



# Synthesis, photophysical and electrochemical study of diisocyano-bridged homodinuclear rhenium(I) diimine complexes



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## ABSTRACT

A new series of diisocyanide-bridged homodinuclear Re(I) complexes  $[(\text{phen})(\text{L}_x)(\text{CO})_2\text{Re}(\text{CNRNC})\text{Re}(\text{CO})_2(\text{L}_x)(\text{phen})]^{2+}$  and their mononuclear analogues  $[\text{Re}(\text{PPh}_3)(\text{CNRNC})(\text{CO})_2(\text{phen})]^+$  [ $\text{L}_x = \text{CO}$  and  $\text{PPh}_3$ ;  $\text{CNRNC} = 1,4\text{-phenylenediisocyanide (CNC}_6\text{H}_4\text{NC)}$  and  $4,4'\text{-biphenyldiisocyanide (CNC}_6\text{H}_4\text{C}_6\text{H}_4\text{NC)}$ ] have been synthesized. The X-ray crystal structures of two of the dinuclear complexes were determined. The photophysics and electrochemistry of these complexes have been investigated. The dicarbonyl phosphino Re(I) phenanthroline complexes display intense MLCT  $[d\pi(\text{Re}) \rightarrow \pi^*(\text{phen})]$  phosphorescence in  $\text{CH}_2\text{Cl}_2$  solution with luminescence quantum yield ( $\phi_{\text{em}}$ ) in the range of 0.127–0.171. In contrast, the tricarbonyl dinuclear Re(I) complexes exhibit LC  $[\pi \rightarrow \pi^*(\text{phen})]$  phosphorescence with  $\phi_{\text{em}}$  from 0.0498 to 0.0625.

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## 1. Introduction

The study of dinuclear complexes is of crucial importance to provide insight into excited-state properties and dynamics as well as photoinduced electron and energy transfer processes [1–8]. Over the past few decades, different homo- or hetero-dinuclear systems (dyads) bridged by various ligands or metal–metal bonding or interactions have been extensively reported [9–36]. These studies had also contributed significantly to the development of supramolecular systems, molecular devices and machines for diverse applications [8].

Due to the rich electrochemical and photophysical properties associated with  $d^6$  transition metal complexes, dyads developed by bridging two  $d^6$  transition metal complex moieties have been extensively developed and investigated [21–36]. In view of excellent electronic communication of bridging aromatic isocyanide ligands [32–33] and as an extension of our recent development of isocyanato Re(I) diimine complexes [37–41], herein, we report the syntheses, photophysical and electrochemical study of a new series of diisocyanide-bridged homodinuclear Re(I) complexes  $[(\text{phen})(\text{L}_x)(\text{CO})_2\text{Re}(\text{CNRNC})\text{Re}(\text{CO})_2(\text{L}_x)(\text{phen})]^{2+}$  and their mono-

nuclear analogues  $[\text{Re}(\text{PPh}_3)(\text{CNRNC})(\text{CO})_2(\text{phen})]^+$  [ $\text{L}_x = \text{CO}$  and  $\text{PPh}_3$ ;  $\text{CNRNC} = 1,4\text{-phenylenediisocyanide (CNC}_6\text{H}_4\text{NC)}$  and  $4,4'\text{-biphenyldiisocyanide (CNC}_6\text{H}_4\text{C}_6\text{H}_4\text{NC)}$ ].

## 2. Experimental

### 2.1. Materials and methods

Anhydrous magnesium sulfate and ammonium hexafluorophosphate were obtained from Aldrich Chemical Company. 1,10-Phenanthroline (phen) monohydrate, triphenylphosphine ( $\text{PPh}_3$ ), silver trifluoromethanesulfonate ( $\text{AgOTf}$ ) and  $[\text{Re}_2(\text{CO})_{10}]$  were purchased from Strem Chemical Company and used without further purification.  $[\text{Re}(\text{CO})_5\text{Br}]$  was synthesized from the reaction between  $[\text{Re}_2(\text{CO})_{10}]$  and bromine according to a literature procedure [42]. Substituted bridging isocyanide ligands  $\text{CNC}_6\text{H}_4\text{NC}$  and  $\text{CNC}_{12}\text{H}_8\text{NC}$  were synthesized from corresponding substituted anilines using the synthetic methodology developed by Ugi and co-workers [43]. *fac*- $[\text{Re}(\text{phen})(\text{CO})_3\text{Br}]$ , *fac*- $[\text{Re}(\text{phen})(\text{CO})_3(\text{MeCN})\text{OTf}]$ , *fac*- $[\text{Re}(\text{phen})(\text{CO})_3(\text{PPh}_3)\text{OTf}]$  and *cis,trans*- $[\text{Re}(\text{CO})_2(\text{phen})(\text{PPh}_3)(\text{MeCN})\text{OTf}]$  were prepared according to slightly modified literature procedures [44]. All solvents were of analytical reagent grade and were used without further purification. Unless specified in the procedure, all the reactions were performed under strictly anhydrous conditions in an inert atmosphere of argon using standard Schlenk techniques.

Abbreviations: phen, 1,10-phenanthroline;  $\text{Me}_3\text{NO}$ , trimethylamine N-oxide;  $\text{AgOTf}$ , silver trifluoromethanesulfonate; LC, ligand-centered; IL, intraligand; MLCT, metal-to-ligand charge transfer; THF, tetrahydrofuran.

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## 2.2. Physical measurements

$^1\text{H}$  NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts ( $\delta$ , ppm) were reported relative to tetramethylsilane ( $\text{Me}_4\text{Si}$ ). All positive-ion ESI mass spectra were recorded on a Perkin-Elmer Sciex API 365 mass spectrometer. The elemental analyses were performed on an Elementar Vario EL III Analyzer. IR spectra of the solid samples as KBr discs were obtained in the range of 4000–400  $\text{cm}^{-1}$  using an AVATAR 360 FTIR spectrometer. 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-TCSPEC spectrofluorometer. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze pump-thaw cycles. Measurements of the EtOH–MeOH (4:1 v/v) glass samples at 77 K were carried out with the dilute EtOH–MeOH sample solutions contained in a quartz tube inside a liquid nitrogen-filled quartz optical Dewar flask. Luminescence quantum yields were determined by the optically dilute method described by Demas and Crosby [45] using quinine sulfate in aqueous sulfuric acid (0.5 M) as reference. Luminescence lifetimes of the samples were measured using time-correlated single photon counting (TCSPEC) technique on the TCSPEC spectrofluorometer in a Fast MCS mode with a NanoLED-375LH excitation source, which has its excitation peak wavelength at 375 nm and pulse width shorter than 750 ps. The photon counting data were analyzed by Horiba Jobin Yvon Decay Analysis Software.

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  $^n\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte at room temperature. The reference electrode was a  $\text{Ag}/\text{AgNO}_3$  (0.1 M in acetonitrile) electrode, and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with a platinum wire as the auxiliary electrode. The working electrode surface was polished with a 1  $\mu\text{m}$   $\alpha$ -alumina slurry (Linde) and then a 0.3  $\mu\text{m}$   $\alpha$ -alumina slurry (Linde) on a microcloth (Buehler Co.). The ferrocenium/ferrocene couple ( $\text{FeCp}_2^{+/0}$ ) was used as the internal reference. All solutions for electrochemical studies were deaerated with pre-purified argon gas prior to measurements.

## 2.3. Preparation of mononuclear rhenium(I) complexes

### 2.3.1. $[\text{Re}(\text{CO})_2(\text{phen})(\text{PPh}_3)(\text{CNC}_6\text{H}_4\text{NC})]\text{PF}_6$ (**1**)

$[\text{Re}(\text{CO})_2(\text{phen})(\text{PPh}_3)(\text{MeCN})]\text{CF}_3\text{SO}_3$  (148 mg, 0.17 mmol) was mixed with  $\text{CNC}_6\text{H}_4\text{NC}$  (27 mg, 0.21 mmol, 1.2 mol equiv.) in THF solution and heated at 60 °C for 1 day. After purification of the target complex by column chromatography on silica gel using dichloromethane-methanol (30:1 v/v) as eluent and subsequent metathesis reaction with ammonium hexafluorophosphate, the target complex was obtained as  $\text{PF}_6^-$  salt. Yellow solids were obtained by slowly diffusing diethyl ether vapor into a concentrated dichloromethane/methanol solution of **1**. Yield: 95 mg, 0.10 mmol; 54%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  6.97–7.01 (m, 6H, phenyl H of  $\text{PPh}_3$ ), 7.13–7.19 (m, 10H, phenyl H of  $\text{PPh}_3$ , phenyl H of isocyanide), 7.28–7.31 (m, 3H, phenyl H of  $\text{PPh}_3$ ), 7.63–7.66 (dd, 2H,  $J = 8.2$ , 5.2 Hz, 3,8-phen H's), 8.12 (s, 2H, 5,6-phen H's), 8.69–8.61 (d, 2H,  $J = 8.1$  Hz, 4,7-phen H's), 8.89–8.91 (d, 2H,  $J = 5.2$  Hz, 2,9-phen H's). ESI-MS:  $m/z$  814  $[\text{M}]^+$ . IR (KBr disc,  $\text{v}/\text{cm}^{-1}$ ) 841  $\nu(\text{P-F})$ , 1893, 1952  $\nu(\text{C=O})$ , 2119  $\nu(\text{C}\equiv\text{N})$ . Elemental Anal. Calc. for **1**· $\text{CH}_3\text{OH}$ : C, 49.65; H, 3.35; N, 5.65. Found: C, 49.37; H, 3.42; N, 5.86%.

### 2.3.2. $[\text{Re}(\text{CO})_2(\text{phen})(\text{PPh}_3)(\text{CNC}_6\text{H}_4\text{C}_6\text{H}_4\text{NC})]\text{PF}_6$ (**2**)

The titled complex was synthesized according to a procedure similar to that used for **1** except  $\text{CNC}_6\text{H}_4\text{C}_6\text{H}_4\text{NC}$  (43 mg,

0.21 mmol, 1.2 mol equiv.) was used instead of  $\text{CNC}_6\text{H}_4\text{NC}$  in the substitution reaction. The complex was obtained as yellow solid. Yield: 106 mg, 0.10 mmol; 61%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  6.99–7.04 (m, 6H, phenyl H of  $\text{PPh}_3$ ), 7.13–7.20 (m, 8H, phenyl H of  $\text{PPh}_3$ , phenyl H of isocyanide), 7.28–7.32 (m, 4H, phenyl H of isocyanide), 7.40–7.43 (m, 2H, phenyl H of isocyanide), 7.46–7.48 (m, 3H, phenyl H of  $\text{PPh}_3$ ), 7.62–7.65 (dd, 2H,  $J = 8.3$ , 5.2 Hz, 3,8-phen H's), 8.17 (s, 2H, 5,6-phen H's), 8.62–8.64 (d, 2H,  $J = 8.2$  Hz, 4,7-phen H's), 8.89–8.90 (d, 2H,  $J = 5.2$  Hz, 2,9-phen H's). ESI-MS:  $m/z$  889  $[\text{M}]^+$ . IR (KBr disc,  $\text{v}/\text{cm}^{-1}$ ) 843  $\nu(\text{P-F})$ , 1890, 1952  $\nu(\text{C=O})$ , 2123  $\nu(\text{C}\equiv\text{N})$ . Elemental Anal. Calc. for **2**· $\text{CH}_3\text{OH}$ : C, 52.86; H, 3.49; N, 5.25. Found: C, 52.78; H, 3.64; N, 5.53%.

## 2.4. Preparation of dinuclear rhenium(I) complexes

### 2.4.1. $[(\text{PPh}_3)(\text{phen})(\text{CO})_2\text{Re}(\text{CNC}_6\text{H}_4\text{NC})\text{Re}(\text{CO})_2(\text{phen})(\text{PPh}_3)]\text{PF}_6$ (**3**)

$[\text{Re}(\text{CO})_2(\text{phen})(\text{PPh}_3)(\text{MeCN})]\text{CF}_3\text{SO}_3$  (50 mg, 0.06 mmol) was mixed with  $\text{CNC}_6\text{H}_4\text{NC}$  (4 mg, 0.03 mmol, 0.45 mol equiv.) in THF solution and heated at ca. 60 °C for 2 days. After removal of solvent, the residue was purified by column chromatography on silica gel using dichloromethane-acetone (2:1 v/v) as eluent. Subsequent metathesis reaction with ammonium hexafluorophosphate gave the target complex as  $\text{PF}_6^-$  salt. Analytically pure yellow crystalline solids were obtained by the slow diffusion of diethyl ether vapor into a dichloromethane/methanol solution (10:1 v/v) of **3**. Yield: 71 mg, 0.04 mmol; 66%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 298 K):  $\delta$  6.99 (s, 4H, phenyl H of isocyanide), 7.04–7.07 (m, 12H, phenyl H of  $\text{PPh}_3$ ), 7.16–7.20 (m, 12H, phenyl H of  $\text{PPh}_3$ ), 7.28–7.32 (m, 6H, phenyl H of  $\text{PPh}_3$ ), 7.62–7.66 (dd, 4H,  $J = 8.2$ , 5.2 Hz, 3,8-phen H's), 8.02 (s, 4H, 5,6-phen H's), 8.53–8.55 (d, 4H,  $J = 8.2$  Hz, 4,7-phen H's), 9.04–9.05 (d, 4H,  $J = 5.2$  Hz, 2,9-phen H's). ESI-MS:  $m/z$  1644  $[\text{M-PF}_6]^+$ . IR (KBr disc,  $\text{v}/\text{cm}^{-1}$ ) 839  $\nu(\text{P-F})$ , 1883, 1947  $\nu(\text{C=O})$ , 2109  $\nu(\text{C}\equiv\text{N})$ . Elemental Anal. Calc. for **3**: C, 48.30; H, 2.98; N, 4.69. Found C, 48.15; H, 3.00; N, 4.72%.

### 2.4.2. $[(\text{PPh}_3)(\text{phen})(\text{CO})_2\text{Re}(\text{CNC}_6\text{H}_4\text{C}_6\text{H}_4\text{NC})\text{Re}(\text{CO})_2(\text{phen})(\text{PPh}_3)]2\text{PF}_6$ (**4**)

The titled complex was synthesized according to a procedure similar to that used for **3** except  $\text{CNC}_6\text{H}_4\text{C}_6\text{H}_4\text{NC}$  (6 mg, 0.03 mmol, 0.45 mol equiv.) was used instead of  $\text{CNC}_6\text{H}_4\text{NC}$  in the substitution reaction. Analytically pure yellow crystals were obtained by the slow diffusion of diethyl ether vapor into a dichloromethane/methanol solution (10:1 v/v) of **4**. Yield: 75 mg, 0.04 mmol; 65%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 298 K):  $\delta$  7.05–7.10 (m, 12H, phenyl H of  $\text{PPh}_3$ ), 7.11–7.13 (d, 4H,  $J = 8.9$  Hz, phenyl H of isocyanide), 7.18–7.22 (m, 12H, phenyl H of  $\text{PPh}_3$ ), 7.29–7.33 (m, 6H, phenyl H of  $\text{PPh}_3$ ), 7.45–7.47 (d, 4H,  $J = 8.8$  Hz, phenyl H of isocyanide), 7.65–7.68 (dd, 4H,  $J = 8.2$ , 5.2 Hz, 3,8-phen H's), 8.05 (s, 4H, 5,6-phen H's), 8.55–8.57 (d, 4H,  $J = 7.9$  Hz, 4,7-phen H's), 9.08–9.10 (d, 4H,  $J = 5.2$  Hz, 2,9-phen H's). ESI-MS:  $m/z$  1720  $[\text{M-PF}_6]^+$ . IR (KBr disc,  $\text{v}/\text{cm}^{-1}$ ) 841  $\nu(\text{P-F})$ , 1889, 1951  $\nu(\text{C=O})$ , 2118  $\nu(\text{C}\equiv\text{N})$ . Elemental Anal. Calc. for **4**: C, 50.16; H, 3.13; N, 4.50. Found: C, 49.97; H, 3.45; N, 4.83%.

### 2.4.3. $[(\text{phen})(\text{CO})_3\text{Re}(\text{CNC}_6\text{H}_4\text{NC})\text{Re}(\text{CO})_3(\text{phen})]2\text{PF}_6$ (**5**)

A solution of  $[\text{Re}(\text{CO})_3(\text{phen})(\text{MeCN})]\text{CF}_3\text{SO}_3$  (80 mg, 0.125 mmol) and  $\text{CNC}_6\text{H}_4\text{NC}$  (7.2 mg, 0.056 mmol, 0.45 mol equiv.) was heated in THF/MeOH (15:1 v/v) solution mixture at ca. 60 °C for 2 days. After removal of solvent, the residue was then purified by column chromatography on silica gel using dichloromethane-methanol (10:1 v/v) as eluent. Subsequent metathesis reaction with ammonium hexafluorophosphate gave the target complex as  $\text{PF}_6^-$  salt. Analytically pure crystals were obtained by slowly diffusing diethyl ether vapor into a dichloromethane/acetone solution (10:1 v/v) of **5**. Yield: 102 mg, 0.078 mmol; 62%.  $^1\text{H}$  NMR (400 MHz, MeOD, 298 K):  $\delta$  7.29 (s, 4H, phenyl H of isocyanide),

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