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Luminescent Rhenium(I) Phenanthroline Complexes with a Benzoxazol-2-ylidene Ligand: Synthesis, Characterization, and Photophysical Study

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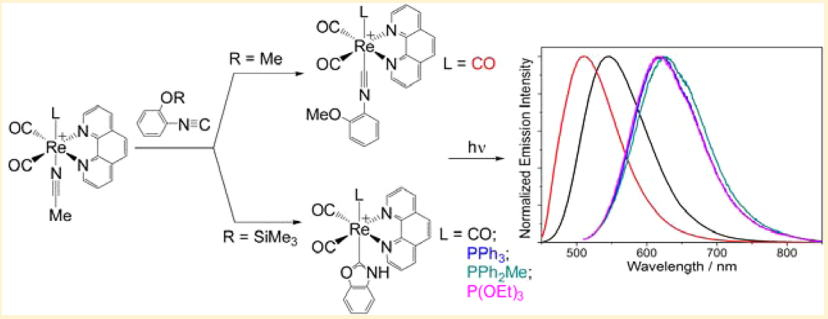
Supporting Information



ABSTRACT: A series of luminescent rhenium(I) phenanthroline complexes containing benzoxazol-2-ylidene ligands with the general formula $\{Re(CO)_3(phen)[\overline{CN(X)C_6H_4\text{-}2\text{-}O}]\}^+$ and *cis,trans*-$\{Re(CO)_2(phen)(L)[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]\}^+$ (X = H, methyl; phen = 1,10-phenanthroline; L = PPh_3, PPh_2Me, $P(OEt)_3$) have been synthesized and characterized. The X-ray crystal structures of most of the carbene complexes and some of their synthetic precursors have also been determined. A new synthetic methodology for the preparation of dicarbonyl rhenium diimine synthetic precursors with a labile acetonitrile ligand, $[Re(CO)_2(phen)(PR_3)(MeCN)]^+$, was developed. Photophysical study shows that these carbene complexes display a green to red ^{3}MLLCT [$d\pi(Re) \rightarrow \pi^*(N{-}N)$] phosphorescence at room temperature. The N-deprotonations of the benzoxazol-2-ylidene ligand in these complexes were investigated.

INTRODUCTION

Transition metal complexes with N-heterocyclic carbene (NHC) were first documented in 1968.[1] However, they have not received significant attention until the first report of a stable NHC ligand[2] and the subsequent application studies of these complexes for various catalytic properties.[3] Compared with free NHC ligands, the carbene ligand in transition metal complexes is much more stable, as its lone-pair electrons on the carbene carbon become unavailable after coordination. Moreover, upon coordination to metal centers with d-electrons, the p_π orbital of the carbene C is stabilized by delocalization of the filled p_π orbital of the adjacent heteroatom and filled d_π orbital of its coordinated metal center. In addition to their unique catalytic properties,[3] many NHC transition metal complexes also display interesting photophysical and luminescent properties.[4] The ease of functionalization, unique electronic properties, and robustness of NHC ligands have made them ideal ligands in the design of tunable luminescent NHC transition metal complexes with enhanced stability and novel photophysical properties.[4] As metal isocyanide complexes are excellent synthetic precursors for NHC metal complexes,[5] we have extended our recent work on luminescent isocyano rhenium(I) diimine complexes[6] to synthesize a new class of tunable luminescent rhenium(I) diimine complexes with NHC ligands. It is anticipated that these NHC rhenium(I) diimine complexes will possess better photo- and thermal stability, as NHC ligands are much less susceptible to nucleophilic attack compared to isocyanide.[3m,7] Herein, we report the synthesis, structures, photophysics, and electrochemistry of a series of carbonyl rhenium(I) phenanthroline complexes with a benzoxazol-2-ylidene ligand. A new synthetic methodology for dicarbonyl rhenium(I) diimine synthetic precursors, *cis,trans*-$[Re(CO)_2(diimine)(PR_3)(MeCN)]^+$, was also described.

Physical Measurements and Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, 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 positive-ion 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 Elementar Vario MICRO Cube elemental analyzer.

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Table 1. Crystal and Structure Determination Data for 1−3 and 5−7

	1	2	3	5	6	7
formula	$C_{22}H_{12}N_3O_4Re$	$C_{22}H_{13}N_3O_4Re\ PF_6$	$C_{23}H_{15}N_3O_4RePF_6$	$C_{34}H_{26}N_3O_3PRePF_6{\cdot}C_3H_6O$	$C_{27}H_{28}N_3O_6PRePF_6{\cdot}0.125C_4H_{10}O$	$C_{23}H_{15}N_3O_4ReCF_3SO_3$
M_w	568.55	714.52	728.56	944.80	861.93	732.65
T/K	133(2)	133(2)	133(2)	133(2)	173(2)	133(2)
a/Å	23.6676(13)	12.1681(3)	8.1807(9)	10.9257(2)	13.7655(1)	8.9977(3)
b/Å	11.3775(2)	11.0649(3)	11.7759(8)	20.0094(3)	19.0956(2)	22.9216(6)
c/Å	17.8694(17)	17.4182(4)	12.6684(9)	17.2111(3)	24.8720(3)	11.8033(3)
α/deg	90.00	90.00	83.666(6)	90.00	90.00	90.00
β/deg	127.018(9)	91.646(2)	81.993(7)	100.859(2)	101.053(10)	91.10(2)
γ/deg	90.00	90.00	75.973(7)	90.00	90.00	90.00
V/Å^3	3842.0(4)	2344.20(10)	1168.75(17)	3695.26(11)	6416.59(11)	2433.88(12)
cryst color	yellow	yellow	yellow	orange	yellow	yellow
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	8	4	2	4	8	4
$F(000)$	2176	1368	700	1864	3386	1416
D_c/g cm^{-3}	1.966	2.025	2.070	1.698	1.784	1.999
dimensions/mm	0.5 × 0.4 × 0.1	0.4 × 0.3 × 0.05	0.3 × 0.1 × 0.01	0.2 × 0.1 × 0.02	0.5 × 0.1 × 0.04	0.7 × 0.1 × 0.05
λ/Å	0.7107	1.5418	1.5418	1.5418	1.5418	1.5418
μ/mm^{-1}	6.36	11.57	11.62	7.91	9.08	11.25
collection range	$3.2 \le \theta \le 25.0°$ (h: −28 to 28; k: −13 to 13; l: −21 to 21)	$4.4 \le \theta \le 67.0°$ (h: −14 to 13; k: −13 to 11; l: −20 to 18)	$3.5 \le \theta \le 67.0°$ (h: −9 to 7; k: −14 to 13; l: −15 to 15)	$3.4 \le \theta \le 67.0°$ (h: −13 to 12; k: −21 to 23; l: −20 to 18)	$3.3 \le \theta \le 67.0°$ (h: −16 to 16; k: −17 to 22; l: −29 to 29)	$3.9 \le \theta \le 71.8°$ (h: −10 to 7; k: −27 to 28;l: −14 to 14)
completeness to theta	99.8%	99.8%	99.3%	99.9%	100%	98.9%
no. of data collected	17 880	8686	7656	14 170	26 237	16 501
no. of unique data	3393	4172	4124	6581	11 443	4719
no. of data used in refinement	3225	4091	4057	6198	10 257	4682
no. of params refined	271	334	343	753	1009	443
R^a	0.018	0.030	0.028	0.023	0.067	0.029
wR^a	0.050	0.076	0.077	0.058	0.158	0.079
goodness-of-fit	1.08	1.14	1.09	1.05	1.25	1.15
maximum shift, $(\Delta/\sigma)_{max}$	0.001	0.002	0.001	0.003	0.001	0.002
residual extrema in final diff map, e Å^{-3}	+1.07, −1.00	+0.88, −2.25	+2.37, −0.91	+0.89, −0.89	+5.02, −3.54	+0.97, −1.63

[a] $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bP]$, where $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$.

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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 MCS or Fast MCS lifetime mode with NanoLED-375LH (λ_{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[8] with an aqueous solution of $[Ru(bpy)_3]Cl_2$ (ϕ_{em} = 0.042[9] with 436 nm excitation) as reference. Cyclic voltammetry 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 $^nBu_4NPF_6$ as the supporting electrolyte at room temperature with a glassy carbon electrode (CH Instruments, Inc.) as working electrode, a platinum wire as the counter electrode, and $Ag/AgNO_3$ (0.01 M in acetonitrile) (CH Instruments, Inc.) as the reference electrode. The working electrode surface was polished with a 1 μm α-alumina slurry and then a 0.3 μm α-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. The acid dissociation constants (pK_a) of **2** and **4**−**6** (0.04 mM) in acetonitrile/water (9:1, v/v, 0.05 M $^nBu_4NPF_6$) were determined by using a potentiometric titration described in the literature.[10]

Crystal Structure Determinations. Single crystals of **1**−**3** and **5**−**7** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether vapor into acetone solutions of the complexes. The crystal structures were determined on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer using graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å) or Mo Kα radiation (λ = 0.7107 Å). The experimental parameters for the structure determination data are summarized in Table 1. All structures were solved by direct methods employing the SHELXS-97 program.[11] Rhenium and many non-hydrogen 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 the SHELXL-97 program.[11] In the final stage of least-squares refinement all non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.5 times that for methyl H atoms and 1.2 times that of the associated carbon or nitrogen and participated in the calculation of final *R*-indices.

EXPERIMENTAL SECTION

Materials and Reagents. $[Re(CO)_5Br]$ was obtained from Strem Chemicals, Inc. 1,10-Phenanthroline (phen), benzoxazole, triphenylphosphine (PPh_3), diphenylmethylphosphine (PPh_2Me), triethylphosphite $[P(OEt)_3]$, dimethyl sulfate, and trimethylamine *N*-oxide dihydrate ($Me_3NO{\cdot}2H_2O$) were obtained from Aldrich Chemical Co. $[Re(CO)_3(phen)(MeCN)](CF_3SO_3)$, $[Re(CO)_3(phen)(PPh_3)](CF_3SO_3)$, $[Re(CO)_3(phen)(PPh_2Me)](CF_3SO_3)$, and $\{Re(CO)_3(phen)[P(OEt)_3]\}(CF_3SO_3)$ were prepared by a slight modification of a literature procedure for related rhenium complexes.[12] 2-Trimethylsiloxyphenyl isocyanide was prepared according to a reported procedure.[13] 2-Methoxyphenyl isocyanide ($2\text{-}MeOC_6H_4NC$) was synthesized from 2-methoxyphenyl formamide[14] using the synthetic methodology developed by Ugi and co-workers.[15] THF and benzene were distilled over sodium prior to use. All other reagents and solvents were of analytical grade and used as received.

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

Synthesis of *cis,trans*-$[Re(CO)_2(phen)(PPh_3)(MeCN)](CF_3SO_3)$. To a solution of $[Re(CO)_3(phen)(PPh_3)](CF_3SO_3)$ (100 mg, 116 μmol) in MeCN (30 mL) was added trimethylamine *N*-oxide dihydrate (19.3 mg, 174 μmol). The resulting solution was refluxed for 18 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane−acetone−acetonitrile (20:10:1 v/v/v) as eluent to give analytically pure complex as an orange solid. Yield: 67.4 mg, 77.0 μmol; 66.4%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.77 (dd, 2H, J = 5.1, 1.4 Hz, 2,9-phen H's), 8.59 (dd, 2H, J = 8.2, 1.4 Hz, 4,7-phen H's), 8.14 (s, 2H, 5,6-phen H's), 7.56 (dd, 2H, J = 8.2, 5.1 Hz, 3,8-phen H's), 7.23 (m, 3H, phenyl H's), 7.12 (m, 6H, phenyl H's), 7.03 (m, 6H, phenyl H's), 2.14 (s, 3H, methyl H's). Positive-ion ESI-MS: m/z 726 $[M - CF_3SO_3]^+$. IR (KBr disk): ν/cm^{-1} 1942, 1871 (C≡O). Anal. Calcd (%) for $C_{35}H_{26}F_3N_3O_5PReS$ (874.84): C 48.05, H 3.00, N 4.80. Found: C 47.86, H 3.32, N 4.41.

Synthesis of *cis,trans*-$[Re(CO)_2(phen)(PPh_2Me)(MeCN)](CF_3SO_3)$. The complex was prepared according to a procedure similar to that for *cis,trans*-$[Re(CO)_2(phen)(PPh_3)(MeCN)](CF_3SO_3)$ except $[Re(CO)_3(phen)(PPh_2Me)](CF_3SO_3)$ (92.8 mg, 116 μmol) was used in place of $[Re(CO)_3(phen)(PPh_3)](CF_3SO_3)$. Yield: 57.9 mg, 71.2 μmol; 61.4%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.98 (dd, 2H, J = 5.2, 1.3 Hz, 2,9-phen H's), 8.61 (dd, 2H, J = 8.1, 1.3 Hz, 4,7-phen H's), 8.12 (s, 2H, 5,6-phen H's), 7.69 (dd, 2H, J = 8.1, 5.2 Hz, 3,8-phen H's), 7.21 (td, 2H, J = 7.4, 1.9 Hz, phenyl H's), 7.09 (td, 4H, J = 7.9, 1.9 Hz, phenyl H's), 6.90 (m, 4H, phenyl H's), 2.16 (s, 3H, methyl H's), 1.57 (d, 3H, J^{PH} = 8.3 Hz, methyl H's). Positive-ion ESI-MS: m/z 664 $[M - CF_3SO_3]^+$. IR (KBr disk): ν/cm^{-1} 1934, 1861 (C≡O). Anal. Calcd (%) for $C_{30}H_{24}F_3N_3O_5PReS$ (821.77): C 44.33, H 2.98, N 5.17. Found: C 44.31, H 2.71, N 4.97.

Synthesis of *cis,trans*-$\{Re(CO)_2(phen)[P(OEt)_3](MeCN)\}(CF_3SO_3)$. The complex was prepared according to a procedure similar to that for *cis,trans*-$[Re(CO)_2(phen)(PPh_3)(MeCN)](CF_3SO_3)$ except $\{Re(CO)_3(phen)[P(OEt)_3]\}(CF_3SO_3)$ (88.8 mg, 116 μmol) was used in place of $[Re(CO)_3(phen)(PPh_3)](CF_3SO_3)$. Yield: 63.3 mg, 81.3 μmol; 70.1%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 9.31 (dd, 2H, J = 5.1, 1.4 Hz, 2,9-phen H's), 8.74 (dd, 2H, J = 8.3, 1.4 Hz, 4,7-phen H's), 8.19 (s, 2H, 5,6-phen H's), 7.95 (dd, 2H, J = 8.3, 5.1 Hz, 3,8-phen H's), 3.66 (q, 6H, J = 7.0 Hz, ethyl H's), 0.90 (t, 9H, J = 7.0 Hz, ethyl H's). Positive-ion ESI-MS: m/z 630 $[M - CF_3SO_3]^+$. IR (KBr disk): ν/cm^{-1} 1949, 1869 (C≡O). Anal. Calcd (%) for $C_{23}H_{26}F_3N_3O_8PReS$ (778.71): C 35.47, H 3.37, N 5.40. Found: C 35.52, H 3.61, N 5.34.

Synthesis of $[Re(CO)_3(phen)(\overline{CNC_6H_4\text{-}2\text{-}O})]$ (1) and $\{Re(CO)_3(phen)[\overline{CN(H)C_6H_4\text{-}2\text{-}O}]\}(PF_6)$ (2). $[Re(CO)_3(phen)(MeCN)](CF_3SO_3)$ (100 mg, 156 μmol) and 2-trimethylsiloxyphenyl isocyanide (35.8 mg, 187 μmol) were dissolved in THF (50 mL). The resulting solution was refluxed overnight. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina using dichloromethane−acetone (9:1 v/v) as eluent to give analytically pure complex **1**, which is the N-deprotonated form of **2**, as a yellow crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.61 (dd, 2H, J = 5.1, 1.3 Hz, 2,9-phen H's), 8.50 (dd, 2H, J = 8.2, 1.3 Hz, 4,7-phen H's), 7.98 (s, 2H, 5,6-phen H's), 7.86 (dd, 2H, J = 8.2, 5.1 Hz, 3,8-phen H's), 7.24 (dd, 1H, J = 7.0, 1.9 Hz, phenyl H's), 7.02 (dd, 1H, J = 7.0, 1.8 Hz, phenyl H's), 6.86 (m, 2H, phenyl H's). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 214.5, 199.6, 198.3, 153.5, 152.7, 147.3, 137.1, 130.4, 127.4, 125.7, 121.4, 121.1, 117.3, 116.3, 108.5. Positive-ion ESI-MS: m/z 570 $[M + H]^+$. IR (KBr disk): ν/cm^{-1} 2009, 1913, 1883 (C≡O). Anal. Calcd (%) for $C_{22}H_{12}N_3O_4Re$ (569.04): C 46.47,

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H 2.13, N 7.39. Found: C 46.47, H 2.11, N 7.53. Protonation of the methanolic solution of **1** with hydrochloric acid (0.1% in MeOH) and subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave complex **2** as a PF_6^- salt. Slow diffusion of diethyl ether vapor into a concentrated acetone solution of the complex gave **2** as a pale yellow crystalline solid. Yield: 74.1 mg, 104 μmol; 66.7%. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K): δ 14.82 (s, 1H, NH's), 9.56 (dd, 2H, J = 5.2, 1.4 Hz, 2,9-phen H's), 9.00 (dd, 2H, J = 8.3, 1.4 Hz, 4,7-phen H's), 8.34 (s, 2H, 5,6-phen H's), 8.16 (dd, 2H, J = 8.3, 5.2 Hz, 3,8-phen H's), 7.46 (m, 2H, phenyl H's), 7.32 (td, 1H, J = 7.7, 1.2 Hz, phenyl H's), 7.26 (td, 1H, 7.7, 1.4 Hz, phenyl H's). ^{13}C NMR (100 MHz, DMSO, 298 K): δ 204.9, 195.2, 192.4, 154.7, 150.9, 146.3, 139.6, 130.5, 127.8, 126.8, 125.8, 125.6, 122.2, 113.1, 111.1. Positive-ion ESI-MS: m/z 570 $[M - PF_6]^+$;. IR (KBr disk): ν/cm^{-1} 2031, 1942, 1912 (C≡O), 839 (P−F). Anal. Calcd (%) for $C_{22}H_{13}F_6N_3O_4PRe$ (714.53): C 36.98, H 1.83, N 5.88. Found: C 36.80, H 1.62, N 5.91.

Synthesis of {Re(CO)$_3$(phen)[$\overline{CN(Me)C_6H_4\text{-}2\text{-}O}$]}(PF$_6$) (3). To a suspension of complex **2** (60 mg, 84.0 μmol) and K_2CO_3 (116 mg, 840 μmol) in acetone (30 mL) was slowly added dimethyl sulfate (79.6 μL, 840 μmol). The reaction mixture was then stirred at room temperature for 18 h. After removal of the solvent under reduced pressure, the residue was redissolved in chloroform and washed with dilute hydrochloric acid (0.1 M) and water. The organic layer was then dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel using dichloromethane−acetone (4:1 v/v) as eluent. It was recrystallized by slow diffusion of diethyl ether vapor into a concentrated acetone solution of the complex to give analytically pure complex **3** as a dark yellow crystalline solid. Yield: 52.4 mg, 71.9 μmol; 85.6%. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K): δ 9.58 (dd, 2H, J = 5.2, 1.4 Hz, 2,9-phen H's), 9.01 (dd, 2H, J = 8.3, 1.4 Hz, 4,7-phen H's), 8.35 (s, 2H, 5,6-phen H's), 8.14 (dd, 2H, J = 8.3, 5.2 Hz, 3,8-phen H's), 7.69 (dd, 1H, J = 8.0, 0.9 Hz, phenyl H's), 7.39 (td, 1H, J = 6.6, 1.8 Hz, phenyl H's), 7.25 (m, 2H, phenyl H's), 4.03 (s, 3H, methyl H's). ^{13}C NMR (100 MHz, d_6-DMSO, 298 K): δ 206.6, 196.1, 192.9, 155.8, 151.6, 147.5, 140.6, 132.3, 131.5, 128.8, 127.6, 126.9, 126.6, 113.8, 111.9, 35.1. Positive-ion ESI-MS: m/z 584 $[M - PF_6]^+$. IR (KBr disk): ν/cm^{-1} 2024, 1919, 1909 (C≡O), 840 (P−F). Anal. Calcd (%) for $C_{23}H_{15}F_6N_3O_4PRe$ (728.55): C 37.92, H 2.08, N 5.77. Found: C 37.71, H 2.18, N 5.53.

Synthesis of *cis,trans*-{Re(CO)$_2$(phen)(PPh$_3$)[$\overline{CN(H)C_6H_4\text{-}2\text{-}O}$]}(PF$_6$) (4). 2-Trimethylsiloxyphenyl isocyanide (15.7 mg, 82.3 μmol) and *cis,trans*-[Re(CO)$_2$(phen)(PPh$_3$)(MeCN)](CF$_3$SO$_3$) (60 mg, 68.6 μmol) were dissolved in THF (30 mL). The resulting solution was refluxed overnight. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina using dichloromethane−acetone (9:1 v/v) as eluent. Subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave the target complex as a PF_6^- salt. It was then further purified by slow diffusion of diethyl ether vapor into a concentrated acetone solution of the complex, giving **4** as a pale yellow crystalline solid. Yield: 46.8 mg, 49.3 μmol; 71.9%. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K): δ 14.15 (s, 1H, NH's), 9.09 (dd, 2H, J = 5.2, 1.1 Hz, 2,9-phen H's), 8.69 (dd, 2H, J = 8.2, 1.1 Hz, 4,7-phen H's), 8.16 (s, 2H, 5,6-phen H's), 7.76 (dd, 2H, J = 8.2, 5.2 Hz, 3,8-phen H's), 7.37 (d, 1H, J = 7.5 Hz, phenyl H's), 7.30 (m, 12H, phenyl H's), 6.98 (m, 6H, phenyl H's). ^{13}C NMR (100 MHz, d_6-DMSO, 298 K): δ 206.7 (d, J^{PC} = 62.6 Hz), 203.3 (d, J^{PC} = 5.5 Hz), 154.0, 151.5, 146.1, 138.5, 132.6 (d, J^{PC} = 11.4 Hz), 132.2, 131.1, 130.4, 130.3, 128.9 (d, J^{PC} = 9.4 Hz), 128.1, 126.8, 125.8, 125.1, 112.7, 111.0. Positive-ion ESI-MS: m/z 803 $[M - PF_6]^+$. IR (KBr disk): ν/cm^{-1} 1937, 1850 (C≡O), 844 (P−F). Anal. Calcd (%) for $C_{39}H_{28}F_6N_3O_3P_2Re$ (948.80): C 49.37, H 2.97, N 4.43. Found: C 49.29, H 3.26, N 4.42.

Synthesis of *cis,trans*-{Re(CO)$_2$(phen)(PPh$_2$Me)[$\overline{CN(H)C_6H_4\text{-}2\text{-}O}$]}(PF$_6$) (5). The complex was prepared according to a procedure similar to that for **4** except *cis,trans*-[Re(CO)$_2$(phen)(PPh$_2$Me)(MeCN)](CF$_3$SO$_3$) (55.7 mg, 68.6 μmol) was used in place of *cis,trans*-[Re(CO)$_2$(phen)(PPh$_3$)(MeCN)](CF$_3$SO$_3$). Yield: 41.2 mg, 46.5 μmol; 67.8%. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K): δ 14.01 (s, 1H, NH's), 9.23 (dd, 1H, J = 5.2, 1.2 Hz, 2,9-phen H's), 8.74 (dd, 2H, J = 8.2, 1.2 Hz, 4,7-phen H's), 8.15 (s, 2H, 5,6-phen H's), 7.89 (dd, 2H, J = 8.2, 5.2 Hz, 3,8-phen H's), 7.35 (d, 1H, J = 7.9 Hz, phenyl H's), 7.32 (d, 1H, J = 8.1 Hz, phenyl H's), 7.22 (m, 3H, phenyl H's), 7.13 (m, 5H, phenyl H's), 6.92 (m, 4H, phenyl H's), 1.54 (d, 3H, J = 7.3 Hz, methyl H's). ^{13}C NMR (100 MHz, d_6-DMSO, 298 K): δ 207.9 (d, J^{PC} = 62.2 Hz), 203.4 (d, J^{PC} = 7.6 Hz), 153.7, 151.6, 146.1, 138.5, 133.8, 133.3, 131.1 (d, J^{PC} = 10.6 Hz), 130.6, 130.0, 128.7 (d, J^{PC} = 9.3 Hz), 128.1, 126.8, 125.7, 125.0, 112.5, 111.0, 13.9 (d, J^{PC} = 30.1 Hz). Positive-ion ESI-MS: m/z 742 $[M - PF_6]^+$. IR (KBr disk): ν/cm^{-1} 1933, 1861 (C≡O), 841 (P−F). Anal. Calcd (%) for $C_{34}H_{26}F_6N_3O_3P_2Re$ (886.73): C 46.05, H 2.96, N 4.74. Found: C 45.83, H 3.13, N 4.73.

Synthesis of *cis,trans*-{Re(CO)$_2$(phen)[P(OEt)$_3$][$\overline{CN(H)C_6H_4\text{-}2\text{-}O}$]}(PF$_6$) (6). The complex was prepared according to a procedure similar to that of **4** except *cis,trans*-[Re(CO)$_2$(phen)[P(OEt)$_3$](MeCN)](CF$_3$SO$_3$) (53.4 mg, 68.6 μmol) was used in place of *cis,trans*-[Re(CO)$_2$(phen)(PPh$_3$)(MeCN)](CF$_3$SO$_3$). Yield: 43.1 mg, 50.5 μmol; 73.7%. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K): δ 14.20 (s, 1H, NH's), 9.45 (dd, 2H, J = 5.2, 0.9 Hz, 2,9-phen H's), 8.91 (dd, 2H, J = 8.2, 0.9 Hz, 4,7-phen H's), 8.30 (s, 2H, 5,6-phen H's), 8.09 (dd, 2H, J = 8.2, 5.2 Hz, 3,8-phen H's), 7.39 (m, 2H, phenyl H's), 7.27 (td, 1H, J = 7.5, 1.2 Hz, phenyl H's), 7.20 (td, 1H, J = 7.2, 1.2 Hz, phenyl H's), 3.62 (q, 6H, J = 7.0 Hz, ethyl H's), 0.77 (t, 9H, J = 7.0 Hz, methyl H's). ^{13}C NMR (100 MHz, d_6-DMSO, 298 K): δ 209.0 (d, J^{PC} = 93.2 Hz), 201.4 (d, J^{PC} = 9.8 Hz), 154.3, 151.6, 146.9, 138.9, 130.9, 130.7, 128.1, 126.8, 125.8, 125.2, 112.8, 111.2, 60.8 (d, J^{PC} = 5.5 Hz), 16.1 (d, J^{PC} = 5.9 Hz). Positive-ion ESI-MS: m/z 709 $[M - PF_6]^+$. IR (KBr disk): ν/cm^{-1} 1940, 1859 (C≡O), 844 (P−F). Anal. Calcd (%) for $C_{27}H_{28}F_6N_3O_6P_2Re$ (852.67): C 38.03, H 3.31, N 4.93. Found: C 38.15, H 3.45, N 4.93.

Synthesis of [Re(CO)$_3$(phen)(2-MeOC$_6$H$_4$NC)](PF$_6$) (7). [Re(CO)$_3$(phen)(MeCN)](CF$_3$SO$_3$) (100 mg, 156 μmol) and 2-MeOC$_6$H$_4$NC (25 mg, 187 μmol) were dissolved in THF (50 mL). The resulting solution was refluxed overnight. After removal of the solvent under reduced pressure, the residue was further purified by column chromatography on alumina using dichloromethane−acetone (9:1 v/v) as eluent. Subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave the target complex as a PF_6^- salt. Slow diffusion of diethyl ether vapor into a concentrated acetone solution of the complex gave **7** as a pale yellow crystalline solid. Yield: 92.8 mg, 127 μmol; 81.4%. ^{1}H NMR (400 MHz, d_6-DMSO, 298 K): δ 9.55 (dd, 2H, J = 5.2, 1.4 Hz, 2,9-phen H's), 9.08 (dd, 2H, J = 8.3, 1.4 Hz, 4,7-phen H's), 8.41 (s, 2H, 5,6-phen H's), 8.20 (dd, 2H, J = 8.3, 5.2 Hz, 3,8-phen H's), 7.38 (m, 2H, phenyl H's), 7.02 (dd, 1H, J = 9.0, 1.1 Hz, phenyl H's), 6.89 (td, 1H, J = 7.9, 1.1 Hz, phenyl H's), 3.38 (s, 3H, methyl H's). ^{13}C NMR (100 MHz, d_6-DMSO, 298 K): δ 192.2, 189.1, 155.9, 155.8, 155.2, 146.8, 140.5, 132.8, 131.2, 128.5, 127.6, 127.5, 121.1, 114.2, 112.9, 56.6. Positive-ion ESI-MS: m/z 584 $[M - PF_6]^+$. IR (KBr disk): ν/cm^{-1} 2181 (C≡N), 2046, 1974, 1943 (C≡O), 839 (P−F). Anal. Calcd (%) for $C_{23}H_{15}F_6N_3O_4PRe$ (728.55): C 37.92, H 2.08, N 5.77. Found: C 37.74, H 2.13, N 5.81.

RESULTS AND DISCUSSION

Synthesis and Characterization. 2-Trimethylsiloxyphenyl isocyanide was prepared from benzoxazole according to a literature method,[13] whereas 2-methoxyphenyl isocyanide (2-MeOC$_6$H$_4$NC) was prepared by dehydration of 2-methoxyphenyl formamide commonly used for the synthesis of isocyanide ligands.[15] On the basis of our recently reported Me$_3$NO-mediated decarbonylation reactions for carbonyl-containing rhenium(I) complexes,[16] the dicarbonyl rhenium phenanthroline acetonitrile precursor complexes, *cis,trans*-[Re(CO)$_2$(phen)(PR$_3$)(MeCN)](CF$_3$SO$_3$), with different phosphine ligands were also prepared. The observations of one set of ^{1}H NMR signals for the two pyridyl moieties in the phenanthroline ligand of all precursor complexes confirm the symmetrical environment of the phenanthroline ligand. This

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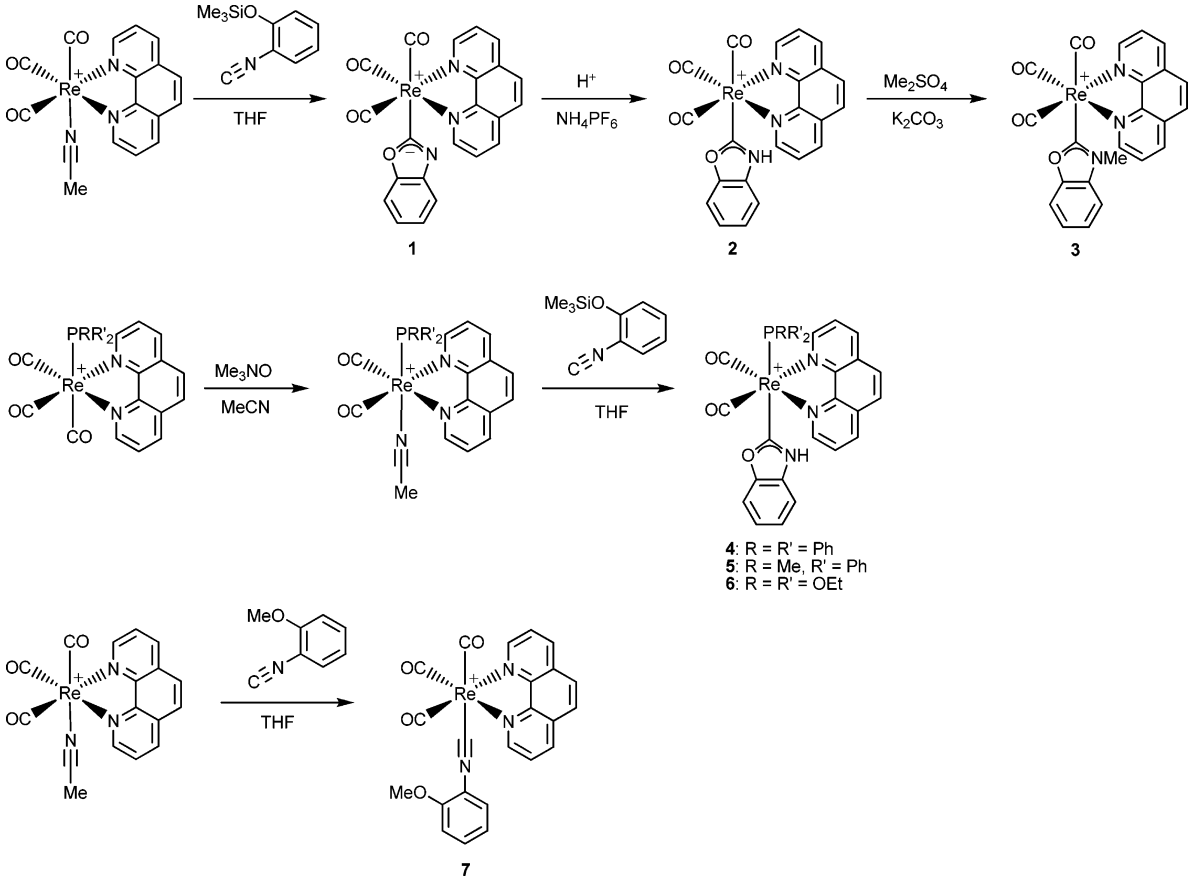
Scheme 1. Synthetic Routes to Complexes 1−7



suggests that the carbonyl ligand *trans* to the phosphine ligand is selectively decarbonylated and substituted with acetonitrile. The geometrical arrangements of ligands in these complexes are further confirmed by the X-ray crystal structures of *cis,trans*-$[Re(CO)_2(phen)(PPh_3)(MeCN)](CF_3SO_3)$ and *cis,trans*-$[Re(CO)_2(phen)(PPh_3Me)(MeCN)](CF_3SO_3)$ (Figure S1, Supporting Information). Although these complexes could also be synthesized using the photochemical ligand substitution reaction reported by Ishitani and co-workers,[17] the current thermal method allows for a larger scale synthesis and easy control and optimization of reaction conditions.

For phosphino rhenium(I) complexes reported by Hahn and co-workers,[5d] the 2-hydroxyphenyl isocyanide ligand coordinates in an isocyanide form without conversion into the benzoxazol-2-ylidene ligand. In contrast, reactions of 2-trimethylsiloxyphenyl isocyanide with precursor acetonitrile complexes, $[Re(CO)_3(phen)(MeCN)](CF_3SO_3)$ and $[Re(CO)_2(phen)(PR_3)(MeCN)](CF_3SO_3)$, gave a series of luminescent carbene-containing rhenium(I) phenanthroline complexes (**1**, **2**, **4**−**6**). This is attributed to the weaker π-back-bonding interaction between the metal center and the 2-hydroxyphenyl isocyanide ligand in the carbonyl rhenium(I) complexes as a result of the competition of strong π-accepting carbonyl ligands. Hence, the isocyanide C is more susceptible to the intramolecular nucleophilic attack to form the carbene ligand.[5b−g,18] The weak π-back-bonding interaction between the Re(I) metal center and the isocyanide ligand can be reflected by the high isocyanide stretching frequency [ν(C≡N) ≈ 2184 cm^{-1}] observed in the analogous complex **7** with the 2-methoxyphenyl isocyanide ligand. As suggested by Hahn and co-workers, the coordinated 2-hydroxyphenyl isocyanide ligand with such a high C≡N stretching frequency would prefer the formation of a carbene ligand.[5b−g,18] The absence of the isocyanide C≡N stretch in the IR spectra of **1**−**6** and the observation of the downfield ^{13}C signals in the range 205 to 215 ppm, which is in the typical range for carbene-^{13}C signals of other benzoxazol-2-ylidene complexes,[5b−g,19] in their ^{13}C NMR spectra are supportive of the formation of a carbene ligand in **1**−**6**.

In the ligand substitution reaction of $[Re(CO)_3(phen)(MeCN)](CF_3SO_3)$ with 2-trimethylsiloxyphenyl isocyanide, neutral complex **1** with an anionic N-deprotonated carbene ligand was obtained. On the other hand, similar reactions for $[Re(CO)_2(phen)(PR_3)(MeCN)](CF_3SO_3)$ gave cationic complexes with neutral carbene ligands. This is attributed to the stronger acidity of the NH proton in the carbene ligand of **2**, as reflected by its lower pK_a value (see below). Acidification of **1** with hydrochloric acid followed by metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave **2** as a PF_6^- salt. Similar to other NHC ligands, the benzoxazol-2-ylidene ligand of **2** could be readily methylated by dimethyl sulfate in the presence of K_2CO_3 to give **3**. All complexes **1**−**7** were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, positive-ion ESI mass spectrometry, and satisfactory elemental analyses. The structures of complexes **1**−**3**, **5**, **6**, and the $CF_3SO_3^-$ salt of **7** were also determined by X-ray crystallography.

X-ray Crystal Structure. The perspective drawings of complex **1** and the complex cations of **2**, **3**, and **5**−**7** are depicted in Figure 1. The experimental details for the crystal structure determinations and selected bond distances and bond angles are summarized in Tables 1 and 2, respectively. The rhenium metal centers of all complexes adopted a distorted octahedral geometry with bite

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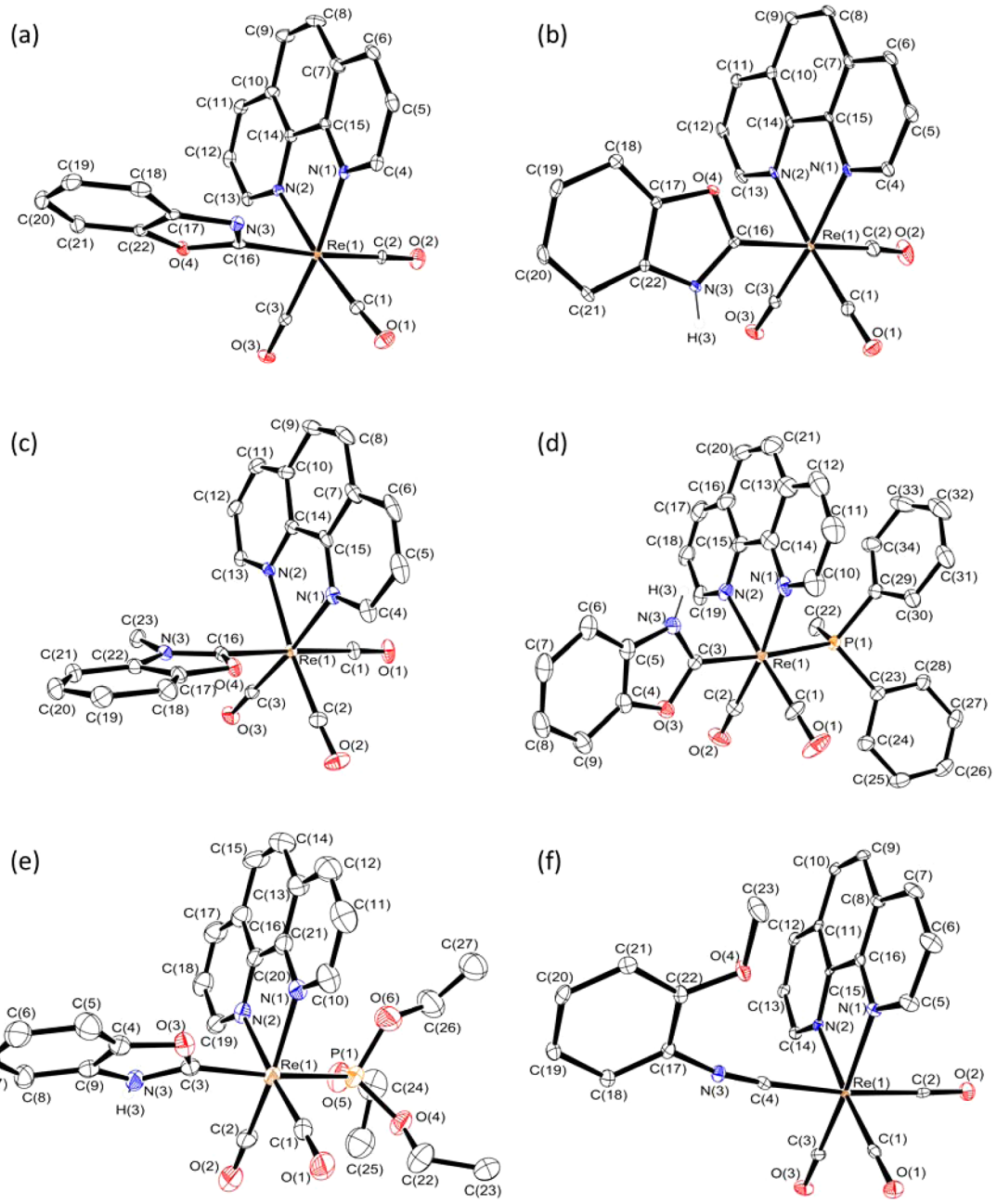

Figure 1. Perspective drawings of (a) **1** and the complex cations of (b) **2**, (c) **3**, (d) **5**, (e) **6**, and (f) **7** with the atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

angles of the phenanthroline ligands from 74.5° to 75.8°, commonly observed in other rhenium(I) phenanthroline complexes.[16,20] In the crystal structures of **1**−**3** and **7**, the three carbonyl ligands show a typical facial arrangement, whereas a *cis* conformation of the carbonyl ligands in the dicarbonyl complexes can be confirmed by the crystal structures of **5** and **6**. This confirms the selectivity of the decarbonylation and subsequent ligand substitution reactions.

For tricarbonyl complexes **1**−**3** and **7**, the Re−C (carbonyl) and C−O (carbonyl) bond lengths are in the ranges 1.92−1.98 and 1.12−1.15 Å, which are similar to those reported for other rhenium(I) tricarbonyl diimine complexes.[16,20] In the structures of the dicarbonyl complexes **5** and **6**, they show shorter average Re−C (carbonyl) bond lengths (1.89 Å vs 1.94 Å) and slightly longer C−O (carbonyl) bond lengths (1.17 vs 1.14 Å) compared to those observed in the tricarbonyl complexes **1**−**3** and **7**. This can be explained by the stronger Re−CO π-back-bonding interaction in the dicarbonyl rhenium(I) complexes compared to that in the tricarbonyl complexes, as phosphines are weaker π-accepting ligands than carbonyl ligands. For benzoxazol-2-ylidene ligands in these structures, the Re−C (carbene) bond lengths are in the range 2.09−2.15 Å, which are in a typical range reported in other rhenium(I) N-heterocyclic carbene complexes.[4a,21] Similarly, due to a stronger π-back-bonding interaction, the Re−C (carbene) bond lengths in **5** and **6** (2.09−2.11 Å) are also shorter than those in **1**−**3** (2.14−2.15 Å). Upon N-deprotonation of the benzoxazol-2-ylidene ligand, the C−N−C angle in the oxazol-2-ylidene moiety decreases from 111.7° in **2**, which is typical for benzoxazol-2-ylidene ligands (~110−112°;[19b,22] 109.9° in **3**, 111.8° in **5**, and 110.6° in **6**), to 106.3° in **1**. This is probably due to the increased electron repulsion for anionic lone-pair electrons

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Table 2. Selected Bond Lengths [Å] and Angles [deg] with Estimated Standard Deviations in Parentheses for Complexes 1−3 and 5−7

			1		
Re(1)−C(1)	1.917(3)	Re(1)−N(2)	2.177(2)	C(3)−O(3)	1.148(4)
Re(1)−C(2)	1.952(3)	Re(1)−C(16)	2.144(3)	C(16)−N(3)	1.354(4)
Re(1)−C(3)	1.915(3)	C(1)−O(1)	1.154(4)	C(16)−O(4)	1.372(4)
Re(1)−N(1)	2.165(3)	C(2)−O(2)	1.147(4)		
C(1)−Re(1)−C(3)	90.21(13)		N(3)−C(16)−O(4)	111.0(3)	
N(1)−Re(1)−N(2)	75.77(10)		C(16)−O(4)−C(22)	106.2(2)	
Re(1)−C(16)−O(4)	123.7(2)		C(16)−N(3)−C(17)	106.3(2)	
Re(1)−C(16)−N(3)	124.9(2)				
			2		
Re(1)−C(1)	1.930(4)	Re(1)−N(2)	2.176(3)	C(3)−O(3)	1.147(5)
Re(1)−C(2)	1.969(4)	Re(1)−C(16)	2.151(4)	C(16)−N(3)	1.328(5)
Re(1)−C(3)	1.924(4)	C(1)−O(1)	1.150(5)	C(16)−O(4)	1.352(5)
Re(1)−N(1)	2.186(3)	C(2)−O(2)	1.139(6)		
C(1)−Re(1)−C(3)	89.37(17)		N(3)−C(16)−O(4)	107.1(3)	
N(1)−Re(1)−N(2)	75.83(11)		C(16)−O(4)−C(17)	108.8(3)	
Re(1)−C(16)−O(4)	123.9(3)		C(16)−N(3)−C(22)	111.7(3)	
Re(1)−C(16)−N(3)	129.0(3)				
			3		
Re(1)−C(1)	1.969(4)	Re(1)−N(2)	2.187(3)	C(3)−O(3)	1.146(5)
Re(1)−C(2)	1.922(4)	Re(1)−C(16)	2.146(3)	C(16)−N(3)	1.329(5)
Re(1)−C(3)	1.936(4)	C(1)−O(1)	1.122(5)	C(16)−O(4)	1.375(5)
Re(1)−N(1)	2.168(3)	C(2)−O(2)	1.146(5)		
C(2)−Re(1)−C(3)	89.45(17)		N(3)−C(16)−O(4)	107.8(3)	
N(1)−Re(1)−N(2)	75.77(12)		C(16)−O(4)−C(17)	108.1(3)	
Re(1)−C(16)−O(4)	116.4(2)		C(16)−N(3)−C(22)	109.9(3)	
Re(1)−C(16)−N(3)	135.3(3)				
			5		
Re(1)−C(1)	1.861(19)	Re(1)−N(2)	2.202(15)	Re(1)−C(3)	2.088(3)
Re(1)−C(2)	1.954(18)	C(1)−O(1)	1.20(2)	C(3)−O(3)	1.370(3)
Re(1)−P(1)	2.436(6)	C(2)−O(2)	1.13(2)	C(3)−N(3)	1.336(4)
Re(1)−N(1)	2.155(16)				
C(1)−Re(1)−C(2)	88.1(5)		N(3)−C(3)−O(4)	106.3(2)	
N(1)−Re(1)−N(2)	74.5(5)		C(3)−O(3)−C(4)	108.5(2)	
Re(1)−C(3)−O(3)	122.95(18)		C(3)−N(3)−C(5)	111.8(2)	
Re(1)−C(3)−N(3)	130.5(2)				
			6		
Re(1)−C(1)	1.890(11)	Re(1)−N(2)	2.184(8)	Re(1)−C(3)	2.105(10)
Re(1)−C(2)	1.864(10)	C(1)−O(1)	1.170(13)	C(3)−O(3)	1.366(13)
Re(1)−P(1)	2.419(10)	C(2)−O(2)	1.177(13)	C(3)−N(3)	1.343(12)
Re(1)−N(1)	2.197(9)				
C(1)−Re(1)−C(2)	88.7(5)		N(3)−C(3)−O(3)	107.2(8)	
N(1)−Re(1)−N(2)	75.4(3)		C(3)−O(3)−C(4)	108.8(8)	
Re(1)−C(3)−O(3)	122.2(7)		C(3)−N(3)−C(9)	110.6(9)	
Re(1)−C(3)−N(3)	130.6(8)				
			7		
Re(1)−C(1)	1.935(4)	Re(1)−N(2)	2.183(3)	C(1)−O(1)	1.146(5)
Re(1)−C(2)	1.984(4)	Re(1)−C(4)	2.076(4)	C(2)−O(2)	1.133(5)
Re(1)−C(3)	1.936(4)	C(4)−N(3)	1.150(5)	C(3)−O(3)	1.145(5)
Re(1)−N(1)	2.167(3)				
C(1)−Re(1)−C(3)	90.91(14)		Re(1)−C(4)−N(3)	173.6(3)	
N(1)−Re(1)−N(2)	75.84(11)		C(4)−N(3)−C(17)	167.5(4)	

in the deprotonated N atom compared to the N−H or N−R bond-pair electrons in benzoxazol-2-ylidene ligands. Moreover, an enlarged O−C−N angle (111.0° in **1** vs 107.1° in **2**), which is similar to the deprotonated benzoxazol-2-ylidene ligands observed in other dicarbene complexes,[18c,19b] is also observed upon N-deprotonation. For the isocyanide ligand in the crystal structure of **7**, the slightly bent C−N−C angle (167.5°) is attributed to the π-back-bonding interaction between the rhenium(I) metal and the isocyanide ligand, which is commonly observed in different metal isocyanide complexes.[16,20f,g,23]

UV−Vis Absorption Spectroscopy. Complexes **1**−**7** dissolve in acetonitrile to give pale yellow to orange solutions,

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Table 3. Photophysical Data for the Rhenium(I) Complexes

complex	medium (T/K)	emission λ_{em}[a]/nm ($\tau_o/\mu s$)	ϕ_{em}[b] (%)	absorption λ_{abs}[c]/nm (ε/dm^3 mol^{-1} cm^{-1})
1	MeCN (298) glass[d] (77)	602 (0.27) 520 (14.0)	1.10	261 (34 660), 283 (25 360), 380 (3940)
2	MeCN (298) glass[d] (77)	545 (1.66) 527 (11.4)	10.2	256 (32 590), 274 sh (37 675), 303 sh (17 935), 332 sh (9250), 373 (3535)
3	MeCN (298) glass[d] (77)	546 (1.26) 522 (16.2)	6.72	261 (44 285), 280 sh (33 585), 375 (5235)
4	MeCN (298) glass[d] (77)	620 (0.26) 558 (7.78)	1.01	267 (31 480), 292 (24 175), 318 (19 965), 349 sh (12 755), 420 (4420)
5	MeCN (298) glass[d] (77)	626 (0.13) 567 (5.96)	0.83	267 (34 215), 292 (23 940), 320 (19 550), 3475 sh (13 825), 421 (4820)
6	MeCN (298) glass[d] (77)	617 (0.21) 556 (5.44)	0.76	265 (40 975), 288 (25 195), 311 (18 985), 340 sh (12 100), 400 (5435)
7	MeCN (298) glass[d] (77)	511 (5.59) 459, 490, 525 (304)	14.5	256 (40 545), 268 (42 575), 295 sh (21 685), 306 sh (19 640), 365 (3380)

[a]Excitation >400 nm. [b]Luminescence quantum yield with excitation at 436 nm. [c]In acetonitrile at 298 K. [d]EtOH–MeOH (4:1 v/v).

depending on the position of their MLCT [dπ(Re) → π^*(phen)] absorption in the visible region. The electronic absorption data of these complexes are summarized in Table 3. All these complexes in acetonitrile show very intense intraligand (IL) $\pi \rightarrow \pi^*$ transitions of phenanthroline, carbene (**1**–**6**), and 2-methoxyphenyl isocyanide (**7**) with molar extinction coefficients on the order of 10^4 dm^3 mol^{-1} cm^{-1} in the range 220–350 nm in the UV region (Figure 2). Similar to other related rhenium(I) diimine complexes,[8] they all exhibit a moderately intense MLCT [dπ(Re) → π^*(phen)] absorption shoulder at ca. 365–421 nm with molar extinction coefficients on the order of 10^3 dm^3 mol^{-1} cm^{-1} and tailing to the visible region down to about 500 nm (Figure 2). The observation of the absorption

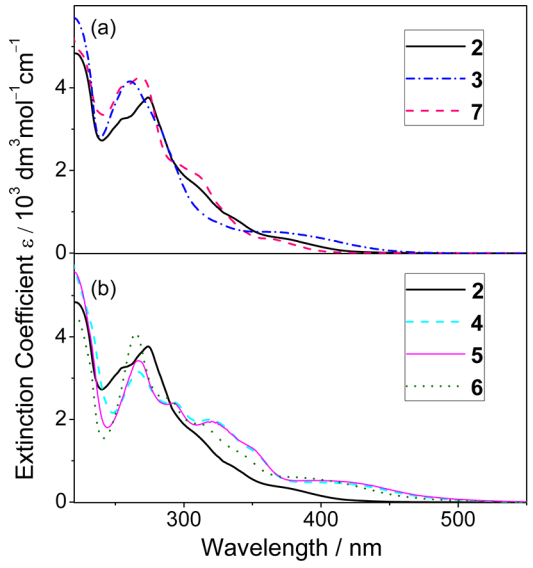

Figure 2. Overlaid UV–vis spectra of (a) **2**, **3**, and **7** and (b) **2**, **4**, **5**, and **6** in acetonitrile at 298 K.

energy in the order **7** (365 nm) > **2** (373 nm) ≈ **3** (375 nm) ≫ **6** (400 nm) > **4** (420 nm) ≈ **5** (421 nm), which is in line with the π-accepting ability of the ancillary ligands, is consistent with the MLCT [dπ(Re) → π^*(phen)] transition. As the dπ(Re) orbital could be better stabilized with a stronger π-accepting ligands, complex **7**, with the strongest π-accepting ancillary ligands, three carbonyl and one isocyanide ligands, shows the highest MLCT [dπ(Re) → π^*(phen)] energy among **1**–**7**. Similarly, significant red-shift of the MLCT absorption could also be observed in **4**–**6** (400–421 nm) compared to that in **2** (373 nm), as a carbonyl ligand in **2** is replaced by weaker π-accepting phosphine ligands. A slightly higher MLCT absorption energy in **6** compared to **4** and **5** is also observed, as $P(OEt)_3$ is a stronger π-accepting ligand compared to PPh_3 and PPh_2Me.[24]

Emission Spectroscopy. All complexes in acetonitrile solution displayed long-lived photoluminescence with λ_{em} in the range 511–626 nm and lifetime (τ) in the range 0.13–5.59 μs (Figure 3, Table 3). These structureless emission bands show a

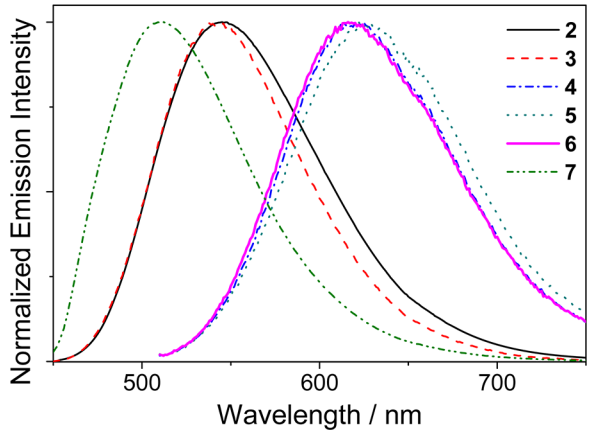

Figure 3. Overlaid normalized emission spectra of complexes **2**–**7** in acetonitrile at 298 K.

significant energy dependence on the electronic properties of the ancillary ligands as reflected by the trends of the λ_{em} in the order **7** (511 nm) ≪ **2** (545 nm) ≈ **3** (546 nm) ≪ **6** (617 nm) < **4** (620 nm) < **5** (626 nm), which is in line with the π-accepting ability of the ancillary ligands and the MLCT absorption (see above). Considerable red-shift of emission energy is observed when the ancillary isocyanide ligand is replaced by a carbene ligand or the carbonyl ligand is replaced by a phosphine ligand, as reflected from the emissions of **7**, **2**, and **6** (Figure 3). Such emission energy trends and the sub-microsecond emission lifetime are suggestive of the ^{3}MLCT [dπ(Re) → π^*(phen)] excited-state origin, probably mixed with some LLCT character.[25]

These complexes also displayed strong photoluminescence in EtOH–MeOH (4:1, v/v) glass at 77 K (Table 3, Figure S2, Supporting Information). With the exception of **7**, the emissions of **1**–**6** in 77 K EtOH–MeOH glassy medium are

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also structureless with a few microsecond emission lifetimes. These emissions show similar emission energy trends to their solution emissions but are all blue-shifted. They are also ascribed to the ^{3}MLLCT excited-state origin. The blue-shifted MLLCT emission of related complexes in 77 K EtOH−MeOH glass relative to the solution emission is commonly observed and were coined as "luminescence rigidochromism".[26] In contrast, **7** in 77 K EtOH−MeOH glassy medium displays a highly structured emission band with vibrational progression spacing of ca. 1380 cm^{-1} and much longer emission lifetime of ca. 304 μs. The significant difference in emission characteristic of **7** in 77 K EtOH−MeOH glass compared to its solution emission as well as those of **1**−**6** and related MLLCT emission of other rhenium(I) diimine complexes in the same medium is suggestive of a different emission origin. In view of the long-lived emission lifetimes and the structured emission bands, the emission of **7** in 77 K glassy medium was ascribed as derived from the triplet ligand-centered (^{3}LC) excited state of the phenanthroline ligand. The change in emissive excited state origin from ^{3}MLLCT at room temperature to ^{3}LC at 77 K glassy medium is probably due to the blue-shift of the ^{3}MLCT state, which becomes higher lying in energy than the ^{3}LC state. Similar observations have also been reported in other related complexes.[27]

Acidity of N−H in the Carbene Ligand. The formation of neutral complex **1** in our initial attempt to prepare carbene complex **2** suggests a high acidity of the NH group in the carbene ligand, which can be readily deprotonated. To study the acidity of the benzoxazol-2-ylidene ligand in different complexes, spectrophotometric titration studies of **2** and **4**−**6** with a non-nucleophilic strong base of ^{n}Bu$_4$NOH were carried out. To avoid UV−vis absorption spectral changes due to alternation of ionic strength during the titration studies, all titrations were performed in 0.1 M ^{n}Bu$_4$NPF$_6$ in acetonitrile in order to maintain a fairly constant ionic strength.

Upon addition of ^{n}Bu$_4$NOH up to a stoichiometric amount of **2** in acetonitrile solution (0.1 M ^{n}Bu$_4$NPF$_6$), a blue-shift of the intense IL $\pi\pi^*$ absorptions and a red-shift of the MLCT [dπ(Re) → π^*(phen)] absorption with well-defined isosbestic points at 271 and 359 nm were observed (Figure 4a). The observation of well-defined isosbestic points together with the identical UV−vis absorption spectrum compared to that of **1** after addition of one molar equivalent of ^{n}Bu$_4$NOH suggests a clean N-deprotonation of the benzoxazol-2-ylidene ligand in **2**. The bathochromic shift of the MLCT absorption of **2** upon deprotonation can be explained by the destabilization of the dπ(Re) orbital due to a significant decrease of the π-accepting ability of the benzoxazol-2-ylidene ligand upon conversion to an anionic carbene ligand. As MLCT energy decreases, the emission of **2** also shows a red-shift and decrease in intensity upon deprotonation (Figure 4b). For analogous complexes **4**−**6** with a phosphine ligand, they also exhibit similar UV−vis and emission spectral changes (Figures S3 and S4, Supporting Information) in the titration with ^{n}Bu$_4$NOH. These changes were also ascribed to the N-deprotonation of the benzoxazol-2-ylidene ligand. To quantify the acidity of the NH proton in the benzoxazol-2-ylidene ligand of these complexes, the acid dissociation constants of the NH proton in **2** and **4**−**6** in acetonitrile−water (9:1, v/v, 0.05 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) have also been determined (Table 4). A significantly lower pK_a for **2** compared to **4**−**6** is noted, suggesting a much more acidic NH proton in the benzoxazol-2-ylidene ligand of **2**. The much stronger acidity of NH protons in **2** can be rationalized by the much stronger electron-withdrawing effect of the *trans*-carbonyl ligand, which can better stabilize the deprotonated anionic carbene ligand, compared to that of the *trans*-phosphine ligands in **4**−**6**. The current deprotonation study shows that the N atom of the benzoxazol-2-ylidene ligand in these complexes can be readily functionalized in the presence of base.

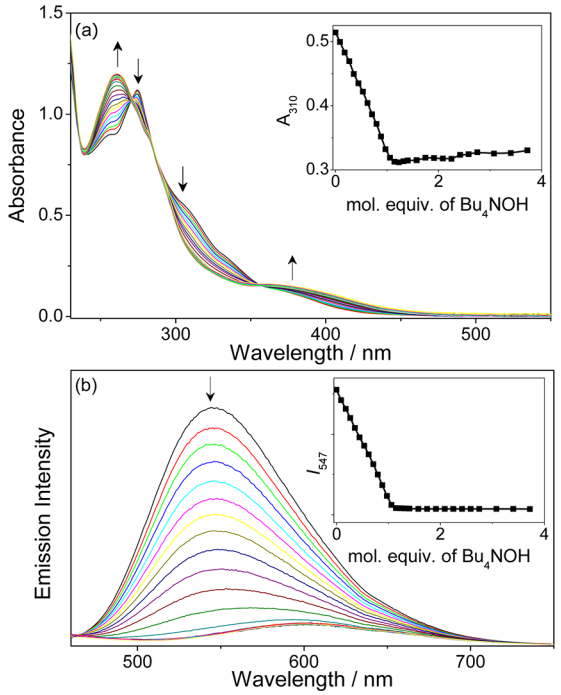

Figure 4. (a) UV−vis absorption and (b) emission spectral changes of **2** (0.0297 mM) in (0.1 M ^{n}Bu$_4$NPF$_6$) acetonitrile solution upon addition of ^{n}Bu$_4$NOH. The insets show the plot of (a) absorbance at 310 nm and (b) emission intensity at 547 nm as a function of mole equivalence of ^{n}Bu$_4$NOH.

Table 4. Summary of pK_a Values of the Complexes 2 and 4−6 in MeCN−H$_2$O (9:1, v/v, 0.05 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) at 298 K

complex	pK_a
2	6.3
4	8.2
5	8.5
6	8.1

Electrochemistry. The electrochemical properties of **1**−**7** in acetonitrile (0.1 M ^{n}Bu$_4$NPF$_6$) were studied by cyclic voltammetry. The electrochemical data are collected in Table 5, and representative cyclic voltammograms are shown in Figure 5. Except for **1**, all other complexes showed one irreversible or quasi-reversible oxidation couple with oxidation potential in the range +1.12 to +1.83 vs SCE, which is ascribed to the typical Re$^{I/II}$ metal-centered oxidation similar to that observed in related tricarbonyl rhenium(I) diimine complexes.[28] The observation of the oxidative potential of the oxidation couple in the order **7** (+1.83 V) ≫ **2** (+1.67 V) ≈ **3** (+1.66 V) ≫ **6** (+1.20 V) > **4** (+1.16 V) > **5** (+1.12 V), which is in line with the π-accepting ability of the ligands and hence the electron richness of the rhenium metal center, is supportive of the Re$^{I/II}$ metal-centered oxidation assignment. For **1**, the second oxidation wave is also assigned to the Re$^{I/II}$ metal-centered oxidation, whereas the additional oxidation wave observed at

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Table 5. Electrochemical Data for 1−7 in Acetonitrile Solution (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) at 298 K[a]

complex	oxidation[b] $E_{1/2}$/V vs SCE (E_{pa}/V vs SCE)	reduction[b] $E_{1/2}$/V vs SCE (E_{pc}/V vs SCE)
1	(+1.10), (+1.69)	−1.43
2	(+1.67)	(−1.30)
3	+1.66	−1.26
4	+1.16	(−1.41)
5	+1.12	(−1.42)
6	+1.20	(−1.41)
7	+1.83	−1.22

[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 peak anodic and peak cathodic potentials, respectively.

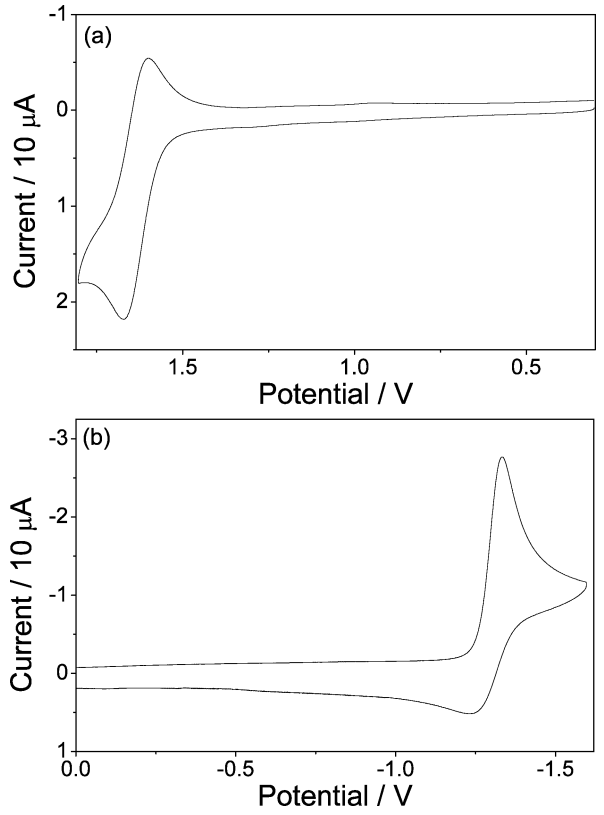

Figure 5. Cyclic voltammograms of (a) the oxidative scan and (b) reductive scan of **3** in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$).

ca. +1.10 V was assigned to the oxidation of the negatively charged N atom on the deprotonated benzoxazol-2-ylidene ligand. In the reductive scan, the first irreversible or quasi-reversible reduction couple of **1**−**7** was determined. The relatively low sensitivity to the change of the ancillary ligands and the close similarity of the potentials for phenanthroline-based reduction observed in related rhenium(I) phenanthroline complexes[20f,g,25b,28] are suggestive of the phenanthroline ligand-centered reduction assignment.

CONCLUSION

A series of luminescent rhenium(I) phenanthroline complexes with benzoxazol-2-ylidene ligands have been synthesized and characterized. A new synthetic methodology for the preparation of dicarbonyl rhenium phenanthroline synthetic precursors was developed. Except **4**, all carbene complexes and two of their precursor complexes have been structurally characterized by X-ray crystallography. The photophysical study on these complexes revealed that all these complexes display green to orange-red MLLCT phosphorescence. In short, the conversion of isocyano rhenium(I) phenanthroline complexes into luminescent carbene-containing rhenium(I) phenanthroline complexes can be achieved. The development of other luminescent rhenium(I) carbene complexes from our previously reported isocyano rhenium(I) diimine complexes and the study of their applications in photocatalysis are currently in progress.

ASSOCIATED CONTENT

Supporting Information

Tables, ORTEP drawings, CIF files, and experimental details for the X-ray crystal structures of *cis,trans*-[Re(CO)$_2$(phen)(PPh$_3$)(MeCN)](CF$_3$SO$_3$), *cis,trans*-[Re(CO)$_2$(phen)(PPh$_3$Me)(MeCN)](CF$_3$SO$_3$), **1**−**3**, and **5**−**7**, emission spectra of **2**−**7** in EtOH−MeOH (4:1, v/v) glassy medium at 77 K, UV−vis and emission spectral changes of **4**−**6** upon addition of ^{n}Bu$_4$NOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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