 5-phen H's), 8.09 (d, 1H, *J* = 8.3 Hz, 6-phen H's), 8.28 (dd, 1H, *J* = 5.1, 8.3 Hz, 8-phen H's), 8.37–8.39 (m, 2H, pyridyl H's), 8.58 (dd, 1H, *J* = 1.4, 8.3 Hz, 4-phen H's), 8.67 (dd, 1H, *J* = 1.4, 8.3 Hz, 7-phen H's), 9.68 (dd, 1H, *J* = 1.4, 5.1 Hz, 2-phen H's), 9.75 (dd, 1H, *J* = 1.4, 5.1 Hz, 9-phen H's). ESI-MS: *m/z* 748 [M]⁺. IR (KBr disk, ν/cm⁻¹) 843 ν(P–F); 1877 ν(C≡O); 1978, 2086 ν(N≡C). Elemental analyses, Calcd for **10**·CH₃COCH₃ (found) %: C 44.17 (44.06), H 2.86 (3.06), N 7.36 (7.13).

cis,cis-[Re(CO)(MeCN)(CNC₆H₄Cl-4)₂(phen)]PF₆ (**11**). A mixture of *cis,cis*-[Re(CO)₂(CNC₆H₄Cl-4)₂(phen)]PF₆ (250 mg, 0.30 mmol) and Me₃NO·2H₂O (40 mg, 0.36 mmol, 1.2 mol equiv.) in argon-degassed THF/MeCN (1:1 v/v, 200 mL) was stirred at 40 °C for 12 h. After removal of the solvent, further purification by column chromatography on silica gel using dichloromethane/acetone (4:1 v/v) as eluent gave the complex as red powdery solid. Yield: 173 mg, 0.18 mmol; 60%. ¹H NMR

(400 MHz, CDCl₃, 298 K): δ 2.18 (s, 3H, MeCN), 6.82 (d, 2H, *J* = 8.6 Hz, phenyl H's), 7.15 (d, 2H, *J* = 8.6 Hz, phenyl H's), 7.42 (s, 4H, phenyl H's), 7.87–8.14 (m, 4H, 3,8-phen and 5,6-phen H's), 8.63 (d, 1H, *J* = 8.1 Hz, 4-phen H's), 8.67 (d, 1H, *J* = 8.1 Hz, 7-phen H's), 9.51 (m, 2H, 2,9-phen H's). ESI-MS: *m/z* 710 [M]⁺. IR (KBr disk, ν/cm⁻¹) 837 ν(P–F); 1860 ν(C≡O); 1937, 2090 ν(N≡C). Elemental analyses, Calcd for **11** (found) %: C 40.71 (40.85), H 2.24 (2.26), N 8.19 (8.28).

trans,cis-[Re(CO)(PPh₃)(CNC₆H₄Cl-4)₂(phen)]PF₆ (**12**). To a solution of **11** (80 mg, 0.07 mmol) in argon-degassed THF (60 mL), PPh₃ (1 g, 3.8 mmol, 53 mol equiv.) was added. The resulting solution was warmed and stirred overnight at 70 °C. After removal of the solvent, analytically pure complex **12** as a brownish orange powdery solid was obtained from the recrystallization by slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of **12**. Yield: 47 mg, 0.04 mmol; 50%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 6.95–7.02 (m, 11H, phenyl H of PPh₃ and phenyl H of CNC₆H₄Cl-4), 7.10–7.14 (m, 6H, phenyl H of PPh₃), 7.25–7.28 (m, 2H, phenyl H of PPh₃), 7.34–7.36 (d, 4H, *J* = 8.8 Hz, phenyl H of CNC₆H₄Cl-4), 7.74 (dd, 2H, *J* = 5.2, 8.1 Hz, 3,8-phen H's), 8.04 (s, 2H, 5,6-phen H's), 8.52 (d, 2H, *J* = 8.1 Hz, 4,7-phen H's), 9.10 (d, 2H, *J* = 5.2 Hz, 2,9-phen H's). ESI-MS: *m/z* 931 [M]⁺. IR (KBr disk, ν/cm⁻¹) 844 ν(P–F); 1897 ν(C≡O); 1986, 2086 ν(N≡C). Elemental analyses, Calcd for **12** (found) %: C 50.19 (49.85), H 2.90 (2.75), N 5.20 (5.45).

Physical Measurements and Instrumentation. ¹H NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (ppm) were reported relative to tetramethylsilane (Me₄Si). All positive-ion electrospray ionization (ESI) mass spectra were recorded on a Perkin-Elmer Sciex API 365 mass spectrometer. The elemental analyses were performed on an Elementar Vario EL III Analyzer. Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady state emission and excitation spectra at room temperature and at 77 K were recorded on a Horiba Jobin Yvon Fluorolog-3-TCSPC spectrofluorometer. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze pump-thaw cycles. Measurements of the EtOH–MeOH (4:1 v/v) glass samples at 77 K were carried out with the dilute EtOH–MeOH sample solutions contained in a quartz tube inside a liquid nitrogen-filled quartz optical Dewar flask. Luminescence quantum yields were determined using the optically dilution method described by Demas and Crosby¹⁰ with an aqueous solution of [Ru(bpy)₃]Cl₂ ($\phi_{em} = 0.042^{11}$ with 436-nm excitation) as the reference. Luminescence lifetimes (τ) of the samples were measured using time-correlated single photon counting (TCSPC) technique on the TCSPC spectrofluorometer in a Fast MCS mode with a NanoLED-375LH excitation source, which has its excitation peak wavelength at 375 nm and pulse width shorter than 750 ps. The photon counting data were analyzed by Horiba Jobin Yvon Decay Analysis Software. Rate constant for nonradiative decay (k_{nr}) is calculated according to the equation: $k_{nr} = [(1 - \phi_{em})/\tau]$.

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. Model CHI 620 Electrochemical Analyzer. Electrochemical measurements were performed in acetonitrile solutions with 0.1 M ⁿBu₄NPF₆ as the supporting electrolyte at room temperature. The reference electrode was a Ag/AgNO₃ (0.1 M in acetonitrile) electrode, and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with a platinum wire as the auxiliary electrode. The working electrode surface was polished with the 1 μm α-alumina slurry (Linde) and then a 0.3 μm α-alumina slurry (Linde) on a microcloth (Buehler Co.). The ferrocenium/ferrocene couple (FeCp₂⁺⁰) was used as the internal calibrant (0.38 V).¹² All solutions for electrochemical studies were deaerated with prepurified argon gas prior to measurements.

X-ray Crystal Structure Determination. The crystal structures were determined on an Oxford Diffraction Gemini S Ultra X-ray single

crystal diffractometer using graphite monochromatized Cu-K α ($\lambda = 1.54178 \text{ \AA}$) or Mo-K α radiation. ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods employing the SHELXL-97 program¹³ on a PC. Re and many non-H atoms were located according to the direct methods. The positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using SHELXL-97 program¹³ on a PC. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by the program SHELXL-97.¹³ The positions of H atoms were calculated based on the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.

RESULTS AND DISCUSSION

Synthesis and Characterization. All isocyanides were synthesized using the synthetic methodology developed by Ugi and co-workers.⁸ With different synthetic strategies, *fac*-[Re(CO)(CNR)₃(N–N)]OTf and *mer*-[Re(CO)(CNR)₃(N–N)]OTf could be prepared from the *fac*-[Re(CO)₃(CNR)₃]OTf and *mer*-[Re(CO)₂(CNR)₃Br] (Scheme 1). The substitution reaction of *fac*-[Re(CO)₃(CNR)₂Br] or [Re(CO)₃Br] with excess isocyanide ligands in refluxing toluene/THF gave *mer*-[Re(CO)₂(CNR)₃Br]. To synthesize facial tri(isocyanido) rhenium(I) complexes, the bromide ligand of *fac*-[Re(CO)₃(CNR)₂Br] was first removed using AgOTf and subsequent reaction with slight excess of isocyanide ligands afforded the target *fac*-[Re(CO)₃(CNR)₃]OTf. Using our recently reported synthetic strategy for *cis,cis*-[Re(CO)₂(CNR)₂(N–N)]⁺,^{6b} photochemical ligand substitution reactions of *fac*-[Re(CO)₃(CNR)₃]OTf and *mer*-[Re(CO)₂(CNR)₃Br] with different diimine ligands were performed. For the syntheses of 1–4 from the corresponding *fac*-[Re(CO)₃(CNR)₃]OTf (R = C₆H₅, 4-BrC₆H₄ or 4-ClC₆H₄), the photochemical substitution reactions were found to be highly stereoselective with the target complexes, *fac*-[Re(CO)(CNR)₃(N–N)]OTf, being the only major product. However, in the preparation of other analogous complexes 6–8, which contain electron-releasing and/or bulky substituents on the isocyanide ligands or diimine ligands, the photosubstitution reactions led to the formation of a 1:1 isomeric mixture of both the facial and the meridional conformations of [Re(CO)(CNR)₃(N–N)]OTf as determined by ¹H NMR spectroscopy. Subsequent metathesis reaction with ammonium hexafluorophosphate gave the target complex as a PF₆[–] salt.

The formations of the two different isomers in the photochemical ligand substitution are likely to be the result of the *fac-mer* photoisomerization of the reaction intermediates since the pure *fac*-isomers 6–8 were found to be highly stable upon prolonged 254-nm excitation for 2 h under similar condition. Except for [Re(CO)(CNC₆H₄Cl-4)₃(^tBu₂bpy)]PF₆, in which the *mer*-isomer 5 can be separated by repeated recrystallization, the *fac*- and *mer*-isomeric mixtures of [Re(CO)(CNR)₃(N–N)]PF₆ are difficult to separate by column chromatography and recrystallization. The photochemical ligand substitution reactions were also successfully carried out with lower energy UV light ($\lambda = 365 \text{ nm}$) as excitation source; however, the ratio of the facial to meridional conformations in the syntheses of 6–8 were not found to improve. On the other hand, the *mer*-[Re(CO)(CNR)₃(N–N)]PF₆ could also be prepared through the photosubstitution reaction of *mer*-[Re(CO)₂(CNR)₃Br] with diimine ligands under similar conditions, but the yields of target products were very low (<10%).

As a result of the strong competition of π -back bonding interactions between the isocyanide ligands and the carbonyl

ligands, the carbonyl ligands, which are *trans*- to the isocyanide ligands, could undergo oxidative decarbonylation reaction by Me₃NO, which was demonstrated to be an effective decarbonylation reagent for metal carbonyl complexes with $\nu(\text{C}\equiv\text{O}) > 2000 \text{ cm}^{-1}$.¹⁴ Through the decarbonylation and the subsequent ligand substitution reactions, synthetic routes for the *fac*- and *mer*-isomers have been developed (Scheme 1). These routes are found to be highly effective in controlling the isomerism of the target complexes. On the basis of this strategy, the *fac*-[Re(CO)(CNR)₃(N–N)]OTf isomer could be obtained from the decarbonylation reactions of two carbonyl ligands in *fac*-[Re(CO)₃(CNR)₃]OTf in THF/acetonitrile (10:1 v/v) solution and the subsequent substitution with a diimine ligand. Similarly, as illustrated in the preparation of 9, the *mer*-[Re(CO)(CNR)₃(N–N)]PF₆ isomer could be obtained from the decarbonylation of *mer*-[Re(CO)₂(CNR)₃Br] and the subsequent substitution with a diimine ligand in the presence of TlOTf for bromide abstraction.

With the successful decarbonylation in these rhenium carbonyl isocyanido complexes, extension of this synthetic methodology to extend the flexibility in the functionalization of these rhenium diimine luminophores was attempted. The *cis,cis*-[Re(CO)(L_x)(CNC₆H₄Cl-4)₂(phen)]PF₆ (L_x = MeCN or pyridine) has been synthesized from *cis,cis*-[Re(CO)₂(CNC₆H₄Cl-4)₂(phen)]PF₆ through the selective decarbonylation of the carbonyl ligand *trans*- to isocyanide ligand with Me₃NO and ligand substitution reaction in MeCN or pyridine (Scheme 2). To confirm the carbonyl ligand that *trans*- to isocyanide ligand is selectively decarbonylated and replaced, the substitution reaction of *cis,cis*-[Re(CO)₂(CNC₆H₄Cl-4)₂(phen)]PF₆ with large excess of CNC₆H₄Cl-4 under similar condition have also been performed, and this reaction gave the *mer*-[Re(CO)(CNC₆H₄Cl-4)₃(phen)]PF₆ as the only major product. Further ligand substitution reaction of labile MeCN ligand in *cis,cis*-[Re(CO)(MeCN)(CNC₆H₄Cl-4)₂(phen)]PF₆ with large excess of PPh₃ ligand at 70 °C was also performed. Surprisingly, the major product obtained from this substitution reaction is the *trans,cis*-[Re(CO)(PPh₃)(CNC₆H₄Cl-4)₂(phen)]PF₆ (12), in which both the *cis*-isocyanide ligands are *trans*- to the phenanthroline, as characterized by the symmetric ¹H NMR signals for the phenanthroline ligand.

All of the complexes are air and thermally stable, and have good solubility in common organic solvents. They gave satisfactory elemental analyses and were characterized by ¹H NMR, IR spectroscopy, and positive-ion ESI mass spectrometry. Complexes 1, 3, 4, 5, 6, 8, 9, and *fac*-[Re(CO)₃(CNC₆H₃¹Pr₂-2,6)₃]OTf were also structurally characterized by X-ray crystallography.

IR and NMR Spectroscopy. All precursor complexes with general formula of *fac*-[Re(CO)₃(CNR)₃]OTf, exhibit two strong C=O stretches and two C≡N stretches (one strong and one weak) at about 1990–2065 cm^{–1} and 2160–2214 cm^{–1}, respectively. The two IR active C=O stretches for the carbonyl ligands and two IR active C≡N stretches of isocyanide ligands are consistent with the facial arrangement of these ligands with C_{3v} symmetry in an octahedral complex.¹⁵ On conversion to the target complexes *fac*-[Re(CO)(CNR)₃(N–N)]⁺, which contain one carbonyl ligand and facial isocyanido ligands of C_s symmetry, the complexes exhibit one C=O stretch and three C≡N stretches, typical for facial arrangement of isocyanido ligands in a distorted octahedral complex with C_s symmetry.^{15,16} Similarly, the *mer*-[Re(CO)(CNR)₃(N–N)]⁺ complexes also display one C=O stretch and three C≡N

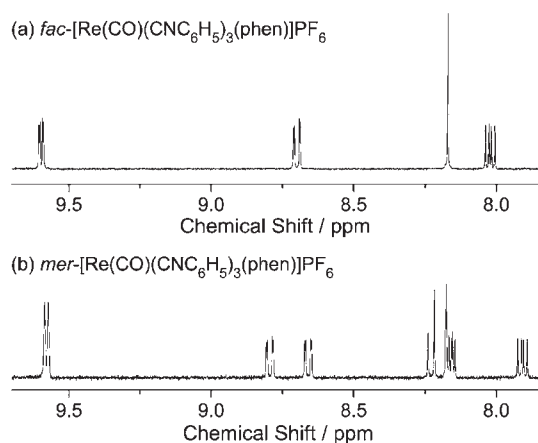


Figure 1. Phenanthroline proton peaks in ^1H NMR spectra of (a) **2** and (b) **9** in CDCl_3 .

stretches. Because of the competition of the π back-bonding interactions between the isocyanide and the carbonyl ligands, the carbonyl stretching frequency for the *fac*- isomer of the phenanthroline complexes in the CH_2Cl_2 solution (Supporting Information, Table S1) increased with the π -accepting ability of the isocyanide ligands [**8** (1934 cm^{-1}) < **7** (1940 cm^{-1}) < **2** (1945 cm^{-1}) < **4** (1949 cm^{-1}) \leq **3** (1951 cm^{-1})]. Also, the *fac*- isomer shows a higher carbonyl stretching frequency than the corresponding *mer*- isomer [**9** (1904 cm^{-1}) < **2** (1945 cm^{-1}); **5** (1906 cm^{-1}) < **6** (1946 cm^{-1})] as the carbonyl ligand is *trans* to the isocyanide in the *fac*- isomer whereas it is *trans* to the diimine ligand in the *mer*- isomer. For the complexes with general formula of $[\text{Re}(\text{CO})(\text{L}_x)(\text{CNR})_2(\text{N}-\text{N})]^+$, they can be characterized by one $\text{C}=\text{O}$ and two $\text{C}\equiv\text{N}$ stretches.

Although the facial and the meridional conformations of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]^+$ cannot be distinguished by the number of IR active $\text{C}=\text{O}$ stretches nor the $\text{C}\equiv\text{N}$ stretches, they can be readily distinguished by the ^1H NMR spectroscopy. Because of the symmetric environment of the bipyridine or phenanthroline ligand in the facial isomer, protons of the two pyridyl moieties of the diimine ligand are chemically equivalent and therefore show one set of ^1H NMR signals (Figure 1a). While for the meridional conformation, the two pyridine moieties of the bipyridine or phenanthroline ligand are of different chemical environments, two different sets of ^1H NMR signals for the two pyridyl moieties of the bipyridine or phenanthroline ligand (Figure 1b) would be observed. Since different sets of ^1H NMR signals of the two pyridyl moieties in the *mer*-isomer show similar coupling patterns and constants, their proton signals were unambiguously assigned based on the two-dimensional (2D) homonuclear correlation spectroscopy (^1H - ^1H COSY). The COSY spectra of the *mer*- isomers (**5** and **9**) suggested that the chemical shifts of one of the pyridyl rings in the diimine ligand are more downfield. This is probably due to the difference of the electronic effects as one of the pyridyl rings is *trans* to the carbonyl ligand and the other is *trans* to the isocyanide ligand. Comparing the *mer*- and *fac*- isomers, the chemical shifts of most of the proton signals in the diimine ligand of the *fac*- isomer are in between those of the two sets of the proton signals at the same ring position of the pyridyl rings in *mer*- isomer and are relatively closer to the upfield pyridyl proton signals of the *mer*- isomer (Figure 1). The overall slightly more downfield signals for the *mer*- isomer compared to the *fac*- isomer is suggestive of the more

electron deficient diimine ligand in the *mer*- isomer, which is consistent with the better π -accepting ability of the carbonyl ligand than the isocyanide ligand. On the basis of these observations and the previous NMR spectroscopic study of $[\text{Mo}(\text{CO})_{4-n}(\text{CNR})_n(\text{bpy})]$ ($n = 0-2$),¹⁷ which show a progressive upfield shifting of the bipyridyl protons on successive replacement of the carbonyl ligand with the isocyanide ligand, the more downfield pyridyl proton signals in the *mer*- isomers are tentatively assigned to those of the pyridyl ring *trans* to the carbonyl ligand.

X-ray Crystal Structure Determination. Diffraction quality crystals of **1**, **3**, **4**, **5**, **6**, **8**, **9**, and *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_3\text{Pr}_2\text{-2,6})_3]\text{OTf}$ were obtained by slow diffusion of diethyl ether vapor into concentrated dichloromethane, methanol, or acetone solutions of the complexes. Both the *fac*- and *mer*- isomers of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ were also confirmed by X-ray crystallography. Perspective drawings of the complex cations of **1**, **3**, **4**, **5**, **6**, **8**, **9**, and *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_3\text{Pr}_2\text{-2,6})_3]\text{OTf}$ are depicted in Figure 2. The experimental details for the crystal structure determinations, and the selected bond distances and bond angles are summarized in Tables 1 and 2, respectively.

The rhenium metal in the crystal structure of *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_3\text{Pr}_2\text{-2,6})_3]\text{OTf}$ adopted an octahedral geometry and owing to the highly symmetric environment, the bond lengths of three $\text{Re}-\text{C}$ (isocyanide), three $\text{Re}-\text{C}$ (carbonyl), and three $\text{C}\equiv\text{N}$ (isocyanide) are very similar with averaged distances of 2.074 \AA , 1.986 \AA , and 1.153 \AA , respectively. These bonding parameters are similar to those reported for other related carbonyl rhenium(I) isocyanide complexes.¹⁵ For the crystal structures of *fac*- $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ (**1**, **3**, **4**, **6**, and **8**) and *mer*- $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ (**5** and **9**), the rhenium metals adopted a distorted octahedral geometry with the bite angles of the diimine ligands ranging from 74.7° to 76.0° , typical of rhenium complexes with diimine ligands.^{2,3} The deviations of the $\text{C}\equiv\text{N}-\text{C}$ bond angle of isocyanide ligands from linearity in these structures are attributed to the π -back-bonding interaction from the rhenium metal center.^{6,18} As a consequence of the competitions for π -back bonding interaction and the difference of *trans*- influence, $\text{C}\equiv\text{N}-\text{C}$ are more linear for isocyanide ligands that are *trans*- to the carbonyl ligand or *trans*- to the isocyanide ligand (averaged angle 173.1°) compared to those *trans*- to the diimine ligand (averaged angle 164.3°).

UV-vis Spectroscopy. The absorption properties of complexes **1-12** in CH_2Cl_2 solution were investigated, and the electronic absorption data are summarized in Table 3. Intense absorptions at $260-340\text{ nm}$ with molar extinction coefficients on the order of $10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ were observed in all complexes. Such absorptions are attributable to the spin allowed intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the isocyanide and diimine moieties. Moreover, one to two additional moderately intense MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{CNR})$] and [$d\pi(\text{Re}) \rightarrow \pi^*(\text{N}-\text{N})$] absorption bands or shoulders with molar extinction coefficients on the order of $10^3\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ were also observed at lower energy region of $385-455\text{ nm}$ (Supporting Information, Figure S1).^{3,6,19} With reference to the previous spectroscopic and computation study of related rhenium isocyanide diimine complexes,²⁰ the higher energy absorption is assigned as the MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{CNR})$] transition.

The lowest energy MLCT absorption bands of **1-9** show strong dependency on the electronic nature of both the isocyanide and diimine ligands (Supporting Information, Figure S2). The absorption energy for complexes with the

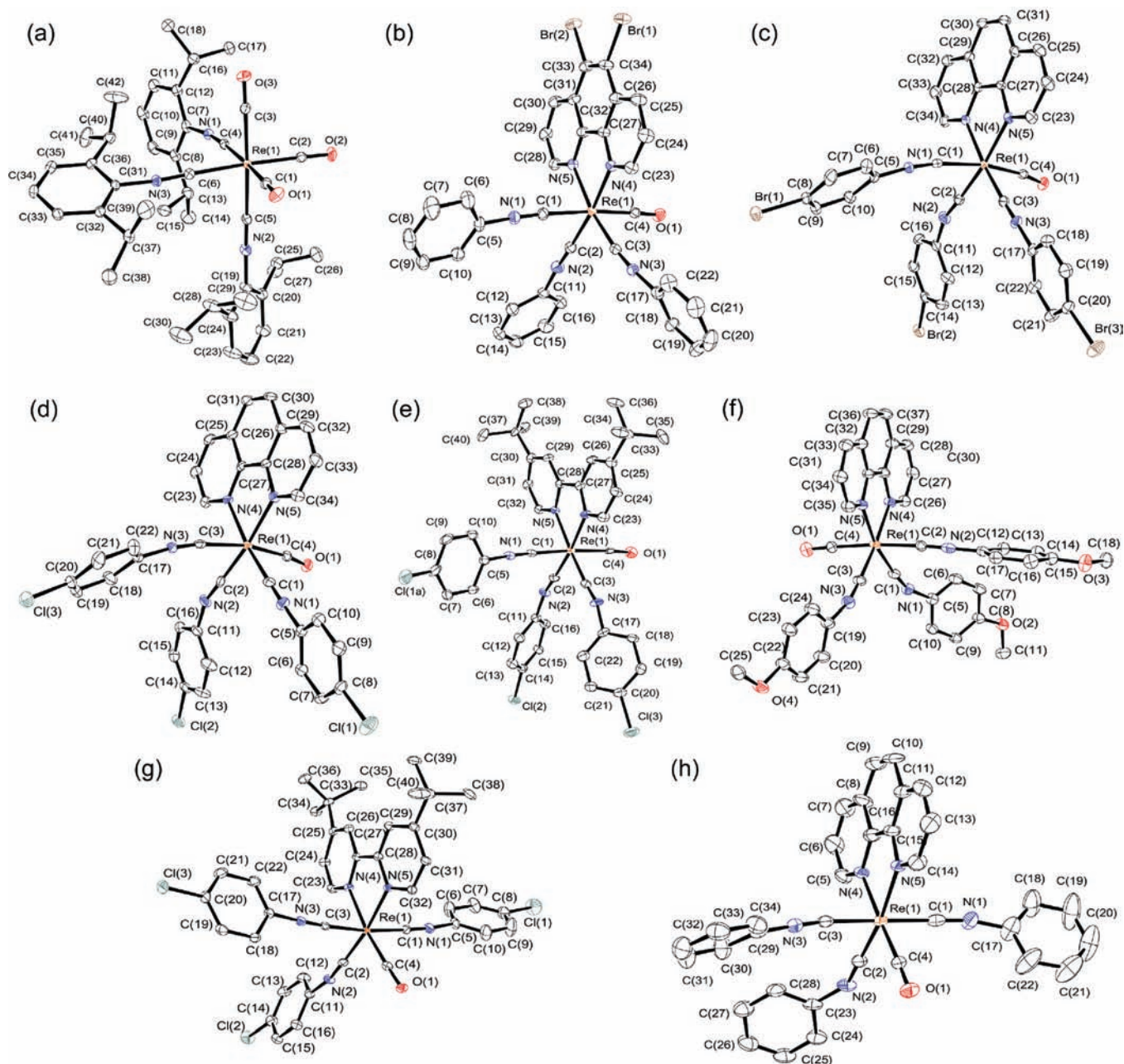


Figure 2. Perspective drawings of the complex cations of (a) *fac*-[Re(CO)₃(CNC₆H₃ⁱPr₂-2,6)₃]OTf, (b) **1**, (c) **3**, (d) **4**, (e) **6**, (f) **8**, (g) **5**, and (h) **9**.

same diimine ligand is progressively lower from those with isocyanide ligands bearing electron-withdrawing substituents to those with electron-releasing substituents, as reflected by the order of λ_{abs} : **4** (411 nm) < **3** (418 nm) < **2** (430 nm) < **7** (437 nm) \approx **8** (436 nm). On the other hand, the absorption energy of the MLCT transition shows an opposite substituent effect on the diimine ligands for complexes with same isocyanide ligands, as exemplified from the trends of λ_{abs} : **2** (430 nm) < **1** (443 nm) and **6** (392 nm) < **4** (411 nm). These observed energy dependences result from the modification of the orbital energy level of $d\pi(\text{Re})$ through the rhenium-isocyanides (Re–CNR) interactions and orbital energy level of $\pi^*(\text{N–N})$ by substituents with different electronic features and therefore consistent with the assignment of MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{N–N})$] transition. Although the

ligand-to-ligand charge transfer (LLCT) [$\pi(\text{CNR}) \rightarrow \pi^*(\text{N–N})$] transitions are also expected to show similar energy dependence, this assignment is disfavored because these lowest-energy absorptions are significantly shifted when one of the isocyanide ligands is replaced by other ligands as reflected from the absorption maxima of **4** (411 nm) < **12** (427 nm) < **11** (435 nm) < **10** (453 nm).

Emission Spectroscopy. Upon excitation with $\lambda < 450$ nm in CH₂Cl₂ solution, complexes **1–12** exhibited an orange to red photoluminescence at room temperature with emission maxima in the range of 607–690 nm (Table 3, Supporting Information, Figure S2). With reference to the previous spectroscopic and computational study of related rhenium diimine complexes,^{1,3,6,19,20} these emissions are ascribed to the metal–ligand-to-ligand charge transfer (MLLCT) [$d\pi(\text{Re})/\pi^*(\text{RNC}) \rightarrow \pi^*(\text{N–N})$]

Table 1. Crystal and Structure Determination Data for 1, 3–6, 8, and 9

	1	3	4	5	6	8	9
Formula	C ₃₄ H ₂₁ Br ₂ F ₆ N ₃ OPRe	C ₃₃ H ₂₁ Br ₃ Cl ₃ F ₆ N ₃ OPRe	C ₃₃ H ₂₂ Cl ₃ F ₆ N ₃ OPRe	C ₄₀ H ₃₆ Cl ₃ N ₃ OReF ₆ P	C ₄₀ H ₃₆ Cl ₃ F ₆ N ₃ OPRe	C ₇₄ H ₃₈ F ₁₂ N ₁₀ O ₈ P ₂ Re ₂	C ₇₄ H ₄₁ F ₁₂ N ₁₀ O _{3.50} P ₂ Re ₂
<i>M_r</i>	1006.55	1204.82	1037.00	1040.26	1040.26	1877.64	1808.67
<i>T</i> , [K]	133(2)	133(2)	173(2)	100(2)	113(2)	133(2)	133(2)
<i>a</i> , [Å]	13.1790(3)	13.1665(2)	12.6678(6)	14.4834(4)	11.6902(3)	24.7197(6)	14.4508(3)
<i>b</i> , [Å]	13.3794(2)	18.3381(3)	17.9925(10)	23.0100(7)	20.5384(6)	19.1464(5)	15.1260(4)
<i>c</i> , [Å]	13.8300(3)	16.5999(3)	16.7007(6)	14.6848(7)	17.7957(4)	15.3390(4)	18.0429(5)
α , [deg]	72.3996(16)	90.00	90.00	90.00	90.00	90.00	86.884(2)
β , [deg]	70.3319(17)	94.5741(15)	94.874(4)	96.219(3)	97.044(3)	91.439(2)	78.297(2)
γ , [deg]	62.2971(19)	90.00	90.00	90.00	90.00	90.00	75.048(2)
<i>V</i> , [Å ³]	2001.73(7)	3995.26(12)	3792.8(3)	4865.1(3)	4240.5(2)	7257.6(3)	3731.10(16)
crystal color	red	orange	orange	yellow	yellow	red	yellow
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$C2/c$	$P\bar{1}$
<i>Z</i>	2	4	4	4	4	4	2
<i>F</i> (000)	964	2296	2016	2056	2056	3696	1782
<i>D_c</i> , [g cm ⁻³]	1.670	2.003	1.816	1.420	1.629	1.718	1.610
crystal dimensions [mm]	0.2 × 0.2 × 0.05	0.2 × 0.2 × 0.05	0.3 × 0.3 × 0.05	0.9 × 0.2 × 0.05	0.5 × 0.4 × 0.05	0.3 × 0.3 × 0.05	0.2 × 0.1 × 0.1
λ , [Å]	1.54178	1.54180	0.71073	1.5418	1.54180	1.54180	1.54180
μ /mm ⁻¹	9.18	12.27	3.67	7.20	8.26	7.66	7.377
collection range	3.45 ≤ θ ≤ 67.0°	3.37 ≤ θ ≤ 67.0°	3.5 ≤ θ ≤ 29.2°	3.59 ≤ θ ≤ 67.0°	3.81 ≤ θ ≤ 67.0°	3.58 ≤ θ ≤ 67.0°	3.7 ≤ θ ≤ 71.4°
completeness to θ	99.9%	100%	99.7%	99.6%	98%	99.9%	96.7%
no. of data collected	33376	15738	14950	35595	16251	14000	24953
no. of unique data	7121	7114	6643	8653	7400	6479	12861
no. of data used in refinement, <i>m</i>	6671	6468	4457	7835	5905	5798	9955
no. of parameters refined, <i>p</i>	472	496	487	520	529	490	891
<i>R^w</i>	0.0277	0.0342	0.0353	0.0524	0.0541	0.0432	0.0710
<i>wR²</i>	0.0712	0.0917	0.0730	0.1463	0.1523	0.1208	0.1983
goodness-of-fit, <i>S</i>	1.053	1.023	0.90	1.055	1.04	1.06	1.06
maximum shift, (Δ / σ) _{max}	0.002	0.002	0.001	0.001	0.001	0.002	0.001
residual extrema in final difference map, e Å ⁻³	+1.685, -0.957	+1.931, -1.117	+1.496, -1.126	+4.494, -2.818	+2.281, -1.685	+2.812, -1.075	+4.705, -2.275
^a $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bP]$, where $P = [2F_c^2 + \text{Max}(F_o, 0)]/3$.							

Table 2. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations (e.s.d.s.) in Parentheses for **1**, **3–6**, **8**, and **9**

1							
Re(1)–N(4)	2.165(3)	Re(1)–N(5)	2.171(3)	Re(1)–C(1)	2.069(4)	Re(1)–C(2)	1.973(4)
Re(1)–C(3)	1.973(4)	Re(1)–C(4)	1.947(4)	C(1)–N(1)	1.152(5)	C(2)–N(2)	1.162(5)
C(3)–N(3)	1.163(5)	C(4)–O(1)	1.144(5)				
C(3)–N(3)–C(17)	173.9(4)	C(1)–N(1)–C(5)	176.5(4)	C(2)–N(2)–C(11)	173.0(4)		
N(4)–Re(1)–N(5)	75.27(11)						
3							
Re(1)–N(4)	2.166(3)	Re(1)–N(5)	2.183(4)	Re(1)–C(1)	2.061(4)	Re(1)–C(2)	1.949(5)
Re(1)–C(3)	1.973(5)	Re(1)–C(4)	1.954(4)	C(1)–N(1)	1.155(6)	C(2)–N(2)	1.178(6)
C(3)–N(3)	1.170(6)	C(4)–O(1)	1.151(5)				
C(1)–N(1)–C(5)	173.2(4)	C(2)–N(2)–C(11)	162.0(5)	C(3)–N(3)–C(17)	173.9(5)		
N(4)–Re(1)–N(5)	75.96(13)						
4							
Re(1)–N(4)	2.178(4)	Re(1)–N(5)	2.181(5)	Re(1)–C(1)	1.974(6)	Re(1)–C(2)	1.930(7)
Re(1)–C(3)	2.061(6)	Re(1)–C(4)	1.959(7)	C(1)–N(1)	1.161(7)	C(2)–N(2)	1.181(8)
C(3)–N(3)	1.146(7)	C(4)–O(1)	1.137(7)				
C(1)–N(1)–C(5)	176.6(6)	C(2)–N(2)–C(11)	160.9(7)	C(3)–N(3)–C(17)	172.4(6)		
N(4)–Re(1)–N(5)	76.18(18)						
5							
Re(1)–N(4)	2.179(4)	Re(1)–N(5)	2.154(4)	Re(1)–C(1)	2.020(5)	Re(1)–C(2)	1.985(5)
Re(1)–C(3)	2.038(5)	Re(1)–C(4)	1.911(5)	C(1)–N(1)	1.157(7)	C(2)–N(2)	1.157(7)
C(3)–N(3)	1.157(7)	C(4)–O(1)	1.154(6)				
C(1)–N(1)–C(5)	174.3(6)	C(2)–N(2)–C(11)	169.7(5)	C(3)–N(3)–C(17)	174.8(5)		
N(4)–Re(1)–N(5)	74.72(15)						
6							
Re(1)–N(4)	2.163(5)	Re(1)–N(5)	2.184(5)	Re(1)–C(1)	2.047(7)	Re(1)–C(2)	1.975(7)
Re(1)–C(3)	1.959(7)	Re(1)–C(4)	1.953(7)	C(1)–N(1)	1.163(9)	C(2)–N(2)	1.175(9)
C(3)–N(3)	1.179(9)	C(4)–O(1)	1.149(9)				
C(1)–N(1)–C(5)	173.7(7)	C(2)–N(2)–C(11)	156.3(7)	C(3)–N(3)–C(17)	157.2(8)		
N(4)–Re(1)–N(5)	74.9(2)						
8							
Re(1)–N(4)	2.179(4)	Re(1)–N(5)	2.169(4)	Re(1)–C(1)	1.983(4)	Re(1)–C(2)	2.047(4)
Re(1)–C(3)	1.963(4)	Re(1)–C(4)	1.975(4)	C(1)–N(1)	1.161(6)	C(2)–N(2)	1.173(6)
C(3)–N(3)	1.171(6)	C(4)–O(1)	1.122(6)				
C(1)–N(1)–C(5)	159.1(5)	C(2)–N(2)–C(12)	171.2(4)	C(3)–N(3)–C(19)	164.4(5)		
N(4)–Re(1)–N(5)	75.92(14)						
9							
Re(2)–N(9)	2.182(8)	Re(2)–N(10)	2.167(7)	Re(2)–C(4)	2.053(10)	Re(2)–C(5)	1.934(11)
Re(2)–C(6)	2.017(12)	Re(2)–C(8)	1.914(10)	C(4)–N(4)	1.147(13)	C(5)–N(5)	1.189(14)
C(6)–N(6)	1.194(15)	C(8)–O(2)	1.158(13)				
C(4)–N(4)–C(39)	176.7(10)	C(5)–N(5)–C(45)	144.5(11)	C(6)–N(6)–C(51)	164.8(11)		
N(9)–Re(2)–N(10)	75.0(3)						

phosphorescence. For complexes **1–9** with general formula of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$, their emission show similar

correlation with the π -accepting ability of the diimine and isocyanide ligands (Figure 3a) [**8** (674 nm) > **7** (650 nm) > **2**

Table 3. UV-vis Absorption and Emission Data for 1–12

	medium (T/K)	emission λ_{em}/nm ($\tau_o/\mu s$)	$\phi_{em}^a \times 10^3$	absorption ^b λ_{abs}/nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$)
1	CH ₂ Cl ₂ (298)	676 (0.031)	5.09	240 (63490), 276 (87500), 290 sh (53810), 313 sh (33140), 330 sh (22750), 386 (11850), 443 sh (9215)
	Glass ^c (77)	595 (1.06)		
2	CH ₂ Cl ₂ (298)	640 (0.075)	19.4	266 (79960), 291 (49440), 338 (21535), 377 (14130), 430 sh (8740)
	Glass ^c (77)	573 (2.01)		
3	CH ₂ Cl ₂ (298)	625 (0.090)	51.9	266 (75140), 293 sh (50905), 344 (28235), 384 (18080), 418 sh (10590)
	Glass ^c (77)	560 (2.21)		
4	CH ₂ Cl ₂ (298)	621 (0.146)	36.7	267 (75080), 293 (53745), 386 sh (19400), 411 sh (11355)
	Glass ^c (77)	561 (4.00)		
5	CH ₂ Cl ₂ (298)	607 (0.0992)	26.5	240 (56570), 288 (67930), 310 (67315), 348 sh (32310), 394 sh (19710)
	Glass ^c (77)	540 (3.24)		
6	CH ₂ Cl ₂ (298)	618 (0.055)	24.4	241 (62990), 285 (78290), 307 sh (54265), 344 (31995), 392 (18355)
	Glass ^c (77)	542 (1.54)		
7	CH ₂ Cl ₂ (298)	650 (0.082)	17.4	267 (72140), 293 (45750), 336 (20770), 384 (12780), 437 (8230)
	Glass ^c (77)	582 (2.16)		
8	CH ₂ Cl ₂ (298)	674 (0.046)	5.14	267 (92200), 293 (62995), 322 sh (30000), 382 (15405), 436 (9575)
	Glass ^c (77)	592 (1.42)		
9	CH ₂ Cl ₂ (298)	625 (0.128)	26.1	268 (76785), 294 (59650), 342 sh (24350), 385 (17715)
	Glass ^c (77)	577 (5.61)		
10	CH ₂ Cl ₂ (298)	690 (0.050)	4.43	271 (62820), 295 (35760), 324 (30360), 374 (16390), 453 (6620)
	Glass ^c (77)	638 (1.02)		
11	CH ₂ Cl ₂ (298)	665 (0.068)	5.57	269 (55400), 292 (33715), 319 (25610), 371 (14615), 435 (7520)
	Glass ^c (77)	609 (1.83)		
12	CH ₂ Cl ₂ (298)	630 (0.217)	37.2	269 (56240), 295 (41920), 323 (32390), 372 (14850), 427 (7005)
	Glass ^c (77)	576 (6.30)		

^a Measured with 436-nm excitation using [Ru(bpy)₃]Cl₂ as the reference. ^b In CH₂Cl₂ at 298 K. ^c EtOH/MeOH = 4:1 (v/v).

(640 nm) > 3 (625 nm) ≥ 4 (621 nm) for phenanthroline complexes with different isocyanide ligands; 1 (676 nm) > 2 (640 nm) for phenylisocyanato complexes with different diimine ligands; 4 (621 nm) > 6 (618 nm) for chlorophenylisocyanato complexes with different diimine ligands] as the lowest-energy MLCT transition. Such emission energy dependence and the sub microsecond lifetime are supportive of the MLLCT phosphorescence assignment. Moreover, because of the higher basicity of the isocyanide ligands compared to carbonyl ligands that results in the formation of a higher-lying $d\pi(\text{Re})$ orbital, the emission energies are in the order of $[\text{Re}(\text{CO})_2(\text{CNR})_2(\text{N}-\text{N})]\text{PF}_6^{6b} > [\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6 > [\text{Re}(\text{CNR})_4(\text{N}-\text{N})]\text{PF}_6^{6a}$ for similar isocyanide and diimine ligands.

As with tris-cyclometalated Ir(III) complexes, $\text{Ir}(\text{C}^{\wedge}\text{N})_3$, where $\text{C}^{\wedge}\text{N}$ = cyclometalating ligand,⁷ the emissions of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ are also sensitive to the isomeric conformations. A slight blue-shift in the emission energy is observed for meridional isomers compared to facial isomers (Figure 3b) [9 (625 nm) vs 2 (640 nm); 5 (607 nm) vs 6 (618 nm)]. As discussed above, the carbonyl ligands can better stabilize $d\pi(\text{Re})$ orbital than the isocyanide ligands. Consequently, when the carbonyl ligand is *trans*- to the diimine ligand in the meridional form, it can stabilize the rhenium metal center to a greater extent through a stronger metal–ligand interaction compared to that in facial conformation, in which the carbonyl ligand is *trans*- to the isocyanide ligand. This could be reflected from the higher metal-centered oxidation potentials for the *mer*-isomers compared to the *fac*-isomers (vide infra).

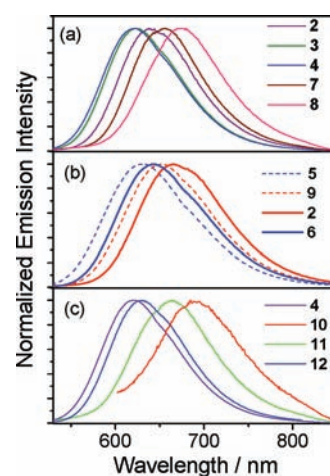


Figure 3. Normalized emission spectra of (a) *fac*-[Re(CNR)₃(CO)(phen)]PF₆ with different isocyanide ligands, (b) *fac*- (solid) and *mer*- (dotted lines) isomers of [Re(CO)(CNC₆H₅)₃(phen)]PF₆ (red lines) and [Re(CO)(CNC₆H₄Cl-4)₃(*t*Bu₂bpy)]PF₆ (blue lines), and (c) [Re(CO)(L_x)(CNC₆H₄Cl-4)₂(phen)]PF₆ with different L_x = CNC₆H₄Cl-4, MeCN, pyridine, PPh₃ in CH₂Cl₂ solution at 298 K.

When one of the isocyanide ligands of *fac*-[Re(CO)(CNC₆H₄Cl-4)₃(phen)]PF₆ is replaced with MeCN or pyridine or triphenylphosphine ligand, the emission energies are in line with the π -acidity of the substituted ligand, as reflected from the emission maxima λ_{em} : 4 (621 nm) < 12 (630 nm) < 11

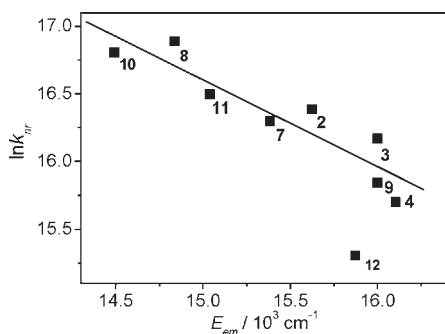


Figure 4. Plot of $\ln k_{nr}$ versus E_{em} (298 K, CH_2Cl_2) for phenanthroline complexes 2–4 and 7–12 with linear least-squares fit.

(665 nm) < 10 (690 nm) (Figure 3c). This is also ascribed to the change of the energy level in the $d\pi(\text{Re})$ orbital as a result of different metal–ligand interaction and is further supportive of the MLLCT excited state assignment. Although the emission lifetimes and the quantum yields varied considerably in the whole series of complexes, the variations for all phenanthroline complexes except 12 were found to follow the energy gap law²¹ as reflected by the linear relationship ($R = 0.92$) between $\ln(k_{nr})$ and emission energy (E_{em}) (Figure 4). The slope of 5.2 eV^{-1} is similar in magnitude compared to those found for other MLCT emitters.²² This correlation suggests that the emissive excited states of these phenanthroline complexes have very similar vibrational and electronic components. The deviation of the emission properties of 12 from the linear correlation may be suggestive of different modes of deactivation or electronic structure of the emissive excited state of 12 compared to other phenanthroline complexes. The emissions of the complexes in low-temperature 77 K EtOH–MeOH (4:1 v/v) glassy medium were also investigated (Table 3). Compared to the solution medium, blue-shifted emissions, because of the luminescence rigidochromic effect,²³ with similar emission energy trends (Supporting Information, Figure S3) were observed. These emissions are also assigned to be derived from an ³MLLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{N}-\text{N})$] excited state origin.

Electrochemistry. The electrochemical properties of the complexes were studied by cyclic voltammetry. Complexes 1–12 generally exhibit a quasi-reversible oxidation, irreversible oxidation wave in the range of +0.81 V to +1.00 V and +1.70 V to +1.90 V vs SCE, respectively. Except for 1, which exhibits two irreversible reduction waves in the reductive scan, a quasi-reversible reduction couple ranged from –1.28 V to –1.45 V vs SCE was recorded in all other complexes. The representative cyclic voltammograms of 3 are shown in Figure 5, and the electrochemical data of 1–12 are summarized in Table 4.

With reference to electrochemical studies of related rhenium complexes⁶ and the sensitivity of the oxidative potentials toward the changes of the isocyanide and diimine ligands, the first oxidation couple and irreversible oxidation wave are tentatively suggested to be the successive metal-centered $\text{Re}^{\text{II/I}}$ and $\text{Re}^{\text{III/II}}$ oxidations. By comparing the first oxidation potentials of different complexes, corresponding to the $\text{Re}^{\text{II/I}}$ couple, the relative energy of the Highest Occupied Molecular Orbital (HOMO) [$d\pi(\text{Re})$] could be revealed. As discussed in the UV–vis absorption and emission properties of these complexes, the $d\pi(\text{Re})$ orbital would be more stabilized with better π -accepting isocyanide ligands; consequently, the first oxidation potentials

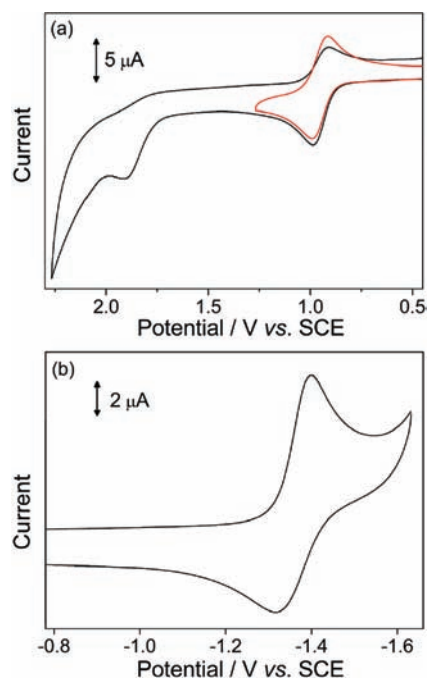


Figure 5. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of 3 in MeCN ($0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6$). Scan rate: 100 mVs^{-1} .

Table 4. Electrochemical Data for 1–12 in Acetonitrile Solution ($0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6$) at 298 K^a

Complex	oxidation, ^b $E_{1/2}/\text{V vs SCE}$	reduction, ^b $E_{1/2}/\text{V vs SCE}$
	($E_{pa}/\text{V vs SCE}$)	($E_{pc}/\text{V vs SCE}$)
1	0.91, (1.90)	(–1.18), (–1.28)
2	0.90, (1.85)	–1.39
3	0.95, (1.90)	–1.37
4	0.98, (1.90)	–1.37
5	1.00, (1.76)	–1.45
6	0.92, (1.80)	–1.45
7	0.93, (1.97)	–1.40
8	0.78, (1.58)	–1.40
9	0.97, (1.85)	–1.41
10	0.81, (1.72)	–1.28
11	0.84, (1.80)	–1.36
12	0.98, (1.71)	–1.39

^a Working electrode, glassy carbon; scan rate, 100 mVs^{-1} . ^b $E_{1/2}$ is $(E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.

for complexes with the same diimine ligands are in line with the π -accepting ability of the corresponding isocyanide ligands: 4 (+0.98 V) > 3 (+0.95 V) > 7 (+0.93 V) > 2 (+0.90 V) > 8 (+0.78 V). Similarly, with the same isocyanide ligands, a higher oxidation potential is observed for complexes with more electron-withdrawing diimine ligand, as reflected by 4 (+0.98 V) > 6 (+0.92 V). The lower-lying $d\pi(\text{Re})$ orbital in *mer*- isomers compared to the *fac*- isomers could be revealed by the slightly higher oxidative potentials for 9 (+0.97 V) and 5 (+1.00 V) relative to those of 2 (+0.90 V) and 6 (+0.92 V), respectively. In the reductive scan, the reversible reduction couple observed in

2–12 is highly sensitive to the nature of the diimine ligand and relatively insensitive to the change of the isocyanide ligand; therefore it is assigned as the one-electron diimine-based reductions that are commonly observed in other rhenium(I) diimine complexes.^{3a,6,19a} The irreversible reduction wave observed in **1** may be attributed to the instability of the reduced phenanthroline ligand in the presence of bromine substituents as similar irreversible diimine-based ligand reductions are commonly observed in metal complexes with bromo-substituted diimine ligands.²⁴

CONCLUSION

New classes of rhenium(I) complexes with general formula of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ and $[\text{Re}(\text{CO})(\text{L}_x)(\text{CNR})_2(\text{N}-\text{N})]\text{PF}_6$ with tunable features have been synthesized and characterized by IR spectroscopy, ¹H NMR, ESI mass spectrometry, and elemental analysis. The photophysical and electrochemical properties of all these complexes were investigated. Both the *fac*- and *mer*- conformations of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$ were also structurally characterized by X-ray crystallography.

In the preparation of the *fac*- and *mer*- conformations of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$, photochemical ligand substitution reactions of *fac*- $[\text{Re}(\text{CO})_3(\text{CNR})_3]\text{OTf}$ and *mer*- $[\text{Re}(\text{CO})_2(\text{CNR})_3\text{Br}]$ with different diimine ligands were performed. However, some of the photochemical ligand substitution reactions gave an isomeric mixture of the target complexes. Another synthetic methodology based on the oxidative decarbonylation reaction by Me_3NO and subsequent ligand substitution reactions were developed and demonstrated to be highly effective in the preparation of both the isomeric pure *fac*- and *mer*- forms of $[\text{Re}(\text{CO})(\text{CNR})_3(\text{N}-\text{N})]\text{PF}_6$. With these new synthetic methodologies, rhenium(I) diimine luminophores capable of functionalized in various orientations and with tailored excited state properties could be achieved.

ASSOCIATED CONTENT

Supporting Information. IR spectral data of complexes **1–12** in CH_2Cl_2 solution, crystal and structure determination data, and selected bond lengths and bond angles for *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_3\text{Pr}_2-2,6)_3]\text{OTf}$, CIF files giving crystallographic data for **1**, **3**, **4**, **5**, **6**, **8**, **9**, and *fac*- $[\text{Re}(\text{CO})_3(\text{CNC}_6\text{H}_3\text{Pr}_2-2,6)_3]\text{OTf}$, bar diagrams showing the absorption and emission energies of complexes **1–12** in CH_2Cl_2 solution at 298 K and overlaid absorption spectra of selected complexes and emission spectra of **1–12** in 77 K EtOH–MeOH (4:1 v/v) glassy medium. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: vinccko@cityu.edu.hk. Fax: (+852)-3442-0522. Phone: (+852)-3442-6958.

ACKNOWLEDGMENT

The work described in this paper was supported by a RGC GRF grant from the Research Grants Council of the Hong Kong (Project No. CityU 101510) and a grant from City University of Hong Kong (Project No. 7002594). A.W.-Y.C. and L.T.-L.L.

acknowledge the receipt of a Postgraduate Studentship from the City University of Hong Kong.

REFERENCES

- (1) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.
- (2) (a) Ranjan, S.; Lin, S.-Y.; Hwang, K.-C.; Chi, Y.; Ching, W.-L.; Liu, C.-S. *Inorg. Chem.* **2003**, *42*, 1248. (b) Lundin, N. J.; Blackman, A. G.; Gordon, K. C.; Officer, D. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 2582. (c) Tse, C.-W.; Man, K. K.-Y.; Cheng, K.-W.; Mak, C. S.-K.; Chan, W.-K.; Yip, C. T.; Liu, Z.-T.; Djuricic, A. B. *Chem.—Eur. J.* **2007**, *13*, 328. (d) Si, Z.; Li, J.; Li, B.; Zhao, F.; Liu, S.; Li, W. *Inorg. Chem.* **2007**, *46*, 6155. (e) Mauro, M.; Procopio, E. Q.; Sun, Y.; Chien, C.-H.; Donghi, D.; Panigati, M.; Mercandelli, P.; Mussini, P.; D'Alfonso, G.; De Cola, L. *Adv. Funct. Mater.* **2009**, *19*, 2607.
- (3) (a) Wrighton, M. S.; Morse, D. L.; Pdungsap, L. *J. Am. Chem. Soc.* **1975**, *97*, 2073. (b) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1983**, 536. (c) Shaw, J. R.; Webb, R. T.; Schmehl, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 1117. (d) Yam, V. W.-W.; Ko, C.-C.; Wu, L.-X.; Wong, K. M.-C.; Cheung, K.-K. *Organometallics* **2000**, *19*, 1820. (e) Yam, V. W.-W.; Ko, C.-C.; Zhu, N. *J. Am. Chem. Soc.* **2004**, *126*, 12734. (f) Ko, C.-C.; Kwok, W.-M.; Yam, V. W.-W.; Phillips, D.-L. *Chem.—Eur. J.* **2006**, *12*, 5840. (g) Abdel-Shafi, A. A.; Bourdelande, J. L.; Ali, S. S. *Dalton Trans.* **2007**, 2510.
- (4) (a) Kotal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, *4*, 2161. (b) Hori, H.; Johnson, F. P. A.; Koike, K.; Ishitani, O.; Ibusuki, T. *J. Photochem. Photobiol. A* **1996**, *96*, 171. (c) Koike, K.; Hori, H.; Ishizuka, M.; Westwell, J. R.; Takeuchi, K.; Ibusuki, T.; Enjouji, K.; Konno, H.; Sakamoto, K.; Ishitani, O. *Organometallics* **1997**, *16*, 5724. (d) Gibson, D. H.; Yin, X. *Chem. Commun.* **1999**, 1411. (e) Hayashi, Y.; Kita, S.; Brunschwig, B. S.; Fujita, E. *J. Am. Chem. Soc.* **2003**, *125*, 11976. (f) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. *J. Am. Chem. Soc.* **2008**, *130*, 2023.
- (5) (a) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 6108. (b) Yoon, D. I.; BergBrennan, C. A.; Lu, H.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 3192. (c) Lewis, J. D.; Perutz, R. N.; Moore, J. N. *J. Phys. Chem. A* **2004**, *108*, 9037. (d) Pope, S. J. A.; Coe, B. J.; Faulkner, S. *Chem. Commun.* **2004**, 1550. (e) Cattaneo, M.; Fagalde, F.; Katz, N. E. *Inorg. Chem.* **2006**, *45*, 6884. (f) Li, M.-J.; Ko, C.-C.; Duan, G.-P.; Zhu, N.; Yam, V. W.-W. *Organometallics* **2007**, *26*, 6091. (g) Uppadine, L. H.; Redman, J. E.; Dent, S. W.; Drew, M. G. B.; Beer, P. D. *Inorg. Chem.* **2001**, *40*, 2860. (h) Lo, K. K.-W.; Hui, W.-K.; Ng, D. C.-M. *J. Am. Chem. Soc.* **2002**, *124*, 9344. (i) Sun, S. S.; Lees, A. J.; Zavalij, P. Y. *Inorg. Chem.* **2003**, *42*, 3445. (j) Lo, K. K.-W.; Hui, W.-K.; Chung, C.-K.; Tsang, K. H.-K.; Lee, T. K.-M.; Li, C.-K.; Lau, J. S.-Y.; Ng, D. C.-M. *Coord. Chem. Rev.* **2006**, *250*, 1724.
- (6) (a) Ng, C.-O.; Lo, L. T.-L.; Ng, S.-M.; Ko, C.-C.; Zhu, N. *Inorg. Chem.* **2008**, *47*, 7447. (b) Ko, C.-C.; Lo, L. T.-L.; Ng, C.-O.; Yiu, S.-M. *Chem.—Eur. J.* **2010**, *16*, 13773.
- (7) (a) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377. (b) Karatsu, T.; Nakamura, T.; Yagai, S.; Kitamura, A.; Yamaguchi, K.; Matsushima, Y.; Iwata, T.; Hori, Y.; Hagiwara, T. *Chem. Lett.* **2003**, *32*, 886. (c) Fletcher, N. C.; Nieuwenhuyzen, M.; Rainey, S. *J. Chem. Soc., Dalton Trans.* **2001**, 2641. (d) Steel, P. J.; Lahousse, F.; Lerner, D.; Marzin, C. *Inorg. Chem.* **1983**, *22*, 1488. (e) Steel, P. J.; Constable, E. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1389. (f) Bond, A. M.; Coiton, R.; McGregor, K. *Inorg. Chem.* **1986**, *25*, 2378.
- (8) (a) Ugi, I.; Fetzter, U.; Eholzer, U.; Knupfer, H.; Offermann, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 472. (b) Weber, W. P.; Gokel, G. W.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1972**, *6*, 530. (c) Obrecht, R.; Herrmann, R.; Ugi, I. *Synthesis* **1985**, *4*, 400. (d) Janza, B.; Studer, A. *Org. Lett.* **2006**, *8*, 1875.
- (9) Schmidt, S. P.; Trogler, W. C.; Basolo, F.; Urbancic, M. A.; Shapley, J. R. *Inorg. Synth.* **2007**, *28*, 160.
- (10) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024.
- (11) Van Houten, J.; Watts, R. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

- (12) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.
- (13) Sheldrick, G. M. *SHELX-97: Programs for Crystal Structure Analysis*, Release 97-2; University of Göttingen: Göttingen, Germany, **1997**.
- (14) (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W.-A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (b) Beck, W.; Gotzfried, F.; Shier, E. *J. Organomet. Chem.* **1978**, *150*, 247. (c) Blumer, D. J.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71. (d) Black, D. S. C.; Deacon, G. B.; Thomas, N. C. *Inorg. Chim. Acta* **1982**, *65*, L75.
- (15) Yang, L.; Cheung, K.-K.; Mayr, A. *J. Organomet. Chem.* **1999**, *585*, 26.
- (16) Garcia Alonso, F. J.; Riera, V.; Valin, M. L.; Moreiras, D.; Vivanco, M.; Solans, X. *J. Organomet. Chem.* **1987**, *326*, C71.
- (17) Connor, J. A.; Overton, C. *J. Chem. Soc., Dalton Trans.* **1982**, 2397.
- (18) (a) Weber, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1515. (b) Pombeiro, A. J. L.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1987**, 319. (c) Fan, J.-S.; Lee, F.-Y.; Chiang, C.-C.; Chen, H.-C.; Liu, S.-H.; Wen, Y.-S.; Chang, C.-C.; Li, S.-Y.; Chi, K.-M.; Lu, K.-L. *J. Organomet. Chem.* **1999**, *580*, 82. (d) Villegas, J. M.; Stoyanov, S. R.; Moore, C. E.; Eichhorn, D. M.; Rillema, D. P. *Acta Crystallogr., Sect. E* **2005**, *61*, m533–m534.
- (19) (a) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401. (b) Worl, L. A.; Duesing, R.; Chen, P.; Ciana, L. D.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849. (c) Kirgan, R. A.; Sullivan, B. P.; Rillema, D. P. *Top. Curr. Chem.* **2007**, *281*, 45. (d) Kumar, A.; Sun, S.-S.; Lees, A. J. *Top. Organomet. Chem.* **2010**, *29*, 1.
- (20) Stoyanov, S. R.; Villegas, J. M.; Cruz, A. J.; Lockyear, L. L.; Reibenspies, J. H.; Rillema, D. P. *J. Chem. Theory. Comput.* **2005**, *1*, 95.
- (21) (a) Feed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272. (b) Fong, F. K. *Theory of Molecular Relaxation*; Wiley: New York, 1975.
- (22) (a) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (c) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3122. (d) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335. (e) Dominey, R. N.; Hauser, B.; Hubbard, J.; Dunham, J. *Inorg. Chem.* **1991**, *30*, 4754. (f) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949.
- (23) (a) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888. (b) Stufkens, D. J. *Comments Inorg. Chem.* **1992**, *13*, 359. (c) Kotch, T. G.; Lees, A. J. *Inorg. Chem.* **1993**, *32*, 2570. (d) Lees, A. J. *Comments Inorg. Chem.* **1995**, *17*, 319.
- (24) (a) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526. (b) Lai, S.-W.; Chan, Q. K.-W.; Zhu, N.; Che, C.-M. *Inorg. Chem.* **2007**, *46*, 11003. (c) Ko, C.-C.; Ng, C.-O.; Feng, H.; Chu, W.-K. *Dalton Trans.* **2010**, *39*, 6475.