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Synthesis, Characterization, and Photophysical and Emission Solvatochromic Study of Rhenium(I) Tetra(isocyano) Diimine Complexes

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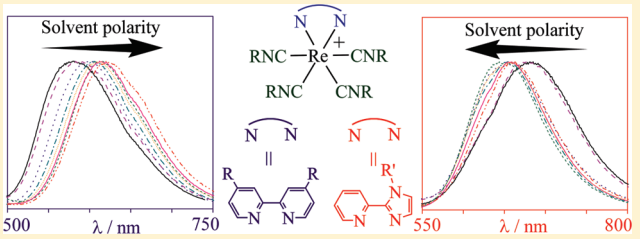
Supporting Information

ABSTRACT: A new series of rhenium(I) tetra(isocyano) diimine complexes ($[Re(CNR)_4(N{-}N)]^+$, where R = 4-IC_6H_4, 4-BrC_6H_4, 4-Br-2,6-$Me_2C_6H_2$, 2,4,6-$Cl_3C_6H_2$, 2,4,6-$Br_3C_6H_2$, 2,4-Cl_2-6-$MeOC_6H_2$ and N−N = bpy, $(MeO)_2$bpy, $^tBu_2$bpy, phen, 1-methyl-2-(2′-pyridyl)imidazole) with various isocyanide and diimine ligands of diverse electronic and steric natures has been synthesized and characterized. The X-ray crystal structures of four of the target complexes were also determined. These complexes were found to show orange to red MLCT ($d\pi(Re) \rightarrow \pi^*(N{-}N)$) phosphorescence. Given the submicrosecond solution emission lifetime, nanosecond transient absorption spectroscopic studies have been performed. The emission solvatochromic behavior and the electrochemical properties of these complexes and their structural correlation have also been reported.



INTRODUCTION

Isocyanides (CNR) are interesting ligands that are capable of coordinating to many different metal centers to give stable organometallic complexes, as they possess excellent π-accepting and σ-donating ability.[1] Since their coordination abilities are similar to those of the carbonyl ligand, the isocyanide analogues of many of the metal carbonyl complexes can be prepared.[1a] However, the synthetic routes for metal carbonyl and isocyanide complexes are generally different.[1a] One of the advantages of using isocyanide ligands over the carbonyl ligand in the design of metal complexes for various applications is that the steric and electronic properties of metal isocyanide complexes can be effectively tuned by changing the substituent on the nitrogen atom. Such flexibility has been demonstrated to be useful and beneficial in the design and study of transition-metal isocyanide complexes for catalytic applications.[2]

Rhenium(I) tricarbonyl diimine complexes have been demonstrated to show rich photophysical and photochemical behavior[3] and are useful in a wide variety of applications.[4] On the basis of the similarity of the carbonyl and the isocyanide ligands in the metal−ligand interaction and taking advantage of the tunability of the isocyanide ligands, we have recently communicated the synthesis and the photophysical studies of a new class of readily tunable rhenium (I) tetra(isocyano) diimine complexes, $[Re(CNR)_4(N{-}N)]^+$.[5] The preliminary study reported in our communication showed that the emissions of some of the complexes are highly sensitive to the change of the solvent environment.[5] To elucidate the emissive excited state and provide insights into the structure relationship of the excited-state properties as well as the emission solvatochromism, herein we report the detailed syntheses, characterization, and photophysical and electrochemical properties of a new series of rhenium(I) tetra(isocyano) diimine complexes with various isocyanide and diimine ligands of diverse electronic and steric natures. Given the submicrosecond solution emission lifetime, nanosecond transient absorption spectroscopic studies have also been carried out.

EXPERIMENTAL SECTION

Materials and Reagents. Ammonium hexafluorophosphate, potassium iodide, and hydrazine hydrate were obtained from Aldrich Chemical Co. Rhenium powder (325 mesh) and thallium triflate (TlOTf) were obtained from Strem Chemicals, Inc. Hydrogen iodide was obtained from International Laboratory Chemical Co. The diimine ligands 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), 4,4′-di-*tert*-butyl-2,2′-bipyridine ($^tBu_2$bpy), and 4,4′-dimethoxy-2,2′-bipyridine ($(MeO)_2$bpy) and substituted anilines 4-iodoaniline, 4-bromoaniline, 4-chloroaniline, 4-fluoroaniline, 2,6-dimethylaniline, 2,4,6-trichloroaniline, 2,4,6-tribromoaniline, 2,4-dichloro-6-methoxyaniline, and 4-bromo-2,6-dimethylaniline were purchased from Aldrich Chemical Co. and used as received. 1-Methyl-2-(2′-pyridyl)imidazole (pimMe) and 1-phenyl-2-(2′-pyridyl)imidazole (pimPh) were prepared according to the literature procedure.[6] The substituted phenyl isocyanide ligands 4-chlorophenyl isocyanide, 2,4,6-trichlorophenyl isocyanide, 4-iodophenyl isocyanide, 2,4-dichloro-6-methoxyphenyl isocyanide, 4-fluorophenyl isocyanide, 4-bromo-2,6-dimethylphenyl isocyanide, 4-bromophenyl isocyanide, 2,4,6-tribromophenyl isocyanide, and 2,6-dimethylphenyl isocyanide were all prepared from the dehydration of the corresponding substituted formamides, which can be readily obtained

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from the reactions between the substituted anilines with formic acid or formic acetic anhydride, using the synthetic methodology developed by Ugi and co-workers.[7] Precursor complexes such as $[Re(CNC_6H_4F\text{-}4)_5I]$, $[Re(CNC_6H_4Cl\text{-}4)_5I]$, and $[Re(CNC_6H_3Me_2\text{-}2,6)_5I]$, were prepared by our previously communicated procedure.[6] All solvents were of analytical reagent grade and used without further purification.

$[Re(CNC_6H_4Br\text{-}4)_5I]$. To a methanolic solution of $K_2[ReI_6]$ (500 mg, 0.49 mmol) was added 4-bromophenyl isocyanide (561 mg, 4.60 mmol). The resulting mixture was stirred overnight. Thereafter, hydrazine hydrate (2.5 mL) was added in a dropwise manner. After the mixture was stirred at room temperature for 2 h, the precipitate was filtered by suction filtration and washed with diethyl ether. Yield: 379 mg, 0.309 mmol; 63%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.05 (d, 2H, J = 7.4 Hz, phenyl H's), 7.27 (d, 8H, J = 7.4 Hz, phenyl H's), 7.41 (d, 2H, J = 7.4 Hz, phenyl H's), 7.50 (d, 8H, J = 7.4 Hz, phenyl H's). ESI-MS: m/z 1228 $\{M\}^+$, 1045 $\{M - CNC_6H_4Br\}^+$. IR (KBr disk, ν/cm^{-1}): 2001, 2063 ν(C≡N). Anal. Calcd (found) for $[Re(CNC_6H_4Br\text{-}4)_5I]$: C 34.37 (34.60); H, 1.65 (1.71); N, 5.73 (5.68).

$[Re(CNC_6H_4I\text{-}4)_5I]$. This complex was synthesized according to a procedure similar to that of $[Re(CNC_6H_4Br\text{-}4)_5I]$, except 4-iodophenyl isocyanide was used in place of 4-bromophenyl isocyanide. Yield: 286 mg, 0.196 mmol; 40%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 6.92 (d, 2H, J = 7.4 Hz, phenyl H's), 7.12 (d, 8H, J = 7.4 Hz, phenyl H's), 7.60 (d, 2H, J = 7.4 Hz, phenyl H's), 7.70 (d, 8H, J = 7.4 Hz, phenyl H's). ESI-MS: m/z 1458 $\{M\}^+$, 1229 $\{M - CNC_6H_4I\}^+$. IR (KBr disk, ν/cm^{-1}): 1993, 2059 ν(C≡N). Anal. Calcd (found) for $[Re(CNC_6H_4I\text{-}4)_5I]$: C, 28.83 (28.75); H, 1.38 (1.18); N, 4.80 (4.65).

$[Re(CNC_6H_2Br_3\text{-}2,4,6)_5I]$. This complex was synthesized according to a procedure similar to that of $[Re(CNC_6H_4Br\text{-}4)_5I]$, except 2,4,6-tribromophenyl isocyanide was used in place of 4-bromophenyl isocyanide. Yield: 453 mg, 0.225 mmol; 46%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.62 (s, 2H, phenyl H's), 7.72 (s, 8H, phenyl H's). ESI-MS: m/z 2013 $\{M\}^+$, 1673 $\{M - CNC_6H_2Br_3\text{-}2,4,6\}^+$. IR (KBr disk, ν/cm^{-1}): 1896, 2027 ν (C≡N). Anal. Calcd (found) for $[Re(CNC_6H_2Br_3\text{-}2,4,6)_5I]$: C, 20.86 (20.89); H, 0.5 (0.77); N, 3.48 (3.46).

$[Re(CNC_6H_2Cl_3\text{-}2,4,6)_5I]$. This complex was synthesized according to a procedure similar to that of $[Re(CNC_6H_4Br\text{-}4)_5I]$, except 2,4,6-trichlorophenyl isocyanide was used in place of 4-bromophenyl isocyanide. Yield: 458 mg, 0.340 mmol; 70%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.28 (s, 2H, phenyl H's), 7.38 (s, 8H, phenyl H's). ESI-MS: m/z 1345 $\{M\}^+$, 1139 $\{M - CNC_6H_2Cl_3\text{-}2,4,6\}^+$. IR (KBr disk, ν/cm^{-1}): 1883, 2037 ν(C≡N). Anal. Calcd (found) for $[Re(CNC_6H_2Cl_3\text{-}2,4,6)_5I]$: C, 31.25 (31.31); H, 0.75 (0.82); N, 5.21 (5.23).

$[Re(CNC_6H_2Cl_2\text{-}2,4\text{-}OMe\text{-}6)_5I]$. This complex was synthesized according to a procedure similar to that of $[Re(CNC_6H_4Br\text{-}4)_5I]$, except 2,4-dichloro-6-methoxyphenyl isocyanide was used in place of 4-bromophenyl isocyanide. Yield: 246 mg, 0.186 mmol; 38%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.83−3.92 (m, 15H, OMe), 6.68−6.91 (m, 2H, phenyl H's), 7.34−7.40 (m, 8H, phenyl H's). ESI-MS: m/z 1323 $\{M\}^+$, 1121 $\{M - CNC_6H_2Cl_2\text{-}2,4\text{-}OMe\text{-}6\}^+$. IR (KBr disk, ν/cm^{-1}); 1891, 1946, 2034 ν(C≡N). Anal. Calcd (found) for $[Re(CNC_6H_2Cl_2\text{-}2,4\text{-}OMe\text{-}6)_5I]$: C, 36.31 (36.28); H, 1.90 (2.01); N, 5.29 (5.38).

$[Re(CNC_6H_2Br\text{-}4\text{-}Me_2\text{-}2,6)_5I]$. This complex was synthesized according to a procedure similar to that of $[Re(CNC_6H_4Br\text{-}4)_5I]$, except 4-bromo-2,6-dimethylphenyl isocyanide was used in place of 4-bromophenyl isocyanide. Yield: 311 mg, 0.27 mmol; 55%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.46 (s, 6H, CH_3), 2.54 (s, 24H, CH_3), 7.15 (s, 2H, phenyl H's), 7.21 (s, 8H, phenyl H's), 7.34−7.40 (m, 8H, phenyl H's). ESI-MS: m/z 1153 $\{M\}^+$, 943 $\{M - CNC_6H_2Br\text{-}4\text{-}Me\text{-}2,6\}^+$. IR (KBr disk, ν/cm^{-1}): 2037, 2062 ν(C≡N). Anal. Calcd (found) for $[Re(CNC_6H_2Br\text{-}4\text{-}Me_2\text{-}2,6)_5I]$: C, 39.64 (39.66); H, 2.96 (3.10); N, 5.14 (5.22).

$[Re(CNC_6H_4I\text{-}4)_4(phen)]PF_6$ (1). The reaction was performed under anhydrous conditions and strictly inert atmosphere of argon using standard Schlenk techniques. $[Re(CNC_6H_4I\text{-}4)_5I]$ (146 mg, 0.1 mmol), phen (40 mg, 0.2 mmol, 2 mol equiv), and TlOTf (53 mg, 0.15 mmol, 1.5 mol equiv.) were mixed in 1,4-dioxane and heated to reflux for 2 days. The resulting suspension was filtered to remove the precipitated TlI. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane/acetone (8/2 v/v) as eluent. The residue was then redissolved in methanol (2 mL). A subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave the target complex as a PF_6^- salt. An analytically pure complex of **1** as a crystalline solid was obtained by the slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of the complex. Yield: 97 mg, 0.068 mmol; 68%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.79 (d, 4H, J = 8.8 Hz, phenyl H's), 7.12 (d, 4H, J = 8.8 Hz, phenyl H's), 7.58 (d, 4H, J = 8.8 Hz, phenyl H's), 7.74 (d, 4H, J = 8.8 Hz, phenyl H's), 8.05 (dd, 2H, J = 8.2, 5.1 Hz, 3,8-phen H's), 8.19 (s, 2H, 5,6-phen H's), 8.70 (dd, 2H, J = 8.2, 1.3 Hz, 4,7-phen H's), 9.60 (dd, 2H, J = 5.1, 1.3 Hz, 2,9-phen H's). ESI-MS: m/z 1283 $\{M - PF_6\}^+$. IR (KBr disk, ν/cm^{-1}): 842 ν(P−F); 1880, 1986, 2056, 2133 ν(C≡N). Anal. Calcd (found) for **1**: C, 33.66 (33.69); H, 1.69 (1.89); N, 5.89 (5.77).

$[Re(CNC_6H_2Br\text{-}4\text{-}Me_2\text{-}2,6)_4(phen)]PF_6$ (2). This complex was synthesized according to a procedure similar to that of **1**, except $[Re(CNC_6H_2Br\text{-}4\text{-}Me_2\text{-}2,6)_5I]$ (145 mg, 0.1 mmol) was used in place of $[Re(CNC_6H_4I\text{-}4)_5I]$ and dichloromethane/acetone (7/3 v/v) was used as eluent in the column chromatography. Yield: 66 mg, 0.049 mmol; 49%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.83 (s, 12H, methyl H's), 2.47 (s, 12H, methyl H's), 7.09 (s, 4H, phenyl H's), 7.52 (s, 4H, phenyl H's), 7.99 (dd, 2H, J = 8.2, 5.1 Hz, 3,8-phen H's), 8.22 (s, 2H, 5,6-phen H's), 8.72 (dd, 2H, J = 8.2, 1.3 Hz, 4,7-phen H's), 9.59 (dd, 2H, J = 5.1, 1.3 Hz, 2,9-phen H's). ESI-MS: m/z 1207 $\{M - PF_6\}^+$. IR (KBr disk, ν/cm^{-1}): 834 ν(P−F); 1920, 1986, 2019, 2111 ν(C≡N). Anal. Calcd (found) for $\mathbf{2}\cdot{}^1/_2CH_2Cl_2$: C, 41.78 (42.03); H, 2.96 (3.03); N, 6.03 (6.15).

$[Re(CNC_6H_2Br_3\text{-}2,4,6)_4(phen)]PF_6$ (3). This complex was synthesized according to a procedure similar to that of **1**, except $[Re(CNC_6H_2Br_3\text{-}2,4,6)_5I]$ (200 mg, 0.1 mmol) was used in place of $[Re(CNC_6H_4I\text{-}4)_5I]$ and dichloromethane/acetone (1/1 v/v) was used as eluent in the column chromatography. Yield: 105 mg, 0.056 mmol; 56%. ^{1}H NMR (400 MHz, DMSO, 298 K): δ 7.92 (s, 4H, phenyl H's), 8.07 (s, 4H, phenyl H's), 8.19 (dd, 2H, J = 8.2, 5.0 Hz, 3,8-phen H's), 8.35 (s, 2H, 5,6-phen H's), 8.96 (dd, 2H, J = 8.2, 1.3 Hz, 4,7-phen H's), 9.75 (d, 2H, J = 5.0 Hz, 2,9-phen H's). ESI-MS: m/z 1726 $\{M - PF_6\}^+$. IR (KBr disk, ν/cm^{-1}): 842 ν(P−F); 1876, 1953, 2026, 2136 ν(C≡N). Anal. Calcd (found) for **3**: C, 25.68 (25.62); H, 0.86 (1.05); N, 4.49 (4.58).

$[Re(CNC_6H_2Cl_3\text{-}2,4,6)_4(phen)]PF_6$ (4). This complex was synthesized according to a procedure similar to that of **1**, except $[Re(CNC_6H_2Cl_3\text{-}2,4,6)_5I]$ (135 mg, 0.1 mmol) was used in place of $[Re(CNC_6H_4I\text{-}4)_5I]$ and dichloromethane/acetone (1/1 v/v) was used as eluent in the column chromatography. Yield: 82 mg, 0.061 mmol; 61%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.25 (s, 4H, phenyl H's), 7.45 (s, 4H, phenyl H's), 8.03 (dd, 2H, J = 8.2, 5.1 Hz, 3,8-phen H's), 8.26 (s, 2H, 5,6-phen H's), 8.82 (dd, 2H, J = 8.2, 1.3 Hz, 4,7-phen H's), 9.63 (dd, 2H, J = 5.1, 1.3 Hz, 2,9-phen H's). ESI-MS: m/z 1192 $\{M - PF_6\}^+$. IR (KBr disk, ν/cm^{-1}): 853 ν(P−F); 1909, 1957, 2037, 2133 ν(C≡N). Anal. Calcd (found) for **4**: C, 35.93 (36.22); H, 1.21 (1.50); N, 6.28 (6.29).

$[Re(CNC_6H_2Cl_2\text{-}2,4\text{-}OMe\text{-}6)_4(phen)]PF_6$ (5). This complex was synthesized according to a procedure similar to that of **1**, except $[Re(CNC_6H_2Cl_2\text{-}2,4\text{-}OMe\text{-}6)_5I]$ (132 mg, 0.1 mmol) was used in place of $[Re(CNC_6H_4I\text{-}4)_5I]$ and dichloromethane/acetone (7/3 v/v) was used as eluent in the column chromatography. Yield: 56 mg, 0.042 mmol; 42%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.57 (m, 12H, OMe), 7.24 (s, 4H, phenyl H's), 7.43 (s, 4H, phenyl H's), 8.02 (dd, 2H, J = 8.2, 5.1 Hz, 3,8-phen H's), 8.25 (s, 2H, 5,6-phen H's), 8.81 (dd, 2H, J = 8.2, 1.3 Hz, 4,7-phen H's), 9.67 (dd, 2H, J = 5.1, 1.3 Hz, 2,9-phen H's). ESI-MS: m/z 1174 $\{M - PF_6\}^+$. IR (KBr disk, ν/cm^{-1}): 849 ν(P−F); 1964, 1993, 2045, 2136 ν(C≡N). Anal. Calcd (found) for **5**: C, 40.05 (40.33); H, 2.14 (1.95); N, 6.37 (6.26).

[Re(CNC$_6$H$_4$I-4)$_4$(bpy)]PF$_6$ (6). This complex was synthesized according to a procedure similar to that of **1**, except bpy (31 mg, 0.2 mmol) was used in place of phen and dichloromethane/acetone (7/3 v/v) was used as eluent in the column chromatography. Yield: 80 mg, 0.057 mmol; 57%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 6.86 (d, 4H, J = 8.6 Hz, phenyl H's), 7.04 (d, 4H, J = 8.6 Hz, phenyl H's), 7.57 (ddd, 2H, J = 8.2, 5.1, 0.9 Hz, 4,4-bipyridyl H's), 7.64 (d, 4H, J = 8.6 Hz, phenyl H's), 7.72 (d, 4H, J = 8.6 Hz, phenyl H's), 8.16 (td, 2H, J = 5.1, 1.5 Hz, 5,5′-bipyridyl H's), 8.59 (d, 2H, J = 8.2 Hz, 3,3′-bipyridyl H's), 9.18 (dd, 2H, J = 5.1, 0.9 Hz, 6,6′-bipyridyl H's). ESI-MS: m/z 1258 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 834 ν(P−F); 1960, 1990, 2052, 2129 ν(C≡N). Anal. Calcd (found) for **6**: C, 32.52 (32.28); H, 1.72 (1.80); N, 5.99 (5.97).

[Re(CNC$_6$H$_4$Br-4)$_4$(bpy)]PF$_6$ (7). This complex was synthesized according to a procedure similar to that of **1**, except bpy (31 mg, 0.2 mmol) and [Re(CNC$_6$H$_4$Br-4)$_5$I] (136 mg, 0.1 mmol) were used in place of phen and [Re(CNC$_6$H$_4$I-4)$_5$I], respectively. Yield: 71 mg, 0.058 mmol; 58%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.02 (d, 4H, J = 8.7 Hz, phenyl H's), 7.19 (d, 4H, J = 8.7 Hz, phenyl H's), 7.45 (d, 4H, J = 8.7 Hz, phenyl H's), 7.54 (d, 4H, J = 8.7 Hz, phenyl H's), 7.59 (ddd, 2H, J = 8.2, 0.9 Hz, 4, 4′-bipyridyl H's), 8.17 (td, 2H, J = 5.7, 1.5 Hz, 5,5′-bipyridyl H's), 8.59 (d, 2H, J = 8.2 Hz, 3,3′-bipyridyl H's), 9.21 (dd, 2H, J = 5.7, 0.9 Hz, 6,6′-bipyridyl H's). ESI-MS: m/z 1074 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 842 ν(P−F); 1949, 2004, 2056, 2136 ν(C≡N). Anal. Calcd (found) for **7**: C, 37.55 (37.48); H, 1.99 (2.07); N, 6.91 (6.88).

[Re(CNC$_6$H$_2$Br-4-Me$_2$-2,6)$_4$((MeO)$_2$bpy)]PF$_6$ (8). This complex was synthesized according to a procedure similar to that of **1**, except [Re(CNC$_6$H$_2$Br-4-Me$_2$-2,6)$_5$I] (145 mg, 0.1 mmol) and (MeO)$_2$bpy (43 mg, 0.2 mmol) were used in place of [Re(CNC$_6$H$_4$I-4)$_5$I] and phen, respectively. Yield: 78 mg, 0.056 mmol; 56%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 2.04 (s, 12H, methyl H's), 2.41 (s, 12H, methyl H's), 4.18 (s, 6H, OMe), 7.00 (dd, 2H, J = 2.6, 6.4 Hz, 5,5′-bipyridyl H's), 7.18 (s, 4H, phenyl H's), 7.30 (s, 4H, phenyl H's), 8.02 (d, 2H, J = 2.6 Hz, 3,3′-bipyridyl H's), 8.90 (d, 2H, J = 6.4 Hz, 6,6′-bipyridyl H's). ESI-MS: m/z 1242 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 845 ν(P−F); 1916, 1953, 2030, 2125 ν(C≡N). Anal. Calcd (found) for **8**·$^1/_2$Et$_2$O: C, 42.15 (42.05); H, 3.47 (3.40); N, 5.90 (5.88).

[Re(CNC$_6$H$_2$Cl$_3$-2,4,6)$_4$((MeO)$_2$bpy)]PF$_6$ (9). This complex was synthesized according to a procedure similar to that of **1**, except [Re(CNC$_6$H$_2$Cl$_3$-2,4,6)$_5$I] (134 mg, 0.1 mmol) and (MeO)$_2$bpy (43 mg, 0.2 mmol) were used in place of [Re(CNC$_6$H$_4$I-4)$_5$I] and phen, respectively. Yield: 87 mg, 0.063 mmol; 63%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 4.20 (s, 6H, OMe), 7.00 (dd, 2H, J = 2.6, 6.4 Hz, 5,5′-bipyridyl H's), 7.32 (s, 4H, phenyl H's), 7.39 (s, 4H, phenyl H's), 8.05 (d, 2H, J = 2.6 Hz, 3,3′-bipyridyl H's), 8.94 (d, 2H, J = 6.4 Hz, 6,6′-bipyridyl H's). ESI-MS: m/z 1228{M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 845 ν(P−F); 1843, 1924, 2030, 2136 ν(C≡N). Anal. Calcd (found) for **9**·Et$_2$O: C, 36.51 (36.59); H, 2.09 (2.19); N, 5.81 (5.68).

Re(CNC$_6$H$_4$Cl-4)$_4$(pimPh)]PF$_6$ (10). This complex was synthesized according to a procedure similar to that of **1**, except [Re(CNC$_6$H$_4$Cl-4)$_5$I] (100 mg, 0.1 mmol) and pimPh (45 mg, 0.2 mmol) were used in place of [Re(CNC$_6$H$_4$I-4)$_5$I] and phen, respectively. Yield: 35 mg, 0.032 mmol; 32%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.01 (d, J = 8.3 Hz, 1H, 4-imidazoyl H's), 7.16 (d, J = 8.7 Hz, 4H, phenyl H's), 7.22−7.44 (m, 15H, phenyl H's, 5-imidazoyl H's, 5-pyridyl H's), 7.56−7.70 (m, 5H, phenyl H's, 4-pyridyl H's), 8.42 (td, 1H, J = 1.3, 7.3 Hz, 3-pyridyl H's), 9.21(d, 1H, J = 5.3 Hz, 6-pyridyl H's). ESI-MS: m/z 958 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 846 ν(P−F); 1860, 2004, 2058, 2136 ν(C≡N). Anal. Calcd (found) for **10**: C, 45.75 (45.89); H, 2.47 (2.29); N, 8.89 (8.68).

[Re(CNC$_6$H$_4$I-4)$_4$(pimMe)]PF$_6$ (11). This complex was synthesized according to a procedure similar to that of **1**, except pimMe (32 mg, 0.2 mmol) was used in place of phen and dichloromethane/acetone (1/1 v/v) was used as eluent in the column chromatography. Yield: 71 mg, 0.050 mmol; 50%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 4.31 (s, 3H, N-methyl H's), 6.87 (d, 4H, J = 8.7 Hz, phenyl H's), 6.99 (d, 4H, J = 8.7 Hz, phenyl H's), 7.39−7.69 (m, 11H, phenyl H's, 4-imidazoyl H's, 5-imidazoyl H's, and 5′-pyridyl H's), 8.24 (t, 1H, J = 8.2 Hz, 4-pyridyl H's), 8.32 (d, 1H, J = 8.2 Hz, 3-pyridyl H's), 9.17 (d, 1H, J = 5.5 Hz, 6-pyridyl H's). ESI-MS: m/z 1258 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 842 ν(P−F); 1909, 1990, 2048, 2129 ν(C≡N). Anal. Calcd (found) for **11**: C, 31.60 (31.73); H, 1.79 (1.84); N, 6.97 (6.94).

Re(CNC$_6$H$_4$Cl-4)$_4$(pimMe)]PF$_6$ (12). This complex was synthesized according to a procedure similar to that of **1**, except [Re(CNC$_6$H$_4$Cl-4)$_5$I] (100 mg, 0.1 mmol) and pimMe (32 mg, 0.2 mmol) were used in place of [Re(CNC$_6$H$_4$I-4)$_5$I] and phen, respectively. Yield: 50 mg, 0.048 mmol; 48%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 4.29 (s, 3H, N-methyl H's), 7.11 (d, J = 8.6 Hz, 4H, phenyl H's), 7.20−7.41 (m, 15H, phenyl H's, 5-imidazoyl H's, 4-imidazoyl H's, 5-pyridyl H's), 8.24 (t, 1H, J = 6.5 Hz, 4-pyridyl H's), 8.42 (d, 1H, J = 8.2 Hz, 3-pyridyl H's), 9.16 (d, 1H, J = 4.8 Hz, 6-pyridyl H's). ESI-MS: m/z 892 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 845 ν(P−F); 1850, 2001, 2056, 2125 ν(C≡N). Anal. Calcd (found) for **12**: C, 42.70 (42.85); H, 2.42 (2.57); N, 9.42 (9.61).

Re(CNC$_6$H$_2$Br-4-Me$_2$-2,6)$_4$(pimMe)]PF$_6$ (13). This complex was synthesized according to a procedure similar to that of **1**, except [Re(CNC$_6$H$_2$Br-4-Me$_2$-2,6)$_5$I] (145 mg, 0.1 mmol) and pimMe (32 mg, 0.2 mmol) were used in place of [Re(CNC$_6$H$_4$I-4)$_5$I] and phen, respectively. Yield: 87 mg, 0.06 mmol; 60%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 2.06 (s, 12H, methyl H's), 2.42 (s, 12H, methyl H's), 4.31 (s, 3H, N-methyl H's), 7.17 (s, 4H, phenyl H's), 7.25 (s, 4H, phenyl H's), 7.30 (s, 1H, 5-imidazoyl H's), 7.39−7.42 (m, 2H, 4-imidazoyl H's, 5-pyridyl H's), 8.24 (t, 1H, J = 8.0 Hz, 4-pyridyl H's), 8.42 (d, 1H, J = 7.8 Hz, 3-pyridyl H's), 9.16 (d, 1H, J = 5.4 Hz, 6-pyridyl H's). ESI-MS: m/z 1182 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 842 ν(P−F); 1916, 1946, 2026, 2118 ν(C≡N). Anal. Calcd (found) for **13**·$^1/_2$CH$_3$COCH$_3$: C, 41.08 (41.21); H, 3.26 (3.34); N, 7.21 (7.08).

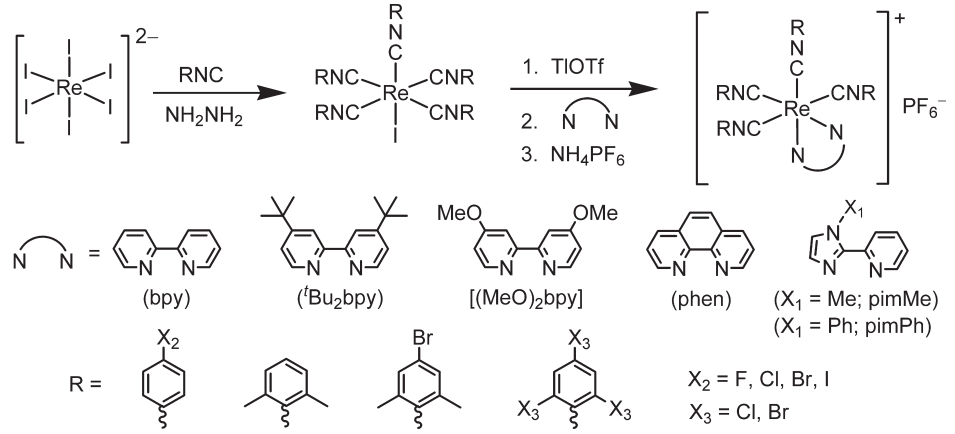
[Re(CNC$_6$H$_4$Cl-4)$_4$((MeO)$_2$bpy)]PF$_6$ (14). The complex has previously been communicated.[6] Yield: 55%. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 4.17 (s, 6H, OMe), 7.06−7.37 (m, 18H, phenyl H's and 5, 5′-bipyridyl H's), 7.95 (d, 2H, J = 2.4 Hz, 3,3′-bipyridyl H's), 8.90 (d, 2H, J = 6.6 Hz, 6,6′-bipyridyl H's). ESI-MS: m/z 953{M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 846 ν(P−F); 1936, 2005, 2058, 2134 ν(N≡C). Anal. Calcd (found) for **14**·$^1/_2$Et$_2$O: C, 44.46 (44.43); H, 2.93 (2.94); N, 7.41 (7.63).

[Re(CNC$_6$H$_4$Cl-4)$_4$(^{t}Bu$_2$bpy)]PF$_6$ (15). The complex has previously been communicated.[6] Yield: 57%. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 1.57 (s, 18H, ^{t}Bu), 7.09−7.14 (m, 4H, phenyl H's), 7.17−7.45 (m, 12H, phenyl H's), 7.65 (dd, 2H, J = 5.9, 1.5 Hz, 5,5′-bipyridyl H's), 8.38 (d, 2H, J = 1.5 Hz, 3,3′-bipyridyl H's), 9.16 (d, 2H, J = 5.9 Hz, 6, 6′-bipyridyl H's). ESI-MS: m/z 1003 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 846 ν(P−F); 1860, 2007, 2061, 2135 ν(C≡N). Anal. Calcd (found) for **15**: C, 48.05 (48.18); H, 3.51 (3.45); N, 7.31 (7.52).

[Re(CNC$_6$H$_4$Cl-4)$_4$(bpy)]PF$_6$ (16). The complex has previously been communicated.[6] Yield: 60%. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 7.07 (m, 4H, phenyl H's), 7.31 (m, 12H, phenyl H's), 7.57 (ddd, 2H, J = 8.2, 5.1, 0.9 Hz, 4,4′-bipyridyl H's), 8.15 (td, 2H, J = 5.1, 1.5 Hz, 5,5′-bipyridyl H's), 8.59 (dd, 2H, J = 8.2, 1.5 Hz, 3,3′-bipyridyl H's), 9.21 (dd, 2H, J = 5.1, 0.9 Hz, 6,6′-bipyridyl H's). ESI-MS: m/z 891 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 846 ν(P−F); 1926, 2003, 2055, 2126 ν(C≡N). Anal. Calcd (found) for **16**: C, 43.99 (44.03); H, 2.33 (2.56); N, 8.10 (8.14).

[Re(CNC$_6$H$_4$F-4)$_4$(bpy)]PF$_6$ (17). The complex has previously been communicated.[6] Yield: 55%. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 6.96−7.34 (m, 16H, phenyl H's), 7.56 (ddd, 2H, J = 8.4, 5.2, 0.9 Hz, 4,4′-bipyridyl H's), 8.16 (td, 2H, J = 5.4, 1.5 Hz, 5,5′-bipyridyl H's), 8.62 (dd, 2H, J = 8.4, 1.5 Hz, 3,3′-bipyridyl H's), 9.22 (dd, 2H, J = 5.6, 0.9 Hz, 6, 6′-bipyridyl H's). ESI-MS: m/z 827 {M − PF$_6$}$^+$. IR (KBr disk, ν/cm^{-1}): 848 ν(P−F); 1941, 2033, 2062, 2137 ν(C≡N). Anal. Calcd (found) for **17**: C, 46.96 (47.36); H, 2.49 (2.55); N, 8.65 (8.91).

Scheme 1. Synthetic Routes to Rhenium(I) Tetra(isocyano) Diimine Complexes



1 R = C_6H_4I-4; N-N = phen
2 R = C_6H_2Br-4-Me_2-2,6; N-N = phen
3 R = $C_6H_2Br_3$-2,4,6; N-N = phen
4 R = $C_6H_2Cl_3$-2,4,6; N-N = phen
5 R = $C_6H_2Cl_2$-2,4-OMe-6; N-N = phen
6 R = C_6H_4I-4; N-N = bpy
7 R = C_6H_4Br-4; N-N = bpy
8 R = C_6H_2Br-4-Me_2-2,6; N-N = $(MeO)_2$bpy
9 R = $C_6H_2Cl_3$-2,4,6; N-N = $(MeO)_2$bpy
10 R = C_6H_4Cl-4; N-N = pimPh
11 R = C_6H_4I-4; N-N = pimMe
12 R = C_6H_4Cl-4; N-N = pimMe
13 R = C_6H_2Br-4-Me_2-2,6; N-N = pimMe
14 R = C_6H_4Cl-4; N-N = $(MeO)_2$bpy
15 R = C_6H_4Cl-4; N-N = $^tBu_2$bpy
16 R = C_6H_4Cl-4; N-N = bpy
17 R = C_6H_4F-4; N-N = bpy
18 R = $C_6H_3Me_2$-2,6; N-N = bpy

$[Re(CNC_6H_3Me_2$-2,6$)_4$(bpy)]PF_6 (18). The complex has previously been communicated.[6] Yield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.02 (s, 12H, Me), 2.49 (s, 12H, Me), 6.96−7.12 (m, 12H, phenyl H's), 7.48 (ddd, 2H, J = 8.1, 5.5, 0.9 Hz, 4,4′-bipyridyl H's), 8.18 (td, 2H, J = 5.3, 1.5 Hz, 5,5′-bipyridyl H's), 8.69 (dd, 2H, J = 8.1, 1.5 Hz, 3,3′-bipyridyl H's), 9.29 (dd, 2H, J = 5.2, 0.9 Hz, 6,6′-bipyridyl H's). ESI-MS: m/z 867 $\{M - PF_6\}^+$. IR (KBr disk, ν/cm^{-1}): 844 ν(P−F); 1962, 1997, 2042, 2123 ν(C≡N). Anal. Calcd (found) for **18**: C, 54.49 (54.93); H, 4.38 (4.22); N, 8.30 (8.59).

General Procedure for Microwave-Assisted Synthesis. To a 10 mL reaction vial containing a suspension of $[Re(CNR)_5I]$ (0.1 mmol) and diimine (0.2 mmol, 2 mol equiv) in THF (5 mL) was added TlOTf (53 mg, 0.15 mmol, 1.5 mol equiv). The resulting suspension was degassed by bubbling argon for 10 min. The vial was then sealed with a septum cap and heated in a microwave reactor for 4 h with a maximum temperature and pressure of 170 °C and 170 psi, respectively. After it was cooled to room temperature, the reaction vial was uncapped and the resulting suspension was filtered to remove the precipitated TlI. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane/acetone (7/3 v/v) as eluent. The residue was then redissolved in methanol (2 mL). A subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave the target complex as a PF_6^- salt.

Physical Measurements and Instrumentation. Microwave reactions were performed using a CEM Discover SP single-mode microwave instrument (CEM Corp., Matthews, NC). Microwave reactions were performed in specially designed Pyrex tubes equipped with a stir bar and sealed with a Teflon/silicon septum. ^{1}H NMR spectra were recorded on a Bruker AV400 (400 MHz) or a Varian (300 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane (Me_4Si). All positive-ion ESI mass spectra were recorded on a PE-SCIEX API 300 triple quadrupole mass spectrometer. The elemental analyses were performed on an Elementar Vario EL III analyzer.

Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission and excitation spectra at room temperature and at 77 K were recorded on a Horiba Jobin Yvon Fluorolog-3-TCSPC spectrofluorometer with a Hamamatsu R928 photomultiplier tube detector. 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 diluted EtOH/MeOH sample solutions contained in a quartz tube inside a liquid nitrogen filled quartz optical Dewar flask. Luminescence quantum yields were determined using the 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. Luminescence lifetimes of the samples were measured using the time-correlated single photon counting (TCSPC) technique on the TCSPC spectrofluorometer in a Fast MCS mode with a NanoLED-375LH excitation source, which has its excitation peak wavelength at 375 nm and a pulse width shorter than 750 ps. The photon counting data were analyzed by Horiba Jobin Yvon decay analysis software. Transient absorption spectra at room temperature were recorded using the spectral mode on a Edinburgh Instruments LP920-KS equipped with an 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 voltammetric measurements were performed by using a CH Instruments, Inc., Model CHI 620 electrochemical analyzer. Electrochemical measurements were performed in acetonitrile solutions with 0.1 M $^nBu_4NPF_6$ as the supporting electrolyte at room temperature. The reference electrode was an $Ag/AgNO_3$ (0.1 M in acetonitrile) electrode, and the working electrode was a glassy-carbon electrode (CH Instruments, Inc.) with a platinum wire as the counter electrode. The working electrode surface was polished with a 1 μm α-alumina slurry (Linde) and then a 0.3 μm α-alumina slurry (Linde) on a microcloth (Buehler Co.). The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference. All solutions for electrochemical studies were deaerated with prepurified argon gas prior to measurements.

Crystal Structure Determinations. The crystal structures of **1**, **4**, **7**, and **12** were determined on an Oxford Diffraction Gemini S Ultra

X-ray single-crystal diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and Cu Kα radiation (λ = 1.541 78 Å), respectively. The structures were solved by direct methods employing the SHELXL-97 program[10] on a PC. Re and many non-H atoms were located according to direct methods. The positions of other non-hydrogen atoms were found after successful refinement by full-matrix least squares using the SHELXL-97 program on a PC.[10] In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by the program SHELXL-97.[10] The positions of H atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final *R* indices.

RESULTS AND DISCUSSION

Synthesis and Characterization. With the dehydration method developed by Ugi and coworkers,[7] isocyanide ligands with different electronic and steric properties were successfully synthesized. The reactions of $K_2[ReI_6]$ with 8 mol equiv of substituted isocyanide ligands (RNC) in a MeOH mixture gave $[Re(CNR)_5I]$.[11] However, in the synthesis of $[Re(CNR)_5I]$, where R = 4-IC_6H_4, 4-BrC_6H_4, 2,4,6-$Cl_3C_6H_2$, 2,4,6-$Br_3C_6H_2$, 6-OMe-2,4-$Cl_2C_6H_2$, 2,6-$(CH_3)_2$-4-BrC_6H_2, with electron-withdrawing substituents, the yield is very low (<15%). The exceptionally low yield could be significantly increased to 40−70% by the addition of the reducing agent hydrazine hydrate. Substitution reactions of $[Re(CNR)_5I]$ with a 2-fold excess of diimine ligands (N−N) in the presence of thallium triflate in 1,4-dioxane under reflux conditions for 2 days gave the target complexes $[Re(CNR)_4(N{-}N)]^+$ (Scheme 1). Since isocyanide ligand is released in the substitution reaction, it also leads to the formation of the rhenium(I) hexa(isocyano) complex $[Re(CNR)_6]^+$ as a major byproduct and the yields of the target complexes are limited to 50−70%. These two complexes can be separated by column chromatography. Attempts to improve the yield of the target complexes by carrying out the substitution reactions with the microwave reactor at elevated temperature and pressure (~170 °C and 170 psi; Figure S1 in the Supporting Information) were made. However, the purity and yield of the target complexes are found to be similar to those of reactions carried out by heating with an oil bath. However, carrying out the substitution reaction in the microwave reactor can significantly shorten the reaction time from 2 days to 4 h. Subsequent metathesis reactions with ammonium hexafluorophosphate and recrystallization by slow diffusion of diethyl ether into concentrated dichloromethane solutions of the complexes gave the analytically pure complexes as orange to red crystals depending on the π-accepting ability of the isocyanide and diimine ligands.

Complexes **1**−**18** were characterized by ^{1}H NMR, IR, and ESI-MS and gave satisfactory elemental analyses. The X-ray crystal structures of **4**, **7**, and **12** and the perchlorate salt of **1** were also determined. All complexes show four C≡N stretches in the 1850−2140 cm^{-1} region, which is consistent with the IR active modes for an octahedral complex with four isocyanide ligands in a C_{2v} symmetry. These four modes (Figure 1) include two A_1 modes involving the in-phase motion of the two trans isocyanides ($1A_1$) and another in-phase motion of the two isocyanide ligands trans to the diimine ligand ($2A_1$), a B_1 mode involving the out-of-phase motion of the trans isocyanides, and another B_2 mode involving the out-of-phase motion of the two isocyanides trans to the diimine ligand. Similar vibrational modes were also assigned for the related rhenium(I) tetracarbonyl bipyridyl systems.[12] On the basis of these vibrational modes, the stretches are assigned to the modes: 2120−2140 cm^{-1} for $1A_1$; 2020−2060 cm^{-1} for B_1; 1950−2000 cm^{-1} for $2A_1$; 1880−1960 cm^{-1} for B_2. The high-energy vibration at ca. 2120−2140 cm^{-1} is very close to the free ligand isocyanide ν(C≡N) stretch (~2130−2140 cm^{-1}), indicating that there was only a weak π-back-bonding interaction between the rhenium metal and one or more isocyanide ligands. These observations are likely to be a result of the competition between the π-back-bonding of the two isocyanide ligands trans to each other. In addition, the hexafluorophosphate anions (PF_6^-) in complexes **1**−**18** are also characterized by the observation of ν(P−F) at ca. 840 cm^{-1}.

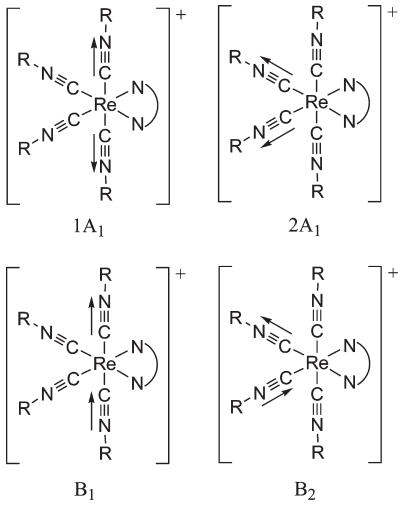


Figure 1. The four IR active stretching modes ($1A_1$, $2A_1$, B_1, and B_2 modes) of $[Re(CNR)_4(N{-}N)]^+$ with C_{2v} symmetry.

X-ray Crystal Structures. Figure 2 depicts the perspective drawings of the complex cations of **4**, **7**, and **12** and perchlorate salt of **1** with their atomic numbering. The crystal and structure determination data are collected in Table S1 (Supporting Information), and selected bond distances and angles are summarized in Table S2 (Supporting Information). The crystal structures of these complexes show similar distorted-octahedral structures with comparable bond lengths and angles. Due to the steric requirements of the bidentate ligands, the bite angles subtended by the nitrogen atoms of chelating diimine ligands at the rhenium center of these complexes are ca. 75°, which is commonly observed in other related complex systems.[3−5] The bond lengths of Re−C and C≡N(isocyanide) are in the ranges of 1.92−2.05 and 1.15−1.19 Å, respectively, similar to those reported for other related rhenium(I) isocyanide complexes.[13] Owing to the π-back-bonding interaction between the isocyanide ligands and the rhenium metal center, the isocyanide ligands in these complexes are nonlinear and show different degrees of bending.[1b,14] In general, the trans isocyanide ligands are more linear, as reflected by the averaged bond angle of C≡N−C (169.4° vs 162.9°) in comparison to those cis isocyanide ligands, which are trans to the diimine ligand. These observations can be rationalized by the competition between the two trans isocyanide ligands for the π-back-bonding and the large trans influence of isocyanide ligands.

UV Spectroscopy. All the complexes dissolve in dichloromethane to give orange to red solutions, which show intense absorptions with molar extinction coefficients on the order of 10^4 $dm^3\,mol^{-1}\,cm^{-1}$ in the region of 230−370 nm (Table 1, Figure 3).

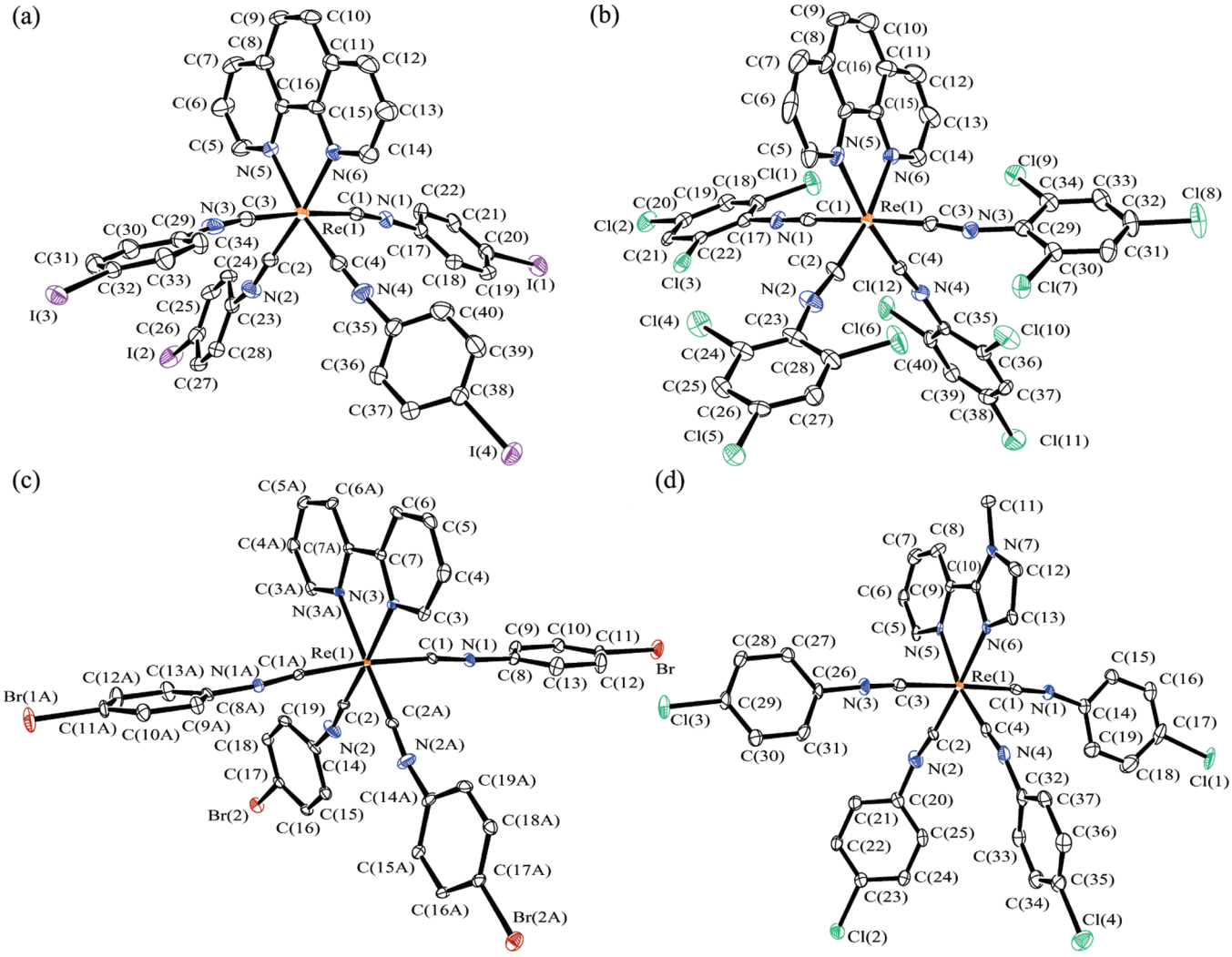


Figure 2. Perspective drawings of the complex cations of (a) **1**, (b) **4**, (c) **7**, and (d) **12** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

These absorptions are ascribed to the intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the substituted phenyl isocyanide and diimine moieties. In addition to intense IL absorptions in the UV region, they also show two to three additional moderately intense absorption bands or shoulders at 370−470 nm. With reference to the previous spectroscopic studies of Re(I) diimine complexes[3−5,15] and the homoleptic metal phenylisocyano complexes of different metal centers,[16] which show metal-to-ligand charge transfer (MLCT) transitions [$d\pi(M) \rightarrow \pi^*(RNC)$] in the region from 250 to 500 nm depending on the nature of the metal center, these moderately intense absorptions are assigned to the MLCT transitions of [$d\pi(Re) \rightarrow \pi^*(RNC)$] and [$d\pi(Re) \rightarrow \pi^*(N-N)$], probably with some mixing of a ligand-to-ligand charge transfer (LLCT) transition of [$\pi(RNC) \rightarrow \pi^*(N-N)$]. The higher energy absorptions at ca. 370−410 nm are assigned to the MLCT [$d\pi(Re) \rightarrow \pi^*(RNC)$] transition, whereas the lowest energy absorption bands are assigned to the MLCT [$d\pi(Re) \rightarrow \pi^*(N-N)$] transition, since π^* orbitals of substituted phenyl isocyanides lie higher in energy than those of the diimine ligands. Moreover, the lowest energy absorption also shows an absorption energy dependence on the π-accepting ability of the diimine and the isocyanide ligands, in line with the MLCT [$d\pi(Re) \rightarrow \pi^*(N-N)$] assignment. For complexes **3**−**5** and **8**−**15**, which contain diimine ligands of relatively higher lying π^* orbitals such as those with electron-donating substituents or a less extensively π-conjugated methylimidazole moiety and/or isocyanide ligands of lower lying π^* orbital due to the presence of electron-withdrawing and π-accepting substituents, the MLCT [$d\pi(Re) \rightarrow \pi^*(N-N)$] and [$d\pi(Re) \rightarrow \pi^*(RNC)$] transitions are close in energy and therefore do not show well-resolved absorption bands or shoulders. The observation of a much higher extinction coefficient for the lowest energy absorption in comparison to those for other complexes is supportive of the mixing of the two MLCT transitions. In addition, all the complexes also exhibit very weak absorption tailing at about 550−650 nm with molar extinction coefficients on the order of 10^2 dm^3 mol^{-1} cm^{-1}, which is ascribed to spin-forbidden ^{3}MLCT transitions.

Emission Spectroscopy. Excitation of dichloromethane solutions of complexes **1**−**18** at λ >350 nm produces orange to red MLCT [$d\pi(Re) \rightarrow \pi^*(N-N)$] phosphorescence with the emission maxima in the range of 612−738 nm (Table 1). These emission bands are found to be sensitive to the nature of the isocyanide and diimine ligands. For complexes with the same isocyanide ligands, a significant blue shift in emission energy is observed when the bipyridyl ligand is replaced by 1-methyl-2-(2′-pyridyl)imidazole, in

Table 1. Photophysical Data for Complexes 1−18

complex	medium (T/K)	emission[a] λ_{em}/nm (τ_o/μs)	$\phi_{em} \times 10^3$	absorption[b] λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})
1	CH_2Cl_2 (298)	674 (0.061)	4.6	269 (72 455), 290 (41 605), 331 (49 520), 385 (28 940), 410 sh (17 080), 465 sh (7890)
	glass[c] (77)	608 (1.69)		
2	CH_2Cl_2 (298)	686 (0.039)	1.7	269 (80 765), 293 (53 240), 327 (68 020), 382 (33 410), 479 (8890)
	glass[c] (77)	610 (1.32)		
3	CH_2Cl_2 (298)	616 (0.241)	43.2	229 (92 790), 267 (89 820), 292 (45 950), 344 (63 475), 381 sh (45 495), 393 sh (42 910), 419 sh (25 665)
	glass[c] (77)	566 (3.38)		
4	CH_2Cl_2 (298)	614 (0.275)	50.3	229 (90 810), 266 (88 270), 293 (45 010), 342 (62 495), 390 sh (43 080), 419 sh (26 195)
	glass[c] (77)	558 (3.28)		
5	CH_2Cl_2 (298)	629 (0.187)	25.4	267 (85 705), 291 (43 810), 341 (58 645), 376 sh (43 965), 430 sh (18 925)
	glass[c] (77)	570 (2.79)		
6	CH_2Cl_2 (298)	684 (0.013)	0.40	254 (58 780), 295 (72 400), 334 (67 420), 383 (38 020), 406 sh (21 155), 450 sh (9440)
	glass[c] (77)	614 (0.72)		
7	CH_2Cl_2 (298)	686 (0.013)	0.50	244 (60 835), 296 (69 680), 331 (60 670), 380 (32 525), 412 sh (14 780), 451 (8205)
	glass[c] (77)	612 (0.68)		
8	CH_2Cl_2 (298)	683 (0.005)	0.49	246 (72 160), 288 (56 440), 335 (74 515), 376 (41 255), 418 sh (16 990)
	glass[c] (77)	584 (0.40)		
9	CH_2Cl_2 (298)	612 (0.039)	3.1	262 (55 525), 283 (41 925), 349 (51 155), 377 sh (37 850), 402 (30 840)
	glass[c] (77)	540 (2.74)		
10	CH_2Cl_2 (298)	645 (0.099)	19.1	242 (59 790), 307 (68 010), 334 (58 405), 380 sh (30 495), 414 sh (18 365)
	glass[c] (77)	574 (2.97)		
11	CH_2Cl_2 (298)	631 (0.173)	27.9	259 (60 170), 307 (64 100), 338 (61 540), 386 (37 605), 411 sh (23 690)
	glass[c] (77)	560 (3.95)		
12	CH_2Cl_2 (298)	632 (0.159)	22.6	240 (54 710), 306 (61 810), 333 (54 475), 385 (30 105), 408 sh (19 840)
	glass[c] (77)	570 (3.95)		
13	CH_2Cl_2 (298)	648 (0.134)	13.8	248 (54 885), 309 (55 005), 333 (53 460), 383 (28 350), 408 sh (17 500)
	glass[c] (77)	566 (3.29)		
14	CH_2Cl_2 (298)	681 (0.007)	0.57	231 (72 610), 252 (52 390), 283 (53 615), 332 (59 270), 375 (33 105), 412 sh (16 160)
	glass[c] (77)	586 (0.46)		
15	CH_2Cl_2 (298)	671 (0.020)	2.9	239 (55 965), 294 (66 050), 331 (57 320), 365 (33 980), 412 sh (15 020)
	glass[c] (77)	586 (0.83)		
16	CH_2Cl_2 (298)	690 (0.012)	1.1	230 (65 215), 296 (78 970), 328 (66 405), 366 (38 610), 408 sh (17 450), 456 sh (9095)
	glass[c] (77)	615 (0.56)		
17	CH_2Cl_2 (298)	698 (0.009)	0.62	235 (38 200), 296 (52 585), 315 (43 390), 358 (22 345), 400 sh (9430), 471 (5520)
	glass[c] (77)	629 (0.41)		
18	CH_2Cl_2 (298)	738 (0.005)	0.16	242 (53 940), 298 (69 555), 322 (52 095), 360 (29 910), 410 sh (9830), 492 (6525)
	glass[c] (77)	642 (0.23)		

[a] Emission maxima are uncorrected values. [b] At 298 K. [c] EtOH/MeOH (4/1 v/v).

comparison to the introduction of electron-donating substituents on the bipyridyl ligand. This can be exemplified by the trends of the emission maxima: **11** (631 nm) ≪ **6** (684 nm); **12** (632 nm) < **10** (645 nm) ≪ **15** (671 nm) < **14** (681 nm) < **16** (690 nm) (Figure 4a). The increase in the MLCT emission energy could be explained by the raising of the energy of the π^* orbital as a result of the introduction of electron-donating substituents or the decrease of the extent of π-conjugation of the diimine ligand. In addition to the direct modification of the LUMO [π^*(N−N)] by changing the diimine ligand to tune the emissive MLCT [dπ(Re) → π^*(N−N)] excited state, the perturbation of the HOMO [dπ(Re)] through the change of isocyanide ligands and their corresponding interactions with rhenium metal center are found to be very effective in tuning the emissive excited state. This could be illustrated by the considerable shift of the MLCT phosphorescence (Figure 4b) for rhenium phenanthrolinyl complexes with different π-accepting isocyanide ligands through the modification of the substituents on the phenyl moiety: **4** (614 nm) ≈ **3** (616 nm) < **5** (629 nm) < **1** (674 nm) < **2** (686 nm) ($\Delta E_{em} \approx 1690$ cm^{-1} from $Cl_3C_6H_2NC$ to $BrMe_2C_6H_2NC$). This could be explained by the difference in the stabilization of the dπ(Re) orbital as a result of the interaction between the dπ(Re) and π^*(RNC) orbitals. Such a π-back-bonding interaction between the metal center and aryl isocyanide ligands, and its variation with the aryl isocyanide ligands of different electronic natures were also commonly observed in other metal isocyanide complexes.[5,15−17] Further tuning of the emissive excited state can be anticipated by simple modification of substituents on the phenyl group of the isocyanide ligands or the replacement of the phenyl group with other functional moieties.

These complexes also display strong photoluminescence with a structureless emission band in solid state and in 77 K EtOH/MeOH (4/1 v/v) glassy medium. As these emissions show trends

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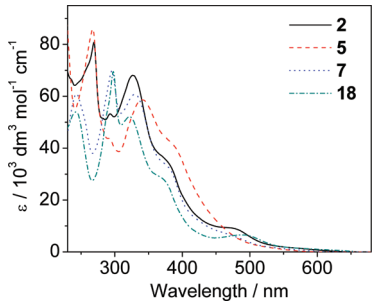

Figure 3. Overlaid absorption spectra of selected complexes **2**, **5**, **7**, and **18** in CH_2Cl_2 solution at 298 K.

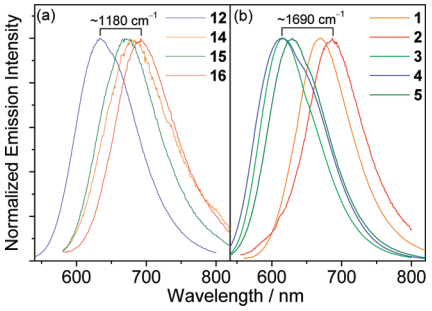

Figure 4. Overlaid uncorrected emission spectra of (a) **12**, **14**−**16** and (b) **1**−**5** in CH_2Cl_2 solution at 298 K.

similar to those of the solution emissions, they are also tentatively assigned as derived from ^{3}MLCT [$d\pi(Re) \rightarrow \pi^*(N-N)$] excited state origin. The blue shift is attributed to the increased rigidity in the glass, which is commonly observed in other related systems. The submicrosecond excited-state lifetime observed in a glassy medium at 77 K is also supportive of its triplet parentage.

The emission of complex **14** was found to be highly sensitive to the solvent environment.[5] To investigate the structure−property relationship of the solvent dependence of the MLCT emission of these complexes, the emissions of **1**−**18** in different solvent media, such as benzene, dioxane, THF, $CHCl_3$, CH_2Cl_2, acetone, MeCN, ethanol, and methanol, were investigated and summarized in Table S3 (Supporting Information). The emissions of these complexes show different solvent dependences as well as different degrees of sensitivity (Table S3, Figure 5). Except for complexes with unsymmetrical diimine ligands (pimMe and pimPh), the emissions of all other complexes show a blue shift in emission energy with decreasing solvent polarity from an acetonitrile solution to a benzene solution. Such a solvent dependence may be due to the increase in the dipole moment of the excited state, which is more stabilized in a polar solvent medium, in comparison to its ground state. Moreover, the emission energies of these complexes are found to correlate well with Dimroth's solvent parameter[18] (Figure 6). Since these complexes do not have any functional moiety capable of forming a hydrogen-bonding interaction and the pyridinium phenoxide dye used for the derivation of Dimroth's solvent parameter[18] can have significant hydrogen-bonding interactions with the protic solvents, the emission data of these complexes obtained in methanol and ethanol deviate from the correlation.

The degree of solvent dependence is found to vary with the nature of diimine ligand and follow the order $(MeO)_2$bpy ≈

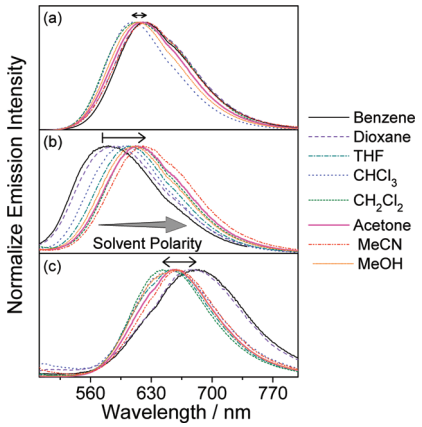

Figure 5. Normalized uncorrected emission spectra of (a) **4**, (b) **9**, and (c) **10** in different solvents at 298 K.

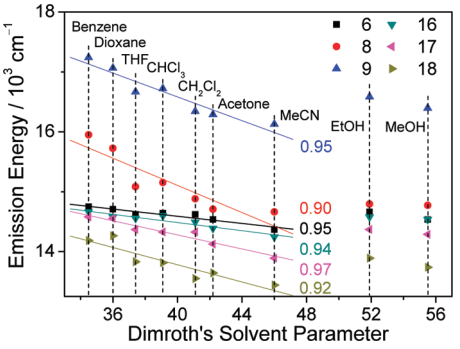

Figure 6. Plot of emission energy of **6**, **8**, **9**, and **16**−**18** in different solvents versus Dimroth's solvent parameter and their linear least-squares fits (—), excluding the data points of methanol and ethanol.

^{t}Bu$_2$bpy ≫ bpy > phen (Figure 5). This is in the reverse order of the π-accepting ability of the diimine ligand. Such a decrease of the solvatochromic shifts with the increasing π-acceptor strength of the diimine ligand is commonly observed in other related metal polypyridyl MLCT chromophores[19] and was attributed to the decrease in charge transfer character as a result of the stronger mixing of the $d\pi$ orbital of metal center and π^* orbital of the diimine ligand by better π-back-bonding interaction. In addition, the degree of solvent dependence is also found to decrease for complexes with 2,4,6-trisubstituted phenyl isocyanide ligands compared to those with 4-monosubstituted phenyl isocyanide ligands. The lower solvent sensitivity of these complexes may be attributed to the better shielding of the excited portions of the complexes in the presence of more sterically bulky isocyanide ligands. Similar shielding effects of the excited state against environmental perturbation were also reported in the emission solvatochromic studies of related MLCT luminophores.[20] Consequently, the MLCT emissions of phenanthroline complexes **2**−**5** with different 2,4,6-trisubstituted phenyl isocyanide ligands are almost insensitive and do not show any obvious emission energy dependence to the polarity of the solvent media. Interestingly, complexes **10**−**12** with unsymmetrically substituted pyridine imidazole ligands show a different solvent dependence, with the lowest energy emission in nonpolar solvents, such as benzene and dioxane, compared to other polar solvents (Figure 5c). This may be attributed to the significant variations

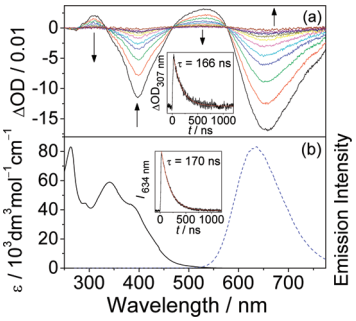

Figure 7. (a) Transient difference spectra of **4** in MeCN solution at 298 K obtained after 355 nm nanosecond laser excitation at different time delays: 0, 60, 120, 180, 240, 300, 360, 420, 480, 540, and 600 ns. (b) Overlaid absorption (solid line) and emission (dashed line) spectra of **4** in MeCN solution. The insets show (a) the absorption−time profile at 307 nm and (b) a luminescence intensity decay trace at 634 nm after 355 nm nanosecond laser excitation and their first-order exponential fit (red line).

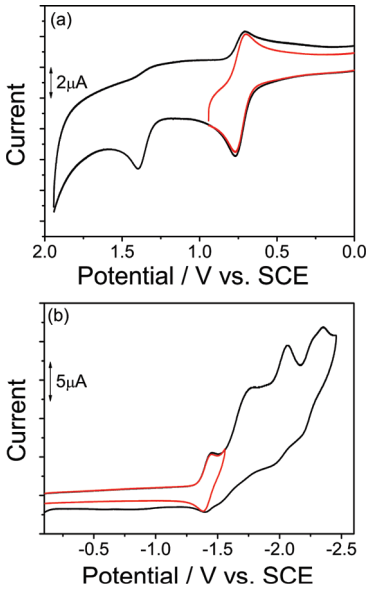

Figure 8. Cyclic voltammograms of (a) the oxidative scan and (b) the reductive scan of **7** in MeCN solution (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$). Scan rate: 100 mV s^{-1}. The red line shows the inset of the oxidative and reductive scan.

of the dipole moments of the complexes in the ground state and the excited state. However, these emissions do not show any correlation with the solvent parameters.

Transient Absorption Spectroscopy. The solution emission lifetime of **4** is on the submicrosecond time scale, which is sufficiently long for a nanosecond transient absorption spectroscopic study. Transient different spectra on the nanosecond time scale after 355 nm nanosecond laser excitation were recorded. Two absorption features peaking at ca. 310 and 525 nm together with a strong ground-state bleaching at ca. 396 nm, which decay in accord with the first-order kinetics with a lifetime of 166 ns, were observed (Figure 7). However, due to the spectral overlapping of the ^{3}MLCT phosphorescence, the excited-state absorptions at λ >570 nm of the complexes cannot be determined. The close resemblance of the lifetimes for these transient absorptions and the luminescence intensity (τ = 170 ns in MeCN) is suggestive of the origin of these transient absorptions being attributed to the emissive excited species. On the basis of the reported absorption for phenanthroline anion radical[21] as well as the previous transient absorption studies of $[Re(CO)_3(phen)Cl]$,[3c] which show similar absorptions, these transient absorptions were also assigned to the absorptions of the reduced phenanthroline. In contrast to the transient absorptions of $[Re(CO)_3(phen)Cl]$,[3c] the transient absorption spectrum of **4** shows a much weaker absorption feature at ca. 310 nm and strong ground-state bleaching peaking at ca. 397 nm. This ground-state bleaching is most likely associated with MLCT [dπ(Re) → π^*(RNC)] and MLCT [dπ(Re) → π^*(phen)] transitions, probably mixed with LLCT [π(RNC) → π^*(N−N)]. The presence of this significant ground-state bleaching for **4**, which is absent in the transient absorption spectrum of $[Re(CO)_3(phen)Cl]$, is consistent with the much stronger MLCT absorptions for **4** as a result of the mixing of different MLCT transitions ([dπ(Re) → π^*(RNC)] and [dπ(Re) → π^*(phen)]). All these observations are in agreement with MLCT phosphorescence assignments.

Electrochemistry. **10**, **12**, and **14**−**18** show one quasi-reversible reduction couple with $E_{1/2}$ in the range of −1.40 to −1.70 V vs SCE in their cyclic voltammograms in acetonitrile (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$) and three irreversible reduction waves with E_{pc} in the ranges of −1.72 to −2.08 V, −2.05 to −2.54 V, and −2.29 to −2.72 V vs SCE, whereas for complexes **1**−**6**, **9**, **11** and **13**, only one irreversible reduction wave with E_{pc} from −1.36 to −1.77 V vs SCE was determined, as these complexes show significant decomposition on scanning to more negative potential. The representative cyclic voltammograms of the oxidative scan and reductive scan of **7** in MeCN solution are shown in Figure 8. The electrochemical data of these complexes in acetonitrile solution (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$) at ambient temperature are summarized in Table 2.

The first quasi-reversible oxidation couple and the irreversible oxidation wave are assigned to the metal-centered Re(I/II) and Re(II/III) oxidation processes, respectively. These oxidation potentials were found to vary with the π-accepting ability of the diimine and the isocyanide ligands. With the same isocyanide ligands, the potential for the oxidation is found to follow the order **1** (+0.74, +1.42 V) ≈ **6** (+0.74, +1.40 V) > **11** (+0.67, +1.27 V), which is in line with the π-accepting ability of the diimine ligands: phen ≈ bpy > pimMe. Similarly, for the phenanthroline complexes with different isocyanide ligands, the trend for the oxidation potential (**4** (+1.05, +1.72 V) ≈ **3** (+1.05, +1.72 V) > **5** (0.98, +1.67 V) > **1** (0.74, +1.42 V)) is consistent with the π-accepting ability of the isocyanide ligands: 2,4,6-$Cl_3C_6H_2NC$ ≈ 2,4,6-$Br_3C_6H_2NC$ >2,4-Cl_2-6-$MeOC_6H_2NC$ > 4-IC_6H_4NC. The increasing metal-centered oxidation potential for complexes with π-accepting ability of the ligands can be attributed to the lower-lying dπ(Re) orbital as a result of a better metal−ligand interaction.

In the reductive scan, the first quasi-reversible couple or irreversible wave of these complexes shows a noticeable cathodic shift for complexes with more electron rich or less π-conjugated diimine ligands and are relatively insensitive to the nature of isocyanide ligands. Therefore, they are assigned to the ligand-centered reduction of the diimine ligands. For the three additional irreversible reduction waves at more negative potentials observed in complexes **7**, **8**, **10**, **12**, and **14**−**18**, the first two irreversible reduction waves are assigned to successive reductions of the isocyanide ligands, as their potentials are highly sensitive to the substituents as well as the π-accepting ability of the

Table 2. Electrochemical Data for Complexes 1−18 in Acetonitrile Solution (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$) 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	0.74 (1.42)[c]	(−1.39)[d,e]
2	0.72 (1.49)[c]	(−1.41)[d,e]
3	1.05 (1.72)[c]	(−1.36)[d,e]
4	1.05 (1.72)[c]	(−1.37)[d,e]
5	0.98 (1.67)[c]	(−1.39)[d,e]
6	0.74 (1.40)[c]	(−1.45)[d,e]
7	0.74 (1.39)[c]	−1.42 (−1.75)[d] (−2.09)[d] (−2.30)[d]
8	0.67 (1.39)[c]	−1.53 (−2.05)[d] (−2.51)[d] (−2.72)[d]
9	1.00 (1.62)[c]	(−1.47)[d,e]
10	0.67 (1.33)[c]	−1.63, (−1.89)[d], (−2.27)[d], (−2.63)[d]
11	0.67 (1.27)[c]	(−1.72)[d,e]
12	0.66 (1.35)[c]	−1.69 (−1.92)[d] (−2.30)[d] (−2.67)[d]
13	0.65 (1.39)[c]	(−1.77)[d,e]
14	0.69 (1.30)[c]	−1.52 (−1.87)[d] (−2.20)[d] (−2.53)[d]
15	0.71 (1.36)[c]	−1.49 (−1.78)[d] (−2.18)[d] (−2.42)[d]
16	0.73 (1.42)[c]	−1.42 (−1.72)[d] (−2.16)[d] (−2.29)[d]
17	0.68 (1.43)[c]	−1.43 (−1.80)[d] (−2.20)[d] (−2.33)[d]
18	0.63 (1.46)[c]	−1.46 (−2.03)[d] (−2.54)[d] (−2.70)[d]

[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 peak anodic and peak cathodic potentials, respectively. [c] Irreversible wave and only E_{pa} reported. [d] Irreversible wave and only E_{pc} reported. [e] Only one irreversible reduction wave was determined, as it shows significant decomposition on scanning to more negative potential.

isocyanide ligands. As the potentials for the third reduction wave show considerable sensitivity on both isocyanide and diimine ligands, it is assigned to metal-centered reduction of Re(I) to Re(0).

CONCLUSION

A new series of luminescent rhenium(I) tetra(isocyano) diimine complexes, $[Re(CNR)_4(N{-}N)]^+$, with isocyanide and diimine ligands of different electronic and steric features has been successfully synthesized and characterized and their photophysical and electrochemical properties have been studied. The X-ray crystal structures of four of the complexes were also determined. Detailed photophysical studies revealed that all complexes displayed orange to red MLCT [$d\pi(Re) \rightarrow \pi^*(N{-}N)$] phosphorescence upon excitation with λ >350 nm. The emissive ^{3}MLCT [$d\pi(Re) \rightarrow \pi^*(N{-}N)$] excited state has been investigated by transient absorption spectroscopy. The emission solvatochromic behaviors of these complexes and their structural correlations have also been reported. By appropriate design of the diimine ligand and alteration of the substituents of isocyanide ligands, the excited-state properties of these complexes and their sensitivity toward the change in environment can be tailored and fine-tuned according to the requirements for different applications.

ASSOCIATED CONTENT

Supporting Information. Tables, figures, and CIF files giving crystal and structure determination data, selected bond lengths and bond angles, and crystallographic data for **1**, **4**, **7**, and **12**, emission data of **1**−**18** in different solvents, and graphs showing the microwave conditions used in the microwave-assisted synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

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