DOI: 10.1002/chem.201000793

# Photochemical Synthesis of Intensely Luminescent Isocyano Rhenium(I) Complexes with Readily Tunable Structural Features

**Chi-Chiu Ko,* Larry Tso-Lun Lo, Chi-On Ng, and Shek-Man Yiu**[a]

**Abstract:** A new class of readily tunable isocyano rhenium(I) diimine luminophores, *cis,cis*-$[Re(CO)_2(CNR)_2(N{-}N)]^+$ ($R = 2,4,6\text{-}Cl_3C_6H_2$, $4\text{-}ClC_6H_4$, $4\text{-}Br\text{-}2,6\text{-}(CH_3)_2C_6H_2$, $2,6\text{-}(CH_3)_2C_6H_3$, $4\text{-}[(CH_3)_2N]C_6H_4$, $4\text{-}(C_6H_5)C_6H_4$, $4\text{-}n\mathrm{Bu}C_6H_4$, *t*Bu), has been synthesized in high yield by a highly selective photochemical substitution reaction. These complexes were characterized by $^1$H NMR and IR spectroscopy, mass spectrometry, and elemental analysis. The X-ray crystal structures of one of the complexes and one of the precursor complexes for the photosubstitution reaction were also determined. As the isocyanide ligands are readily tunable, complexes with excellent solubility in benzene or other nonpolar solvents could be designed through slight modification of the isocyanide ligands with a short *n*Bu substituent. With the characteristic strong infrared absorptions of the carbonyl (C≡O) and isocyanide (C≡N) stretches as well as the high solubility of the reactant and product in benzene, which is the solvent for the photoreaction, the photosubstitution reaction of $[Re(CO)_3(n\mathrm{Bu}C_6H_4NC)_2Br]$ with 4,4′-di-*tert*-butyl-2,2′-bipyridine was also studied by in situ IR spectroscopy. The photophysical and electrochemical properties of these complexes were also investigated. Except for the complex with $[(CH_3)_2N]C_6H_4NC$ ligands, all complexes displayed intense luminescence with quantum yields of up to 0.37 in degassed $CH_2Cl_2$ solution at room temperature. These emissions were assigned as the phosphorescence derived from the metal-to-ligand charge transfer [dπ(Re)→π*(N−N)] excited state. The emissive excited states of these complexes have also been characterized by transient absorption spectroscopic studies. The capability of tuning the emissive excited-state energy through the modification of the isocyanide ligands could be reflected by the significant shifting of the phosphorescence from 530 to 620 nm with the same phenanthroline ligand.

**Keywords:** charge transfer • isocyanide ligands • luminescence • photochemistry • rhenium

## Introduction

The luminescence behavior of the rhenium(I) tricarbonyl diimine complexes was first reported by Wrighton and Morse in 1974.[1] Following these pioneering works, quite a number of rhenium(I) tricarbonyl α,α′-diimine complexes, $[Re(CO)_3(L_a)(N{-}N)]^{n+}$ ($L_a$ = axial ligand; $n = 0$ or 1), capable of displaying phosphorescence and rich excited-state properties associated with their long-lived $^3$MLCT (MLCT: metal-to-ligand charge transfer) excited state, were reported in the literature.[2] In addition to its long-lived luminescence, the characteristic intense carbonyl (C≡O) stretches, which can be readily probed by time-resolved IR spectroscopy to follow the excited-state dynamics, are exceptionally sensitive to changes of the microenvironment, conformation, as well as the electron-density distribution,[3] and therefore can serve as protein labels to study the protein dynamics.[4] Such characteristics have made this class of complex unique amongst other polypyridyl transition-metal complexes with d$^6$ metal centers, which also exhibit long-lived MLCT phosphorescence. With a suitable functionalization of the diimine ligand, these complexes can be used as building blocks for photosensitizers,[5] luminescent probes, and sensors[6] as well as the materials for electroluminescent and photovoltaic devices.[7] Although spectacular achievements and potential applications of these complexes have been demonstrated,[5–7] one of the limitations of these systems is that modification and fine-tuning of the physical and excited-state properties with their functions being maintained are challenging. Tedious organic synthesis on the diimine ligands would be required, because the carbonyl co-ligands cannot be functionalized and are difficult to substitute with other ligands,

---

[a] Dr. C.-C. Ko, L. T.-L. Lo, C.-O. Ng, Dr. S.-M. Yiu
Department of Biology and Chemistry
City University of Hong Kong
Tat Chee Avenue, Kowloon, Hong Kong (China)
Fax: (+852) 2788-7406
E-mail: vinccko@cityu.edu.hk

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000793.

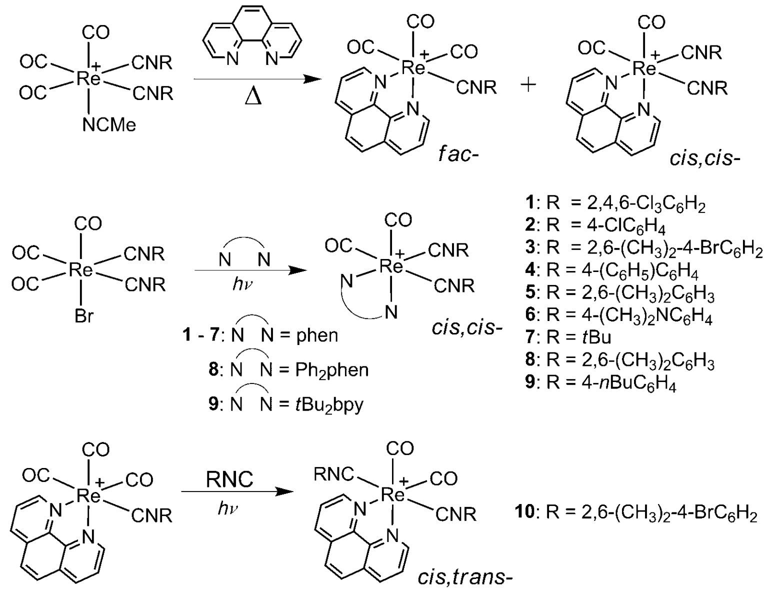
though there has been some success in the replacement of the carbonyl ligand with phosphine ligands.[8] As a consequence, the luminescence, photoreactivity, excited-state properties, and other physical properties can mainly be modified or fine-tuned by variation of the α,α′-diimine ligands and/or one ancillary ligand (monodentate axial ligand). It is anticipated that the exploration and development of rhenium(I) complex systems through the employment of other readily tunable π-accepting ligands to replace these carbonyl ligands would lead to readily tunable luminescent rhenium(I) systems with desirable as well as novel excited-state and physical properties. It would also open up the possibility for the extension of the rhenium diimine luminophore towards the construction of highly functionalized molecular systems of widely diverse solubility and property by simply altering the substituent group on the tunable π-accepting ligands.

Isocyanides (R−N≡C:), which are isoelectronic to the carbonyl ligand (O≡C:), can coordinate to the metal center (M) in a terminal mode ($L_nM{-}C{\equiv}N{-}R$). Because of their good and unique π-accepting and σ-donating ability, isocyanides can stabilize both high- and low-valent metal centers.[9] Moreover, with the synthetic methodologies[10] developed by Ugi et al.[10a] and Weber et al.,[10b] the electronic and steric features of isocyanide ligands could simply and readily be tuned through variation of the substituent on the nitrogen atom. Moreover, metal isocyanides also exhibit strong and characteristic C≡N stretches, which also allow the study of the excited-state dynamics with time-resolved IR spectroscopy. Thus, they are ideal ligands that can be used in the replacement of the carbonyl ligands to provide a tunable feature for the complexes, and can concurrently retain the feasibility of probing the complexes with IR spectroscopy so that the excited-state dynamics could also be readily investigated through time-resolved IR spectroscopy.

We have recently communicated the synthesis and photophysical studies of a new class of readily tunable tetra(isocyano) rhenium(I) diimine complexes, $[Re(CNR)_4(N{-}N)]^+$ ($R = 4\text{-}ClC_6H_4$; $4\text{-}FC_6H_4$; $2,6\text{-}(CH_3)_2C_6H_3$), with highly environment sensitive excited-state properties.[11] To enhance the capability in tuning the excited-state properties with simple and slight variations of the isocyanide ligands as well as the extension of our previous studies, which demonstrated the interesting excited-state properties associated with $[Re(CNR)_4(N{-}N)]^+$, we decided to develop another new class of isoelectronic rhenium(I) complexes containing both carbonyl and isocyanide ligands, $[Re(CO)_2(CNR)_2(N{-}N)]^+$. Since the carbonyl and isocyanide stretches are well separated, it could provide another dimension for probing the changes of the excited state as well as the microenvironment. In contrast to the most commonly used thermal ligand substitution reaction in the preparation of the rhenium(I) complexes,[1–6] novel microscale high-yield photochemical ligand substitution reactions, which show an excellent stereoselectivity for the preparation of these complexes, are reported. With the characteristic C≡O and C≡N stretches, the photochemical ligand substitution reaction has also been studied by in situ IR spectroscopy. The photophysical properties of these highly luminescent *cis*,*cis*-dicarbonyl diisocyano rhenium(I) diimine complexes are also described.

## Results and Discussion

**Synthesis and characterization**: All isocyanide ligands were synthesized by the dehydration of formamide, which can readily be prepared by either the reaction of the corresponding amine with formic acid in toluene heated at reflux or the reaction of the corresponding amine with acetic formic anhydride, by using the method developed by Ugi and co-workers.[10a] The substitution reactions of $[Re(CO)_5Br]$ with 2.05 mole equivalents of substituted isocyanide ligands (RNC) in a THF/benzene (1:1 v/v) mixture gave *fac*-$[Re(CO)_3(CNR)_2Br]$ in quantitative yield. Attempts to carry out substitution reactions on *fac*-$[Re(CO)_3(CNR)_2(MeCN)]^+$, which is prepared by reaction of *fac*-$[Re(CO)_3(CNR)_2Br]$ with silver triflate in acetonitrile under reflux heating conditions, with an excess of diimine ligands (N−N) resulted in the formation of a mixture of *cis*,*cis*-$[Re(CO)_2(CNR)_2(N{-}N)]^+$ and *fac*-$[Re(CO)_3(CNR)(N{-}N)]^+$ (Scheme 1). However, these two complexes are very difficult



Scheme 1. Synthetic routes and reactivity of rhenium isocyanide complexes. phen = 1,10-phenanthroline, bpy = bipyridine.

to separate by column chromatography. To enhance the stereoselectivity of the ligand substitution reaction, photosubstitutions of *fac*-[Re(CO)$_3$(CNR)$_2$Br] with four equivalents of diimine ligand in benzene solution were performed with broadband or UV excitation. Both excitations give *cis,cis*-[Re(CO)$_2$(CNR)$_2$(N−N)]Br (Scheme 1) as the only major product but with significantly different reaction rates. Subsequent metathesis reaction with ammonium hexafluorophosphate and recrystallization by slow diffusion of diethyl ether vapor into concentrated dichloromethane solutions of the complexes gave the analytically pure complexes as yellow to orange crystals. The *cis,trans* isomer (*cis,trans*-[Re(CO)$_2$-{CNC$_6$H$_2$(CH$_3$)$_2$-2,6-Br-4}$_2$(phen)]$^+$) can also be synthesized by stereoselective photosubstitution reaction of *fac*-[Re(CO)$_3$(CNR)(N−N)]$^+$ with acetonitrile, followed by thermal substitution reaction with the isocyanide ligands (Scheme 1). Complexes **1**–**10** and their precursor complexes, *fac*-[Re(CO)$_3$(CNR)$_2$Br], were characterized by $^1$H NMR and IR spectroscopy and ESI-MS, and gave satisfactory elemental analyses. All the precursor complexes, *fac*-[Re(CO)$_3$-(CNR)$_2$Br], display three intense carbonyl stretches in the region of 1895–2040 cm$^{-1}$, and one medium and one weak C≡N stretch in the region of 2145–2200 cm$^{-1}$, thus confirming the facial arrangement of the tricarbonyl complex in an octahedral environment.[12] The all-*cis* configuration of the ligands in complexes **1**–**9** would result in an unsymmetrical chemical environment for the two isocyanide ligands and the bipyridine or phenanthroline ligand, as revealed by the observation of two different sets of $^1$H NMR signals for the two pyridyl moieties of the bipyridine or phenanthroline ligands as well as for the two identical isocyanide ligands.

The facial carbonyl arrangement of the precursor complexes and the all-*cis* configuration of the dicarbonyl diisocyano rhenium(I) diimine complexes were confirmed by X-ray crystal structural studies. Single crystals of *fac*-[Re(CO)$_3$(CN*t*Bu)$_2$Br] and **3** suitable for X-ray diffraction studies were obtained by slow evaporation of a diethyl ether solution of *fac*-[Re(CO)$_3$(CN*t*Bu)$_2$Br] and slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of **3**, respectively. The experimental details of the crystal structure determinations and selected bond lengths and bond angles are summarized in Tables 1 and 2, respectively. Perspective drawings of [Re(CO)$_3$(CN*t*Bu)$_2$Br] and the complex cation of **3** are depicted in Figure 1. The slight deviation of the C-N-C bond angle of isocyanide ligands from linearity in both structures is attributed to the π-backbonding interaction from the rhenium metal center. For complex **3**, the rhenium metal center adopted a distorted octahedral geometry with ligands arranged in an all-*cis* configuration. The angle subtended by the nitrogen atoms of phenanthroline at the rhenium center, N(1)-Re(1)-N(2), is 75.8°, which is much smaller than the ideal angle of 90° in a regular octahedral geometry. The deviation from the ideal angle of 90° is

Table 1. Crystal and structure determination data for crystals of *fac*-[Re(CO)$_3$(CN*t*Bu)$_2$Br] and **3**.

| | [Re(CO)$_3$(CN*t*Bu)$_2$Br] | **3** |
|---|---|---|
| formula | C$_{13}$H$_{18}$BrN$_2$O$_3$Re | C$_{33}$H$_{26}$Br$_2$Cl$_2$F$_6$N$_4$O$_2$PRe |
| $M_r$ | 516.40 | 1072.47 |
| $T$ [K] | 293(2) | 173(2) |
| $a$ [Å] | 6.19900(10) | 16.2410(6) |
| $b$ [Å] | 9.9166(2) | 14.1713(4) |
| $c$ [Å] | 29.3406(3) | 17.7914(6) |
| $\alpha$ [°] | 90 | 90 |
| $\beta$ [°] | 90 | 111.937(4) |
| $\gamma$ [°] | 90 | 90 |
| $V$ [Å$^3$] | 1803.65(5) | 3798.3(2) |
| crystal color | colorless | yellow |
| crystal system | orthorhombic | monoclinic |
| space group | $P2_12_12_1$ | $P2_1/c$ |
| $Z$ | 4 | 4 |
| $F$(000) | 976 | 2064 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.902 | 1.875 |
| crystal dimensions [mm] | 0.3×0.2×0.1 | 0.4×0.3×0.1 |
| $\lambda$ [Å] (Cu$_{K\alpha}$) | 1.54178 | 1.54178 |
| $\mu$ [mm$^{-1}$] | 15.843 | 10.998 |
| collection range | $4.46 \leq \theta \leq 71.05°$<br>($h$: −7–7;<br>$k$: −11–10;<br>$l$: −35–35) | $4.11 \leq \theta \leq 66.99°$<br>($h$: −19–18;<br>$k$: −11–16;<br>$l$: −21–21) |
| completeness to $\theta$ | 99.9 % | 99.9 % |
| no. of data collected | 13 130 | 13 438 |
| no. of unique data | 3170 | 6758 |
| no. of data used in refinement, $m$ | 3156 | 5986 |
| no. of parameters refined, $p$ | 188 | 473 |
| $R$[a] | 0.0163 | 0.0545 |
| $wR$[a] | 0.0398 | 0.1550 |
| goodness-of-fit, $S$ | 1.090 | 1.127 |
| maximum shift, $(\Delta/\sigma)_{max}$ | 0.004 | 0.001 |
| residual extrema in final difference map [eÅ$^{-3}$] | +0.494, −0.283 | +2.211, −1.202 |

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

Table 2. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses for *fac*-[Re(CO)$_3$(CN*t*Bu)$_2$Br] and **3**.

| | | | | |
|---|---|---|---|---|
| [Re(CO)$_3$(CN*t*Bu)$_2$Br] | Re(1)−C(1) | 1.940(5) | C(1)−O(1) | 1.101(6) |
| | Re(1)−C(3) | 1.957(4) | C(2)−O(2) | 1.136(5) |
| | Re(1)−C(2) | 1.969(4) | C(3)−O(3) | 1.115(6) |
| | Re(1)−C(5) | 2.093(4) | C(4)−N(1) | 1.148(5) |
| | Re(1)−C(4) | 2.094(4) | C(5)−N(2) | 1.146(5) |
| | C(4)-N(1)-C(6) | 177.9(5) | C(5)-N(2)-C(10) | 171.0(4) |
| **3** | Re(1)−C(1) | 1.919(10) | C(1)−O(1) | 1.138(12) |
| | Re(1)−C(2) | 1.964(11) | C(2)−O(2) | 1.142(13) |
| | Re(1)−C(3) | 1.972(8) | C(3)−N(3) | 1.171(11) |
| | Re(1)−C(4) | 2.077(8) | C(4)−N(4) | 1.145(11) |
| | N(1)-Re(1)-N(2) | 75.8(3) | C(4)-N(4)-C(27) | 174.4(10) |
| | C(3)-N(3)-C(19) | 166.2(8) | | |

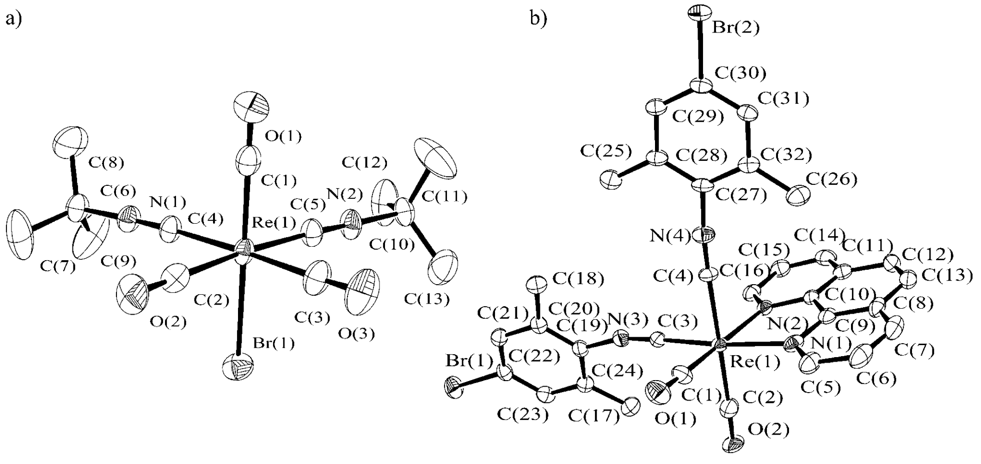


Figure 1. Perspective drawings of a) [Re(CO)$_3$(CN*t*Bu)$_2$Br] and b) the complex cation of **3** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30 % probability level.

due to the steric requirement of the chelating phenanthroline ligands, which is commonly observed in other related complex systems.[2] The isocyanide ligand *trans* to the carbonyl ligand showed longer Re–C (2.077 vs. 1.972 Å) and shorter C≡N (1.145 vs. 1.171 Å) distances with more linear bond angles of C≡N–C (174.4 vs. 166.2°) compared with that *trans* to the phenanthroline ligand. These observations are most likely attributable to competition between the isocyanide ligand and the carbonyl ligand for the π backbonding and the large *trans* influence of the carbonyl group.

The photosubstitution reaction of *fac*-[Re(CO)$_3$(CNR)$_2$Br] with diimine ligand in [D$_6$]benzene excited by UV light was also investigated by in situ IR spectroscopy, which showed the real-time IR spectral changes throughout the reaction. [D$_6$]Benzene was used as it is transparent in the IR absorption region of the C≡O and C≡N stretches of the metal carbonyl and isocyanide complexes. To obtain signals with reasonably good signal-to-noise ratio in the in situ IR spectroscopic study, high concentrations of the reactants and products are required. To ensure the complete solubility of the precursor complex and the reaction products throughout the reaction at concentrations sufficient for the in situ IR spectroscopic study, the photosubstitution reaction of the *n*-butyl-substituted isocyano rhenium(I) precursor complex with 4,4′-di-*tert*-butyl-2,2′-bipyridine (*t*Bu$_2$bpy) was investigated so that both the reactant and the major reaction product could have excellent solubility in [D$_6$]benzene. The IR spectra of a mixture of 15 mM *fac*-[Re(CO)$_3$(CNC$_6$H$_4$*n*Bu-4)$_2$Br] with 60 mM *t*Bu$_2$bpy in [D$_6$]benzene solution in the wavenumber range of 1890 to 2200 cm$^{-1}$ recorded at various times after photoexcitation at 254 nm are displayed in Figure 2 and the absorption–time profiles at selected wavenumbers are shown in the insets of Figure 2. Before UV irradiation, *fac*-[Re(CO)$_3$(CNC$_6$H$_4$*n*Bu-4)$_2$Br] displayed three C≡O (1932, 1996, and 2041 cm$^{-1}$) and two C≡N (2156 and 2190 cm$^{-1}$) stretches of the carbonyl and isocyanide ligands, respectively. On UV excitation, these C≡O and C≡N bands decreased in intensity with a single exponential decay function, from which a time constant of 85.7 min was obtained. The concomitant growth of new absorptions with a similar time constant of 88.5 min at 1910, 1962 and 2096, 2170 cm$^{-1}$, which can be assigned to the two C≡O and two C≡N stretches of the final product *cis,cis*-[Re(CO)$_2$(CNC$_6$H$_4$*n*Bu-4)$_2$(*t*Bu$_2$bpy)]Br, respectively, was also observed. The shifts of the C≡O and C≡N absorptions to lower stretching frequencies on conversion from the starting precursor complex to the final complex are in agreement with the substitution of a stronger π-accepting carbonyl ligand with the diimine ligand, thus rendering a better π-backbonding interaction between the rhenium metal center and the unsubstituted carbonyl and isocyanide ligands. Several fairly well defined isosbestic points at approximately 2180, 2142, 2054, 2027, 2010, 1983, 1942, and 1924 cm$^{-1}$ were also noted in the IR absorption spectral traces. The similar time constants for the decay of the absorptions of the starting precursor complex and the growth of absorptions of the final product as well as the apparent isosbestic points are suggestive of a clean conversion process between these two distinct species.

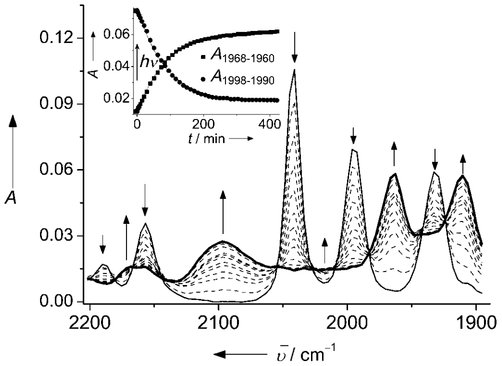


Figure 2. In situ IR spectra of a reaction mixture of 15 mM *fac*-[Re(CO)$_3$(CNC$_6$H$_4$*n*Bu-4)$_2$Br] and 60 mM *t*Bu$_2$bpy in [D$_6$]benzene solution in the wavenumber range of 1890 to 2200 cm$^{-1}$ recorded at various times (0, 20, 40, 60, 80, 120, 140, 160, 180, 240, 300, 360, and 420 min) after photoexcitation at 254 nm. The inset shows the absorption (*A*) spectral changes at selected wavenumbers.

To elucidate the mechanism of the photosubstitution reaction, the reaction between *fac*-[Re(CO)$_3$(CNC$_6$H$_4$*n*Bu-4)$_2$Br] and 10 mole equivalents of 4-*t*Bupy was also investigated. However, no disubstituted pyridyl complex, only monosubstituted *cis,cis*-[Re(CO)$_2$(CNC$_6$H$_4$*n*Bu-4)$_2$(4-*t*Bupy)Br], was isolated. This result is consistent with the previous photosubstitution study on [Re(CO)$_5$X] (X = Cl, Br, I) with pyridine (py) or triphenylphosphine (PPh$_3$) reported by Wrighton and co-workers,[13] in which only one of the equatorial carbonyl ligands of [Re(CO)$_5$X] was replaced, thus resulting in the formation of *cis*-[Re(CO)$_4$(py)X] or *cis*-[Re(CO)$_4$(PPh$_3$)X] as the only product. With reference to the photosubstitution behavior of [Re(CO)$_5$X] as well as the observation of only monoequatorial CO substitution when 4-*t*Bupy was used in the photosubstitution of *fac*-[Re(CO)$_3$(CNC$_6$H$_4$*n*Bu-4)$_2$Br], the initial step of the photosubstitution reactions of *fac*-[Re(CO)$_3$(CNC$_6$H$_4$*n*Bu-4)$_2$Br] most probably undergoes a dissociative mechanism of CO substitution similar to that of [Re(CO)$_5$X].[13] When diimine ligands were used in the photosubstitution reactions, further substitution of the bromo ligand was observed to give *cis,cis*-[Re(CO)$_2$(CNC$_6$H$_4$*n*Bu-4)$_2$(*t*Bu$_2$bpy)]Br as the final product.

**UV/Vis absorption and emission properties**: The electronic absorption spectra of **1**–**10** showed intense absorptions at 265–330 nm, with molar extinction coefficients on the order of $10^4$ $\text{M}^{-1}\text{cm}^{-1}$. With reference to the previous spectroscopic studies of the free isocyanide ligands and their transition-metal complexes,[14] these absorptions were assigned to intraligand (IL) π→π* transitions of the isocyanide and diimine moieties. For **7**, it showed a moderately intense absorption band at 430 nm, corresponding to the MLCT transition of [dπ(Re)→π*(N–N)]. For other complexes with substituted phenylisocyanide ligands, one to two additional moderately intense absorption shoulders with molar extinction coefficients on the order of $10^3$ $\text{M}^{-1}\text{cm}^{-1}$ in the region of 340–440 nm were observed, and were ascribed to mixed MLCT transitions of [dπ(Re)→π*(RNC)] and [dπ(Re)→π*(N–N)] and with some mixing of a [π(RNC)→π*(N–N)] ligand-to-ligand charge transfer (LLCT) transition.[2m,8,14] The lowest-energy absorption shoulders showed an energy dependence on the π-accepting ability of the diimine and the isocyanide ligands, in agreement with an assignment of a predominant MLCT [dπ(Re)→π*(N–N)] transition. The photophysical data of complexes **1**–**10** are summarized in Table 3.

Table 3. Photophysical data for complexes **1**–**10**.

| Complex | Medium ($T$ [K]) | Emission[a] $\lambda_{em}$ [nm] ($\tau_o$ [μs]) | $\phi_{em}$[b] | Absorption[c] $\lambda_{abs}$ [nm] ($\varepsilon$ [$\text{M}^{-1}\text{cm}^{-1}$]) |
|---|---|---|---|---|
| **1** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 530 (3.37)<br>497 (10.5) | 0.37 | 255 (43 770), 273 (49 950), 316 (25 960), 366 (14 550), 413 sh (3980) |
| **2** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 553 (2.97)<br>517 (11.3) | 0.34 | 272 (68 040), 325 (20 370), 355 (14 210), 426 sh (4100) |
| **3** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 551 (3.17)<br>510 (8.85) | 0.35 | 272 (73 380), 324 (20 370), 357 (14 330), 427 sh (3800) |
| **4** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 558 (3.29)<br>515 (10.7) | 0.28 | 275 (65 110), 285 (65 750), 310 (47 800), 360 (20 700), 427 sh (5230) |
| **5** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 562 (2.88)<br>508 (8.89) | 0.31 | 269 (70 930), 320 (14 190), 355 (10 880), 428 sh (3350) |
| **6** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 620 (0.002)<br>553 (8.10) | 0.006 | 272 (68 040), 325 (20 370), 355 (14 210), 460 sh (3780) |
| **7** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 576 (1.72)<br>528 (12.5) | 0.08 | 262 (39 430), 288 (16 610), 369 (5780), 430 sh (3050) |
| **8** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 573 (5.45)<br>532 (15.4) | 0.31 | 279 (486200), 350 (10 460), 440 sh (3240) |
| **9** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 556 (0.90)<br>503 (4.54) | 0.23 | 246 (39 550), 275 (56 630), 352 (10 400), 425 sh (2970) |
| **10** | CH$_2$Cl$_2$ (298)<br>glass[d] (77) | 555 (2.17)<br>513 (6.92) | 0.30 | 267 (43 210), 294 (40 520), 329 (19 790), 352 (17 040), 411 sh (3820) |

[a] Excitation at 400 nm. Emission maxima are uncorrected values. [b] Luminescence quantum yield with excitation at 436 nm. [c] Dichloromethane at 298 K. sh = shoulder. [d] EtOH–MeOH (4:1 v/v).

With the exception of complex **6**, all complexes in CH$_2$Cl$_2$ solution at room temperature display long-lived ($\tau_o$ = 0.90–3.3 μs) and intense yellow to orange-red emission (Figure 3a) with luminescence quantum yields in the range of 0.08–0.37 with 436 nm excitation (Table 3). These structureless emission bands show a large variation in the emission maxima for the same phenanthroline ligand as a function of the isocyanide ligand (CNR) with 530, 551, 553, 558, 562, 578, and 620 nm for R = 2,4,6-Cl$_3$C$_6$H$_2$, 4-Br-2,6-(CH$_3$)$_2$C$_6$H$_2$, 4-ClC$_6$H$_4$, 2,6-(CH$_3$)$_2$C$_6$H$_3$, 4-(C$_6$H$_5$)C$_6$H$_4$, *t*Bu, and 4-[(CH$_3$)$_2$N]C$_6$H$_4$, respectively. This emission energy is in line with the decreasing π-accepting ability of the isocyanide ligands, which is suggestive of an assignment of a $^3$MLCT [dπ(Re)→π*(N–N)] origin. The higher MLCT [dπ(Re)→π*(N–N)] energy for the complexes with better π-accepting isocyanide ligands can be attributed to the better stabilization of the dπ(Re) orbital as a result of the stronger interaction between the dπ(Re) and π*(RNC) orbitals. This has also been supported by the more positive potential for the metal-centered oxidation of complexes with better π-accepting isocyanide ligands (see below). Through alteration of the substituents on the isocyanide ligands and the corresponding interactions, the phosphorescence can be readily shifted from 530 to 620 nm with the same phenanthroline ligand. Consequently, it can provide a simple and predicta-

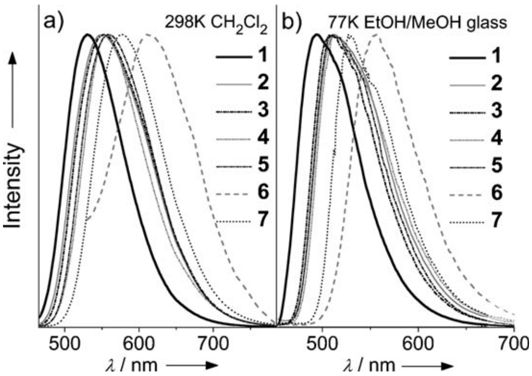


Figure 3. Normalized emission spectra of [Re(CO)$_2$(CNR)$_2$(phen)]$^+$ (complexes **1**–**7**) in a) CH$_2$Cl$_2$ solution at 298 K and b) EtOH–MeOH (4:1 v/v) glass at 77 K.

ble way of tuning the emissive excited state with desirable energy.

Moreover, the luminescence quantum yields of the MLCT phosphorescence of this class of complexes are fairly high, which may be attributed to the strong ligand-field strengths of the carbonyl and isocyanide ligands that led to an increase in the energy of the common deactivating d–d ligand-field state. The extended microsecond excited-state lifetimes for these emissions are also supportive of a phosphorescence assignment. In contrast to the analogous carbonyl complex $[Re(bpy)(CO)_4]^+$, which was found to show structured LC phosphorescence (448 nm) with the triplet ligand-centered ($^3$LC) state as the lowest-lying emissive state,[15] the much lower energy MLCT state for complexes **1**–**10** can be rationalized by the higher basicity of the isocyanide ligands compared to that of the carbonyl ligands that results in the formation of a higher-lying dπ(Re) orbital. The much lower quantum yield for complex **6** is probably due to the presence of the lone-pair electrons on the dimethylamino groups, which can quench the emissive $^3$MLCT state by photoinduced electron transfer. Unlike $[Re(CNR)_4(N{-}N)]^+$,[11] which show highly environment sensitive MLCT emissions, the MLCT absorption and emission of $[Re(CO)_2(CNR)_2(N{-}N)]^+$ are only slightly shifted with different solvents.

All complexes also exhibit intense luminescence with a structureless emission band in low-temperature 77 K EtOH–MeOH (4:1 v/v) glass. A similar emission energy dependence (Figure 3b) and a blueshift in emission energies relative to those in the solution state were also observed. Such a blueshift is typical for the MLCT phosphorescence in other related metal complexes.[1a,2k,16] These emissions have also been assigned as being derived from an excited state of $^3$MLCT [dπ(Re)→π*(N−N)] origin.

To provide further insights into the nature of the emissive excited states of these complexes, transient absorption spectroscopy on a nanosecond to microsecond timescale after 355 nm nanosecond laser excitation was carried out on acetonitrile solutions of complexes **1**–**3**, **5**, and **7**, which have the common phenanthroline ligand with various isocyanide ligands. In general, all complexes display two absorption features peaking at approximately 300–310 and 480–520 nm, respectively (Figure 4 and Figure S2, Supporting Information). However, the transient absorption signals at $\lambda > 520$–570 nm (depending on the emission energy for different complexes) could not be obtained as they overlapped significantly with the photoluminescence of the complexes (Figure S2, Supporting Information). The transient absorption decays for all the complexes follow first-order exponential kinetics with lifetimes consistent with their corresponding luminescence intensity decays. The close agreement of these decay profiles with the phosphorescence decays is suggestive of their identical origin. Complex **7** shows very intense absorption at 308 nm and broad absorption at 510 nm in the transient absorption spectra. In view of the close resemblance of these absorption features with the transient absorption spectrum of $[Re(CO)_3(phen)Cl]$[2b] and the absorptions of the phenanthroline anion radical,[17] these absorptions are ascribed to the reduced phenanthroline anion radical, typical of the absorption of the triplet MLCT state. In contrast to **7**, complexes **1**–**3** and **5** only show very weak to weak absorptions at about 300–310 nm with very strong ground-state bleaching at 310–400 nm, at which **1**–**3** and **5** showed stronger ground-state absorptions than **7** (Figures S1 and S2f, Supporting Information). With reference to the previous spectroscopic studies of the related metal isocyanide complexes,[14] this ground-state bleaching is most likely associated with the MLCT [dπ(Re)→π*(RNC)], LLCT [π(RNC)→π*(phen)], and MLCT [dπ(Re)→π*(phen)] transitions. The weaker ground-state absorption and the absence of the ground-state bleaching for **7** in the region of 310–400 nm is consistent with the much higher energies for MLCT [dπ(Re)→π*(*t*BuNC)] and LLCT [π(*t*BuNC)→π*(phen)] transitions as a result of the much lower-lying π and higher-lying π* orbitals of the isocyanide ligands for the nonconjugated *tert*-butyl substituent.[14c] In light of the close similarity of the absorptions in the visible region and the weak absorption at approximately 300 nm for these complexes and **7**, the transient absorptions for these complexes are also tentatively assigned to the absorptions of the reduced phenanthroline, characteristic of the triplet MLCT excited state.

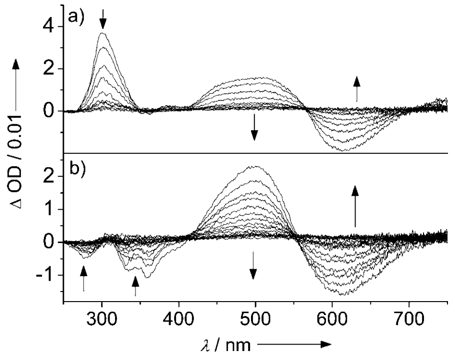


Figure 4. Transient difference spectra of a) **7** and b) **2** in MeCN solution at 298 K obtained after 355 nm nanosecond excitation at different time delays: a) 0, 0.2, 0.5, 0.8, 1.2, 1.6, 2.0, 2.5, 3.0, and 4.0 μs; b) 0, 0.4, 0.8, 1.2, 1.6, 2.2, 2.8, 3.4, 4.0, 5.2, 5.8, and 8.2 μs. OD: optical density.

**Electrochemistry**: The electrochemical properties of the complexes were investigated by cyclic voltammetry. All complexes displayed a quasi-reversible oxidation and a quasi-reversible reduction couple at $E_{1/2}$ in the range of +1.07 to +1.58 V versus SCE and −1.26 to −1.42 V versus SCE, respectively. The electrochemical data of **1**–**10** are summarized in Table 4 and representative cyclic voltammograms of **7** are shown in Figure 5. The oxidation couple is found to be dependent on the electron-richness of the metal center and thus it is sensitive to the electronic property of both the isocyanide and diimine ligands. Therefore, it is tentatively assigned to the metal-centered oxidation from $Re^I$ to $Re^{II}$, as is commonly observed in the related tricarbonyl rhenium(I) diimine system.[2a,b,5f] As a result of the stabiliza-

Table 4. Electrochemical data for **1**–**10** in acetonitrile solution (0.1 M $n\mathrm{Bu_4NPF_6}$) at 298 K.[a]

| Complex | Oxidation $E_{1/2}$ [V] versus SCE[b] ($\Delta E_p$ [mV])[c] | Reduction $E_{1/2}$ [V] versus SCE[b] ($\Delta E_p$ [mV])[c] |
|---|---|---|
| **1** | +1.58 (70) | −1.26 (70) |
| **2** | +1.40 (63) | −1.31 (62) |
| **3** | +1.41 (65) | −1.29 (65) |
| **4** | +1.35 (67) | −1.32 (68) |
| **5** | +1.38 (62) | −1.31 (72) |
| **6** | (+1.07),[d] (+1.45)[d] | −1.36 (67) |
| **7** | +1.28 (63) | −1.36 (75) |
| **8** | +1.37 (75) | −1.28 (62) |
| **9** | +1.31 (79) | −1.42 (62) |
| **10** | +1.46 (62) | −1.31 (63) |

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

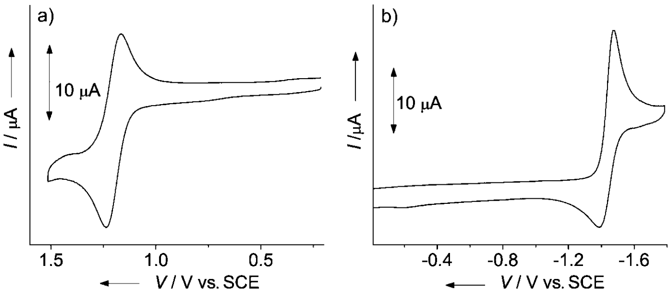


Figure 5. Cyclic voltammograms of the a) oxidative scan and b) reductive scan of **7** in MeCN (0.1 M $n\mathrm{Bu_4NPF_6}$).

tion of the metal center through the π-backbonding interaction between rhenium and the π-acceptor ligands, the potential for the Re$^{II/I}$ couple is found to show an anodic shift with increasing π-accepting ability of the isocyanide ligands for the same diimine ligand. Thus, for complexes with the phenanthroline ligand, **1** with the best π-accepting 2,4,6-$\mathrm{Cl_3C_6H_2NC}$ shows the most positive potential (+1.58 V). The observation of the second oxidation wave for **6** is ascribed to the oxidation of the $\mathrm{NMe_2}$ moiety. On the other hand, for the reduction couple, the reduction potential is dependent on the electron-richness and hence the π-accepting ability of the diimine ligands. Complex **9**, with the electron-donating *tert*-butyl substituents on the bipyridine ligand, shows the most negative potential (−1.42 V) for its reduction couple, whereas complex **8** with phenyl substituents on the phenanthroline ligand gives the least negative potential (−1.28 V), indicative of its greater ease of reduction. The strong dependence of this reduction process on the nature of the diimine ligands, together with its relative insensitivity to the nature of the isocyanide ligands, suggested the assignment of a phenanthroline- or bipyridine-based ligand-centered reduction. Similar metal-centered oxidation and diimine ligand-based reduction are also commonly observed in the related [$\mathrm{Re(CO)_3(N{-}N)X}$] complexes.[2a,b,5f]

## Conclusion

A new class of intensely luminescent isocyano rhenium(I) diimine complexes, *cis,cis*-[$\mathrm{Re(CO)_2(CNR)_2(N{-}N)}$]$^+$, with readily tunable isocyanide ligands has been synthesized in high yield through a highly selective photochemical substitution reaction of *fac*-[$\mathrm{Re(CO)_3(CNR)_2Br}$] with diimine ligands. These complexes have been characterized by $^1$H NMR and IR spectroscopy, mass spectrometry, and elemental analysis. The X-ray crystal structures of [$\mathrm{Re(CO)_3(CN}t\mathrm{Bu)_2Br}$] and *cis,cis*-[$\mathrm{Re(CO)_2(CNC_6H_2Br\text{-}4\text{-}(CH_3)_2\text{-}2,6)_2(phen)}$]$\mathrm{PF_6}$ have also been determined. The excellent yield and high selectivity of this photosubstitution reaction were revealed by in situ IR spectroscopy. The photophysical and electrochemical properties of these complexes have been investigated. Detailed studies revealed that all the complexes except **6** displayed intense long-lived luminescence with quantum yields of up to 0.37 in degassed dichloromethane solution at room temperature. These emissions were ascribed to being derived from an excited state of predominantly $^3$MLCT [dπ(Re)→π*(N−N)] origin. The emissive excited state was further investigated by transient absorption spectroscopy. With the current photochemical synthetic strategy, a new class of air-stable, robust, and highly luminescent rhenium complexes of general formula *cis,cis*-[$\mathrm{Re(CO)_2(CNR)_2(N{-}N)}$]$^+$ could be readily prepared. It has also been shown that both the physical and excited-state properties of this class of complexes could be readily tuned through the modification of either the diimine ligand or the isocyanide ligands. It is envisaged that, through rational design of diimine and isocyanide ligands with different functional properties, this class of complexes could be used in the development of photosensitizers, luminescent probes, and sensors as well as materials for electroluminescent devices and solar-energy conversion.

## Experimental Section

**Materials and reagents**: 1,10-Phenanthroline (phen), 4,7-diphenyl-1,10-phenanthroline ($\mathrm{Ph_2phen}$), 4,4′-di-*tert*-butyl-2,2′-bipyridine ($t\mathrm{Bu_2bpy}$), *tert*-butyl isocyanide, and [$\mathrm{Re_2(CO)_{10}}$] were purchased from Strem Chemical Company and used without further purification. Substituted phenyl isocyanide ligands, 4-$\mathrm{C_6H_5C_6H_4NC}$, 4-$\mathrm{ClC_6H_4NC}$, 2,4,6-$\mathrm{Cl_3C_6H_2NC}$, 2,6-$\mathrm{(CH_3)_2}$-4-$\mathrm{BrC_6H_2NC}$, 4-[$\mathrm{(CH_3)_2N}$]$\mathrm{C_6H_4NC}$, 4-$n\mathrm{BuC_6H_4NC}$, and 2,6-$\mathrm{(CH_3)_2C_6H_3NC}$, were prepared from the corresponding substituted anilines by using the synthetic methodology developed by Ugi and co-workers.[10a,18] [$\mathrm{Re(CO)_5Br}$] and [$\mathrm{Re(CO)_3\{CNC_6H_2Br\text{-}4\text{-}(CH_3)_2\text{-}2,6\}(phen)}$]$\mathrm{PF_6}$ were synthesized according to modified literature procedures for the related metal complexes.[2m,19] All solvents were of analytical reagent grade and were used without further purification.

**Physical measurements and instrumentation**: Photosubstitution reactions were carried out either by broadband excitation with a 120 W PAR 38 incandescent lamp or UV-light excitation with a Pen-Ray mercury lamp (11SC-1; $\lambda = 254$ nm). $^1$H NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane ($\mathrm{Me_4Si}$). 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. In situ IR spectra for the photochemical ligand substitution reaction in [D$_6$]benzene solution were recorded by the attenuated total reflection (ATR) method on a Mettler Toledo ReactIR 45m spectrometer equipped with a flexible AgX fiber conduit and 9.5 mm SiComp immersion probe.

Electronic absorption spectra were recorded on a Hewlett–Packard 8453 diode-array spectrophotometer. Steady-state emission and excitation spectra at room temperature and at 77 K were recorded on a Horiba Jobin Yvon Fluorolog-3-TCSPC spectrofluorometer. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze–pump–thaw cycles. Measurements of the EtOH–MeOH (4:1 v/v) glass samples at 77 K were carried out with the dilute EtOH–MeOH sample solutions contained in a quartz tube inside a liquid-nitrogen-filled quartz optical Dewar flask. Luminescence quantum yields were determined by using the optical dilution method described by Demas and Crosby[20] with an aqueous solution of [Ru(bpy)$_3$]Cl$_2$ ($\phi_{em}=0.042$[21] with 436 nm excitation) as the reference. Luminescence lifetimes of the samples were measured by the time-correlated single photon counting (TCSPC) technique on a TCSPC spectrofluorometer in the fast MCS mode with a NanoLED-375LH excitation source, which had 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. Transient absorption spectra at room temperature were recorded by using the spectral mode on an Edinburgh Instruments LP920-KS spectrometer equipped with an intensified charge-coupled device (ICCD) detector. The excitation source for the transient absorption measurement was the third harmonic output (355 nm; 6–8 ns fwhm pulse width) of a Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd:YAG laser (10 Hz).

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc., Model CHI 620 electrochemical analyzer. Electrochemical measurements were performed in acetonitrile solutions with $n$Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte at room temperature. The reference electrode was a 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 auxiliary 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.

**X-ray crystal structure determination**:[22] The crystal structures were determined on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer using graphite-monochromated Cu$_{K\alpha}$ radiation ($\lambda=1.54178$ Å). The structure was solved by direct methods employing the SHELXL-97 program.[23] Re 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.[23] In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by the program SHELXL-97.[23] The positions of H atoms were calculated based on the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final $R$ indices. CCDC-771483 ([Re(CO)$_3$(CN$t$Bu)$_2$Br]) and CCDC-771484 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Syntheses**: All ligand substitution reactions were carried out under strictly anaerobic conditions in an inert atmosphere of argon by using standard Schlenk techniques.

**General synthetic procedure for *fac*-[Re(CO)$_3$(CNR)$_2$Br]**: A mixture of [Re(CO)$_5$Br] (100 mg, 0.25 mmol) and the corresponding isocyanide ligand (0.51 mmol, 2.05 mole equiv) was dissolved in THF/benzene (1:1 v/v; 30 mL). The resulting solution was heated to reflux for 10 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with dichloromethane/$n$-hexane as eluent. Crystallization by slow evaporation of a concentrated diethyl ether or acetone solution of the complex gave the analytically pure complex as off-white crystals.[24]

***cis,cis*-[Re(CO)$_2$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$(phen)]PF$_6$ (1)**: A mixture of *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$Br] (100 mg, 0.13 mmol) and 1,10-phenanthroline (95 mg, 0.52 mmol, 4 mole equiv) was dissolved in argon-degassed benzene (20 mL). The resulting solution was then irradiated with UV light ($\lambda=254$ nm) for 2.5 h at room temperature with a Pen-Ray mercury lamp (11SC-1) in a water-cooled quartz jacket, during which the solution gradually turned orange and yellow solids precipitated. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with dichloromethane/methanol (19:1 v/v) as eluent. The residue was then redissolved in methanol (2 mL). Subsequent metathesis reaction with a saturated methanolic solution of ammonium hexafluorophosphate gave the target complex as a PF$_6^-$ salt. Yellow crystals were obtained from slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of **1**. Yield 70% (90 mg, 0.09 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta=7.28$ (s, 2H; phenyl H), 7.53 (s, 2H; phenyl H), 8.05 (dd, $J=5.3$, 8.2 Hz, 1H; 3-phen H), 8.13 (dd, $J=5.3$, 8.2 Hz, 1H; 8-phen H), 8.26 (d, $J=8.8$ Hz, 1H; 5-phen H), 8.30 (d, $J=8.8$ Hz, 1H; 6-phen H), 8.85 (d, $J=8.2$ Hz, 1H; 4-phen H), 8.92 (d, $J=8.2$ Hz, 1H; 7-phen H), 9.48 (d, $J=5.2$ Hz, 1H; 9-phen H), 9.53 ppm (d, $J=5.2$ Hz, 1H; 2-phen H); ESI-MS: $m/z$ 836 $[M]^+$; IR (KBr disc): $\tilde{\nu}=838$ $\nu$(P−F), 1928, 1972 $\nu$(C≡O), 2056, 2148 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **1**: C 34.31, H 1.23, N 5.72; found: C 34.06, H 1.48, N 5.80.

***cis,cis*-[Re(CO)$_2$(CNC$_6$H$_4$Cl-4)$_2$(phen)]PF$_6$ (2)**: The complex was synthesized according to a procedure similar to that used for **1**, except that *fac*-[Re(CO)$_3$(CNC$_6$H$_4$Cl-4)$_2$Br] (82 mg, 0.13 mmol) was used in place of *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$Br] in the substitution reaction. Yield 73% (80 mg, 0.09 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta=7.00$–7.56 (m, 8H; phenyl H), 7.93 (dd, $J=5.2$, 8.3 Hz, 1H; 3-phen H), 8.11 (d, $J=8.9$ Hz, 1H; 5-phen H), 8.16 (d, $J=8.9$ Hz, 1H; 6-phen H), 8.22 (dd, $J=5.2$, 8.3 Hz, 1H; 8-phen H), 8.66 (dd, $J=1.3$, 8.3 Hz, 1H; 4-phen H), 8.70 (dd, $J=1.3$, 8.3 Hz, 1H; 7-phen H), 9.53 (dd, $J=1.3$, 5.2 Hz, 1H; 9-phen H), 9.64 ppm (dd, $J=1.3$, 5.2 Hz, 1H; 2-phen H); ESI-MS: $m/z$ 697 $[M]^+$; IR (KBr disc): $\tilde{\nu}=838$ $\nu$(P−F), 1905, 1968 $\nu$(C≡O), 2107, 2169 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **2**: C 39.92, H 1.91, N 6.65; found: C 40.12, H 2.10, N 6.66.

***cis,cis*-[Re(CO)$_2$(CNC$_6$H$_2$Br-4-(CH$_3$)$_2$-2,6)$_2$(phen)]PF$_6$ (3)**: The complex was synthesized according to a procedure similar to that used for **1**, except that *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Br-4-(CH$_3$)$_2$-2,6)$_2$Br] (100 mg, 0.13 mmol) was used in place of *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$Br] in the substitution reaction. Yield 62% (80 mg, 0.08 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta=1.83$ (s, 6H; methyl H), 2.55 (s, 6H; methyl H), 7.11 (s, 2H; phenyl H), 7.36 (s, 2H; phenyl H), 7.99 (dd, $J=5.1$, 8.2 Hz, 1H; 3-phen H), 8.18 (dd, $J=5.1$, 8.2 Hz, 1H; 8-phen H), 8.21 (d, $J=8.8$ Hz, 1H; 5-phen H), 8.26 (d, $J=8.8$ Hz, 1H; 6-phen H), 8.77 (dd, $J=1.3$, 8.2 Hz, 1H; 4-phen H), 8.86 (dd, $J=1.3$, 8.2 Hz, 1H; 7-phen H), 9.48 (dd, $J=1.3$, 5.1 Hz, 1H; 9-phen H), 9.53 (dd, $J=1.3$, 5.1 Hz, 1H; 2-phen H); ESI-MS: $m/z$ 843 $[M]^+$; IR (KBr disc): $\tilde{\nu}=838$ $\nu$(P−F), 1913, 1968 $\nu$(C≡O), 2085, 2151 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **3**: C 38.66, H 2.45, N 5.67; found: C 38.42, H 2.72, N 5.66.

***cis,cis*-[Re(CO)$_2$(CNC$_6$H$_4$C$_6$H$_5$-4)$_2$(phen)]PF$_6$ (4)**: The complex was synthesized according to a procedure similar to that used for **1**, except *fac*-[Re(CO)$_3$(CNC$_6$H$_4$C$_6$H$_5$-4)$_2$Br] (92 mg, 0.13 mmol) was used in place of *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$Br] in the substitution reaction. Yield 50% (60 mg, 0.06 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta=7.29$–7.76 (m, 18H; phenyl H), 7.97 (dd, $J=5.2$, 8.2 Hz, 1H; 3-phen H), 8.16 (d, $J=9.1$ Hz, 1H; 5-phen H), 8.19–8.26 (m, 2H; 6,8-phen H), 8.71 (d, $J=8.2$ Hz, 1H; 4-phen H), 8.79 (d, $J=8.2$ Hz, 1H; 7-phen H), 9.56 (d, $J=5.2$ Hz, 1H; 9-phen H), 9.64 ppm (d, $J=5.2$, Hz, 1H; 2-phen H); ESI-MS: $m/z$ 781 $[M]^+$; IR (KBr disc): $\tilde{\nu}=838$ $\nu$(P−F), 1909, 1961 $\nu$(C≡O), 2093, 2151 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **4**·CH$_2$Cl$_2$: C 48.72, H 2.79, N 5.54; found: C 48.92, H 2.75, N 5.64.

***cis,cis*-[Re(CO)$_2$(CNC$_6$H$_3$(CH$_3$)$_2$-2,6)$_2$(phen)]PF$_6$ (5)**: The complex was synthesized according to a procedure similar to that for **1**, except *fac*-[Re(CO)$_3$(CNC$_6$H$_3$(CH$_3$)$_2$-2,6)$_2$Br] (80 mg, 0.13 mmol) was used in place of *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$Br] in the substitution reaction. Yield

65% (70 mg, 0.08 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 1.84$ (s, 6H; methyl H), 2.58 (s, 6H; methyl H), 6.94–7.21 (m, 6H; phenyl H), 7.99 (dd, $J = 5.2$, 8.2 Hz, 1H; 3-phen H), 8.01 (dd, $J = 5.2$, 8.2 Hz, 1H; 8-phen H), 8.27 (d, $J = 8.9$ Hz, 1H; 5-phen H), 8.36 (d, $J = 8.9$ Hz, 1H; 6-phen H), 8.83 (dd, $J = 1.3$, 8.2 Hz, 1H; 4-phen H), 9.00 (dd, $J = 1.3$, 8.2 Hz, 1H; 7-phen H), 9.49 (dd, $J = 1.3$, 5.2 Hz, 1H; 9-phen H), 9.54 ppm (dd, $J = 1.3$, 5.2 Hz, 1H; 2-phen H); ESI-MS: *m/z* 685 $[M]^+$; IR (KBr disc): $\tilde{\nu} = 838$ $\nu$(P−F), 1902, 1957 $\nu$(C≡O), 2089, 2155 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **5**: C 46.32, H 3.16, N 6.75; found: C 46.10, H 3.27, N 6.41.

***cis,cis*-[Re(CO)$_2$(CNC$_6$H$_4$(N(CH$_3$)$_2$)-4)$_2$(phen)]PF$_6$ (6)**: The complex was synthesized according to a procedure similar to that used for **1**, except *fac*-[Re(CO)$_3$(CNC$_6$H$_4$(N(CH$_3$)$_2$)-4)$_2$Br] (84 mg, 0.13 mmol) was used in place of *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$Br] in the substitution reaction. Yield 44% (60 mg, 0.07 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta =$ 2.91 (s, 6H; *N*-methyl H), 3.05 (s, 6H; *N*-methyl H), 6.43–7.40 (m, 8H; phenyl H), 7.91 (dd, $J = 5.1$, 8.2 Hz, 1H; 3-phen H), 8.01 (m, 2H; 5,8-phen H), 8.22 (d, $J = 8.9$ Hz, 1H; 6-phen H), 8.68 (dd, $J = 1.3$, 8.2 Hz, 1H; 4-phen H), 8.80 (dd, $J = 1.3$, 8.2 Hz, 1H; 7-phen H), 9.49 (dd, $J = 1.3$, 5.1 Hz, 1H; 9-phen H), 9.53 ppm (dd, $J = 1.3$, 5.1 Hz, 1H; 2-phen H); ESI-MS: *m/z* 715 $[M]^+$; IR (KBr disc): $\tilde{\nu} = 838$ $\nu$(P−F), 1895, 1953 $\nu$(C≡O), 2107, 2159 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **6**: C 44.70, H 3.28, N 9.77; found: C 44.49, H 3.46, N 9.83.

***cis,cis*-[Re(CO)$_2$(CN*t*Bu)$_2$(phen)]PF$_6$ (7)**: The complex was synthesized according to a procedure similar to that used for **1**, except that *fac*-[Re(CO)$_3$(CN*t*Bu)$_2$Br] (66 mg, 0.13 mmol) was used in place of *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$Br] in the substitution reaction. Yield 42% (40 mg, 0.05 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 1.21$ (s, 9H; methyl H), 1.69 (s, 9H; methyl H), 7.85–7.88 (m, 1H; 3-phen H), 8.12–8.22 (m, 3H; 5,6,8-phen H), 8.63 (dd, $J = 1.2$, 8.2 Hz, 1H; 4-phen H), 8.73 (dd, $J = 1.3$, 8.2 Hz, 1H; 7-phen H), 9.35 (dd, $J = 1.2$, 5.1 Hz, 1H; 9-phen H), 9.46 ppm (dd, $J = 1.3$, 5.1 Hz, 1H; 2-phen H); ESI-MS: *m/z* 589 $[M]^+$; IR (KBr disc): $\tilde{\nu} = 838$ $\nu$(P−F), 1895, 1953 $\nu$(C≡O), 2129, 2173 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **7**: C 39.29, H 3.57, N 7.64; found: C 39.29, H 3.80, N 7.61.

***cis,cis*-[Re(CO)$_2$(CNC$_6$H$_3$(CH$_3$)$_2$-2,6)$_2$(Ph$_2$phen)]PF$_6$ (8)**: The complex was synthesized according to a procedure similar to that for **5**, except Ph$_2$phen (173 mg, 0.52 mmol) was used in place of phen in the substitution reaction. Yield 63% (80 mg, 0.08 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 1.97$ (s, 6H; methyl H), 2.61 (s, 6H; methyl H), 6.97–7.20 (m, 6H; phenyl H), 7.58–7.68 (m, 10H; phenyl H), 7.88 (d, $J =$ 5.4 Hz, 1H; 6-phen H), 8.10 (d, $J = 5.4$ Hz, 1H; 7-phen H), 8.19–8.24 (m, 2H; 3,8-phen H), 9.58 (d, $J = 5.4$ Hz, 1H; 9-phen H), 9.60 ppm (d, $J =$ 5.4 Hz, 1H; 2-phen H); ESI-MS: *m/z* 837 $[M]^+$; IR (KBr disc): $\tilde{\nu} = 838$ $\nu$-(P−F), 1913, 1964 $\nu$(C≡O), 2089, 2151 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **8**$\cdot$Et$_2$O: C 54.59, H 4.20, N 5.31; found: C 54.87, H 4.21, N 5.05.

***cis,cis*-[Re(CO)$_2$(CNC$_6$H$_4$*n*Bu-4)$_2$(*t*Bu$_2$bpy)]PF$_6$ (9)**: The complex was synthesized according to a procedure similar to that used for **1**, except *fac*-[Re(CO)$_3$(CNC$_6$H$_4$*n*Bu-4)$_2$Br] (87 mg, 0.13 mmol) and *t*Bu$_2$bpy (140 mg, 0.52 mmol) were used in place of *fac*-[Re(CO)$_3$(CNC$_6$H$_2$Cl$_3$-2,4,6)$_2$Br] and phen in the substitution reaction. Yield 63% (80 mg, 0.08 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 0.85$–0.96 (m, 6H; CH$_2$CH$_2$CH$_2$*CH$_3$*), 1.26–1.42 (m, 4H; CH$_2$CH$_2$*CH$_2$*CH$_3$), 1.49 (d, $J =$ 2.0 Hz, 18H; *t*Bu H), 1.59–1.72 (m, 4H; CH$_2$*CH$_2$*CH$_2$CH$_3$), 2.55 (t, $J =$ 7.6 Hz, 2H; *CH$_2$*CH$_2$CH$_2$CH$_3$), 2.67 (t, $J = 7.6$ Hz, 2H; *CH$_2$*CH$_2$CH$_2$CH$_3$), 7.14–7.39 (m, 8H; phenyl H), 7.51–7.56 (m, 1H; 5-bpy H), 7.71–7.75 (m, 1H; 5′-bpy H), 8.35 (s, 2H; 3,3′-bpy H), 8.99 (d, $J = 3.9$ Hz, 1H; 6-bpy H), 9.00 ppm (d, $J = 3.9$ Hz, 1H; 6′-bpy H); ESI-MS: *m/z* 829 $[M]^+$; IR (KBr disc): $\tilde{\nu} = 842$ $\nu$(P−F), 1913, 1964 $\nu$(C≡O), 2100, 2159 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **9**$\cdot$Et$_2$O: C 52.71, H 5.77, N 5.35; found: C 52.97, H 5.61, N 5.41.

***cis,trans*-[Re(CO)$_2$(CNC$_6$H$_2$Br-4-(CH$_3$)$_2$-2,6)$_2$(phen)]PF$_6$ (10)**: [Re(CO)$_3$(phen)(CNC$_6$H$_2$Br-4-(CH$_3$)$_2$-2,6)]PF$_6$ (104 mg, 0.13 mmol) was added to a solution of 2,6-(CH$_3$)$_2$-4-BrC$_6$H$_2$NC (34 mg, 0.16 mmol) in argon-degassed THF (30 mL). The resulting solution was then irradiated with UV light ($\lambda = 254$ nm) for 5 h at room temperature with a Pen-Ray mercury lamp (11SC-1) in a water-cooled quartz jacket. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with dichloromethane/acetone (7:3 v/v) as eluent. Subsequent recrystallization by slow diffusion of diethyl ether vapor into a concentrated methanolic solution of **10** afforded the analytically pure complex as a light yellow powder. Yield 31% (40 mg, 0.04 mmol); $^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta = 1.91$ (s, 12H; methyl H), 7.15 (s, 4H; phenyl H), 8.07 (dd, $J = 5.3$, 8.1 Hz, 2H; 3,8-phen H), 8.30 (s, 2H; 5,6-phen H), 8.89 (d, $J = 8.1$ Hz, 2H; 4,7-phen H), 9.46 ppm (d, $J =$ 5.3 Hz, 2H; 2,9-phen H); ESI-MS: *m/z* 843 $[M]^+$; IR (KBr disc): $\tilde{\nu} = 838$ $\nu$(P−F), 1906, 1975 $\nu$(C≡O), 2096 cm$^{-1}$ $\nu$(N≡C); elemental analysis calcd (%) for **10**: C 38.66, H 2.45, N 5.67; found: C 38.91, H 2.75, N 5.64.

## Acknowledgements

The work described herein was supported by an RGC GRF grant from the Research Grants Council of Hong Kong (Project No. CityU 101008) and a grant from City University of Hong Kong (Project No. 7008032). The flash photolysis system was supported by a Special Equipment Grant from the University Grants Committee of Hong Kong (SEG CityU02). L.T.-L.L. acknowledges the receipt of a Postgraduate Studentship from the City University of Hong Kong. Prof. I. T. Horváth and Q. Long are gratefully acknowledged for their advice on the in situ IR spectroscopic measurement. Prof. V. W.-W. Yam is also thanked for her helpful comments and discussions.

---

[1] a) M. S. Wrighton, D. L. Morse, *J. Am. Chem. Soc.* **1974**, *96*, 998–1003; b) J. C. Luong, H. Faltynak, M. S. Wrighton, *J. Am. Chem. Soc.* **1979**, *101*, 1597–1598.

[2] a) J. C. Luong, L. Nadjo, M. S. Wrighton, *J. Am. Chem. Soc.* **1978**, *100*, 5790–5795; b) K. Kalyanasundaram, *J. Chem. Soc. Faraday Trans. 2* **1986**, *82*, 2401–2415; c) L. A. Worl, R. Duesing, P. Chen, L. D. Ciana, T. J. Meyer, *J. Chem. Soc. Dalton Trans.* **1991**, 849–858; d) L. Sacksteder, M. Lee, J. N. Demas, B. A. DeGraff, *J. Am. Chem. Soc.* **1993**, *115*, 8230–8238; e) H. Hori, F. P. A. Johnson, K. Koike, K. Takeuchi, T. Ibusuki, O. Ishitani, *J. Chem. Soc. Dalton Trans.* **1997**, 1019–1023; f) V. W.-W. Yam, V. C.-Y. Lau, K.-K. Cheung, *Organometallics* **1995**, *14*, 2749–2753; g) T. A. Oriskovich, P. S. White, H. H. Thorp, *Inorg. Chem.* **1995**, *34*, 1629–1631; h) W. B. Connick, A. J. Di Bilio, M. G. Hill, J. R. Winkler, H. B. Gray, *Inorg. Chim. Acta* **1995**, *240*, 169–174; i) R. V. Slone, D. I. Yoon, R. M. Calhoun, J. T. Hupp, *J. Am. Chem. Soc.* **1995**, *117*, 11813–11814; j) K. D. Benkstein, J. T. Hupp, C. L. Stern, *J. Am. Chem. Soc.* **1998**, *120*, 12982–12983; k) S.-S. Sun, A. J. Lees, *J. Am. Chem. Soc.* **2000**, *122*, 8956–8967; l) V. W.-W. Yam, *Chem. Commun.* **2001**, 789–796; m) J. M. Villegas, S. R. Stoyanov, W. Huang, D. P. Rillema, *Dalton Trans.* **2005**, 1042–1051; n) R. A. Kirgan, B. P. Sullivan, D. P. Rillema, *Top. Curr. Chem.* **2007**, *281*, 45–100.

[3] a) D. R. Gamelin, M. W. George, P. Glyn, F. W. Grevels, F. P. A. Johnson, W. Klotzbucher, S. L. Morrison, G. Russell, K. Schaffner, J. J. Turner, *Inorg. Chem.* **1994**, *33*, 3246–3250; b) J. R. Schoonover, G. F. Strouse, *Chem. Rev.* **1998**, *98*, 1335–1355; c) D. M. Dattelbaum, K. M. Omberg, J. R. Schoonover, R. L. Martin, T. J. Meyer, *Inorg. Chem.* **2002**, *41*, 6071–6079; d) D. J. Liard, M. Busby, P. Matousek, M. Towrie, A. Vlček, Jr., *J. Phys. Chem. A* **2004**, *108*, 2363–2369; e) G. Li, K. Parimal, S. Vyas, C. M. Hadad, A. H. Flood, K. D. Glusac, *J. Am. Chem. Soc.* **2009**, *131*, 11656–11657.

[4] a) A. J. Di Bilio, B. R. Crane, W. A. Wehbi, C. N. Kiser, M. M. Abu-Omar, R. M. Carlos, J. H. Richards, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2001**, *123*, 3181–3182; b) B. R. Crane, A. J. Di Bilio, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2001**, *123*, 11623–11631; c) W. Belliston-Bittner, A. R. Dunn, Y. H. Le Nguyen, D. J. Stuehr, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **2005**, *127*, 15907–15915; d) A. M. Blanco-Rodríguez, M. Busby, C. Grădinaru, C. R. Crane, A. J. Di Bilio, P. Matousek, M. Towrie, B. S. Leigh, J. S. Richards, A. Vlček, Jr., H. B. Gray, *J. Am. Chem. Soc.* **2006**, *128*,

4365–4370; e) A. M. Blanco-Rodríguez, M. Busby, K. Ronayne, M. Towrie, C. Grădinaru, J. Sudhamsu, J. Sýkora, M. Hof, S. Záliš, A. J. Di Bilio, C. R. Crane, H. B. Gray, A. Vlček Jr. , *J. Am. Chem. Soc.* **2009**, *131*, 11788–11800.

[5] a) M. S. Wrighton, D. L. Morse, L. Pdungsap, *J. Am. Chem. Soc.* **1975**, *97*, 2073–2079; b) J. Hawecker, J.-M. Lehn, R. Ziessel, *J. Chem. Soc. Chem. Commun.* **1983**, 536–538; c) J. R. Shaw, R. T. Webb, R. H. Schmehl, *J. Am. Chem. Soc.* **1990**, *112*, 1117–1123; d) V. W.-W. Yam, C.-C. Ko, L.-X. Wu, K. M.-C. Wong, K.-K. Cheung, *Organometallics* **2000**, *19*, 1820–1822; e) V. W.-W. Yam, C.-C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 12734–13735; f) C.-C. Ko, W.-M. Kwok, V. W.-W. Yam, D.-L. Phillips, *Chem. Eur. J.* **2006**, *12*, 5840–5848; g) A. A. Abdel-Shafi, J. L. Bourdelande, S. S. Ali, *Dalton Trans.* **2007**, 2510–2516.

[6] a) D. B. MacQueen, K. S. Schanze, *J. Am. Chem. Soc.* **1991**, *113*, 6108–6110; b) D. I. Yoon, C. A. BergBrennan, H. Lu, J. T. Hupp, *Inorg. Chem.* **1992**, *31*, 3192–3194; c) V. W.-W. Yam, A. S.-F. Kai, *Chem. Commun.* **1998**, 109–110; d) L. H. Uppadine, J. E. Redman, S. W. Dent, M. G. B. Drew, P. D. Beer, *Inorg. Chem.* **2001**, *40*, 2860–2869; e) S. J. A. Pope, B. J. Coe, S. Faulkner, *Chem. Commun.* **2004**, 1550–1551; f) S. S. Sun, A. J. Lees, P. Y. Zavalij, *Inorg. Chem.* **2003**, *42*, 3445–3455; g) P. De Wolf, S. Heath, J. Thomas, *Chem. Commun.* **2002**, 2540–2541; h) A. Dirksen, C. J. Kleverlaan, J. N. H. Reek, L. De Cola, *J. Phy. Chem. A.* **2005**, *109*, 5248–5256; i) K. K.-W. Lo, W.-K. Hui, C.-K. Chung, K. H.-K. Tsang, T. K.-M. Lee, C.-K. Li, J. S.-Y. Lau, D. C.-M. Ng, *Coor. Chem. Rev.* **2006**, *250*, 1724–1736; j) S.-T. Lam, N. Zhu, V. W.-W. Yam, *Inorg. Chem.* **2009**, *48*, 9664–9670.

[7] a) C.-W. Tse, K. K.-Y. Man, K.-W. Cheng, C. S.-K. Mak, W.-K. Chan, C.-T. Yip, Z.-T. Liu, A. B. Djurisic, *Chem. Eur. J.* **2007**, *13*, 328–335; b) F. He, Y. Zhou, S. Liu, L. Tian, H. Xu, H. Zhang, B. Yang, Q. Dong, W. Tian, Y. Ma, J. Shen, *Chem. Commun.* **2008**, 3912–3914; c) M. Mauro, E. Q. Procopio, Y. Sun, C.-H. Chien, D. Donghi, M. Panigati, P. Mercandelli, P. Mussini, G. D'Alfonso, L. De Cola, *Adv. Funct. Mater.* **2009**, *19*, 2607–2614.

[8] a) O. Ishitani, K. Kanai, Y. Yamada, K. Sakamoto, *Chem. Commun.* **2001**, 1514–1515; b) S. Sato, T. Morimoto, O. Ishitani, *Inorg. Chem.* **2007**, *46*, 9051–9053; c) Y. Yamamoto, S. Sawa, Y. Funada, T. Morimoto, M. Falkenstrom, H. Miyasaka, S. Shishido, T. Ozeki, K. Koike, O. Ishitani, *J. Am. Chem. Soc.* **2008**, *130*, 14659–14674.

[9] a) L. Malatesta, *Prog. Inorg. Chem.* **1959**, *1*, 284–298; b) J. M. Bassett, G. K. Barker, M. Green, J. A. Howard, G. A. Stone, W. C. Wolsey, *J. Chem. Soc. Dalton Trans.* **1981**, 219–227.

[10] a) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, K. Offermann, *Angew. Chem* **1965**, *77*, 492–504; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 472–485; b) W. P. Weber, G. W. Gokel, *Tetrahedron Lett.* **1972**, *13*, 1637; c) D. Lentz, *Angew. Chem.* **1994**, *106*, 1377–1393; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1315–1331, and references therein; d) T. Yonezawa, K. Imamura, N. Kimizuka, *Langmuir* **2001**, *17*, 4701–4703; e) D. Prosperi, *Synlett.* **2006**, 786–789.

[11] C.-O. Ng, L. T.-L. Lo, S.-M. Ng, C.-C. Ko, N. Zhu, *Inorg. Chem.* **2008**, *47*, 7447–7449.

[12] a) J. R. Wagner, D. G. Hendricker, *J. Inorg. Nucl. Chem.* **1975**, *37*, 1375–1379; b) H. D. Kaesz, R. Bau, D. Hendrickson, J. M. Smith, *J. Am. Chem. Soc.* **1967**, *89*, 2844–2851.

[13] M. S. Wrighton, D. L. Morse, H. B. Gray, D. K. Ottesen, *J. Am. Chem. Soc.* **1976**, *98*, 1111–1119.

[14] a) I. Ugi, R. Meyr, *Chem. Ber.* **1960**, *93*, 239–248; b) K. R. Mann, M. Cimolino, G. L. Geoffroy, G. S. Hammond, A. A. Orio, G. Albertin, H. B. Gray, *Inorg. Chim. Acta* **1976**, *16*, 97–101; c) G. L. Geoffory, M. S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, **1980**, pp. 259–276; d) D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Springer, New York, **1994**, pp. 216–270.

[15] R. J. Shaver, D. P. Rillema, *Inorg. Chem.* **1992**, *31*, 4101–4107.

[16] a) A. J. Lees, *Chem. Rev.* **1987**, *87*, 711–743; b) D. J. Stufkens, *Comments Inorg. Chem.* **1992**, *13*, 359–385.

[17] C. Turró, Y. C. Chung, N. Leventis, M. E. Kuchenmeister, P. J. Wagner, G. E. Leroi, *Inorg. Chem.* **1996**, *35*, 5104–5106.

[18] a) R. Obrecht, R. Herrmann, I. Ugi, *Synthesis* **1985**, 400–403; b) B. Janza, A. Studer, *Org. Lett.* **2006**, *8*, 1875–1878.

[19] S. P. Schmidt, W. C. Trogler, F. Basolo, M. A. Urbancic, J. R. Shapley, *Inorg. Synth.* **1990**, *28*, 160–162.

[20] G. A. Crosby, J. N. Demas, *J. Phys. Chem.* **1971**, *75*, 991–1024.

[21] J. van Houten, R. Watts, *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858.

[22] For experimental details, see the Supporting Information.

[23] SHELX-97, G. M. Sheldrick, SHELX-97: Programs for Crystal Structure Analysis (Release 97–2), University of Göttingen, Germany, **1997**.

[24] For characterization data of *fac*-[Re(CO)$_3$(CNR)$_2$Br], see the Supporting Information.

Received: March 30, 2010
Revised: August 13, 2010