www.rsc.org/dalton

Dalton

# A spectroscopic and computational study on the effects of methyl and phenyl substituted phenanthroline ligands on the electronic structure of Re(I) tricarbonyl complexes containing 2,6-dimethylphenylisocyanide<sup>†</sup>

John M. Villegas, Stanislav R. Stoyanov, Wei Huang and D. Paul Rillema\*

Department of Chemistry, Wichita State University, 1845 N. Fairmount St., Wichita, KS, 67260-0051, USA. E-mail: paul.rillema@wichita.edu

Received 29th September 2004, Accepted 21st January 2005 First published as an Advance Article on the web 10th February 2005

[Re(CO)<sub>3</sub>(CNx)(L)]<sup>+</sup>, where CNx = 2,6-dimethylphenylisocyanide, forms complexes with L = 1,10-phenanthroline (1), 4-methyl-1,10-phenanthroline (2), 4,7-dimethyl-1,10-phenanthroline (3), 3,4,7,8-tetramethyl-1,10-phenanthroline (4), 2,9-dimethyl-1,10-phenanthroline (5) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (6). The metal–ligand-to-ligand charge transfer transition (MLLCT) absorption bands follow the series: 3 (27 800 cm<sup>-1</sup>) > 1, 2, 4 and 5 (27 500 cm<sup>-1</sup>) > 6 (26 600 cm<sup>-1</sup>). Density functional theory (DFT) geometry optimizations reveal elongated Re–N (L) distances of 2.28 and 2.27 Å for 5 and 6, respectively, compared to 2.23 Å for 1–4. The reversible reduction potentials ( $E_{1/2(red)}$ ) of 1–4 are linearly dependent on the B3LYP calculated LUMO energies. Time-dependent (TD) DFT and conductor-like polarizable continuum model (CPCM) calculated singlet excited states deviate by 700 cm<sup>-1</sup> or less from the experimental absorption maxima and aid in the spectral assignments. The <sup>3</sup>MLLCT emitting state energies are within 900 cm<sup>-1</sup> of the experimental 77 K emission energies for 1–6. The 77 K emission energies,  $E_{1/2(red)}$ , and the room temperature emission quantum yields ( $\phi_{LUMOem}$ ) decrease in the order 1 > 2 > 3 > 4 whereas  $E_{LUMO}$  and the room temperature emission energies follow the opposite trend. The emission lifetimes ( $\tau_{cm}$ ) decrease in the order 3 > 4 > 2 > 1 > 5 with 3 having the highest emission lifetime values of 26.9 µs at room temperature and 384 µs at 77 K and complex 5 having the lowest emission lifetimes of 4.6 µs at room temperature and 51 µs and 77 K.

# Introduction

Studies of the photophysical and photochemical properties of heterocyclic diimine complexes of the rhenium(I) tricarbonyl moiety are of interest due to their photophysical properties which are similar in some respects to ruthenium(II) polypyridyl complexes.<sup>1</sup> Such Re(I) complexes are ideally suited for solar energy conversion dyes<sup>2,3</sup> since they display intense luminescence in the visible region of the spectrum with long emission lifetimes.<sup>4</sup> The origin of the emission was attributed to the metal-to-ligand charge transfer (MLCT) state based on broad and structureless emission bands which were sensitive to changes in the nature of the environment.<sup>5–11</sup> The photochemical and photophysical properties of these complexes can be fine-tuned by changing the chormophoric, bidentate ligand and/or the ancillary "spectator" ligands.

Our group has been systematically examining the electronic and photophysical properties of Ru(II) and Re(I) complexes containing diimine and 2,6-dimethylphenylisocyanide (CNx) ligands by comparing their properties to those calculated by density functional theory (DFT).<sup>12</sup> Linear relationships of  $E_{1/2(ox)}$  and  $E_{1/2(red)}$  versus the B3LYP<sup>13</sup> calculated highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, respectively, for a series of isoelectronic ruthenium(II) diimine complexes were reported from our laboratory.<sup>14</sup> Others reported correlations of timedependent (TD) DFT calculated singlet and triplet excitedstate energies and spatial distributions with time-resolved IR studies for rhenium(I) tricarbonyl diimine complexes that contained ancillary py ligands<sup>15</sup> and good agreement between the computed and the experimental absorption bands of

† Electronic supplementary information (ESI) available: The optimized geometries (Table S1), the percent orbital contributions (Table S2) and the calculated singlet excited-state energies of the six complexes (Table S3), and additional comments. See http://www.rsc.org/suppdata/dt/b4/b415079a/

 $\label{eq:constraint} \begin{array}{l} [\operatorname{Re}(\operatorname{CO})_3(4,4'/5,5'\text{-bpy})\operatorname{Cl}] \mbox{ complexes.}^{16a} \mbox{ Picosecond flash photolysis measurements were used to assign the emissive state of } [\operatorname{Re}(\operatorname{CO})_3(\operatorname{dppz})(\operatorname{py})]^+ \mbox{ (dppz = dipyrido}[3,2-a:2',3'-c] \mbox{ phenazine}) as an intraligand {}^3\pi \rightarrow \pi^* \mbox{ (phenazine) state which has been supported by TDDFT results.}^{16b} \mbox{ Additionally, correlations between TDDFT calculated MLCT states and UV-vis spectra were reported for } [\operatorname{Re}(\operatorname{CO})_3\operatorname{Cl}(\operatorname{N-N})]^+ \mbox{ (N-N = 7,8-diphenyl-2,5-bis(phenylamino)-$p$-quinonediimine).}^{16c} \end{array}$ 

The TDDFT method treats molecules in the gas phase and does not always give the right excited-state energies in solution.<sup>17,18</sup> Hence, TDDFT and the conductor-like polarizable continuum model (CPCM) were combined and the UV-vis absorption energies of [Ru(bpy)<sub>2</sub>(CNx)Cl]<sup>+</sup> were calculated. The computed singlet excited-state energies correlated linearly in a series of seven solvents of varied polarity.<sup>17a</sup> The tandem use of TDDFT and CPCM has also produced dramatic changes in the singlet excited-state energies and assignments for other ruthenium(II) and osmium(II) polypyridyl complexes<sup>19</sup> and is the current method of choice for calculating energies of excited states in similar complexes.

 $[\text{Re}(\text{CO})_3(\text{phen})(\text{py})]^+$  complexes have longer emission lifetimes ( $\tau_{\text{em}}$ ) and higher emission quantum yields ( $\phi_{\text{LUMOem}}$ ) than their bpy analogs.<sup>11,20</sup> The CNx ligand was also found to enhance these important photophysical parameters when substituted for py in [Re(CO)\_3(bpy)(py)]^+.<sup>12b</sup> Here we have combined the effects of both the phen and the CNx ligands and report a series of [Re(CO)\_3(CNx)(phen)]^+ complexes where methyl groups were attached to the 2-, 3-, 4-, 7- and 9-positions and phenyl groups were attached to the 4- and 7-positions of the phen ligand.

# **Experimental**

# Materials

The ligand 2,4-dimethylphenylisocyanide was purchased from Fluka and ligands 1,10-phenanthroline, 4-methyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline were purchased

1042

DOI: 10.1039/b4150798

from GFS Chemicals. The ligands 2,9-dimethyl-1,10-phenanthroline (neocuproine), 3,4,7,8-tetramethyl-1-10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline were purchased from Aldrich. Optima grade methanol was purchased from Fischer Scientific while acetonitrile was purchased from Sigma-Aldrich. AAPER Alcohol and Chemical Company was the source of absolute ethanol. [Re(CO)<sub>5</sub>CI] was purchased from Aldrich. Ethanol and methanol were used in a 4 : 1 (v/v) mixture to prepare solutions for emission and emission lifetime studies. All purchased reagents were used without further purification. Elemental analyses were obtained from M–H–W Laboratories, Phoenix, AZ.

# Instrumentation and physical measurements

UV-vis spectra were obtained using a Hewlett-Packard model 8452A diode array spectrophotometer and IR spectra were acquired using a Nicolet Avatar 360 FT-IR spectrophotometer. Proton NMR spectra were obtained using a Varian Mercury 300 FT NMR spectrometer. An EG & G PAR model 263A potentiostat/galvanostat was used to obtain cyclic voltammo-grams. Measurements were carried out in a typical H-cell using a platinum disk working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode in acetonitrile. The supporting electrolyte used was 0.1 M tetrabutylammo-nium hexafluorophosphate (TBAH). Ferrocene was added as a reference.

The sample preparation for emission studies involved dissolving a small amount of sample ( $\approx 2$  mg) in the appropriate solvent and the absorbance of the solution was measured. The concentration of the solution was altered in order to achieve an absorbance of about 0.10 at the lowest energy transition. Such a concentration provided enough material for data acquisition but excluded self-quenching processes. A 3-4 mL aliquot of the solution was then placed in a 10 mm diameter Suprasil (Heraeus) non-fluorescent quartz tube equipped with a tip-off manifold. The sample was then freeze-pump-thaw degassed for at least three cycles (to approximately 75 milliTorr) removing any gasses from the sample. The manifold was then closed and the sample was allowed to equilibrate at room temperature. The solvent evaporation was assumed to be negligible, therefore the concentrations were assumed to remain constant throughout this procedure. The corrected emission spectra were collected using a Spex Tau3 Fluorometer.

The emission quantum yields were then calculated using eqn. (1), where  $\phi_{\text{LUMOx}}$  is the emission quantum yield of the sample and  $\phi_{\text{LUMOxd}}$  is the emission quantum yield for the standard  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,  $A_{\text{std}}$  and  $A_x$  represent the absorbance of the standard and the sample, respectively, while  $I_{\text{std}}$  and  $I_x$  are the integrals of the emission envelope of the standard and the sample, respectively.<sup>21</sup>

$$\phi_{\text{LUMOx}} = (A_{\text{std}}/A_{\text{x}})(I_{\text{x}}/I_{\text{std}})\phi_{\text{LUMOstd}}$$
(1)

The excited state lifetimes were determined by exciting the sample at 355 nm using the third harmonic of a Continuum Surlite Nd:YAG laser run at  $\approx 20$  mJ (10 ns pulse)<sup>-1</sup>. The oscilloscope control and data curve fitting analysis was accomplished using the Origin 6.1 program by OriginLab Corporation. The excited state lifetime experiments were conducted as previously published.<sup>22</sup>

### Preparation of fac-[Re(CO)<sub>3</sub>(CNx)(L)](PF<sub>6</sub>)

The complexes were synthesized according to previously published procedures<sup>23,24</sup> which were modified as follows: a 0.55 mmole sample of [Re(CO)<sub>5</sub>CI] was added to an equimolar amount of the phenanthroline-based ligand in a 125 mL round-bottomed flask. Approximately 50 mL of absolute ethanol was added and the mixture was refluxed for 2–4 hours. A yellowish-colored precipitate formed in the solution which was cooled to room temperature and filtered. After drying in a vacuum oven

for 3–5 hours, about 0.20 mmole of the product was added to an equimolar amount of AgCF<sub>3</sub>SO<sub>3</sub> in a 125 mL round-bottomed flask. Again, approximately 50 mL of absolute ethanol was added and the mixture was refluxed for 4–6 hours. The solution was cooled to room temperature and the AgCl precipitate was removed by filtration. An equimolar amount of the CNx ligand dissolved in 10 mL of ethanol was added to the filtrate and the solution was refluxed again for another 3–5 hours. The solvent was reduced in volume (about 5–10 mL) under vacuum. A saturated NH<sub>4</sub>PF<sub>6</sub> solution (15 mL) in water was then added and the solution was completed). The precipitate was collected by filtration, dried in a vacuum oven and weighed.

(1) *fac*-[Re(CO)<sub>3</sub>(CNx)(phen)](PF<sub>6</sub>). Color: yellow. Yield: 97%. Anal. Calcd. for ReC<sub>24</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>PF<sub>6</sub>: C, 39.67; H, 2.36; N, 5.78%. Found: C, 39.49; H, 2.20; N, 5.63%. (KBr pellet): 2170, 2037, 1937, 1632, 1605, 1521, 1431, 1227, 1151, 841, 779, 724, 634, 558, 507, 471 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO):  $\delta$  (ppm) 1.72 (s, 6H), 7.06 (d, 2H, J = 7.5 Hz), 7.19 (dd, 1H, J = 0.9, 8.1 Hz), 8.18 (dd, 2H, J = 3.3, 5.1 Hz), 8.38 (s, 2H), 9.06 (dd, 2H, J =1.2, 8.4 Hz), 9.57 (dd, 2H, J = 1.5, 5.1 Hz).

(2) fac-[Re(CO)<sub>3</sub>(CNx)(4-Me-phen)](PF<sub>6</sub>). Color: light yellow. Yield: 89%. Anal. Calcd. for ReC<sub>25</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>PF<sub>6</sub>: C, 40.54; H, 2.59; N, 5.67%. Found: C, 39.54; H, 2.40; N, 5.70%. (KBr pellet): 2171, 2036, 1964, 1935, 1653, 1635, 1576, 1522, 1473, 1431, 1384, 1261, 1168, 1032, 842, 782, 727, 635, 612, 558, 508, 421 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO):  $\delta$  (ppm) 1.72 (s, 6H), 2.97 (s, 3H), 7.05 (d, 2H, J = 7.5 Hz), 7.19 (dd, 1H, J = 0.9, 7.2 Hz), 8.03 (dd, 1H, J = 0.6, 5.4 Hz), 8.17 (dd, 1H, J = 3.0, 5.4 Hz), 8.43 (dd, 2H, J = 9.3, 13.8), 9.06 (dd, 1H, J = 1.5, 8.4 Hz), 9.41 (d, 1H, J = 5.4 Hz), 9.56 (dd, 1H, J = 1.5, 5.1 Hz).

(3) *fac*-[Re(CO)<sub>3</sub>(CNx)(4,7-Me<sub>2</sub>-phen)](PF<sub>6</sub>). Color: offwhite. Yield: 92%. Anal. Calcd. for ReC<sub>26</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>PF<sub>6</sub>: C, 41.38; H, 2.81; N, 5.57%. Found: C, 41.19; H, 2.74; N, 5.70%. (KBr pellet): 2171, 2035, 1695, 1933, 1653, 1608, 1577, 1525, 1425, 1386, 1233, 1171, 1035, 839, 781, 726, 634, 612, 558, 483, 419 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO):  $\delta$  (ppm) 1.72 (s, 6H), 2.98 (s, 6H), 7.05 (d, 2H, J = 7.5 Hz), 7.19 (dd, 1H, J = 0.9, 8.1 Hz), 8.02 (dd, 2H, J = 0.6, 5.4 Hz), 8.46 (s, 2H), 9.40 (d, 2H, J =5.1 Hz).

(4) fac-[Re(CO)<sub>3</sub>(CNx)(3,4,7,8-Me<sub>4</sub>-phen)](PF<sub>6</sub>). Color: light yellow. Yield: 92%. Anal. Calcd. for ReC<sub>28</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>PF<sub>6</sub>: C, 42.97; H, 3.22; N, 5.37%. Found: C, 42.17; H, 3.42; N, 5.29%. (KBr pellet): 2170, 2036, 1967, 1929, 1653, 1624, 1531, 1431, 1388, 1248, 1177, 843, 781, 723, 634, 614, 579, 558 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO):  $\delta$  (ppm) 1.68 (s, 6H), 2.63 (s, 6H), 2.86 (s, 6H), 7.04 (d, 2H, J = 7.5 Hz), 7.19 (dd, 1H, J = 0.9, 7.8 Hz), 8.46 (s, 2H), 9.29 (s, 2H).

(5) fac-[Re(CO)<sub>3</sub>(CNx)(2,9-Me<sub>2</sub>-phen](PF<sub>6</sub>). Color: light yellow. Yield: 66%. Anal. Calcd. for ReC<sub>26</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>PF<sub>6</sub>: C, 41.38; H, 2.80; N, 5.57%. Found: C, 41.25; H, 2.79; N, 5.36%. (KBr pellet): 2175, 2052, 1966, 1926, 1902, 1628, 1592, 1506, 1439, 1383, 1167, 1037, 838, 774, 730, 662, 646, 616, 558 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO):  $\delta$  (ppm) 1.72 (s, 6H), 3.30 (s, 6H), 7.06 (d, 2H, J = 7.5 Hz), 7.20 (dd, 1H, J = 0.9, 8.4 Hz), 8.18 (d, 2H, J =8.4 Hz), 8.24 (s, 2H), 8.86 (d, 2H, J = 8.4 Hz).

(6) *fac*-[Re(CO)<sub>3</sub>(CNx)(2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>-phen)](PF<sub>6</sub>). Color: yellow. Yield: 97%. Anal. Calcd. for ReC<sub>38</sub>H<sub>29</sub>N<sub>3</sub>O<sub>3</sub>PF<sub>6</sub> (containing 2 moles H<sub>2</sub>O): C, 48.41; H, 3.52; N, 4.46%. Found: C, 48.20; H, 3.40; N, 4.60%. (KBr pellet): 2172, 2034, 1966, 1927, 1653, 1627, 1570, 1490, 1446, 1387, 1031, 841, 775, 710, 637, 617, 558, 484, 419 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO):  $\delta$  (ppm) 1.79 (s, 6H), 3.35 (s, 6H), 7.10 (d, 2H, J = 7.2 Hz), 7.23 (dd, 1H, J = 1.2, 7.2 Hz), 7.65 (m, 10H), 8.04 (s, 2H), 8.23 (s, 2H).

# Results

# Synthesis

The synthesis of the complexes was carried out according to the scheme presented in Fig. 1. [Re(CO)<sub>5</sub>Cl] was first allowed to react with the phenanthroline-based ligand (L) to form a neutral complex with the general formula [Re(CO)<sub>3</sub>(L)Cl]. The product was next allowed to react with AgCF<sub>3</sub>SO<sub>3</sub> thereby removing the chloro ligand from the coordination sphere by precipitating AgCl and replacing it with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>. The CNx ligand then replaced CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> by reaction of [Re(CO)<sub>3</sub>(L)(CF<sub>3</sub>SO<sub>3</sub>)] with a slight excess of CNx added to the filtrate. After refluxing the solution for about three hours and reducing the volume by rotary evaporation, the final product was precipitated by adding a saturated solution of NH<sub>4</sub>PF<sub>6</sub> and diluting it with more water until precipitation was complete. The products were obtained in relatively high yield.

$$\begin{array}{ccc} \text{Re}(\text{CO})_{5}\text{Cl} & \stackrel{L}{\longrightarrow} & \text{Re}((\text{CO})_{3}(\text{L})\text{Cl} & \stackrel{\text{AgCF}_{3}\text{SO}_{3}}{\longrightarrow} & \text{Re}(\text{CO})_{3}(\text{L})(\text{CF}_{3}\text{SO}_{3}) \\ & \stackrel{\text{EtOH}}{\longrightarrow} & \text{EtOH} \end{array}$$

 $\operatorname{Re}(\operatorname{CO})_{3}(\operatorname{L})(\operatorname{CF}_{3}\operatorname{SO}_{3}) \xrightarrow{\operatorname{CNx}} \operatorname{NH}_{4}\operatorname{PF}_{6} \operatorname{fac-[\operatorname{Re}(\operatorname{CO})_{3}(\operatorname{CNx})(\operatorname{L})](\operatorname{PF}_{6})} fac-\operatorname{Fac-[\operatorname{Re}(\operatorname{CO})_{3}(\operatorname{CNx})(\operatorname{L})](\operatorname{PF}_{6})]$ 

Fig. 1 Schematic diagram of the synthesis of the complexes.

Fig. 2 shows a schematic diagram of the Re(1) tricarbonyl isocyanide complexes with the phenanthroline-based ligands. As noted for this series of complexes, the 2-, 3-, 4-, 7-, 8- and/or 9-positions (peripheral) of the parent phenanthroline ligand were modified by replacing the hydrogen atoms with electron-donating methyl and/or electron withdrawing phenyl groups.



Fig. 2 Structures of the complexes used in the study.

#### **Electronic absorption studies**

The electronic absorption properties of the complexes were studied at room temperature using 4:1 (v/v) ethanol–methanol

Complex	$E_{ m exp}/10^3{ m cm}^{-1}\ (\epsilon/{ m M}^{-1}{ m cm}^{-1})$	$E_{\rm calc}/10^3~{\rm cm}^{-1}$	Assignment
1	27.5 (3 300)	28.2	MLCT
	33.3 (15 000)	33.5	MCDCT
	37.0 (40 000)	37.1	CDLCT
	38.5 (38 000)	38.4	LLCT
2	27.5 (3 000) 36.8 (42 000) 38.8 (39 000) 43.9 (43 000)	27.1 36.8 39.2	MLLCT LC MLLCT LC
3	27.8 (4000)	28.4	MLLCT
	32.3 (15000)	32.9	MLLCT
	36.8 (51000)	37.1	LC
4	27.5 (3 000)	27.7	MLLCT
	32.5 (18 000)	32.3	LC
	36.0 (42 000)	36.1	MCDCT
	40.3 (37 000)	40.4	LCDCT
5	27.5 (2000) 32.9 (19000) 35.7 (29000) 38.8 (37000) 43.5 (35000)	27.4 32.8 35.4/36.0 39.4	MLLCT MLLCT MLLCT/MCDCT LCDCT LC
6	26.6 (4 800)	26.6	LMLCT
	30.7 (19 000)	31.2	LMLCT
	33.8 (48 000)	33.8	LC
	38.5 (42 000)	38.6	MLLCT

<sup>*a*</sup> In 4 : 1 (v/v) ethanol–methanol. <sup>*b*</sup> In ethanol.

as solvent and spectra are shown in Fig. 3. The absorption coefficients of the transitions involved were determined from Beer's Law studies using at least five dilution points. The probable assignments of these bands were made on the basis of the computational assignment of the singlet excited states and the documented optical transitions of similar type of complexes.<sup>3-6,25</sup> The results are listed in Table 1.

The lowest energy transitions of the complexes were assigned as metal–ligand-to-ligand-charge transfer (MLLCT) while those at higher energies were assigned as ligand  $\pi \rightarrow \pi^*$  transitions. It is important to note that since the MLLCT bands occur as broad shoulders, the exact positions of the bands as well as the extinction coefficients were subject to error.

The MLLCT maxima for complexes 1 to 5 were located in the narrow range of 27 500–27 800 cm<sup>-1</sup>. For **6**, where two phenyl groups were located in the 4- and 7-positions and two methyl groups were attached in the 2- and 9-positions of the phen ligand, the MLLCT band red-shifted by 900 cm<sup>-1</sup> relative to **1**. The positions of the intraligand  $\pi \rightarrow \pi^*$  transitions for the series of complexes studied occurred over a broader range from 32 000 to 44 000 cm<sup>-1</sup>.

#### **Electrochemical studies**

The redox potentials of the complexes in the series were determined by cyclic voltammetry and are listed in Table 2. All complexes in the series showed irreversible oxidation waves in the range of 1.90–2.03 V.

The reduction potentials decreased in the following order: 1 (-1.18 V) > 2 (-1.25 V) > 3 (-1.33 V) > 4 (-1.42 V) as the number of methyl substituents in the 3, 4, 7 and 8-positions of the parent ligand was increased. The reduction potentials for the two complexes 5 and 6 containing methyl groups in the 2,9-positions were the same within experimental error  $(-1.25 \pm 0.01 \text{ V})$ .



Fig. 3 Experimental absorption spectra of complexes 1–6 and calculated singlet excited- states. The excited states are shown as vertical bars with height equal to the extinction coefficient.<sup>18a</sup>  $\blacksquare =$  MLLCT or MLCT,  $\star =$  LLCT,  $\blacktriangle = \pi \rightarrow \pi^*$ ,  $\Phi =$  MCDCT,  $\blacklozenge =$  LCDCT (ligand  $\rightarrow$  delocalized).

Table 2 Electrochemical properties of the complexes in CH<sub>3</sub>CN at room temperature

Complex	$E_{1/2(ox)}/V^a$	$E_{1/2(\mathrm{red})}/\mathrm{V}^{a}\left(\mathrm{L}\right)$
1 2 3 4	$2.01^{b}$ $1.93^{b}$ $1.90^{b}$ $1.92^{b}$	-1.18 -1.25 -1.33 -1.42
5 6	$2.02^{b}$ $2.03^{b}$	-1.26 -1.25

<sup>*a*</sup> Potential in V vs. SSCE (scan rate =  $250 \text{ mV s}^{-1}$ ). <sup>*b*</sup> Irreversible oxidation

**Emission properties** 

The emission properties and excited state lifetimes of the complexes were determined both at room temperature and at 77 K in 4 : 1 (v/v) ethanol-methanol. The results are listed in Table 3. Overlays of the room temperature and 77 K emission spectra of the six complexes are shown in Fig. 4. The emission maxima of the complexes were shifted to higher energies at 77 K compared to room temperature. Temperature-dependent emission studies were not conducted because the complexes underwent photodecomposition upon continuous exposure to laser light.

Table 3	Calculated <sup>3</sup> MLLCT	state energies <sup>a</sup>	and emission	properties of	f the compl	lexes at 77 K	and room tem	perature <sup>b</sup>

		$E_{\rm exp}/10^3~{\rm cm}^{-1}$		$\tau_{\rm em}/\mu s$		$\phi_{ ext{LUMOem}}{}^{c}$
Complexes	$E_{\rm calc}/10^3{\rm cm}^{-1}$	77 K	RT	77 K	RT	RT
1	22.6	21.8 20.4 19.1 17.7 (s)	19.7	65	8.6	0.77
2	22.6	21.7 20.2 18.9 17.6 (s)	19.8 20.7 (s)	148	10.1	0.70
3	22.0	21.5 20.1 18.7 17.5 (s)	20.8 19.8	384	26.9	0.61
4	21.7	21.5 20.0 18.7 17.4 (s)	21.0 19.8	254	20.8	0.52
5	21.9	22.1 20.7 19.5 18.1 (s)	20.1	61	4.6	0.22
6	21.4	20.2 19.1 17.8 (s)	18.9	101	40.7	0.39

<sup>*a*</sup> In ethanol. <sup>*b*</sup> In 4 : 1 (v/v) EtOH–MeOH; s = shoulder. <sup>*c*</sup> Relative to  $[Ru(bpy)^3]^{2+}$  (ref. 22).

wave.



Fig. 4 Emission spectra of the complexes at 77 K (---), curve-fitted (···) and at room temperature (---) in 4:1 (v/v) ethanol-methanol.

After converting the wavelength (abscissa) values into energy, the emission spectral data were fit to eqn. (2), where the summation was carried out over the two sets of six vibrational levels.<sup>26</sup> The parameters were as follows:  $I_0$  was equal to 0, A was the peak area,  $n_1$ ,  $n_2 = 0$  to 5,

$$I(E) = I_0 + A[\sum_{n_1} \sum_{n_2} [(E_0 - n_1\omega_1 - n_2\omega_2)/E_0]^4 (S_1^{n_1}/n_1!) (S_2^{n_2}/n_2!) \exp\{-4 \log^2 [(E - E_0 + n_1\omega_1 + n_2\omega_2)/v_{1/2}]^2\}]$$
(2)

 $E_0$  was the zero-zero energy,  $\omega_1$  and  $\omega_2$  represented the energies of the high and low vibrational frequency acceptor modes,  $S_1$ and  $S_2$  were the measures of the distortion in the high and low frequency acceptor modes<sup>27</sup> and  $v_{1/2}$  was the full-width at halfmaximum of the zero-zero vibronic component in the emission spectra. The maximum intensity was adjusted to 1 for the curvefitting analysis.

The results of the emission spectral curve fitting at 77 K (Fig. 4) are listed in Table 4. The values of the high frequency modes at about  $1400 \text{ cm}^{-1}$  corresponded to ring breathing modes

of the phenanthroline ligands. The low frequency modes for the six complexes were assigned as metal–ligand vibrations.

# **Computational technique**

The singlet ground-state geometries of the complexes 1-6 were optimized in the gas phase using the B3LYP<sup>13</sup> functional of the Gaussian '03<sup>28</sup> program package. For the Re valence shell a (8s7p6d)/[6s5p3d] Gaussian-type orbital (GTO) was used whereas the Stuttgart–Dresden (SDD) effective core potential (ECP)<sup>29</sup> was used for the Re core. The all-electron 6-311G\* basis set<sup>30</sup> was applied for O, N, C, and H atoms. Selected metal–ligand bond lengths are listed in Table 5. The singlet ground state optimized geometries of the complexes are listed in Table S1.†

The singlet excited-states<sup>31</sup> of complexes **1–6** in ethanol were calculated using the non-equilibrium TDDFT<sup>32</sup>/CPCM<sup>33</sup> method based on the singlet ground-state geometry optimized in the gas phase.<sup>34</sup> The TDDFT/CPCM calculations are non-equilibrium calculations with respect to the polarization

Table 4 Emission spectral curve fitting parameters of complexes 1–6 in 4 : 1 (v/v) EtOH–MeOH at 77 K<sup>a</sup>

Parameter	1	2	3	4	5	6
$E_{\rm em}/{\rm cm}^{-1}$	21 800	21 700	21 500	21 500	22 100	20 200
$E_0/cm^{-1}$	21 800	21,654	21,502	21,456	22,094	20,695
$\omega_1/\text{cm}^{-1}$	1395	1415	1402	1420	1443	1464
$S_1$	0.89	0.89	0.94	0.94	1.10	0.91
$\omega_2/\mathrm{cm}^{-1}$	545	544	502	558	593	502
$\overline{S_2}$	0.63	0.68	0.57	0.58	0.90	1.67
$v_{1/2}$	510	554	500	569	637	730
Ă	0.90	0.86	0.93	0.94	0.84	0.48

<sup>*a*</sup> Error limits are as follows:  $E_0, \pm 6.0 \text{ cm}^{-1}, \omega, \pm 15 \text{ cm}^{-1}, S, \pm 0.02, v_{1/2}, \pm 20 \text{ cm}^{-1}, A, \pm 002.$ 

Table 5	Calculated	Re-ligand	distances	in Å	for com	plexes 1	-6
	Careaterea			*** * *			

Complex	Re–C (CNx)	Re-C (CO trans to CNx)	Re–C (CO cis to CNx)	Re–N (phen)
1	2.10	2.01	1.96	2.23
2	2.10	2.01	1.96	2.23
3	2.10	2.00	1.96	2.23
4	2.10	2.00	1.95	2.23
5	2.10	2.00	1.95	2.28
6	2.10	2.00	1.95	2.27

process between the solvent reaction field and the charge density of the electronic state indicated in the input. For singlet excited states this is the singlet ground state.<sup>35</sup> The TDDFT output contained information for the excited-state energies and oscillator strengths (f) and a list of the excitations that give rise to each excited state, the orbitals involved as well as the wavefunction coefficients of the excitations. The singlet excited states of the six complexes are presented in Fig. 3 as vertical bars with its height equal to the extinction coefficient calculated from the oscillator strength.<sup>18</sup>

The lowest-lying triplet state geometries of the six complexes were calculated using unrestricted B3LYP in the gas phase. The spin contamination from states of higher multiplicity was low. The value of  $\langle S^2 \rangle$  was 2.017 for **1** and **5**, 2.016 for **2**, 2.036 for **3** and **4**, 2.019 for **6**. The energies of the lowest-lying triplet states were higher than these of the corresponding ground states by 22 600 cm<sup>-1</sup> for **1** and **2**, 22 000 cm<sup>-1</sup> for **3**, 21 700 cm<sup>-1</sup> for **4**, 21 900 cm<sup>-1</sup> for **5**, 20 400 cm<sup>-1</sup> for **6** (Fig. 5). The lowestlying triplet states for complexes **1–6** were <sup>3</sup>MLLCT states. These states featured single occupancy of the HOMO and the LUMO.



Fig. 5 Triplet excited-state energy diagram for complexes 1-6

A number of triplet excited states were computed based on the lowest-lying triplet-state geometry for complexes 1-6. The four low-lying triplet excited states are listed in Table 6 and shown in Fig. 5, even if the *f* value was low.

#### Discussion

#### Geometry optimization

The distances between the Re atom and the ligand atoms bound to it are listed in Table 5. The Re–N and Re–C (CO *cis* to CNx) varied across the series. The Re–N distance for complexes **5** and **6** of 2.28 and 2.27 Å, respectively, was longer than 2.23 Å for complexes **1–4**, due to the steric hindrance caused by the methyl groups in the 2- and 9-positions. The Re–N bond elongation in **5** and **6** was accompanied by a 0.01 Å bond shortening of the Re– C (CO *cis* to CNx) distance relative to **1–4**. In the acetonitrile analog of complex **6**, *fac*-[Re(CO)<sub>3</sub>(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)(CH<sub>3</sub>CN)]<sup>+</sup>, the Re–N (2,9-diemthyl-4,7diphenyl-1,10-phenanthroline) distances were 2.211(3) and 2.215(3) Å,<sup>36</sup> shorter by  $\approx 0.05$  Å than our calculated value of 2.27 Å. The 0.05 Å overestimation of Re–N (diimine) distance is the same as reported earlier when B3LYP theory was used.<sup>12</sup>

# Molecular orbital analysis

The molecular orbital energy diagram in Fig. 6 shows the twelve frontier orbitals of complexes 1–6. In Fig. 7 schematic diagrams of the HOMOs and the LUMOs of the six complexes



**Fig. 6** Molecular orbital energy diagram for six occupied (H) and six virtual (L) frontier orbitals of the complexes in the singlet ground state in ethanol.  $a = Re_d$ , CNx,  $b = Re_d$ , CO, c = CO, d = delocalize,  $m = Re_d$ , p = phen-based ligand and x = CNx. For example, orbitals H-3 and H-4 of complex **5** are assigned as p, m & x where H-3 is on the phen-based ligand (p) and  $Re_d$  (m) but H-4 is on the CNx ligand (x).



Fig. 7 Schematic diagram of the HOMO and the LUMO of complexes 1–6.

are shown. The HOMOs of complexes 1–5 contained 45% or more  $Re_d$  contributions and 28% or more CNx ligand contributions. The HOMO of complex 6, however, contained a 47% contribution from 2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>-phen ligand and only a 31%  $Re_d$  contribution (Fig. 7). The character of the HOMO and HOMO-2 of complexes 1–5 as well as of HOMO-1 of complexes 1 and 2 was similar to the character of the corresponding orbitals for the [Re(bpy)(CO)<sub>3</sub>(CNx)]<sup>+</sup> complex.<sup>12b</sup> The LUMOs and LUMOs + 1 of complexes 1–6 contained 77 and 98% diimine

**Table 6** Calculated triplet excited-states of complexes 1–6 in ethanol based on the lowest-lying triplet state geometry.  $E_{\text{VER}}$  is the energy of the vertical transition, f is the oscillator strength,  $\psi_o$  and  $\psi_v$  are the occupied and the virtual orbitals that define the transition. The transition type is determined based on the change in the spatial distribution from occupied to virtual orbital. The absolute value of the transition coefficient for each transition is given in parentheses. H = HOMO and L = LUMO (see text for calculation details)

State	f	$\psi_{ m o}  ightarrow \psi_{ m v}$	Туре	$E_{\rm ver}/10^3~{\rm cm}^{-1}$
Complex 1				
1	0.01	$H-2 \rightarrow H(0.7)$	$Re_d, CO \rightarrow Re_d, CNx$	27.6
		$H-1 \rightarrow H(0.6)$	$\operatorname{Re}_{d} \rightarrow \operatorname{Re}_{d}, \operatorname{CNx}$	
2	0.00	$H-4 \rightarrow H(1.0)$	phen, $CNx \rightarrow Re_d$ , $CNx$	28.6
3	0.01	$L \rightarrow L + 1 (0.8)$	LC $\pi \to \pi^*$	28.9
4	0.10	$H-1 \rightarrow H(0.7)$	$\operatorname{Re}_{d} \rightarrow \operatorname{Re}_{d}, \operatorname{CNx}$	30.4
		$H-2 \rightarrow H(0.5)$	$\operatorname{Re}_{d}, \operatorname{CO} \rightarrow \operatorname{Re}_{d}, \operatorname{CNx}$	
Complex 2				
1	0.00	$H-1 \rightarrow H(1.0)$	$\text{Re}_4 \rightarrow \text{Re}_4$ , $\text{CNx}$	27.2
2	0.01	$L \rightarrow L + 1 (0.9)$	$LC \pi \rightarrow \pi^*$	28.5
3	0.00	$H-4 \rightarrow H(1.0)$	4-Me-phen, $CNx \rightarrow Re_4$ , $CNx$	29.0
4	0.09	$H-2 \rightarrow H(0.8)$	$\operatorname{Re}_{d}, \operatorname{CO} \rightarrow \operatorname{Re}_{d}, \operatorname{CNx}$	30.8
Complex 3				
1	0.02	$L \rightarrow L + 1 (1.0)$	$LC \pi \rightarrow \pi^*$	26.8
2	0.02	$H-1 \rightarrow H(0.9)$	$\operatorname{Re}_{d}$ , 4,7- $\operatorname{Me}_{2}$ -phen $\rightarrow \operatorname{Re}_{d}$ , CNx	29.4
3	0.02	$H-2 \rightarrow H(1.0)$	$\operatorname{Re}_{d}, \operatorname{CO} \to \operatorname{Re}_{d}, \operatorname{CNx}$	30.6
4	0.00	$H-3 \rightarrow H(1.0)$	$CNx \rightarrow Re_d, CNx$	31.4
Complex 4				
1	0.02	$L \to L + 1 (1.0)$	LC $\pi \to \pi^*$	26.8
2	0.02	$H-1 \rightarrow H(0.9)$	$\text{Re}_{d}, \text{Me}_{4}\text{-phen} \rightarrow \text{Re}_{d}, \text{CNx}$	29.4
3	0.03	$H-2 \rightarrow H(0.9)$	$Re_d, CO \rightarrow Re_d, CNx$	30.6
4	0.00	$H-3 \rightarrow H(1.0)$	$\dot{CNx} \rightarrow Re_d, \dot{CNx}$	31.6
Complex 5	0.01	$\mathbf{H} 1 \rightarrow \mathbf{H} (0.7)$	Pr 20 Ma share Pr CNr	27.2
1	0.01	$H^{-1} \rightarrow H(0, 7)$	$\operatorname{Re}_d$ , 2,9- $\operatorname{Me}_2$ -pnen $\rightarrow$ $\operatorname{Re}_d$ , $\operatorname{CNx}$	27.3
2	0.01	$\Pi^{-2} \rightarrow \Pi (0.0)$	$\operatorname{Re}_d, \operatorname{CO} \to \operatorname{Re}_d, \operatorname{CNX}$	20.0
2	0.01	$L \rightarrow L + I(0.9)$	$L \subset n \to n^{-1}$	20.0
5	0.01	$\Pi - 4 \rightarrow \Pi (0.7)$ $\Pi - 2 \rightarrow \Pi (0.6)$	$2,9$ -Me <sub>2</sub> -phen, Ke <sub>d</sub> $\rightarrow$ Ke <sub>d</sub> , Chx P <sub>2</sub> CO $\rightarrow$ P <sub>2</sub> CNy	29.1
4	0.05	$\Pi^{-2} \rightarrow \Pi (0.0)$	$\operatorname{Re}_d, \operatorname{CO} \to \operatorname{Re}_d, \operatorname{CNx}$	20.2
4	0.05	$\Pi -4 \rightarrow \Pi (0.0)$	2.9-Me <sub>2</sub> -pilen, $\text{Re}_d \rightarrow \text{Re}_d$ , $\text{CNx}$	30.3
		$\Pi^{-3} \rightarrow \Pi(0.3)$	$2,9$ -Me <sub>2</sub> -pilen $\rightarrow$ Ke <sub>d</sub> , Civx	
		$\Pi$ -2 $\rightarrow$ $\Pi$ (0.4) $\Pi$ 1 $\rightarrow$ $\Pi$ (0.4)	$Re_d, CO \rightarrow Re_d, CNX$ $Re_d, 20 Me n hen > Re_d CNx$	
		$\Pi^{-1} \rightarrow \Pi (0.4)$	$\operatorname{Re}_d$ , 2,9- $\operatorname{Me}_2$ -plien $\rightarrow$ $\operatorname{Re}_d$ , CINX	
Complex 6				
1	0.02	$H-1 \rightarrow H(0.9)$	$\text{Re}_{d}, \text{Me}_{2}\text{-}\text{Ph}_{2}\text{-}\text{phen} \rightarrow \text{Me}_{2}\text{-}\text{Ph}_{2}\text{-}\text{phen}, \text{Re}_{d}$	27.4
2	0.00	$L \rightarrow L + 1 (1.0)$	LC $\pi \to \pi^*$	28.0
3	0.10	$H-2 \rightarrow H(0.8)$	$\text{Re}_{d}, \text{Me}_{2}\text{-}\text{Ph}_{2}\text{-}\text{phen} \rightarrow \text{Me}_{2}\text{-}\text{Ph}_{2}\text{-}\text{phen}, \text{Re}_{d}$	29.6
4	0.03	$H-3 \rightarrow H(0.9)$	$Me_2$ -Ph <sub>2</sub> -phen, $Re_d \rightarrow Me_2$ -Ph <sub>2</sub> -phen, $Re_d$	30.1

ligand contributions, respectively. The LUMOs + 2 of complexes **1–6** contained 46% CNx character and 20% CO character. The LUMO, LUMO + 2 and LUMO + 1 of [Re(bpy)(CO)<sub>3</sub>(CNx)]<sup>+</sup> contained a 82% bpy ligand contribution<sup>12b</sup> similar to the LUMOs, LUMOs + 1 and LUMOs + 2 of complexes **1–6**, respectively. The percentages of molecular orbital contributions for complexes **1–6** are listed in Table S2.<sup>†</sup>

The HOMO–LUMO gap increased in the order:  $32\ 100\ (1) < 32\ 300\ (2) < 32\ 700\ (3) < 33\ 000\ cm^{-1}\ (4)$  as the number of methyl substituents increased. Upon addition of the sterically hindering methyl groups in the 2- and 9-positions, the HOMO–LUMO gap decreased by 200 cm<sup>-1</sup> for 5 (32\ 500\ cm^{-1}) relative to isomer 3 (32\ 700\ cm^{-1}). The smallest HOMO–LUMO gap of 31\ 500\ cm^{-1} was calculated for 6 due to the sterically hindering methyl groups located in the 2- and 9-positions and the two phenyl groups located in the 4,7-positions.

#### **Electrochemical behavior**

The redox potentials of importance in discussing the electrochemistry of the complexes are those derived from the processes involving the HOMO and the LUMO.<sup>23</sup> The HOMO consisted mainly of the  $d\pi$  orbitals located on the metal center while the dominant contribution to the LUMO was from the  $\pi^*$  orbital of the phen-based ligand. The oxidations, then, involved the removal of an electron from a mixed heritage orbital consisting of considerable  $d\pi$  character with a rather large contribution of CNx (28%) character which perhaps accounts for the irreversible electrochemical behavior. The one-electron reduction on the other hand, involved addition of an electron to the  $\pi^*$  orbital localized on the diimine moiety consistent with the observation of emission decay involving the ring breathing vibronic mode obtained from the emission curve fitting analysis.<sup>37</sup>

The irreversible oxidation potentials of the methyl substituted complexes 2, 3 and 4 were less than 1 but the values did not change proportionally to the number of methyl groups. The increase in the number of methyl substituents attached to the parent phen ligand caused a decrease in the reduction potentials in the order 1 > 2 > 3 > 4. The linear relationship ( $R^2 =$  $0.98 \pm 0.01$ ) between the reduction potentials and the LUMO energies for complexes 1-4 is shown in Fig. 8. A slope of  $-0.51 \pm 0.05$  was obtained. Both  $E_{1/2(\text{red})}$  ( $R^2 = 0.98 \pm 0.03$ ) and  $E_{\text{LUMO}}$  ( $R^2 = 1.00 \pm 0.01$ ) were linearly dependent on the Hammett substituent constants  $\sigma_{\rm T}$  ( $\sigma_{\rm t} = \sigma_{\rm p} + \sigma_{\rm m}$ )<sup>38</sup> for 1-4. The slope of the line for  $E_{1/2(\text{red})}$  versus  $\sigma_T$  (Fig. 9) was  $0.48 \pm 0.04$  with an intercept of  $-1.18 \pm 0.01$ , similar to -1.16reported for [Re(CO)<sub>3</sub>(Etpy)(bpy)]<sup>+</sup> complexes with meta and para substituents located on the bpy ring.<sup>39</sup> The slope of  $E_{LUMO}$ versus  $\sigma_{\rm T}$  (Fig. 10) was  $-0.25 \pm 0.01$  and the intercept was  $-2.82 \pm 0.01$ .



Fig. 8 Linear dependence of  $E_{1/2(\text{red})}$  and the LUMO energies for complexes 1–4.



Fig. 9 Linear dependence of  $E_{1/2(\text{red})}$  and  $\sigma_{\text{T}}$  for complexes 1–4.



Fig. 10 Linear dependence of  $E_{\text{LUMO}}$  and  $\sigma_{\text{T}}$  for complexes 1–4.

The addition of the methyl groups in the 2- and 9-positions in complex **5** produced reduction and oxidation potentials that were higher by 0.07 and 0.12 V than the corresponding values for isomer **3**. Addition of phenyl groups in **6** did not alter the redox potentials compared to **5**. The energy difference  $\Delta E_{1/2}$ , where  $\Delta E_{1/2} = E_{1/2(ox)} - E_{1/2(red)}$ , and the HOMO–LUMO energy gap increased in the order **1**, **2** < **3** < **4** indicating the parallel relationship between the thermodynamic and electronic energy spacings.<sup>25,40-42</sup>

#### Singlet excited states and UV-Vis absorption spectra

In Fig. 3 the calculated singlet excited states of complexes 1-6 with f > 0.01 are shown as vertical bars with height equal to the

molar absorptivity coefficient ( $\varepsilon$ ). The excited states expressed with the taller bars have higher contributions to the experimental peaks. The symbol on the bar corresponds to the type of the singlet excited state as follows:  $\blacksquare = MLLCT, \star = LLCT, \blacktriangle =$  $\pi \to \pi^*, \bullet = MCDCT$  (metal to complex-delocalized charge transfer) and  $\blacklozenge$  = both LCDCT (ligand to complex-delocalized charge transfer) and CDLCT (complex-delocalized to ligand charge transfer).43 Here we use several abbreviations for the computational assignment of the singlet excited states for a more appropriate description of the excited states that had large contributions from excitations involving delocalized molecular orbitals. For example, the MLLCT states involve transfer of electronic charge from both the Re atom and the CNx ligand to the diimine ligand. The major contributing excitation in these states is from an occupied orbital that contains mainly Re<sub>d</sub> and CNx ligand contributions to a virtual orbital that contains primarily a diimine ligand contribution, e.g. HOMO  $\rightarrow$  LUMO for complexes 1-5. In the MCDCT singlet excited states the major contributing excitation is from an occupied molecular orbital that contains mainly Re<sub>d</sub> contributions to a virtual orbital that contains high contributions from three or more different moieties, e.g. HOMO-2  $\rightarrow$  LUMO + 3 of complex 1. Since calculated excited state  $\varepsilon$  values do not correlate very well with the experimental ones,<sup>17</sup> we based our assignment primarily on the correlation of the calculated excited state energies with the experimental peak energies.

The singlet excited states in the range of 25000-30000 cm<sup>-1</sup> were assigned as MLLCT states for complexes 1-5. The lowestlying excited states with f > 0.01 were within 700 cm<sup>-1</sup> from the experimental lowest-energy absorption peaks and were assigned based on the singlet excited states for the six complexes. Several excited states were calculated for complexes 1–6 that were related to the transitions in the range 30 000–40 000 cm<sup>-1</sup> and assigned as phen ligand  $\pi \to \pi^*$ , MCDCT or LCDCT. The absorption profile of complex 5 differed from the profiles of complexes 1– 4 because the most intense peak was at 38 800 cm<sup>-1</sup> and there were pronounced shoulders at 32 900 and 35 700 cm<sup>-1</sup>. Singlet excited states 17 ( $\epsilon = 28\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) at 36500 cm<sup>-1</sup> and 21 ( $\varepsilon = 26\,100$  M<sup>-1</sup> cm<sup>-1</sup>) at 37 300 cm<sup>-1</sup> for complex 5 were associated with LMLCT and 2,9-phen ligand  $\pi \rightarrow \pi^*$  transitions and assigned as LMLCT (black) based on the higher transition coefficient.<sup>43</sup> Singlet excited states 14 at 35400 cm<sup>-1</sup> and 15 at  $36\,000 \text{ cm}^{-1}$  were computed for 5 and assigned as MLLCT and MCDCT states, respectively. State 14 was red-shifted by 300 cm<sup>-1</sup> and state 15 was blue-shifted by 300 cm<sup>-1</sup> relative to the experimental shoulder at 35 700 cm<sup>-1</sup> (Table 1). For complex 6, excited state 17 ( $\varepsilon = 21700 \text{ M}^{-1} \text{ cm}^{-1}$ ) at 33800 cm<sup>-1</sup> was primarily a 2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>-phen ligand  $\pi \rightarrow \pi^*$  transition and had the same energy as the most intense absorption peak. The MLLCT excited state 32 at 38 600 cm<sup>-1</sup> was only blue-shifted by 100 cm<sup>-1</sup> relative to the experimental peak at 38 500 cm<sup>-1</sup>. The agreement between singlet excited-state energies and absorption maxima presented in Table 1 is very good. The singlet excitedstates are listed in Table S3.<sup>†</sup>

#### **Triplet excited states**

The lowest-lying triplet states for the six complexes were of <sup>3</sup>MLLCT origin. These states featured single-electron occupancy of both the HOMO and the LUMO. The calculated <sup>3</sup>MLLCT state energies generally decreased in the order  $1 \approx 2 > 3 > 4 > 6$  similar to the 77 K experimental emission energies. The calculated <sup>3</sup>MLLCT energies were 500–1200 cm<sup>-1</sup> higher than the corresponding experimental emission energies for complexes 1–3 and 6. Four upper lying triplet excited states were computed based on these <sup>3</sup>MLLCT states and listed in Table 6. The <sup>3</sup>d–d excited states 1 for complexes 1, 2 and 5 were based on transitions from HOMO-1 and HOMO-2 to the HOMO, where the three orbitals contained 43% or higher Re<sub>d</sub> character. The <sup>3</sup>LC excited states 1 for complexes 3 and 4 were based on LUMO to LUMO + 1 transitions, where the

two orbitals contained 81% or higher contributions from the respective phen derivative ligands. For complex **6** however, triplet excited state 1 was based on a transition from the HOMO-1 to HOMO, where the HOMO-1 contained 43% Re<sub>d</sub> and 26% 2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>-phen character whereas the HOMO contained 47% 2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>-phen and 31% Re<sub>d</sub> character. Excited state 1 of complex **6** was assigned as a mixed <sup>3</sup>d–d and <sup>3</sup>LC state as shown in Fig. 5. Most of the higher energy states listed in Table 6 were either <sup>3</sup>d–d or <sup>3</sup>LC states.

The excited states 1 for complexes 1-6 were located more than  $4\,600 \text{ cm}^{-1}$  above the <sup>3</sup>MLLCT states (Fig. 5). The energies of the higher-lying triplet states were determined by single electron vertical excitations from the lowest lying <sup>3</sup>MLLCT state; hence the reported excited state energies were not the minima.<sup>44</sup>

### **Emission properties**

The emission spectra of the complexes are shown in Fig. 4. The complexes were emissive both at room temperature and at 77 K. Selected emission properties, including the excited state lifetimes of the six complexes are listed in Table 3. The room temperature emission spectrum of complex 1 featured a bell shape envelope typical for <sup>3</sup>MLCT emitters with a maximum at 19700 cm<sup>-1</sup>. For **2**, a shoulder appeared at higher energy in addition to the maximum at 19800 cm<sup>-1</sup>. For 3 and 4 containing additional methyl groups, the low energy absorption remained at the same energy as for 1 and 2, but the emission profile now featured two well defined peaks located at higher energy that were 1000 cm<sup>-1</sup> apart in **3** and 1200 cm<sup>-1</sup> apart in **4**. The appearance of the fine structure in the room temperature spectra of 3 and 4 could be due to the mixing between the <sup>3</sup>MLLCT and <sup>3</sup>LC states (Fig. 5). An alternative explanation used to explain the increased <sup>3</sup>LC character of the emitting <sup>3</sup>MLCT state based on B3LYP calculations for fac-[Re(CO)<sub>3</sub>(bpy)(4ethylpyridine)]<sup>+</sup> was mixing of diimine ligand  $\pi \to \pi^*$  character into the emitting <sup>3</sup>MLCT state.<sup>15a</sup> Overall, the room temperature emission energies of the complexes increased in the order 1 <2 < 3 < 4. The room temperature emission profiles of complexes 5 and 6 were bell-shaped curves and the maxima were located at 20 100 and 18 900 cm<sup>-1</sup>, respectively.

The 77 K emission spectra of the complexes were more structured (Fig. 4) and shifted to higher energies due to the temperature dependence of the <sup>3</sup>MLLCT state energy.<sup>12,23*b*</sup> The peak maxima were located at 21 800 cm<sup>-1</sup> for complex 1, 21 700 cm<sup>-1</sup> for complex 2, at 21 500 cm<sup>-1</sup> for 3, at 21 500 cm<sup>-1</sup> for 4, at 22 100 cm<sup>-1</sup> for 5 and at 20 200 cm<sup>-1</sup> for 6. The 77 K emission energies of complexes 1, 5 and 6 were 700, 1000 and 500 cm<sup>-1</sup> greater than the energies of their respective py analogs in the same solvent.<sup>23</sup>

The values of the  $\tau_{em}$  at room temperature and at 77 K were determined by exponential decay curve-fitting analysis. The room temperature  $\tau_{em}$  values increased sequentially from 8.6 µs for 1 to 10.1 µs for 2, 20.8 µs for 4 and 26.9 µs for 3. However, for 5 and 6 containing the sterically hindered methyl groups,  $\tau_{em}$  dropped to 4.6 µs in 5 but increased to 40.4 µs for 6 which was greater than for any of the others. In like manner, an increase of the emission lifetime from 15.3 µs for [Re(CO)<sub>3</sub>(py)(2,9-Me<sub>2</sub>-phen)]<sup>+</sup> to 22.1 µs for [Re(CO)<sub>3</sub>(py)(2,9-Me<sub>2</sub>-4,7-Ph<sub>2</sub>-phen)]<sup>+</sup> in the same solvent has been reported.<sup>23</sup>

A parallel trend for  $\tau_{em}$  values was also observed at 77 K for the complexes in this series. The  $\tau_{em}$  value of 148 µs for complex **2** was more than twice as large as the  $\tau_{em}$  value of 65 µs for complex **1**. The  $\tau_{em}$  value increased even more to 384 µs and 254 µs in **3** and **4**, respectively. As expected, a decrease to 61 µs was noted in **5** relative to **1**. When the two phenyl substituents were attached in **6**, the  $\tau_{em}$  value increased to 101 µs. The 77 K emission lifetimes for complexes **1**, **5** and **6** were several times higher than the reported 11.7, 15.3 and 22.1 µs for their respective py analogs in the same solvent.<sup>23</sup> Overall, the emission lifetimes increased in the order **5** < **1** < **2** < **4** < **3** both at room temperature and at 77 K. By definition, the decay rate constant, k, is related to the sum of the radiative and non-radiative decay rate,  $k_r$  and  $k_{nr}$ , respectively ( $k = k_r + k_{nr}$ ). Thus, the decrease in the emission lifetime of **5** compared to **1** could be attributed to the increase in the  $k_{nr}$  term. This decrease could also be attributed to the steric effects of the methyl groups in the 2- and 9-positions. The emission lifetime was enhanced in **6** due to the added phenyl groups in the parent phen ligand. However,  $\tau_{em}$  of **6** did not dramatically increase at 77 K compared to room temperature as exhibited by the other five complexes. This is most likely due to the geometry of **6** in the glass where the phenyl groups are not coplanar with the phen moiety. According to the geometry optimization, the angles between the approximate planes of the phenyl rings and the phen ligand were in the range 52–56°.

The emission quantum yields ( $\phi_{LUMOem}$ ) were not directly related with the room temperature emission lifetimes for the complexes.  $\phi_{LUMOem}$  decreased gradually from 0.77 for complex 1 to 0.70 for 2, 0.61 for 3, and 0.52 for 4. Complex 5 had the lowest  $\phi_{LUMOem}$  value of 0.22. The addition of phenyl groups in 6 caused  $\phi_{LUMOem}$  to increase to 0.39. The  $\phi_{LUMOem}$  of complexes 1, 3, 5 and 6 were significantly higher than 0.18, 0.29, 0.17 and 0.17 reported for their respective py analogs in acetonitrile.<sup>23</sup>

# Conclusions

A series of six complexes with the general formula  $[Re(CO)_3(CNx)(L)](PF_6)$  where L is a 1,10-phenanthroline derivative with one, two and four methyl groups in the peripheral 3-, 4-, 7- and 8-positions or in the sterically hindering 2- and 9-positions, the latter coupled with phenyl substituents on 4and 7-positions, were synthesized and investigated using both computational and spectroscopic methods. The conclusions follow: (1) The complexes exhibited typical MLLCT electronic transitions that were located near 27 500 cm<sup>-1</sup> for the methyl derivatives with one exception, the MLLCT electronic transition for 6 was red-shifted relative to 27 500 cm<sup>-1</sup>. (2)  $E_{1/2(\text{red})}$  was linearly dependent on  $E_{LUMO}$ . (3) The complexes were highly emissive at both room temperature and 77 K. (4) The emission energies at room temperature increased in the order 1 < 2 < 23 < 4 but at 77 K followed the opposite trend. (5) The emission quantum yields ranged from 0.77 for 1 to 0.22 for 5 and were significantly higher than 0.089 for the standard, [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and their py analogs. (6) The emission lifetimes both at room temperature and at 77 K increased in the order 5 < 1 < 2 < 4 < 13 and were in the microsecond time scale.

# Acknowledgements

We thank the support of National Science Foundation under Grant No. EIA-0216178 and Grant No. EPS-0236913, matching support from the State of Kansas and the Wichita State University High Performance Computing Center, the Wichita State University Office of Research Administration, the Department of Energy, and Parker Fellowships (J. M. V., H. W. and S. R. S.).

# References

- A. Juris, S. Campagna, I. Bidd, J.-M. Lehn and R. Ziessel, *Inorg. Chem.*, 1988, 27, 4007–4011.
- (a) T. J. Meyer, *Pure Appl. Chem.*, 1986, **58**, 1193; (b) J. V. Caspar, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1984, **23**, 2098; (c) E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1985, **24**, 2755; (d) E. M. Kober, B. P. Sullivan, W. J. Dressick, J. V. Caspar and T. J. Mayer, *J. Am. Chem. Soc.*, 1980, **102**, 1383.
- 3 M. S. Wrighton and G. L. Geoffroy, Organometallic Photochemistry, Academic Press: New York, 1979, ch 2.
- 4 J. C. Luong, L. Nadjo and M. Wrighton, J. Am. Chem. Soc., 1978, 100, 5790.
- 5 M. Wrighton and D. L. Morse, J. Am. Chem. Soc., 1974, 96, 998.
- 6 P. J. Giordano and M. S. Wrighton, J. Am. Chem. Soc., 1979, 101, 2888.
- 7 A. Lees, J. Chem. Rev., 1987, 87, 711.

- 8 P. J. Giordano, S. M. Fredericks, M. S. Wrighton and D. L. Morse, J. Am. Chem. Soc., 1978, 100, 2257.
- 9 S. M. Fredericks, J. C. Luong and M. S. Wrighton, J. Am. Chem. Soc., 1979, 101, 7415.
- 10 W. K. Smothers and M. S. Wrighton, J. Am. Chem. Soc., 1983, 105, 1067
- 11 R. M. Leasure, L. Sacksteder, D. Nesselrodt, G. A. Reitz, J. N. Demas and B. A. DeGraff, Inorg. Chem., 1991, 30, 3722.
- 12 (a) J. M. Villegas, S. R. Stoyanov, J. Reibenspies and D. P. Rillema, Organometallics, 2005, 24, 395-404; (b) S. R. Stoyanov, J. M. Villegas, A. J. Cruz, L. L. Lockyear, J. Reibenspies and D. P. Rillema, J. Chem. Theory Comput., 2005, 1, 95-106; (c) J. M. Villegas, S. R. Stoyanov, W. Huang and D. P. Rillema, Inorg. Chem., 2004, in press.
- 13 (a) A. D. Becke, J. Chem. Phys., 1993, 98, 5648; (b) C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785; (c) S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys., 1980, 58, 1200.
- 14 S. R. Stoyanov, J. M. Villegas and D. P. Rillema, Inorg. Chem., 2002, 41, 2941.
- 15 (a) D. M. Dattelbaum, K. M. Omberg, J. R. Schoonover, R. L. Martin and T. J. Meyer, Inorg. Chem., 2002, 41, 6071-6079; (b) D. M. Dattelbaum, R. L. Martin, J. R. Schoonover and T. J. Mever, J. Phys. Chem. A, 2004, 108, 3518; (c) D. M. Dattelbaum, K. M. Omberg, J. P. Hay, N. L. Gebhart, R. L. Martin, J. R. Schoonover and T. J. Meyer, J. Phys. Chem. A, 2004, 108, 3527.
- 16 (a) L. Yang, A.-M. Ren, J.-K. Feng, X.-J. Liu, Y.-G. Ma, M. Zhang, X.-D. Liu, J.-C. Shen and H.-X. Zhang, J. Phys. Chem. A, 2004, 108, 6797; (b) J. Dyer, W. J. Blau, C. G. Coates, C. M. Creely, J. D. Gavey, M. W. George, D. C. Grills, S. Hudson, J. M. Kelly, P. Matousek, J. J. McGarvey, J. McMaster, A. W. Parker, M. Towrie and J. A. Weinstein, Photochem. Photobiol. Sci., 2003, 2, 542; (c) S. Frantz, J. Rall, I. Hartenbach, T. Schleid, S. Zalis and W. Kaim, Chem.-A Eur. J., 2004, 10, 149.
- 17 (a) S. R. Stoyanov, J. M. Villegas and D. P. Rillema, Inorg. Chem. Commun., 2004, 7, 838-841; (b) J. M. Villegas, S. R. Stoyanov, W. Huang, L. L. Lockyear, J. Reibenspies and D. P. Rillema, Inorg. Chem., 2004, 43, 6383-6396.
- 18 (a) J. E. Monat, J. H. Rodriguez and J. K. McCusker, J. Phys. Chem. A, 2002, 106, 7399; (b) J. H. Rodrigues, D. E. Wheeler and J. K. McCusker, J. Am. Chem. Soc., 1998, 120, 12051.
- 19 J.-F. Guillemoles, V. Barone, L. Joubert and C. Adamo, J. Phys. Chem. A, 2002, 106, 11345.
- 20 L. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. DeGraff, Inorg. Chem., 1990, 29, 4335.
- 21 (a) J. N. Demas and G. A. Crosby, J. Phys. Chem., 1971, 75, 991;
  (b) M. J. Cook, A. B. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, A. L. Glasper and D. J. Robbins, J. Chem. Soc., Perkin Trans. 2, 1984, 1293.
- 22 J. M. Villegas, S. R. Stoyanov and D. P. Rillema, Inorg. Chem., 2002, 41. 6688.
- 23 L. Wallace and D. P. Rillema, Inorg. Chem., 1993, 32, 3936-3843.
- 24 R. J. Shaver and D. P. Rillema, Inorg. Chem., 1992, 31, 4101.
- 25 A. Juris, P. Belser, F. Barigelletti, A. von Zelewsky and V. Balzani, Inorg. Chem., 1986, 25, 256.
- 26 (a) J. V. Caspar, PhD Thesis, University of North Carolina, Chapel Hill, NC, 1982; (b) G. H. Allen, R. P. White, D. P. Rillema and T. J. Meyer, J. Am. Chem. Soc., 1984, 106, 2613.
- 27 The spatial distribution of the singly occupied orbitals in the excited state can be determined from the vibrational frequency acceptor modes. Example: for the MLCT state the high frequency acceptor mode would be the ligand ring breathing mode and the low frequency acceptor mode would be related to the vibrations of metal-ligand bonds. The coefficients  $S_1$  and  $S_2$  are indicative of the relative contributions of the high and the low vibrational modes to the fine vibronic structure of the emission.
- 28 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, T. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth,

P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, revision B.03, Gaussian, Inc., Pittsburgh, PA, 2003. 29 D. Andrae, U. Hauessermann, M. Dolg, H. Stoll and H. Preuss,

- Theor. Chim. Acta, 1990, 77, 123.
- 30 (a) A. D. McLean and G. S. Chandler, J. Chem. Phys., 1980, 72, 5639; (b) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys., 1980, 72, 650.
- 31 The CPCM is designed to account for the bulk physical properties of the solvent. It does not account for specific solvent-solute interactions. The TDDFT is known to perform well for the computing of charge transfer excited states between closely spaced moieties. The tandem use of CPCM and TDDFT is currently the most suitable computational approach for the treatment of the solvent effects to the transition metal complexes excited state energies.
- 32 (a) R. E. Stratmann, G. E. Scuseria and M. J. Frisch, J. Chem. Phys, 1998, 109, 8218; (b) R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett., 1996, 256, 454; (c) M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, J. Chem. Phys., 1998, 108, 4439.
- 33 (a) M. Cossi and V. Barone, J. Chem. Phys., 2001, 115, 4708; (b) V. Barone and M. Cossi, J. Phys. Chem. A, 1998, 102, 1995; (c) M. Cossi, N. Rega, G. Scalmani and V. Barone, J. Comput. Chem., 2003, **24**, 669,
- 34 Geometry optimization in solvents was not achieved. Partial optimizations (change in distance of less than 0.001 Å and change in angles of less than 0.01°) followed by TDDFT/CPCM calculation produced excited-state energies that were not in better agreement with the experimental excited-state energies than the excited state energies based on the gas phase optimized geometry.
- 35 Æ. Frisch, M. J. Frisch and G. W. Trucks, Gaussian 03 User's Reference, version 7.0, Gaussian Inc., Carnegie, PA, 2003, p. 206.
- 36 S.-S. Sun, P. Y. Zavalij and A. J. Lees, Acta Crystallogr., Sect. E, 2001, 57, m119.
- 37 (a) B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining and T. J. Meyer, J. Chem Soc., Chem. Commun., 1985, 1414; (b) H. D. Abruna and A. I. Breiks, J. Electroanal. Chem. Interfacial Electrochem., 1986, 201, 347; (c) T. R. O'Toole, B. P. Sullivan, M. R. M. Bruce, L. D. Margerum, R. W. Murray and T. J. Meyer, J. Electroanal. Chem. Interfacial Electrochem., 1989, 259, 217.
- 38 A. J. Gordon and R. A. Ford, The Chemist's Companion, 1972, John Wiley & Sons, New York, pp. 145–146.
- 39 J. K. Hino, L. Della Ciana, W. J. Dressick and B. P. Sullivan, Inorg. Chem., 1992, 31, 1072.
- 40 J. V. Caspar and T. J. Meyer, Inorg. Chem., 1983, 22, 2444.
- 41 A. Juris, S. Campagna, I. Bidd, J. M. Lehn and R. Zeissel, Inorg. Chem., 1988, 27, 4007.
- 42 L. Della Ciana, W. J. Dressick, D. Sandrini, M. Maestri and M. Ciano, Inorg. Chem., 1990, 29, 2792.
- 43 These assignments were made based on the major contributing excitation. The singlet excited-states had contributions from several excitations. For those presented with solid bars there was a major contributing excitation (with a transition coefficient for the major excitation being higher than the transition coefficient of the other excitations by more than 0.2). For some singlet excited-states, however, there was more than one contributing excitation with high transition coefficient. Singlet excited-states that contained contributions from several excitations with transition coefficients that were within 0.2 of the major excitation transition coefficient are assigned as mixed singlet excited-states and are presented with dotted vertical bars.
- 44 The triplet excited states were calculated based on the lowest-lying triplet state geometry because according to Kasha's rule this state would be the emitting state. Thus the triplet excited states were determined based on the most stable triplet geometry. The TDDFT calculations did not account for spin-orbit coupling. For third-row transition metal complexes the treatment of spin-orbit coupling could lower the predicted triplet state energies by 1700-2500 cm<sup>-1</sup> as outlined in C. Makedonas, C. A. Mitsopoulou, F. J. Lahoz and A. I. Balana, Inorg. Chem., 2003, 42, 8853-8865.

1051 Dalton Trans., 2005, 1042-1051