Inorganic Chemistry
Article
pubs.acs.org/IC

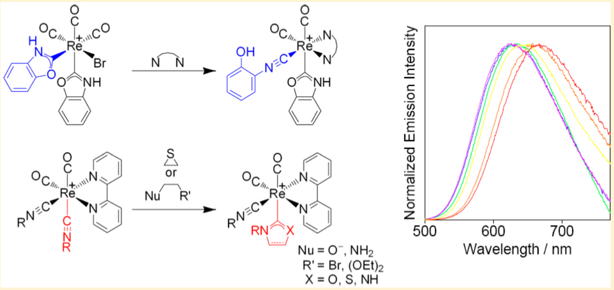
# Synthesis, Characterization, and Photophysical Study of Luminescent Rhenium(I) Diimine Complexes with Various Types of N-Heterocyclic Carbene Ligands

Chi-On Ng, Shek-Man Yiu, and Chi-Chiu Ko*

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

*Supporting Information*

**ABSTRACT:** A series of luminescent Re(I) diimine complexes with various types of N-heterocyclic carbene (NHC) ligands has been synthesized through the reaction between isocyano Re(I) diimine complexes with different nucleophiles. These Re(I) NHC complexes were characterized by $^1$H and $^{13}$C NMR and IR spectroscopy, mass spectrometry, and elemental analysis. One of the precursor complexes *fac*-$\{Re(CO)_3[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]_2Br\}$ and five of the Re(I) diimine complexes with different types of NHC ligands were also structurally characterized by X-ray crystallography. In the preparation of these Re(I) NHC complexes, it is found that the reactivity of the isocyanide ligands in the synthetic complex precursors is significantly affected by the electronic nature of the *trans* ligand. All these complexes displayed $^3$MLCT [d$\pi$(Re) → $\pi^*$(N−N)] phosphorescence in degassed $CH_2Cl_2$ and $CH_3CN$ solutions at room temperature. Through the study of the photophysical and electrochemical properties of these Re(I) NHC complexes, the electronic properties of different types of NHC ligands were investigated.



## INTRODUCTION

The rapid development of transition metal complexes with N-heterocyclic carbene (NHC) ligands over the past two decades can be attributed to their outstanding performance in catalytic applications.[1] The unique and outstanding properties of these complexes can be explained by the excellent $\sigma$-donating ability, stability, and the ease of functionalization of the NHC ligands, which allows for the tuning of their electronic and steric properties.[2] In addition to the extensive studies of their catalytic applications,[1] there has been a growing interest in the study of luminescent metal−NHC complexes.[3] These luminescent NHC-containing transition metal complexes not only exhibit novel photophysical properties but also led to the development of highly efficient OLED.[4]

To prepare transition metal complexes with NHC ligands, the most common synthetic strategies[5] include (i) direct metalation,[6] (ii) *in situ* deprotonation of azolium salt,[7] (iii) transmetalation,[8] and (iv) cleavage of electron-rich olefins.[9] Apart from the incorporation of NHC ligands, transition metal isocyanides also serve as good synthetic precursors for NHC complexes through the reactions with suitable nucleophiles.[10] On the basis of this reactivity, various nucleophile-containing isocyanide ligands, which can be readily converted to NHC ligands through an intramolecular attack on the isocyanide carbon atom, have been designed to prepare different metal NHC complexes.[11] Through the coordination of 2-trimethylsiloxyphenyl isocyanide into the carbonyl Re(I) phenanthroline complexes, we have recently reported a series of luminescent Re(I) complexes with the benzoxazol-2-ylidene ligand $\{Re(CO)_2(L)(phen)[\overline{CN(X)C_6H_4\text{-}2\text{-}O}]\}^+$ (X = H, methyl; L = CO, $PPh_3$, $PPh_2Me$, $P(OEt)_3$).[12] To further extend this work based on our previously reported isocyano rhenium(I) diimine complexes,[13] in this Article, we describe the synthesis, structures, photophysics, and electrochemistry of rhenium(I) diimine complexes with N,O-, N,N- and N,S- NHC ligands. The influence of the ancillary ligands on the reactivity of the isocyanide ligand was also investigated.

## EXPERIMENTAL SECTION

**Materials and Reagents.** $[Re(CO)_5Br]$ was obtained from Strem Chemicals, Inc. 2,2′-Bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine ($Me_2bpy$), 4,4′-di-*tert*-butyl-2,2′-bipyridine ($^t\!Bu_2bpy$), 1,10-phenanthroline (phen), benzoxazole, and *n*-butyllithium were obtained from Aldrich Chemical Co. Phosphoryl chloride ($POCl_3$), triethylamine, and formic acid were obtained from Uni-chem Chemical Reagent. 2-Bromoethanol, 2-bromoethylamine hydrobromide, thiirane, and 2,2-diethoxyethanamine were obtained from J&K Scientific Company. 2-Trimethylsiloxyphenyl isocyanide ($2\text{-}(OSiMe_3)C_6H_4NC$) and 4-chlorophenyl isocyanide ($4\text{-}ClC_6H_4NC$) were prepared according to reported literature procedures.[14] *fac*-$[Re(CO)_3(CNC_6H_4Cl\text{-}4)_2Br]$ and *cis,cis*-$[Re(CO)_2(CNC_6H_4Cl\text{-}4)_2(bpy)]Br$ were synthesized by slight modification of the corresponding literature procedures for related rhenium complexes.[13]

**Physical Measurements and Instrumentation.** Photosubstitution reactions were carried out in the photoreactor described

Received: November 9, 2013
Published: March 5, 2014

ACS Publications © 2014 American Chemical Society

previously[13] with a Pen-Ray mercury lamp (11SC-1; $\lambda$ = 254 nm) as the excitation source. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts ($\delta$, ppm) were reported relative to tetramethylsilane ($Me_4Si$). IR spectra were obtained from KBr discs by using a Perkin-Elmer Spectrum 100 FTIR spectrophotometer. All ESI mass spectra were recorded on a PE-SCIEX API 150 EX single quadrupole mass spectrometer. Elemental analyses of all compounds were performed on an Elemetar Vario MICRO Cube elemental 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 SPEX 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. The emission lifetimes were measured in the fast MCS lifetime mode with NanoLED-375LH ($\lambda_{ex}$ = 375 nm; pulse width < 750 ps) as the excitation source. The photon counting data were analyzed by Horiba Jobin Yvon Decay Analysis Software. Luminescence quantum yields were measured by the optically dilute method described by Demas and Crosby[15] with an aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\phi_{em}$ = 0.04[16] with 436 nm excitation) as the standard solution. Transient absorption spectra at room temperature were recorded by using the spectral mode on an Edinburgh Instruments LP920-KS spectrometer equipped with an intensified charge-coupled device (ICCD) detector. The excitation source for the transient absorption measurement was the third harmonic output (355 nm; 6−8 ns fwhm pulse width) of a Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd:YAG laser (10 Hz). Cyclic voltammetry measurements were performed by using a CH instrument, Inc., model CHI 620 electrochemical analyzer. Cyclic voltammetric measurements were performed in acetonitrile solutions with 0.1 M $^nBu_4NPF_6$ as the supporting electrolyte at room temperature with a glassy carbon electrode (3-mm diameter, CH Instruments, Inc.) as a working electrode, a platinum wire coil as the counter electrode, and $Ag/AgNO_3$ (10 mM in acetonitrile) electrode (CH Instruments, Inc.) as the reference electrode. The working electrode surface was polished with a 1-mm $\alpha$-alumina slurry and then a 0.3-mm $\alpha$-alumina slurry (Linde) on a microcloth (Buehler Co.). The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference. All solutions for electrochemical studies were deaerated with prepurified argon gas prior to measurements.

**Synthesis.** All reactions were performed under strictly anaerobic and anhydrous conditions in an inert atmosphere of argon using standard Schlenk techniques.

***fac*-{Re(CO)$_3$[$\overline{\text{CN(H)C}_6\text{H}_4\text{-2-O}}$]$_2$(Br)}.** $[Re(CO)_5(Br)]$ (200 mg, 492 $\mu$mol) and 2-$(OSiMe_3)C_6H_4NC$ (235 mg, 1.23 mmol) in THF−benzene (1:1, v/v, 50 mL) was refluxed overnight. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane−*n*-hexane (3:2, v/v) as eluent. Recrystallization by slow diffusion of hexane into concentrated chloroform solution of the complex gave the analytically pure complex as off-white crystalline solid. Yield: 259 mg, 441 $\mu$mol; 89.5%. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): $\delta$ 11.78 (s, 2H, NH), 7.60 (m, 2H, phenyl H), 7.44 (m, 2H, phenyl H), 7.34 (m, 4H, phenyl H). $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ 208.99, 193.54, 189.88, 152.76, 129.22, 125.58, 125.29, 111.77, 111.73. Positive-ion ESI-MS *m*/*z*: 508.7 $[M - Br]^+$. IR (KBr disc) $\nu$/cm$^{-1}$: 2028, 1949, 1902 $\nu$(C≡O). Anal. Calcd (%) for $C_{17}H_{10}BrN_2O_5Re$ (587.93): C 34.70, H 1.71, N 4.76. Found: C 34.39, H 1.91, N 4.63.

***cis*,*cis*-{Re(CO)$_2$[CNC$_6$H$_4$(OH)-2][$\overline{\text{CN(H)C}_6\text{H}_4\text{-2-O}}$](bpy)}(PF$_6$) (1).** A benzene solution (30 mL) of *fac*-{Re(CO)$_3$[$\overline{\text{CN(H)C}_6\text{H}_4\text{-2-O}}$]$_2$(Br)} (100 mg, 170 $\mu$mol) and bpy (106 mg, 680 $\mu$mol) was irradiated with UV light ($\lambda$ = 254 nm) for 3 h at room temperature with a Pen-Ray mercury lamp (11SC-1) in a water-cooled quartz jacket. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane−acetonitrile (9:1, v/v) as eluent. Subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave complex **1** as a $PF_6^-$ salt. Recrystallization by slow diffusion of diethyl ether vapor into a concentrated acetone solution of **1** gave analytically pure complex **1** as brownish orange crystalline solid. Yield: 41.4 mg, 53.0 $\mu$mol; 31.2%. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): $\delta$ 9.32 (d, 1H, *J* = 5.0 Hz, 6/6′-bpy H), 9.14 (d, 1H, *J* = 5.0 Hz, 6/6′-bpy H), 8.32 (d, 1H, *J* = 8.2 Hz, 3/3′-bpy H), 8.24 (d, 1H, *J* = 8.2 Hz, 3/3′-bpy H), 8.13 (dd, 1H, *J* = 8.6, 8.2 Hz, 4/4′-bpy H), 7.79 (dd, 1H, *J* = 8.6, 8.2 Hz, 4/4′-bpy H), 7.58 (dd, 1H, *J* = 8.6, 5.0 Hz, 5/5′-bpy H), 7.42 (d, 1H, *J* = 7.5 Hz, phenyl H), 7.32 (d, 1H, *J* = 7.8 Hz, phenyl H), 7.24 (d, 1H, *J* = 8.3 Hz, phenyl H), 7.18 (dd, 2H, *J* = 8.5, 8.3 Hz, phenyl H), 7.09 (dd, 1H, *J* = 8.5, 7.8 Hz, phenyl H), 6.98 (dd, 1H, *J* = 8.3, 7.5 Hz, phenyl H), 6.92 (dd, 1H, *J* = 8.6, 5.0 Hz, 5/5′-bpy H), 6.84 (dd, 1H, *J* = 8.5, 7.8 Hz, phenyl H). $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ 208.90, 198.44, 194.90, 167.10, 155.94, 155.74, 154.03, 153.20, 152.60, 151.45, 139.18, 138.66, 129.48, 128.94, 128.22, 127.31, 125.98, 125.41, 124.84, 123.45, 123.43, 121.07, 118.65, 116.61, 113.58, 110.78. Positive-ion ESI-MS *m*/*z*: 637.1 $[M - PF_6]^+$. IR (KBr disc) $\nu$/cm$^{-1}$: 2084 $\nu$(C≡N), 1946, 1891 $\nu$(C≡O), 843 $\nu$(P—F). Anal. Calcd (%) for $C_{26}H_{18}N_4O_4RePF_6{\cdot}0.5(CH_3)_2CO$ (810.66): C 40.74, H 2.61, N 6.91. Found: C 40.45, H 2.52, N 6.71.

***cis*,*cis*-{Re(CO)$_2$[CNC$_6$H$_4$(OH)-2][$\overline{\text{CN(H)C}_6\text{H}_4\text{-2-O}}$](Me$_2$bpy)}(PF$_6$) (2).** The complex was prepared according to a procedure similar to that for **1** except $Me_2bpy$ (125 mg, 680 $\mu$mol) was used in place of bpy. Yield: 57.2 mg, 70.7 $\mu$mol; 41.6%. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): $\delta$ 9.23 (d, 1H, *J* = 5.8 Hz, 6/6′-bpy H), 9.16 (d, 1H, *J* = 4.9 Hz, 6/6′-bpy H), 8.02 (s, 1H, 3/3′-bpy H), 7.98 (s, 1H, 3/3′-bpy H), 7.55 (d, 1H, *J* = 7.6 Hz, phenyl H), 7.36 (d, 1H, *J* = 5.3 Hz, 5/5′ bpy), 7.28 (d, 1H, *J* = 5.8 Hz, 5/5′ bpy H), 7.19 (m, 2H, phenyl H), 7.13 (m, 3H, phenyl H), 7.05 (m, 1H, phenyl H), 6.77 (dd, 1H, *J* = 7.3, 6.2 Hz, phenyl H), 2.62 (s, 3H, methyl H), 2.51 (s, 3H, methyl H). $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ 206.40, 200.78, 196.60, 167.79, 155.70, 155.63, 153.61, 152.37, 151.94, 150.26, 149.59, 128.44, 127.84, 127.58, 124.78, 124.58, 123.66, 123.36, 123.27, 123.01, 119.75, 118.16, 117.81, 114.74, 109.63, 21.37, 21.29. Positive-ion ESI-MS *m*/*z*: 665.1 $[M - PF_6]^+$. IR (KBr disc) $\nu$/cm$^{-1}$: 2080 $\nu$(C≡N), 1946, 1891 $\nu$(C≡O), 843 $\nu$(P—F). Anal. Calcd (%) for $C_{28}H_{22}N_4O_4RePF_6{\cdot}0.5Et_2O$ (846.73): C 42.55, H 3.21, N 6.62. Found: C 42.53, H 3.32, N 7.05.

***cis*,*cis*-{Re(CO)$_2$[CNC$_6$H$_4$(OH)-2][$\overline{\text{CN(H)C}_6\text{H}_4\text{-2-O}}$]($^t$Bu$_2$bpy)}(PF$_6$) (3).** The complex was prepared according to a procedure similar to that for **1** except $^tBu_2bpy$ (182 mg, 680 $\mu$mol) was used in place of bpy. Yield: 64.0 mg, 71.6 $\mu$mol; 42.1%. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): $\delta$ 9.38 (d, 1H, *J* = 6.0 Hz, 6/6′-bpy H), 9.16 (d, 1H, *J* = 6.0 Hz, 6/6′-bpy H), 8.00 (d, 1H, *J* = 1.8 Hz, 3/3′-bpy H), 7.96 (d, 1H, *J* = 1.8 Hz, 3/3′-bpy H), 7.51 (m, 2H, phenyl H, 5/5′-bpy H), 7.38 (dd, 1H, *J* = 6.0, 1.8 Hz, 5/5′-bpy H), 7.16 (m, 3H, phenyl H), 7.02 (m, 2H, phenyl H), 6.93 (dd, 1H, *J* = 8.4, 7.6 Hz, phenyl H), 6.81 (dd, 1H, *J* = 8.3, 7.2 Hz, phenyl H), 1.49 (s, 9H, methyl H), 1.36 (s, 9H, methyl H). $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ 204.09, 201.87, 197.60, 170.42, 161.98, 161.67, 157.35, 155.97, 155.90, 154.10, 152.46, 152.34, 141.17, 128.22, 124.11, 124.03, 124.00, 123.78, 122.20, 121.43, 119.98, 118.86, 118.79, 118.26, 116.29, 108.82, 35.44, 35.36, 30.46, 30.33. Positive-ion ESI-MS: *m*/*z*: 749.2 $[M - PF_6]^+$. IR (KBr disc) $\nu$/cm$^{-1}$: 2083 $\nu$(C≡N), 1942, 1887 $\nu$(C≡O), 840 $\nu$(P—F). Anal. Calcd (%) for $C_{34}H_{34}F_6N_4O_4PRe$ (894.18): C 45.69, H 3.83, N 6.27. Found: C 45.78, H 3.59, N 6.21.

***cis*,*cis*-{Re(CO)$_2$[CNC$_6$H$_4$(OH)-2][$\overline{\text{CN(H)C}_6\text{H}_4\text{-2-O}}$](phen)}(PF$_6$) (4).** The complex was prepared according to a procedure similar to that for **1** except phen (123 mg, 680 $\mu$mol) was used in place of bpy. Yield: 49.4 mg, 61.4 $\mu$mol; 36.1%. $^1$H NMR (400 MHz, $CDCl_3$, 298 K): $\delta$ 9.63 (d, 1H, *J* = 4.8 Hz, 2/9-phen H), 9.62 (d, 1H, *J* = 4.8 Hz, 2/9-phen H), 8.63 (d, 1H, *J* = 8.3 Hz, 4/7-phen H), 8.44 (d, 1H, *J* = 8.0 Hz, 4/7-phen H), 8.05 (d, 1H, *J* = 8.9 Hz, 5/6-phen H), 8.00 (d, 1H, *J* = 8.9 Hz, 5/6-phen H), 7.97 (dd, 1H, *J* = 8.3, 4.8 Hz, 3/8-phen H), 7.61 (dd, 1H, *J* = 8.3, 4.8 Hz, 3/8-phen H), 7.35 (d, 1H, *J* = 7.6 Hz, phenyl H), 7.30 (m, 2H, phenyl H), 7.19 (dd, 2H, *J* = 8.3, 7.6 Hz, phenyl H), 7.08 (d, 1H, *J* = 8.3 Hz, phenyl H), 6.92 (m, 2H, phenyl H). $^{13}$C NMR (100 MHz, $CDCl_3$, 298 K): $\delta$ 208.12, 198.94, 195.36, 167.13, 155.82, 154.07, 153.37, 151.46, 147.19, 137.86, 137.55, 130.75, 130.60, 130.58, 129.03, 127.76, 127.70, 126.22, 125.98, 125.15, 124.78, 124.62, 119.64, 119.27, 117.51, 113.20, 110.59, 100.00. Positive-ion ESI-MS: *m*/*z*: 660.9

$[\mathrm{M}-\mathrm{PF_6}]^+$. IR (KBr disc) $\nu/\mathrm{cm^{-1}}$: 2085 $\nu(\mathrm{C{\equiv}N})$, 1942, 1888 $\nu(\mathrm{C{\equiv}O})$, 841 $\nu(\mathrm{P{-}F})$. Anal. Calcd (%) for $\mathrm{C_{28}H_{18}F_6N_4O_4PRe}$ (806.05): C 41.74, H 2.25, N 6.95. Found: C 41.97, H 2.07, N 6.81.

***cis,cis*-{Re(CO)$_2$(CNC$_6$H$_4$Cl-4)[$\overline{\mathrm{CN(4\text{-}ClC_6H_4)C_2H_4O}}$](bpy)}(PF$_6$) (5).** To a solution of 2-bromoethanol (0.52 mL, *d* = 1.763 g/mL, 2.36 mmol) in THF (30 mL) at 0 °C was added, in a dropwise manner, $^n$BuLi (1.2 mL, 2.5 M in hexane). After the mixture stirred at 0 °C for 15 min, *cis,cis*-$[\mathrm{Re(CO)_2(CNC_6H_4Cl\text{-}4)_2(bpy)}]\mathrm{Br}$ (90 mg, 119 μmol) was added. The resulting solution was stirred at room temperature for 16 h. Thereafter, deionized water (30 mL) was added. The resulting mixture was then extracted with chloroform (30 mL) and dried over $\mathrm{MgSO_4}$. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane–acetonitrile–methanol (9:1:0.1, v/v/v) as eluent. Subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave complex **5** as a $\mathrm{PF_6}^-$ salt. Recrystallization by slow diffusion of diethyl ether vapor into a concentrated acetone solution of **5** gave the target complex as pale orange crystalline solid. Yield: 55.7 mg, 64.6 μmol; 54.1%. $^1$H NMR (400 MHz, DMSO, 298 K): $\delta$ 8.85 (d, 1H, *J* = 5.6 Hz, 6/6′-bpy H), 8.76 (d, 1H, *J* = 5.6 Hz, 6/6′-bpy H), 8.75 (d, 1H, *J* = 7.6 Hz, 3/3′-bpy H), 8.73 (d, 1H *J* = 7.3 Hz, 3/3′-bpy H), 8.31 (dd, 1H, *J* = 8.0, 7.9 Hz, 4/4′-bpy H), 8.27 (dd, 1H, *J* = 8.0, 7.9 Hz, 4/4′-bpy H), 7.69 (dd, 1H, *J* = 7.9, 5.6 Hz, 5/5′-bpy H), 7.62 (dd, 1H, *J* = 7.9, 5.6 Hz, 5/5′-bpy H), 7.60 (d, 2H, *J* = 8.7 Hz, phenyl H), 7.44 (d, 2H, *J* = 8.7 Hz, phenyl H), 7.35 (d, 2H, *J* = 8.7 Hz, phenyl H), 7.27 (d, 2H, *J* = 8.7 Hz, phenyl H), 4.35 (t, 2H, *J* = 9.8 Hz, $\mathrm{CH_2}$), 3.87 (t, 2H, *J* = 9.8 Hz, $\mathrm{CH_2}$). $^{13}$C NMR (100 MHz, DMSO, 298 K): $\delta$ 215.59, 198.75, 194.56, 164.20, 155.87, 155.47, 153.47, 152.66, 139.62, 139.10, 136.43, 133.83, 131.88, 129.77, 129.48, 128.94, 128.48, 127.61, 124.06, 123.99, 71.63, 54.11. Positive-ion ESI-MS *m*/*z*: 717.8 $[\mathrm{M}-\mathrm{PF_6}]^+$. IR (KBr disc): $\nu/\mathrm{cm^{-1}}$: 2084 $\nu(\mathrm{C{\equiv}N})$, 1946, 1891 $\nu(\mathrm{C{\equiv}O})$, 843 $\nu(\mathrm{P{-}F})$. Anal. Calcd (%) for $\mathrm{C_{28}H_{20}Cl_2F_6N_4O_3PRe}$ (862.56): C 38.99, H 2.34, N 6.50. Found: C 38.75, H 2.47, N 6.43.

***cis,cis*-{Re(CO)$_2$(CNC$_6$H$_4$Cl-4)[$\overline{\mathrm{CN(4\text{-}ClC_6H_4)C_2H_4N}}$(H)](bpy)}(PF$_6$) (6).** The complex was prepared according to a procedure similar to that for **5** except 2-bromoethylamine hydrobromide (680 mg, 332 μmol) was used in place of 2-bromoethanol, and purification was performed by column chromatography on silica gel using dichloromethane–methanol (95:5, v/v) as eluent. Yield: 59.0 mg, 68.4 μmol; 57.3%. $^1$H NMR (400 MHz, DMSO, 298 K): $\delta$ 8.79 (d, 1H, *J* = 4.8 Hz, 6/6′-bpy H), 8.66 (d, 1H, *J* = 8.4 Hz, 3/3′-bpy H), 8.64 (d, 1H, *J* = 8.4 Hz, 3/3′-bpy H), 8.58 (d, 1H, *J* = 5.4 Hz, 6/6′-bpy H), 8.42 (s, 1H, NH), 8.26 (dd, 1H, *J* = 8.4, 7.9 Hz, 4/4′-bpy H), 8.19 (dd, 1H, *J* = 8.4, 7.9 Hz, 4/4′-bpy H), 7.57 (m, 3H, phenyl H and 5/5′-bpy H), 7.53 (d, 2H, *J* = 8.8 Hz, phenyl H), 7.44 (dd, 1H, *J* = 7.9, 5.4 Hz, 5/5′-bpy H), 7.18 (d, 2H, *J* = 8.6 Hz, phenyl H), 6.92 (d, 2H, *J* = 8.6 Hz, phenyl H), 3.61 (t, 2H, *J* = 9.8 Hz, $\mathrm{CH_2}$), 3.43 (t, 2H, *J* = 9.8 Hz, $\mathrm{CH_2}$). $^{13}$C NMR (100 MHz, DMSO, 298 K): $\delta$ 201.77, 199.52, 194.39, 165.14, 155.20, 154.75, 153.35, 152.69, 139.99, 139.34, 138.67, 132.20, 131.75, 129.71, 129.29, 128.89, 128.82, 127.79, 127.60, 127.44, 124.05, 124.03, 53.86, 45.17. Positive-ion ESI-MS *m*/*z*: 717.0 $[\mathrm{M}-\mathrm{PF_6}]^+$. IR (KBr disc) $\nu/\mathrm{cm^{-1}}$: 2082 $\nu(\mathrm{C{\equiv}N})$, 1946, 1886 $\nu(\mathrm{C{\equiv}O})$, 838 $\nu(\mathrm{P{-}F})$. Anal. Calcd (%) for $\mathrm{C_{28}H_{21}Cl_2N_2O_2RePF_6}$ (861.58): C 39.03, H 2.46, N 8.13. Found: C 39.20, H 2.94, N 8.20.

***cis,cis*-{Re(CO)$_2$(CNC$_6$H$_4$Cl-4)[$\overline{\mathrm{CN(4\text{-}ClC_6H_4)C_2H_4S}}$](bpy)}(PF$_6$) (7).** To a solution of *cis,cis*-$[\mathrm{Re(CO)_2(CNC_6H_4Cl\text{-}4)_2(bpy)}]\mathrm{Br}$ (50 mg, 66.4 μmol) in THF (40 mL) was added thiirane (0.10 mL, *d* = 1.01 g/mL, 1.66 mmol). The reaction mixture was heated to 45 °C and stirred at this temperature for 2 days. After cooling to room temperature and removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane–methanol (95:5, v/v) as eluent. Subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave complex **7** as a $\mathrm{PF_6}^-$ salt. Recrystallization by slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of **7** gave the target complex as orange crystalline solid. Yield: 23.4 mg, 26.6 μmol; 40.1%. $^1$H NMR (400 MHz, DMSO, 298 K): $\delta$ 8.87 (d, 1H, *J* = 5.2 Hz, 6/6′-bpy H), 8.75 (d, 1H, *J* = 8.9 Hz, 3/3′-bpy H), 8.73 (d, 1H, *J* = 8.9 Hz, 3/3′-bpy H), 8.67 (d, 1H, *J* = 5.2 Hz, 6/6′-bpy H), 8.33 (dd, 1H, *J* = 8.9, 5.2 Hz, 4/4′-bpy H), 8.27 (dd, 1H, *J* = 8.9, 5.2 Hz, 4/4′-bpy H), 7.71 (dd, 1H, *J* = 5.2 Hz, 5/5′-bpy H), 7.61 (m, 3H, phenyl H, 5/5′-bpy H), 7.53 (d, 2H, *J* = 8.7 Hz, phenyl H), 7.35 (d, 2H, *J* = 8.4 Hz, phenyl H), 7.19 (d, 2H, *J* = 8.4 Hz, phenyl H), 4.31 (t, 2H, *J* = 9.6 Hz, $\mathrm{CH_2}$), 3.13 (m, 2H, $\mathrm{CH_2}$). $^{13}$C NMR (100 MHz, DMSO, 298 K): $\delta$ 233.51, 198.56, 195.12, 163.35, 155.70, 155.14, 153.53, 152.91, 141.43, 139.87, 139.18, 133.68, 132.08, 129.84, 129.65, 128.37, 127.99, 127.95, 127.88, 127.70, 124.29, 124.21, 67.15, 54.88. Positive-ion ESI-MS *m*/*z*: 734.0 $[\mathrm{M}-\mathrm{PF_6}]^+$. IR (KBr disc) $\nu/\mathrm{cm^{-1}}$: 2096 $\nu(\mathrm{C{\equiv}N})$, 1938, 1878 $\nu(\mathrm{C{\equiv}O})$, 843 $\nu(\mathrm{P{-}F})$. Anal. Calcd (%) for $\mathrm{C_{28}H_{20}Cl_2N_4O_3SRePF_6{\cdot}H_2O}$ (896.64): C 37.51, H 2.47, N 6.25. Found: C 37.37, H 2.72, N 6.28.

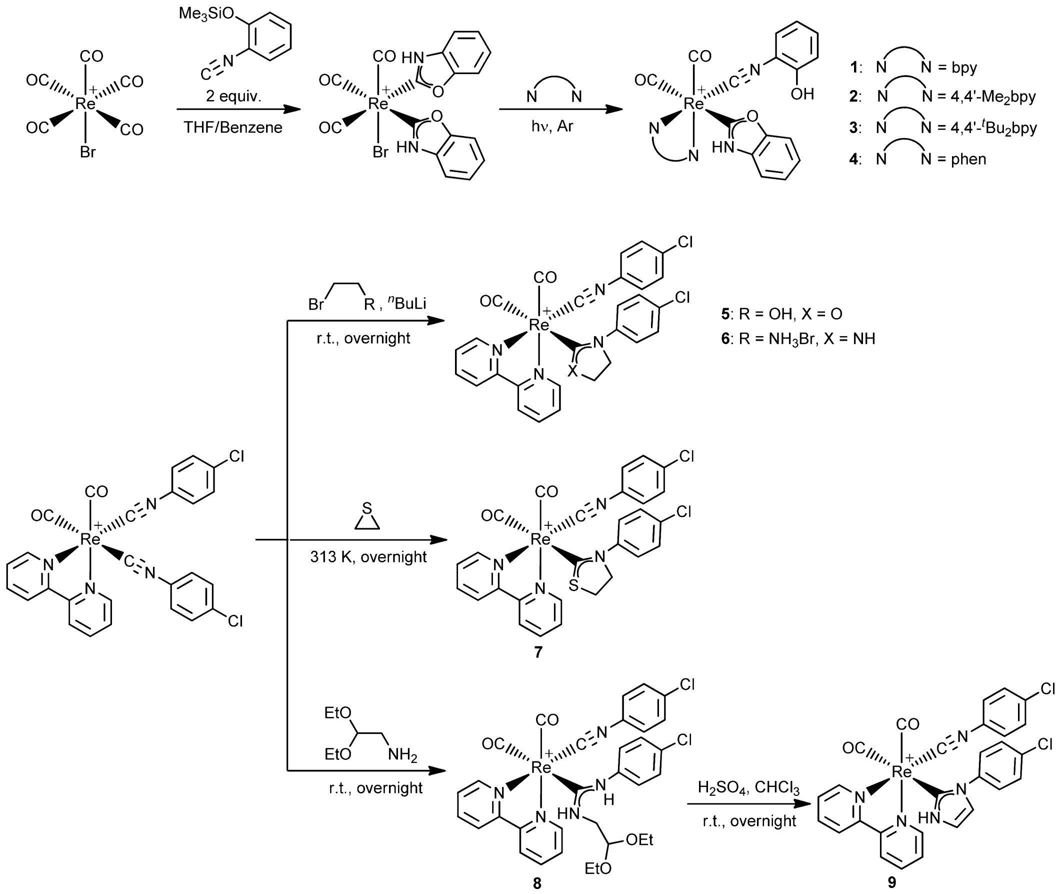
***cis,cis*-{Re(CO)$_2$(CNC$_6$H$_4$Cl-4){C[N(H)(4-ClC$_6$H$_4$)][N(H)CH$_2$CH(OEt)$_2$]}(bpy)}(PF$_6$) (8).** To a solution of *cis,cis*-$[\mathrm{Re(CO)_2(CNC_6H_4Cl\text{-}4)_2(bpy)}]\mathrm{Br}$ (50 mg, 66.4 μmol) in THF (40 mL) was added 2,2-diethoxyethanamine (0.241 mL, *d* = 0.916 g/mL, 1.66 mmol). After stirring at room temperature for 16 h and removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane–methanol (95:5, v/v) as eluent. Subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave complex **8** as a $\mathrm{PF_6}^-$ salt. Recrystallization by slow diffusion of diethyl ether vapor into a concentrated acetone solution of **8** gave the target complex as yellow crystalline solid. Yield: 19.9 mg, 20.9 μmol; 31.5%. $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta$ 9.12 (d, 1H, *J* = 5.5 Hz, 6/6′ bpy H), 8.49 (s, 1H, NH), 8.26 (d, 1H, *J* = 8.3 Hz, 3/3′ bpy H), 8.17 (m, 2H, 3/3′ bpy H and 6/6′ bpy H), 8.11 (dd, 1H, *J* = 8.3, 7.56 Hz, 4/4′ bpy H), 7.90 (dd, 1H, *J* = 8.3, 7.5 Hz, 4/4′ bpy H), 7.72 (dd, 1H, J = 7.5, 6.5 Hz, 5/5′ bpy H), 7.45 (d, 2H, *J* = 6.1 Hz, phenyl H), 7.43 (d, 2H, *J* = 6.1 Hz, phenyl H), 7.13 (d, 2H, *J* = 8.7 Hz, phenyl H), 7.01 (dd, 1H, *J* = 7.5, 6.5 Hz, 5/5′ bpy H), 6.85 (d, 2H, *J* = 8.6 Hz, phenyl H), 4.38 (t, 1H, *J* = 5.1 Hz, $\mathrm{CH_2}\mathit{CH}\mathrm{(OEt)_2}$), 3.58 (m, 4H, $\mathit{CH_2}\mathrm{CH_3}$), 3.29 (t, 2H, *J* = 5.1 Hz, $\mathit{CH_2}\mathrm{CH(OEt)_2}$), 1.14 (t, 3H, *J* = 7.0 Hz, $\mathrm{CH_3}$), 1.02 (t, 3H, *J* = 7.0 Hz, $\mathrm{CH_3}$). $^{13}$C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta$ 208.11, 200.59, 193.14, 164.69, 155.39, 155.02, 153.25, 152.68, 138.81, 138.48, 137.29, 133.25, 132.28, 129.65, 129.21, 128.39, 127.60, 126.92, 126.07, 123.32, 122.99, 101.24, 64.21, 63.90, 46.93, 15.28. Positive-ion ESI-MS *m*/*z*: 806.9 $[\mathrm{M}-\mathrm{PF_6}]^+$. IR (KBr disc) $\nu/\mathrm{cm^{-1}}$: 2073 $\nu(\mathrm{C{\equiv}N})$, 1917, 1867 $\nu(\mathrm{C{\equiv}O})$, 842 $\nu(\mathrm{P{-}F})$. Anal. Calcd (%) for $\mathrm{C_{32}H_{31}Cl_2N_5O_4RePF_6}$ (951.70): C 40.38, H 3.28, N 7.36. Found: C 40.14, H 3.58, N 7.47.

***cis,cis*-{Re(CO)$_2$(CNC$_6$H$_4$Cl-4)[$\overline{\mathrm{CN(4\text{-}ClC_6H_4)C_2H_2N}}$(H)](bpy)}(PF$_6$) (9).** To the bromide salt of **8** (50 mg, 56.4 μmol) in chloroform (30 mL) solution was added concentrated sulfuric acid (98%, 3.33 μL). The resulting mixture was stirred at room temperature for 3 days. Thereafter, deionized water (30 mL) was added and extracted with $\mathrm{CHCl_3}$ (30 mL). After removal of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane–methanol (9:1, v/v) as eluent. Subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave complex **9** as a $\mathrm{PF_6}^-$ salt. Recrystallization by slow diffusion of diethyl ether vapor into a concentrated acetone solution of **9** gave the target complex as orange crystalline solid. Yield: 31.9 mg, 37.2 μmol; 65.9%. $^1$H NMR (400 MHz, DMSO, 298 K): $\delta$ 12.22 (s, 1H, NH), 8.87 (d, 1H, *J* = 5.5 Hz, 6/6′-bpy H), 8.70 (d, 1H, *J* = 5.5 Hz, 6/6′-bpy H), 8.60 (d, 1H, *J* = 8.5 Hz, 3/3′-bpy H), 8.57 (d, 1H, *J* = 8.5 Hz, 3/3′-bpy H), 8.24 (dd, 1H, *J* = 8.5, 5.5 Hz, 4/4′-bpy H), 8.17 (dd, 1H, *J* = 8.5, 5.5 Hz, 4/4′-bpy H), 7.60 (m, 3H, phenyl H’s, 5/5′-bpy H), 7.53 (d, 2H, *J* = 8.9 Hz, phenyl H), 7.46 (dd, 1H, *J* = 8.5, 5.5 Hz, 5/5′-bpy H), 7.26 (m, 4H, phenyl H, imidazolin-2-ylidyl H), 6.98 (d, 2H, *J* = 8.7 Hz, phenyl H’s). $^{13}$C NMR (100 MHz, DMSO, 298 K): $\delta$ 200.05, 195.00, 175.51, 165.71, 155.70, 155.26, 153.80, 153.12, 139.82, 139.16, 138.42, 134.14, 132.22, 130.20, 129.57, 129.32, 128.94, 128.28, 128.09, 127.96, 124.66, 124.60, 124.59, 120.33. Positive-ion ESI-MS *m*/*z*: 714.9 $[\mathrm{M}-\mathrm{PF_6}]^+$. IR (KBr disc): $\nu/\mathrm{cm^{-1}}$: 2083 $\nu(\mathrm{C{\equiv}N})$, 1939, 1883 $\nu(\mathrm{C{\equiv}O})$, 839 $\nu(\mathrm{P{-}F})$. Anal. Calcd (%) for $\mathrm{C_{28}H_{19}Cl_2N_5O_2RePF_6{\cdot}0.5H_2O}$ (868.57): C 38.72, H 2.32, N 8.06. Found: C 38.97, H 2.62, N 8.28.

## ■ RESULTS AND DISCUSSION

**Synthesis and Characterization.** The bis(isocyano) and bis(carbene) precursor complexes, *fac*-$[\mathrm{Re(CO)_3(CNC_6H_4Cl\text{-}4)_2Br}]$ and *fac*-$\{\mathrm{Re(CO)_3}[\overline{\mathrm{CN(H)C_6H_4\text{-}2\text{-}O}}]_2\mathrm{Br}\}$, were synthesized by

**Scheme 1. Synthetic Routes to Complexes 1−9**



the ligand substitution reactions of [Re(CO)$_5$Br] with 2 mol equiv of 4-ClC$_6$H$_4$NC and 2-(OSiMe$_3$)C$_6$H$_4$NC, respectively, according to our recently reported procedure for the preparation of bis(isocyano) complexes [Re(CO)$_3$(CNR)$_2$Br] (Scheme 1).[13] The formation of the bis(carbene) precursor complex can be characterized by the characteristic downfielded $^{13}$C NMR signal (209 ppm) of the carbene ligands[2a,e,h,5−12,17] as well as the absence of the isocyanide (C≡N) stretch in the IR spectrum. The geometrical arrangement and the carbene ligands were further confirmed by the X-ray crystallography (see below). The carbene ligand formation is due to the result of the coordination of 2-trimethylsiloxyphenyl isocyanide and its subsequent intramolecular cyclization through the nucleophilic attack on the isocyanide carbon with the oxygen atom as described by Hahn and co-worker.[11c−e] Interestingly, the photoligand substitution reaction of the bis(carbene) precursor complex with the diimine ligand would lead to the formation of *cis*-dicarbonyl Re(I) diimine complexes with one carbene ligand and one 2-hydroxyphenyl isocyanide ligand (**1**−**4**). The close resemblance of the spectroscopic characterizations of **1**−**4** suggested that they are of the same geometrical isomerism. The *cis* carbonyl ligands, which are *trans* to two different types of ligands, are characterized by the two carbonyl $^{13}$C NMR signals in the typical range (190−200 ppm) of Re carbonyl complexes.[12,18] The presence of one carbene and one isocyanide ligand is confirmed by the characteristic downfield carbene $^{13}$C NMR signal at 204−209 ppm[17] and isocyanide $^{13}$C NMR signal at 167−171 ppm,[11d,19] respectively. The *cis* carbonyl ligand arrangement and the presence of 2-hydroxyphenyl isocyanide ligand are further characterized by the two carbonyl $\nu$(C≡O) stretches in the region 1887−1946 cm$^{-1}$ and one isocyanide $\nu$(C≡N) stretch at *ca.* 2080−2085 cm$^{-1}$. With reference to the IR stretches of *cis,cis*-[Re(CO)$_2$(CNR)$_2$(N−N)]$^+$,[13] such a low C≡N stretching frequency suggested that the isocyanide ligand is not *trans* to the carbonyl ligand. On the basis of these characterization data, a geometrical isomer of the Re(I) complex with the *cis* carbonyl ligands, one *trans* to diimine and the other one *trans* to carbene ligand, and the isocyanide ligand *trans* to the diimine ligand can be proposed. Such a geometrical isomerism is confirmed by the X-ray crystal structure of **1** (see below). This confirmed the possibility of the interconversion between 2-hydroxyphenyl isocyanide and its cyclized N,O-heterocyclic carbene form, which depends on the relative stability of the metal−isocyanide and metal−carbene forms.[11d] On substituting the carbonyl ligand, which is *trans* to the carbene in the bis(carbene) precursor complex, with the diimine ligand, the $\pi$-back-donation from the Re metal center to the carbene ligand (*trans* to the diimine ligand) is significantly enhanced. As a result, the interaction between p$\pi$(C$_{\text{carbene}}$) and p$\pi$(O) is weakened, thus opening up the heterocyclic carbene ligand to produce the isocyanide form.

Apart from using nucleophile-containing isocyanide ligand to synthesize Re(I) NHC complexes, attempts to convert the isocyano Re(I) diimine complexes to Re(I) NHC complexes by the reactions with suitable nucleophiles were also carried out. *cis,cis*-[Re(CO)$_2$(CNC$_6$H$_4$Cl-4)$_2$(bpy)]Br, which can be readily obtained in high yield based on our recently reported photosubstitution reaction between *fac*-[Re(CO)$_3$(CNC$_6$H$_4$Cl-4)$_2$Br] and bpy,[13] was chosen as synthetic precursor to test the reactivity of isocyanide ligands in these Re(I) complexes. It is interesting to find that only one of the isocyanide ligands, which is *trans* to the carbonyl ligand, was converted to carbene ligands despite the

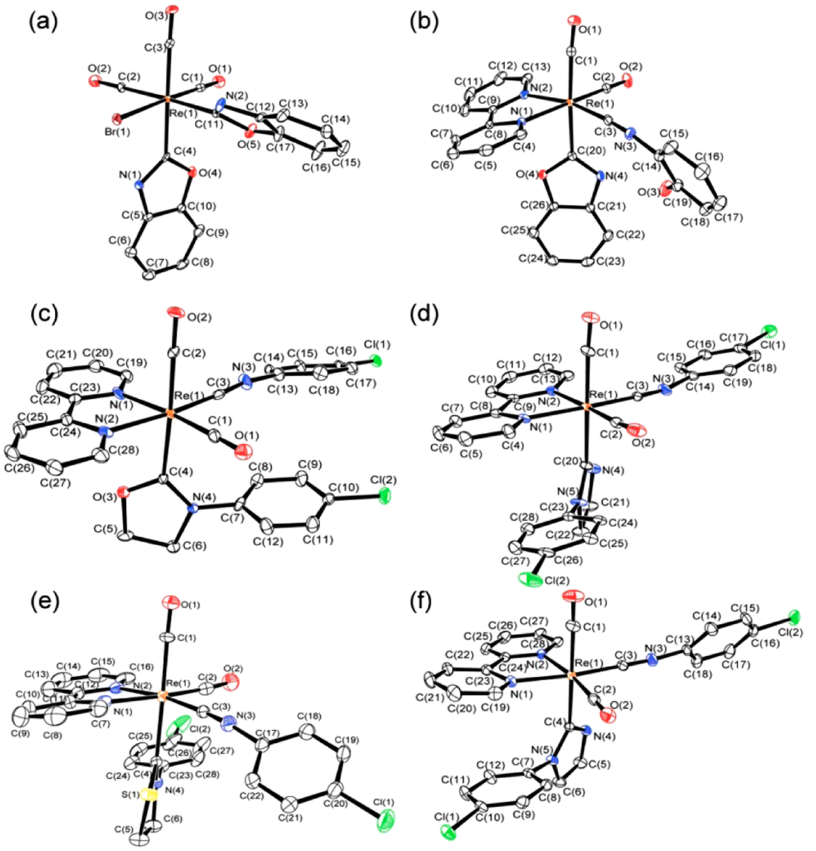


**Figure 1.** Perspective drawings of (a) $\{Re(CO)_3[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]_2(Br)\}$ and the complex cations of (b) **1**, (c) **5**, (d) **6**, (e) **7**, and (f) **9** with the atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

addition of large excess (25 mol equiv) of nucleophiles. Such reactivity is illustrated by the formation of complexes **5**−**8**, which contain only one carbene ligand, from the reaction between *cis*,*cis*-$[Re(CO)_2(CNC_6H_4Cl\text{-}4)_2(bpy)]Br$ and 25 mol equiv of deprotonated 2-bromoethanol, 2-bromoethanamine, thiirane, and diethoxyethanamine. Unlike the isocyanide ligand that is *trans* to the carbonyl ligand, the isocyanide ligand *trans* to diimine ligand is much less reactive or even unreactive toward these nucleophiles under the same reaction condition. The lower reactivity of this isocyanide ligand can be explained by the stronger $\pi$-back-donation from the rhenium metal center, which renders the isocyanide carbon more electron rich and therefore less susceptible to nuclecophilic attack. The lower reactivity of the isocyanide ligand *trans* to the diimine ligand in **5**−**8** is consistent with the more stable 2-hydroxyphenyl isocyanide form for ligand that is *trans* to the diimine ligand in **1**−**4**. This was also observed in other 2-hydroxyphenyl isocyanide complexes with electron-rich metal centers and strong $\pi$-back-donation.[20] The subsequent reaction of **8** with concentrated sulfuric acid in chloroform at room temperature gave the NHC complex **9**.

The geometrical arrangements of the ligands in complexes **5**−**9** were confirmed structurally by X-ray crystallography (see below). Similar to **1**−**4**, complexes **5**−**9** were also characterized by one medium isocyanide C≡N stretch and two strong C≡O (carbonyl) stretches in their IR spectra as well as the characteristic downfielded carbene $^{13}C$ NMR signals in the range 175−234 ppm and isocyanide $^{13}C$ NMR signals in the range 163−166 ppm in their $^{13}C$ NMR spectra. The close similarity of the stretching frequencies of C≡N and C≡O stretches in the IR spectra of **5**−**9** compared to those in **1**−**4** are consistent with their similar ligand arrangements. In addition to $^1H$ and $^{13}C$ NMR and IR spectroscopies, complexes **1**−**9** and their precursor complexes were also characterized by ESI-MS and gave satisfactory elemental analyses.

**X-ray Crystal Structure Determination.** The structures of *fac*-$\{Re(CO)_3[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]_2(Br)\}$, **1**, **5**−**7**, and **9** were characterized by X-ray crystallography. The perspective drawings of *fac*-$\{Re(CO)_3[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]_2(Br)\}$ and the complex cations of **1**, **5**−**7**, and **9** are depicted in Figure 1. The experimental details for the crystal structure determinations and selected bond distances and bond angles are summarized in Table S1 in the Supporting Information and Table 1, respectively.

In the crystal structure, the bis(carbene) precursor complex, *fac*-$\{Re(CO)_3[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]_2(Br)\}$, adopted an octahedral geometry with three carbonyl ligands arranged in a facial geometry. In contrast, the crystal structures of Re(I) diimine complexes (**1**, **5**−**7**, and **9**) adopted a distorted octahedral geometry with the bite angles of the diimine ligands in the range 74.1−75.5°, typical of Re(I) diimine complexes.[12,18,21] The geometrical arrangement of the ligands in **1**, **5**−**7**, and **9**, i.e., the two unsymmetrical *cis* carbonyl ligands (one *trans* to the diimine and the other *trans* to the carbene ligand), are confirmed in these X-ray crystal structures. The presence of 2-hydroxyphenyl isocyanide ligand *trans* to diimine ligand corroborated the lower reactivity of this isocyanide ligand toward the nucleophilic attack. The Re−C (carbonyl), Re−C (carbene), and Re−C (isocyanide) bond lengths in these complexes are in the ranges

**Table 1. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations (esd's) in Parentheses for $\{Re(CO)_3[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]_2(Br)\}$, 1, 5−7, and 9**

| | | | | | |
|---|---|---|---|---|---|
| *fac*-$\{Re(CO)_3[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]_2(Br)\}$ | | | | | |
| Re(1)−C(1) | 1.888(8) | C(4)−O(4) | 1.353(8) | N(1)−C(5) | 1.390(9) |
| Re(1)−C(2) | 1.972(7) | C(4)−N(1) | 1.348(9) | O(4)−C(10) | 1.398(9) |
| Re(1)−C(3) | 1.945(7) | C(11)−O(5) | 1.357(8) | N(2)−C(12) | 1.403(9) |
| Re(1)−C(4) | 2.118(7) | C(11)−N(2) | 1.339(9) | O(5)−C(17) | 1.397(9) |
| Re(1)−C(11) | 2.136(7) | | | | |
| Re(1)−C(4)−O(4) | 123.2(5) | N(2)−C(11)−O(5) | 106.0(6) | C(11)−N(2)−C(12) | 112.4(6) |
| Re(1)−C(4)−N(1) | 130.1(5) | C(4)−N(1)−C(5) | 111.6(6) | C(11)−O(5)−C(17) | 109.1(5) |
| N(1)−C(4)−O(4) | 106.7(6) | C(4)−O(4)−C(10) | 108.4(5) | | |
| **1** | | | | | |
| Re(1)−C(1) | 1.957(3) | C(3)−N(3) | 1.165(5) | C(23)−C(24) | 1.386(6) |
| Re(1)−C(2) | 1.904(3) | C(20)−O(4) | 1.353(4) | N(4)−C(21) | 1.394(4) |
| Re(1)−C(3) | 1.982(3) | C(20)−N(4) | 1.326(4) | O(4)−C(26) | 1.387(4) |
| Re(1)−C(20) | 2.141(3) | | | | |
| N(1)−Re(1)−N(2) | 74.62(11) | N(4)−C(20)−O(4) | 107.0(3) | C(20)−O(4)−C(26) | 108.8(2) |
| C(3)−N(3)−C(14) | 168.2(3) | C(20)−N(4)−C(21) | 111.9(3) | | |
| **5** | | | | | |
| Re(1)−C(1) | 1.908(9) | C(3)−N(3) | 1.180(12) | C(5)−C(6) | 1.525(13) |
| Re(1)−C(2) | 1.926(10) | C(4)−N(4) | 1.334(13) | N(4)−C(6) | 1.478(11) |
| Re(1)−C(3) | 1.947(9) | C(4)−O(3) | 1.310(11) | O(3)−C(5) | 1.487(10) |
| Re(1)−C(4) | 2.181(10) | | | | |
| N(1)−Re(1)−N(2) | 75.5(3) | N(4)−C(4)−O(3) | 110.9(8) | C(4)−O(3)−C(5) | 110.5(7) |
| C(3)−N(3)−C(13) | 170.3(10) | C(4)−N(4)−C(6) | 113.2(8) | | |
| **6** | | | | | |
| Re(1)−C(1) | 1.959(7) | C(3)−N(3) | 1.178(9) | C(21)−C(22) | 1.511(11) |
| Re(1)−C(2) | 1.926(6) | C(20)−N(4) | 1.322(9) | N(4)−C(21) | 1.465(9) |
| Re(1)−C(3) | 1.958(6) | C(20)−N(5) | 1.350(9) | N(5)−C(22) | 1.497(8) |
| Re(1)−C(20) | 2.189(6) | | | | |
| N(1)−Re(1)−N(2) | 74.4(2) | N(4)−C(20)−N(5) | 107.3(5) | C(20)−N(5)−C(22) | 112.2(6) |
| C(3)−N(3)−C(14) | 168.9(7) | C(20)−N(4)−C(21) | 115.3(6) | | |
| **7** | | | | | |
| Re(1)−C(1) | 1.958(7) | C(3)−N(3) | 1.157(10) | C(5)−C(6) | 1.503(12) |
| Re(1)−C(2) | 1.905(10) | C(4)−N(4) | 1.316(9) | N(4)−C(6) | 1.476(9) |
| Re(1)−C(3) | 1.989(7) | C(4)−S(1) | 1.732(7) | S(2)−C(5) | 1.819(8) |
| Re(1)−C(4) | 2.183(6) | | | | |
| N(1)−Re(1)−N(2) | 74.8(2) | N(4)−C(4)−S(1) | 109.5(5) | C(4)−S(1)−C(5) | 95.4(4) |
| C(3)−N(3)−C(17) | 168.8(8) | C(4)−N(4)−C(6) | 119.1(6) | | |
| **9** | | | | | |
| Re(1)−C(1) | 1.931(5) | C(3)−N(3) | 1.173(6) | C(5)−C(6) | 1.346(7) |
| Re(1)−C(2) | 1.910(5) | C(4)−N(4) | 1.359(6) | N(4)−C(5) | 1.371(6) |
| Re(1)−C(3) | 1.975(5) | C(4)−N(5) | 1.362(6) | N(5)−C(6) | 1.382(6) |
| Re(1)−C(4) | 2.179(5) | | | | |
| N(1)−Re(1)−N(2) | 74.13(13) | N(4)−C(4)−N(5) | 102.4(4) | C(4)−N(5)−C(6) | 111.8(4) |
| C(3)−N(3)−C(13) | 172.9(6) | C(4)−N(4)−C(5) | 113.2(4) | | |

1.89−1.97, 2.12−2.19, and 1.94−1.99 Å, respectively, which are commonly observed in related tricarbonyl Re(I),[3a,21] NHC Re(I),[3a,12,17b−d] and isocyano Re(I) complexes.[12,13,22] The deviations of the isocyanide ligands from linearity as reflected by the C≡N—C bond angles in the range 168°−173° are due to the $\pi$-back bonding interaction between the Re(I) metal center and the isocyanide ligand.[22]

In NHC ligands of these structures, the heteroatom−carbene (X−C (carbene); X = N, O, and S) bond distances are much shorter than the other X−C bond in the NHC ligands. This can be explained by $p_\pi$−$p_\pi$ interactions between the heteroatoms and carbene carbon, which render a stronger and shorter X−C bond. Due to the steric requirement, the bond angle (X−C−N) at the carbene carbon for the same heteroatom X increases with the C−C bond distance of the NHC ligand. As a result, the bond angles at carbene atom in these complexes follow the order oxazolidin-2-ylidene (110.9°) > benzoxazol-2-ylidene (106.0°−107.0°) and imidazolidin-2-ylidene (107.3°) > imidazol-2-ylidene (102.4°).

**UV−Vis Absorption Properties.** Complexes **1**−**9** dissolve in dichloromethane to give yellow to orange-red solutions. The photophysical data of these complexes are collected in Table 2. Intense absorptions at *ca.* 235−345 nm with molar extinction coefficients on the order of $10^4$ $dm^3$ $mol^{-1}$ $cm^{-1}$ were observed in the electronic absorption spectra of these complexes (Figure 2). These absorptions were assigned to intraligand $\pi \rightarrow \pi^*$ transitions of the isocyanide, carbene, and diimine ligands. Similar to other isocyano Re(I) diimine complexes,[22b−d] all these complexes also exhibit two moderately intense absorption bands or shoulders at *ca.* 345−438 nm with molar extinction coefficients on the order of $10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$ and tailing to

### Table 2. Photophysical Data of 1−9

| complex | medium ($T$/K) | emission[a] $\lambda_{em}$/nm ($\tau_o$/$\mu$s) | $\phi_{em}$[b]/% | absorption[c] $\lambda_{abs}$/nm ($\varepsilon$/$M^{-1}$ $cm^{-1}$) |
|---|---|---|---|---|
| **1** | $CH_2Cl_2$ (298) | 634 (0.14) | 2.37 | 245 (29 455), 285 (33 700), 300 sh (29 690), 348 sh (10 115), 376 sh (6630), 432 sh (3160) |
| | $CH_3CN$ (298) | 651 (0.06) | | |
| | glass[d] (77) | 589 (3.05) | | |
| **2** | $CH_2Cl_2$ (298) | 630 (0.13) | 2.24 | 250 (31 865), 281 (37 150), 300 sh (31 315), 344 sh (12 050), 377 sh (6715), 423 sh (3500) |
| | $CH_3CN$ (298) | 643 (0.08) | | |
| | glass[d] (77) | 579 (3.40) | | |
| **3** | $CH_2Cl_2$ (298) | 626 (0.18) | 3.67 | 249 (29 340), 282 (33 780), 297 sh (29 575), 348 sh (10 635), 419 sh (3670) |
| | $CH_3CN$ (298) | 641 (0.10) | | |
| | glass[d] (77) | 560 (4.46) | | |
| **4** | $CH_2Cl_2$ (298) | 632 (0.75) | 6.20 | 264 (40 300), 290 (24 845), 311 (20 285), 349 sh (8960), 425 sh (3965) |
| | $CH_3CN$ (298) | 647 (0.37) | | |
| | glass[d] (77) | 592 (9.10) | | |
| **5** | $CH_2Cl_2$ (298) | 633 (0.14) | 2.35 | 234 (35 970), 284 (35 845), 347 sh (10 295), 381 sh (6290), 428 sh (3970) |
| | $CH_3CN$ (298) | 649 (0.07) | | |
| | glass[d] (77) | 565 (3.68) | | |
| **6** | $CH_2Cl_2$ (298) | 659 (0.04) | 0.47 | 242 (33 290), 285 (29 555), 314 sh (18 930), 342 sh (8770), 400 (4390), 437 sh (3270) |
| | $CH_3CN$ (298) | 670 (0.03) | | |
| | glass[d] (77) | 593 (2.69) | | |
| **7** | $CH_2Cl_2$ (298) | 643 (0.10) | 1.23 | 256 (32 490), 278 (38 860), 301 sh (32 040), 367 sh (7990), 433 sh (3710) |
| | $CH_3CN$ (298) | 658 (0.04) | | |
| | glass[d] (77) | 570 (4.00) | | |
| **8** | $CH_2Cl_2$ (298) | 664 (0.04) | 0.32 | 241 (38 285), 285 (35 315), 307 sh (25 335), 343 sh (9815), 394 (4985), 436 sh (3840) |
| | $CH_3CN$ (298) | 681 (0.02) | | |
| | glass[d] (77) | 586 (2.30) | | |
| **9** | $CH_2Cl_2$ (298) | 666 (0.05) | 0.42 | 239 sh (33 845), 286 (35 245), 306 sh (25 260), 342 sh (9755), 408 (4685), 438 sh (4000) |
| | $CH_3CN$ (298) | 681 (0.02) | | |
| | glass[d] (77) | 590 (3.40) | | |

[a] Excitation at $\lambda \geq 400$ nm. Emission maxima are corrected values. [b] Luminescence quantum yield with excitation at 436 nm. [c] Dichloromethane at 298 K. [d] EtOH−MeOH (4:1, v/v).

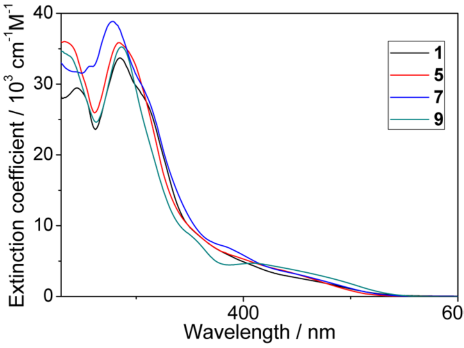


**Figure 2.** Overlaid UV−vis absorption spectra of selected complexes in dichloromethane at 298 K.

the visible region down to *ca.* 550 nm. These absorption bands or shoulders are ascribed to the MLCT [d$\pi$(Re) → $\pi$*(RNC)] and the MLCT [d$\pi$(Re) → $\pi$*(N−N)] transition admixing with the LLCT [$\pi$(RNC) → $\pi$*(N−N)] transition. With reference to previous spectroscopic and computation studies on isocyano rhenium(I) diimine complexes,[23] the $\pi$*(RNC) orbital is higher-lying in energy than that of the $\pi$*(N−N) orbital. Thus, the higher-energy absorption in this region is assigned to the MLCT [d$\pi$(Re) → $\pi$*(RNC)] transition, whereas the lowest-energy absorption is assigned to MLCT [d$\pi$(Re) → $\pi$*(N−N)] transition.

**Emission Spectroscopy.** All these complexes in dichloromethane solution displayed orange to red MLCT [d$\pi$(Re) → $\pi$*(N−N)] phosphorescence with structureless emission bands (Figure 3) and lifetimes ($\tau_o$) in the range 0.04−0.75 $\mu$s (Table 2). The MLCT phosphorescence assignment is supported by the trend of their emission energy for complexes **1**−**4** with the same isocyanide and carbene ligands, **3** (626 nm) > **2** (630 nm) > **1** (634 nm) (Figure 3a), which is in line with expected energy of $\pi$*(N−N). Besides, the MLCT phosphorescence energy also follows the order of the $\pi$-accepting ability of all other ancillary ligands for complexes with the same diimine ligand.[24] Thus, the relative $\pi$-accepting ability of the NHC carbene ligands can be elucidated by comparing the MLCT phosphorescence of **5**−**9**, in which only the NHC ligand is varied. From the trend of emission

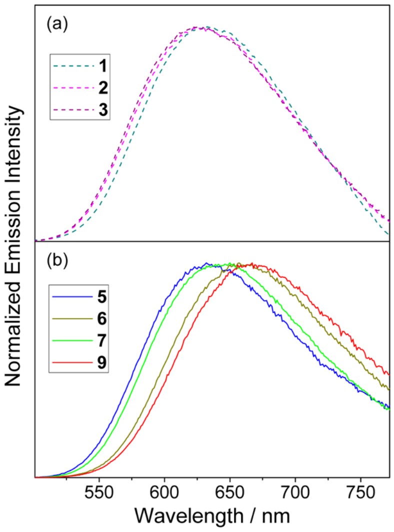


**Figure 3.** Overlaid emission spectra of (a) **1**−**3**, and (b) **5**−**7** and **9** in dichloromethane at 298 K.

energy, which is in the order **5** (633 nm) > **7** (643 nm) > **6** (659 nm) (Figure 3b), it is suggested that the $\pi$-accepting ability of NHC ligands and the d$\pi$(Re)−p$\pi$(NHC) interaction follow the order N,O-NHC ≥ N,S-NHC > N,N-NHC. The weakest $\pi$-accepting ability of N,N-NHC ligand can be attributed to the better $\pi$-delocalization between the lone-pair electrons of both nitrogen atoms and carbene carbon, which renders the vacant p$\pi$($C_{carbene}$) orbital higher-lying in energy. Further fine-tuning of the emission properties can be achieved through the modification of the substituents on the nitrogen atom and/or carbon atoms of the NHC ligands as illustrated from the difference of the emission energy between **6** (659 nm) and **9** (666 nm). Similar to other Re(I) bipyridyl complexes,[25] the rate constants of the nonradiative decay of these complexes are 2 orders of magnitudes higher than those of their radiative decay and decreased with increasing $\pi$-accepting ability of the NHC ligands as well as the emission energy (Table S2, Supporting Information). The variations of the emission characteristics of the bipyridyl complexes in this series follow the energy gap law as reflected by the linear correlation ($R$ = 0.92) between emission energy ($E_{em}$) and ln($k_{nr}$) (Figure 4). This suggests that the vibrational and electronic components of their emissive excited states for these structurally related bipyridyl complexes are similar. The close resemblance of the slope (−12.34 eV$^{-1}$) in $E_{em}$−ln($k_{nr}$) plot (Figure 4) to that of [Re(CO)$_3$(bpy)(L)] (−11.97 eV$^{-1}$)[25a] is suggestive of a similar nonradiative deactivation of their emissive excited state.

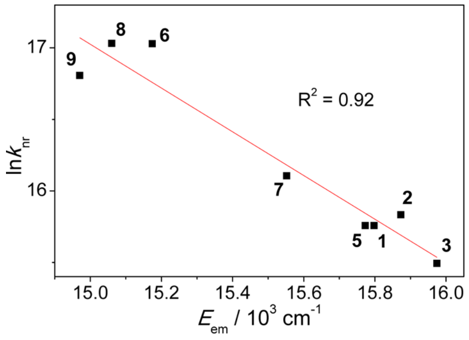


**Figure 4.** Plot of ln $k_{nr}$ vereus $E_{em}$ (298 K, $CH_2Cl_2$) for biypridyl complexes.

As with other tricarbonyl Re(I) diimine complexes,[3a,26] the emissions of these complexes in the acetonitrile solutions are slightly red-shifted compared to those in dichloromethane (Table 2 and Supporting Information Figure S1). In a comparison of the emission of the phenanthroline complex **4** in $CH_3CN$ solution with those of our previously reported phenanthroline complexes with the same benzoxzol-2-ylidene ligand,[12] the emission energy follows the order {Re(CO)$_3$(phen)[$\overline{\text{CN(H)C}_6\text{H}_4\text{-2-O}}$]} (562 nm)[12,27] ≫ **4** (647 nm) ≥ {Re(CO)$_2$(phen)[$\overline{\text{CN(H)C}_6\text{H}_4\text{-2-O}}$](PR$_3$)} (651−661 nm).[12,27] This trend is ascribed to variation of the energy level of d$\pi$(Re) orbital as a result of the different $\pi$-acidity of the ancillary ligand (CO ≫ $CNC_6H_5OH$ ≥ $PR_3$). On the basis of the emission energies of these NHC complexes, it can be deduced that the $\pi$-accepting ability of these NHC ligands is slightly weaker than that of triphenylphosphine, but is stronger than those of substituted pyridines.

These complexes also displayed MLCT phosphorescence in 77 K EtOH−MeOH (4:1, v/v) glassy medium (Supporting Information Figure S2). These emissions also show structureless emission bands with similar energy trend but are considerably blue-shifted and longer-lived compared to their solution emissions. The considerably blue-shifted emission in the low-temperature glassy medium is due to the rigidochromic effect commonly observed in MLCT emitters.[28]

**Transient Absorption Properties.** For further insights into the emissive excited states of these NHC complexes, nanosecond transient absorption spectroscopic study was carried out for the bipyridyl complexes **1**, **5**, and **6**. As there is strong MLCT phosphorescence at $\lambda$ > 545 nm, the transient absorption of these complexes at the same region could not be obtained due to the overlapping. In general, all these complexes show one narrow and one board absorption features peaking at *ca.* 368−374 nm and *ca.* 491−510 nm, respectively (Figure 5 and Supporting Information Figure S3). The decays of these absorption features both follow first-order exponential kinetics with lifetimes in close agreement with that of their phosphorescence in the same solution. This suggested the transient absorption is of the same origin as the emission. The maxima of these absorption features are similar to those in the transient absorption spectrum of [Re(CO)$_3$(bpy)-Cl][26a] and therefore were also assigned the absorptions of reduced bpy of the $^3$MLCT excited state. Although the maxima and bands of these transient absorption features are similar to those of [Re(CO)$_3$(bpy)Cl],[26a] the intensity of the high energy absorption relative to the lower energy absorption is apparently much weaker. This is probably due to the overlapping of the ground state bleaching of the MLCT [d$\pi$(Re)→$\pi$*(RNC)] transition,[13,23] which is also observed in the transient absorption study of the isocyano Re(I) complexes.[13]

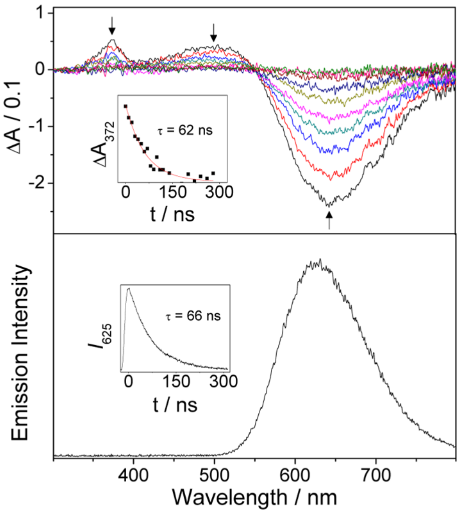


**Figure 5.** Transient difference spectra of **5** in $CH_3CN$ solution at 298 K obtained after 355 nm nanosecond excitation at different time delays: 0, 20, 40, 60, 80, 100, 120, 160, 200, 280 ns.

**Electrochemistry.** The electrochemical properties of complexes **1**−**9** in acetonitrile (0.1 M $^n$Bu$_4$NPF$_6$) were studied by cyclic voltammetry. The electrochemical data are collected in Table 3, and representative cyclic voltammograms are shown in Figure 6. Except for **8**, all complexes show a quasireversible metal-centered oxidation Re(I/II)[21c,22c,d,29] from +1.05 to +1.19 V versus SCE (Table 3). This assignment is further supported by the potential varied with the $\pi$-accepting ability of all ligands. For complex **8**, the metal-centered oxidation is irreversible. The irreversibility is probably due to the instability of the *N*-(4-chlorophenylamino),*N*′-[(2,2-diethoxyethyl)amino]carbene ligand. In the reductive scan, a quasireversible reductive couple in

**Table 3. Electrochemical Data of 1–9 in Acetonitrile Solution (0.1 M $^n$Bu$_4$NPF$_6$) at 298 K**[a]

| complex | oxidation $E_{1/2}$/V vs SCE[b] ($\Delta E_p$/mV)[c] | reduction $E_{1/2}$/V vs SCE[b] ($\Delta E_p$/mV)[c] |
|---|---|---|
| **1** | +1.08 (91) | −1.48 (61), (−2.01)[e] |
| **2** | +1.05 (87) | −1.56 (69), (−2.13)[e] |
| **3** | +1.05 (100) | −1.61 (78), (−2.26)[e] |
| **4** | +1.08 (105) | −1.44 (108), (−2.16)[e] |
| **5** | +1.17 (97) | −1.40 (75), (−1.96)[e] |
| **6** | +1.13 (77) | −1.37 (74), (−1.89)[e] |
| **7** | +1.19 (95) | −1.36 (99), (−1.71)[e] |
| **8** | (+1.12)[d] | −1.33 (124), (−1.85)[e] |
| **9** | +1.09 (65) | −1.36 (77), (−1.89)[e] |

[a] Working electrode, glassy carbon; scan rate, 100 mV s$^{-1}$. [b] $E_{1/2}$ is $(E_{pa} + E_{pc})/2$; $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak potentials, respectively. [c] $\Delta E_p$ is $|E_{pa} - E_{pc}|$. [d] Irreversible oxidation; anodic peak potential ($E_{pa}$/V vs SCE). [e] Irreversible reduction; cathodic peak potential ($E_{pc}$/V vs SCE).

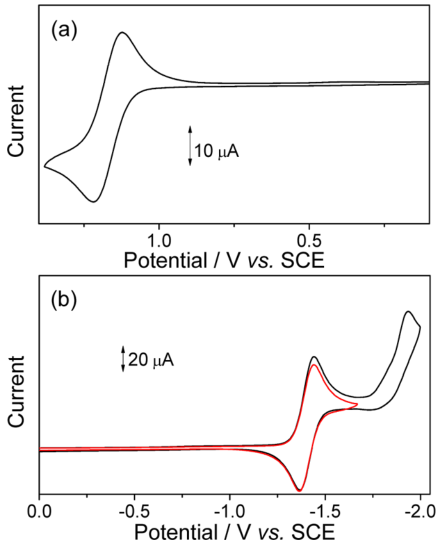


**Figure 6.** Cyclic voltammograms of (a) the oxidative scan and (b) the reductive scan of **5** in acetonitrile (0.1 M $^n$Bu$_4$NPF$_6$).

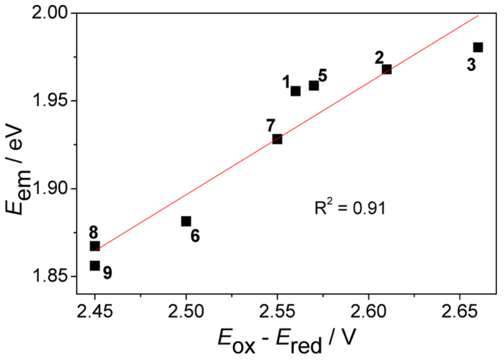


**Figure 7.** Plot of $E_{em}$ (298 K, $CH_2Cl_2$) versus potential difference of oxidation and reduction for the bipyridyl complexes with linear least-squares fit.

the range −1.33 to −1.61 V versus SCE and an irreversible reduction wave in the range −1.71 to −2.26 V versus SCE were observed (Table 3). As the potentials of the first quasireversible couples are relatively insensitive to the change in the NHC ligands as reflected by the similar reduction potentials for **5**–**9** and are in line with the π-accepting ability of the diimine ligands for **1**–**4**, they are assigned to the diimine-based reduction. The potential difference between the metal-centered Re(I/II) oxidation and the diimine-based reduction for the bipyridyl complexes also show a linear correlation with the phosphorescence emission energy (Figure 7). This is further supportive of the MLCT [dπ(Re) → π*(bpy)] emission assignment as both the filled dπ(Re) and the empty π*(bpy) orbitals are involved in the MLCT excited state. Such correlations are commonly observed in different MLCT phosphorescent emitters.[26b,30] With reference to previous electrochemical study of tricarbonyl Re(I) diimine,[21a,29b,31] the second irreversible reduction wave was tentatively assigned to the metal-centered reduction of Re(I) to Re(0).

## ■ CONCLUSION

A new series of luminescent NHC-containing isocyano rhenium(I) diimine complexes, *cis,cis*-[Re(CO)$_2$(CNR)(NHC)(N–N)]$^+$, has been synthesized and characterized by IR and $^1$H and $^{13}$C NMR spectroscopies, ESI mass spectrometry, and elemental analysis. The bis(carbene) precursor complex *fac*-[Re(CO)$_3$($\overline{\mathrm{CN(H)C_6H_4\text{-}2\text{-}O}}$)$_2$Br] and some of the NHC-containing Re(I) diimine complexes (**1**, **5**–**7**, and **9**) were also structurally characterized by X-ray crystallography. Various synthetic pathways for the preparation of luminescent N,O-, N,N-, and N,S-NHC complexes have also been investigated. The interconversions between the benzoxoal-2-ylidene ligand and 2-hydroxyphenyl isocyanide ligand were demonstrated in the preparation of **1**–**4**. The photophysical and electrochemical properties of all these complexes were studied, through which the relative π-accepting ability of various types of NHC ligands was evaluated. This should provide insights into the development of other luminescent NHC transition metal complexes as well as the tuning of their emission properties for various applications. Preliminary experiments showed that these NHC-containing Re(I) diimine complexes are active photocatalysts for reduction of $CO_2$. The study of their detailed photocatalytic properties are currently in progress.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

CIF data giving crystallographic data and the structure determination data for *fac*-[Re(CO)$_3$($\overline{\mathrm{CN(H)C_6H_4\text{-}2\text{-}O}}$)$_2$Br], **1**, **5**–**7**, and **9**; radiative and nonradiative decay rate constants of **1**–**9**; emission spectra of **1**–**9** in acetonitrile at 298 K and in EtOH–MeOH (4:1, v/v) glassy medium at 77 K; and transient absorption spectra of **1**, **5**, and **6**. 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.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The work described in this Article was supported by the Hong Kong University Grants Committee Area of Excellence Scheme (AoE/P-03-08) and a General Research Fund (Project CityU 101212). C.-O.N. acknowledges the receipt of a postgraduate studentship from City University of Hong Kong.

## REFERENCES

(1) (a) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247. (b) Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, 2006. (c) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. (d) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (e) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Chem. Rev.* **2009**, *109*, 3859. (f) Kühl, O. *Functionalised N-Heterocyclic Carbene Complexes*; John Wiley & Sons: Chichester, 2010.

(2) (a) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Perrin, L.; Clot, E.; Eisenstein, O.; Loch, J.; Crabtree, R. H. *Inorg. Chem.* **2001**, *40*, 5806. (c) Tafipolsky, M.; Scherer, W.; Öfele, K.; Artus, G.; Pedersen, B.; Herrmann, W. A.; McGrady, G. S. *J. Am. Chem. Soc.* **2002**, *124*, 5865. (d) Strassner, T. *Top. Organomet. Chem.* **2004**, *13*, 1. (e) Präsang, C.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2005**, *127*, 10182. (f) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874. (g) Radius, U.; Bickelhaupt, F. M. *Coord. Chem. Rev.* **2009**, *253*, 678. (h) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687. (i) Martin, D.; Melaimi; Soleilhavoup, M.; Betrand, G. *Organometallics* **2011**, *30*, 5304.

(3) (a) Xue, W.-M.; Chan, M. C.-W.; Su, Z.-M.; Cheung, K.-K.; Liu, S.-T.; Che, C.-M. *Organometallics* **1998**, *17*, 1622. (b) Unger, Y.; Zeller, A.; Ahrens, S.; Strassner, T. *Chem. Commun.* **2008**, 3263. (c) Unger, Y.; Meyer, D.; Molt, O.; Schildknecht, C.; Münster, I.; Wagenblast, G.; Strassner, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 10214. (d) Friese, V.; Nag, S.; Wang, J.; Santoni, M.-P.; Rodrigue-Witchel, A.; Hanan, G. S; Schaper, F. *Eur. J. Inorg. Chem.* **2011**, 39. (e) Hudson, Z. M.; Sun, C.; Helander, M. G.; Chang, Y.-L.; Lu, Z.-H.; Wang, S. *J. Am. Chem. Soc.* **2012**, *134*, 13930. (f) Darmawan, N.; Yang, C.-H.; Mauro, M.; Raynal, M.; Heun, S.; Pan, J.; Buchholz, H.; Braunstein, P.; De Cola, L. *Inorg. Chem.* **2013**, *52*, 10756. (g) Uesugi, H.; Tsukuda, T.; Takao, K.; Tsubomura, T. *Dalton Trans.* **2013**, *42*, 7396.

(4) (a) Sajoto, T.; Djurovich, P. I.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E.; Holmes, R. J.; Forrest, S. R. *Inorg. Chem.* **2005**, *44*, 7992. (b) Haneder, S.; Da Como, E.; Feldmann, J.; Lupton, J. M.; Lennartz, C.; Erk, P.; Fuchs, E.; Molt, O.; Muenster, I.; Schildknecht, C.; Wagenblast, G. *Adv. Mater.* **2008**, *20*, 3325. (c) Chang, C.-F.; Cheng, Y.-M.; Chi, Y.; Chiu, Y.-C.; Lin, C.-C.; Lee, G.-H.; Chou, P.-T.; Chen, C.-C.; Chang, C.-H.; Wu, C.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 4542. (d) Sasabe, H.; Takamatsu, J.-I.; Motoyama, T.; Watanabe, S.; Wagenblast, G.; Langer, N.; Molt, O.; Fuchs, E.; Lennartz, C.; Kido, J. *Adv. Mater.* **2010**, *22*, 5003. (e) Li, K.; Guan, X.; Ma, C.-W.; Lu, W.; Chen, Y.; Che, C.-M. *Chem. Commun.* **2011**, *47*, 9075. (f) Zhang, X.; Wright, A. M.; DeYonker, N. J.; Hollis, T. K.; Hammer, N. I.; Webster, C. E.; Valente, E. J. *Organometallics* **2012**, *31*, 1664.

(5) (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (b) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.

(6) (a) Raubenheimer, H. G.; Roos, M.; Otte, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1722. (b) Arduengo, A. J., III; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Organometallics* **1993**, *12*, 3405. (c) Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, G. R. J. *Chem.—Eur. J.* **1996**, *2*, 1627. (d) Raubenheimer, H. G.; Stander, Y.; Marais, E. K.; Thompson, C.; Kruger, G. J.; Cronje, S.; Deetlefs, M. *J. Organomet. Chem.* **1999**, *590*, 158.

(7) (a) Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141. (b) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42. (c) Schönherr, H.-J.; Wanzlick, H.-W. *Chem. Ber.* **1970**, *103*, 1037.

(8) (a) Bonati, F.; Burini, A.; Pietroni, B. R. *J. Organomet. Chem.* **1989**, *375*, 147. (b) Hahn, F. E.; Meier, N.; Pape, T. *Z. Naturforsch.* **2006**, *61b*, 820. (c) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642.

(9) (a) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F.; Manojlović-Muir, L.; Muir, K. W. *Chem. Commun.* **1971**, 400. (b) Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 541.

(10) (a) Ito, Y.; Hirao, T.; Tsubata, K.; Saegusa, T. *Tetrahedron Lett.* **1978**, *18*, 1535. (b) Beck, W.; Weigand, W.; Nagel, U.; Schaal, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 377. (c) Beck, G.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *10*, 1344. (d) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 85. (e) Bertani, R.; Mozzon, M.; Michelin, R. A. *Inorg. Chem.* **1988**, *27*, 2809. (f) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185.

(11) (a) Barrel, K.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 599. (b) Plaia, U.; Stolzenberg, H.; Fehlhammer, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 2172. (c) Hahn, F. E.; Tamm, M. *Chem. Commun.* **1993**, 842. (d) Hahn, F. E.; Tamm, M. *Organometallics* **1995**, *14*, 2597. (e) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175. (f) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lügger, T.; Fehlhammer, W. P. *Chem.—Eur. J.* **2003**, *9* (3), 704. (g) Edwards, P. G.; Hahn, F. E. *Dalton Trans.* **2011**, *40*, 10278.

(12) Ko, C.-C.; Ng, C.-O.; Yiu, S.-M. *Organometallics* **2012**, *31*, 7074.

(13) Ko, C.-C.; Lo, L. T.-L.; Ng, C.-O.; Yiu, S.-M. *Chem.—Eur. J.* **2010**, *16*, 13773.

(14) (a) Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offermann, K. *Angew. Chem., Int. Ed., Engl.* **1965**, *4*, 472. (b) Jutzi, P.; Gilge, U. *J. Organomet. Chem.* **1983**, *246*, 159.

(15) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(16) Ishida, H.; Tobita, S.; Hasegawa, Y.; Katoh, R.; Nozaki, K. *Coord. Chem. Rev.* **2010**, *254*, 2449.

(17) (a) Tapu, D.; Dixon, D. A.; Roe, C. *Chem. Rev.* **2009**, *109*, 3385. (b) Casson, L. A.; Muzzioli, S.; Raiteri, P.; Skelton, B. W.; Stagni, S.; Massi, M.; Brown, D. H. *Dalton Trans.* **2011**, *40*, 11960. (c) Li, X.-W.; Li, H.-Y.; Wang, G.-F.; Chen, F.; Li, Y.-Z.; Chen, X.-T.; Zheng, Y.-X.; Xue, Z.-L. *Organometallics* **2012**, *31*, 3829. (d) Chen, C.-H.; Liu, Y.-H.; Peng, S.-M.; Chen, J.-T.; Liu, S.-T. *Dalton Trans.* **2012**, *41*, 2747.

(18) (a) Sun, S.-S.; Lees, A. J.; Zavalij, P. Y. *Inorg. Chem.* **2003**, *42*, 3445. (b) Ng, C.-O.; Lai, S.-W.; Feng, H.; Yiu, S.-M.; Ko, C.-C. *Dalton Trans.* **2011**, *40*, 10020.

(19) Hahn, F. E.; Tamm, M.; Lügger, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1356.

(20) Hahn, F. E.; Tamm, M. *J. Chem. Soc., Chem. Commun.* **1995**, 569.

(21) (a) Tapolsky, G.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 2285. (b) Lin, R.; Fu, Y.; Prock Guarr, T. F. *Inorg. Chem.* **1992**, *31*, 4346. (c) Ko, C.-C.; Ng, C.-O.; Feng, H.; Chu, W.-K. *Dalton Trans.* **2010**, *39*, 6475. (d) Lo, L. T.-L; Lai, S.-W.; Yiu, S.-M.; Ko, C.-C. *Chem. Commun.* **2013**, *49*, 2311.

(22) (a) Yang, L.; Cheung, K.-K.; Mayr, A. *J. Organomet. Chem.* **1999**, *585*, 26. (b) Ng, C.-O.; Lo, L. T.-L.; Ng, S.-M.; Ko, C.-C.; Zhu, N. *Inorg. Chem.* **2008**, *47*, 7447. (c) Ko, C.-C.; Siu, J. W.-K.; Cheung, A. W.-Y.; Yiu, S.-M. *Organometallics* **2011**, *30*, 2701. (d) Cheung, A. W.-Y.; Lo, L. T.-L.; Ko, C.-C.; Yiu, S.-M. *Inorg. Chem.* **2011**, *50*, 4798.

(23) (a) 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. (b) Villegas, J. M.; Stoyanov, S. R.; Huang, W.; Rillema, R. *Dalton Trans.* **2005**, 1042.

(24) (a) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335. (b) Stufkens, D. J.; Vlček, A., Jr. *Coord. Chem. Rev.* **1998**, *177*, 127. (c) Ko, C.-C.; Cheung, A. W.-Y.; Lo, L. T.-L.; Siu, J. W.-K.; Ng, C.-O.; Yiu, S.-M. *Coord. Chem. Rev.* **2012**, *256*, 1546.

(25) (a) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (b) Kumar, A.; Sun, S.-S.; Lees, A. J. *Top. Organomet. Chem.* **2010**, *29*, 37.

(26) (a) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans.* **1986**, *282*, 2401. (b) Worl, L. A.; Duesing, R.; Chen, P.; Ciana, L. D.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849. (c) MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 7470.

(27) Emission maxima are corrected values and thus are different from the uncorrected emission maxima reported in ref 12.

(28) (a) Stufkens, D. J. *Comments Inorg. Chem.* **1992**, *13*, 359. (b) Kotch, T. G.; Lees, A. J. *Inorg. Chem.* **1993**, *32*, 2570.

(29) (a) Wallace, L.; Rillema, D. P. *Inorg. Chem.* **1993**, *32*, 3836. (b) Moya, S. A.; Guerrero, J.; Pastene, R.; Schmidt, R.; Sariego, R.; Sartori, R.; Sanz-Aparicio, J.; Fonseca, I.; Martínez-Ripoll, M. *Inorg. Chem.* **1994**, *33*, 2341.

(30) (a) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 4115. (b) Barqawi, K. R.; Llobet, A.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7751. (c) Baiano, J. A.; Murphy, W. R., Jr. *Inorg. Chem.* **1991**, *30*, 4594.

(31) Tsubaki, H.; Tohyama, S.; Koike, K.; Saitoh, H.; Ishitani, O. *Dalton Trans.* **2005**, 385.