Synthesis, characterisation and photophysical studies of leucotriarylmethanes-containing ligands and their rhenium(I) tricarbonyl diimine complexes†

Chi-Chiu Ko,* Chi-On Ng, Hua Feng and Wing-Kin Chu

Received 4th January 2010, Accepted 7th May 2010
First published as an Advance Article on the web 15th June 2010
DOI: 10.1039/b927167h

A series of pyridine- and bipyridine-containing leucotriarylmethane ligands has been successfully synthesised and incorporated into tricarbonyl rhenium(I) diimine complexes. The X-ray crystal structures of two of the complexes have also been determined. The photoreactivity, photophysical and electrochemical properties of these ligands and their rhenium complexes were investigated. The photo-ionisation of the leucotriarylmethanes in the free ligands and their metal complexes and the subsequent change in absorption properties were also studied. Additionally, the electrochemistry of these ligands and complexes were investigated.

Introduction

Leucotriarylmethanes are well known to exhibit photochromism due to their reversible photo-ionisation reactions, which give the coloured triphenylmethyl cation and the counter anion upon UV-light excitation.[1] Owing to these properties, they are widely used in many applications such as colourless copying papers, photoimaging systems, photo-responsive polymers, reversible photomechanical transfer materials and photocontrollable vesicle formation.[1b,2] In recent years, the design and study of ligands with photochromic moieties, such as stilbenes, azo compounds, spirooxazines, spiropyrans and diarylethenes, and their coordination compounds have received considerable attention, as these metal complexes have been demonstrated to show novel and perturbed photochromic behaviour with their characteristic functionality being switchable by the photochromic reactivity.[3] To extend the design of photochromic diarylethene and spirooxazine-containing ligands and their transition metal complexes,[3d-3i] we have designed the first series of leucotriarylmethanes-containing ligands and their transition metal complexes. In this study, we describe the syntheses, characterisation, photophysics, photochemistry and electrochemistry of two leucotriarylmethane-containing ligands and their rhenium(I) tricarbonyl diimine complexes.

Experimental

Reagent and materials

[Re(CO)$_5$Br] was obtained from Strem Chemicals, Inc. Methyl isonicotinate, 4-bromo-*N*,*N*-dimethylaniline, 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (^{t}Bu$_2$bpy), 5-nitro-1,10-phenanthroline (NO$_2$phen) and 1,10-phenanthroline (phen) were obtained from Aldrich Chemical Company. 5,6-Dibromo-1,10-phenanthroline (Br$_2$phen) and 4′-methyl-2,2′-bipyridine-4-carboxylic acid were prepared by a slight modification of a reported procedure.[4] [Re(CO)$_3$(N–N)(MeCN)](CF$_3$SO$_3$) (N–N = ^{t}Bu$_2$bpy, phen, Br$_2$phen, NO$_2$phen) were synthesized according to literature method.[5] ^{n}Bu$_4$NPF$_6$ was obtained from Aldrich Chemical Company and recrystallised three times from ethanol and dried *in vacuo* at 100 °C for 24 h before use for electrochemical measurements. Acetonitrile was distilled over CaH$_2$ under argon. THF was distilled over sodium prior to use. All other reagents and solvents were of analytical grade and were used as received.

Synthesis

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

Bis(4-(dimethylamino)phenyl)(pyridin-4-yl) methanol (L1OH). To a THF solution of 4-bromo-*N*,*N*-dimethylaniline (1 g, 5.0 mmol) at −78 °C, *n*-BuLi (3.125 mL, 1.6 M, 5.0 mmol) was added in a dropwise manner. The resulting mixture was allowed to stir at −78 °C for 1 h. Thereafter, methyl isonicotinate (0.343 g, 2.5 mmol) in THF (5 mL) was added dropwise. The resulting solution was allowed to slowly warm to room temperature over 3 h, after which the reaction was quenched by the addition of water (30 mL) and extracted with CHCl$_3$ (3 × 30 mL). The chloroform extract was then washed with H$_2$O and dried over MgSO$_4$. After removal of the solvent under reduced pressure, the residue was further purified by column chromatography on alumina using CHCl$_3$ as an eluent to afford analytically pure **L1OH** as a white powdery solid. Yield: 450 mg, 1.30 mmol; 52%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, TMS): δ 2.66 (s, 1H, –OH), 2.95 (s, 12H, NCH$_3$), 6.65 (d, 4H, J = 8.9 Hz, phenyl protons at 2,2′,6,6′ positions), 7.09 (d, 4H, J = 8.9 Hz, phenyl protons at 3,3′,5,5′ positions), 7.30 (d, 2H, J = 4.6 Hz, pyridyl protons at 3,5 positions), 8.51 (d, 2H, J = 4.6 Hz, pyridyl protons at 2,6 positions); positive-ion ESI-MS: m/z: 348.5 [M + H]$^+$; IR (KBr disc): ν/cm^{-1}: 3125 (O–H); elemental analyses calcd (%) for $C_{22}H_{25}N_3O{\cdot}0.25H_2O$ (351.9): C 75.08, H 7.30, N 11.96; found: C 75.30, H 7.02, N 11.91.

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China. E-mail: vinccko@ctyu.edu.hk; Fax: 852-2788-7406; Tel: 852-3442-6958

† CCDC reference numbers 760665 and 760666. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b927167h

Bis(4-(dimethylamino)phenyl)(pyridin-4-yl) acetonitrile (L1). Concentrated hydrochloric acid (0.267 mL) was added dropwise to a solution of **L1OH** (1 g, 2.89 mmol) in DMSO (30 mL) at 65 °C, after which the solution changed from pale yellow to greenish blue. KCN (1.03 g, 16 mmol) in H_2O (5 mL) was then added dropwise into the resulting greenish blue mixture and stirred at this temperature for an additional 30 min. It was then poured over deionised water (900 mL) to commence precipitation. The crude product was filtered and air dried. Further purification by column chromatography on alumina using CH_2Cl_2 as the eluent resulted in analytically pure **L1** as a white powder. Yield: 291 mg, 0.81 mmol; 28%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 2.96 (s, 12H, NCH_3), 6.63 (d, 4H, J = 8.9 Hz, phenyl protons at 2,2′,6,6′ positions), 7.02 (d, 4H, J = 8.9 Hz, phenyl protons at 3,3′,5,5′ positions), 7.22 (d, 2H, J = 4.6 Hz, pyridyl protons at 3,5 positions), 8.59 (d, 2H, J = 4.6 Hz, pyridyl protons at 2,6 positions); positive-ion ESI-MS: m/z: 357 $[M + H]^+$; IR (KBr disc): ν/cm^{-1}: 2230 (C≡N); elemental analyses calcd (%) for $C_{23}H_{24}N_4$ (356.46): C 77.50, H 6.79, N 15.72; found: C 77.40, H 6.78, N 15.55.

Methyl 4′-methyl-2,2′-bipyridine-4-carboxylate. Concentrated sulfuric acid (0.96 mL) was added dropwise to 4′-methyl-2,2′-bipyridine-4-carboxylic acid (500 mg, 2.33 mmol) in methanol (20 mL) at 0 °C. The resulting solution was refluxed overnight and poured into H_2O (100 mL). After neutralisation with aqueous sodium hydroxide solution (25%) to pH 8, the mixture was extracted with $CHCl_3$ (3 × 50 mL). The combined extracts was washed with H_2O and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the white solid was further purified by column chromatography on silica gel using $CHCl_3$ as the eluent to afford analytically pure methyl 4′-methyl-2,2′-bipyridine-4-carboxylate as a white powdery solid. Yield: 419 mg, 1.84 mmol; 79%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 2.46 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 7.18 (d, 1H, J = 4.9 Hz, proton at 5′ position), 7.87 (d, 1H, J = 5.0 Hz, proton at 5 position), 8.25 (s, 1H, proton at 3′ position), 8.58 (d, 1H, J = 4.9 Hz, proton at 6′ position), 8.82 (d, 1H, J = 5.0 Hz, proton at 6 position), 8.93 (s, 1H, proton at 3 position); positive-ion ESI-MS: m/z: 229 $[M + H]^+$; IR (KBr disc): ν/cm^{-1}: 1735 (C=O); elemental analyses calcd (%) for $C_{13}H_{12}N_2O_2$ (228.3): C 68.41, H 5.30, N 12.27; found: C 68.12, H 5.71, N 12.05.

Bis(4-(dimethylamino)phenyl)(4′-methyl-2,2′-bipyridin-4-yl) methanol (L2). The title compound was synthesised according to a procedure similar to that of **L1OH**, except that methyl 4′-methyl-2,2′-bipyridine-4-carboxylate (300 mg, 1.31 mmol) was used in place of methyl isonicotinate. After purification by column chromatography on alumina using CH_2Cl_2 as the eluent, analytically pure **L2** was obtained as a pale yellow powder. Yield: 141 mg, 0.32 mmol; 25%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 2.68 (s, 3H, bipyridyl CH_3), 2.94 (s, 12H, NCH_3), 6.66 (d, 4H, J = 8.9 Hz, phenyl protons at 2,2′,6,6′ positions), 7.09 (d, 1H, J = 4.9, bipyridyl proton at 5′ position) 7.16 (d, 4H, J = 8.9 Hz, phenyl protons at 3,3′,5,5′ positions), 7.25 (dd, 1H, J = 5.3, 1.8 Hz, bipyridyl proton at 5 position), 8.18 (s, 1H, bipyridyl proton at 3′ position), 8.49 (d, 1H, J = 4.9 Hz, bipyridyl proton at 6′ position), 8.51 (dd, 1H, J = 1.8 Hz, 0.7 Hz, bipyridyl proton at 3 position), 8.57 (dd, 1H, J = 5.3, 0.7 Hz, bipyridyl proton at 6 position); positive-ion ESI-MS: m/z: 439 $[M + H]^+$; IR (KBr disc): ν/cm^{-1}: 3395 (O–H); elemental analyses calcd (%) for $C_{28}H_{30}N_4O$ (438.56): C 76.68, H 6.89, N 12.78; found: C 76.42, H 6.81, N 12.57.

$[Re(CO)_3(^tBu_2bpy)(L1)](PF_6)$ (1). The complex was prepared by modification of a literature method for the related Re(I) diimine complexes.[5] $[Re(CO)_3(^tBu_2bpy)(CH_3CN)](CF_3SO_3)$ (100 mg, 0.14 mmol) and **L1** (52.6 mg, 0.15 mmol) were dissolved in THF (30 mL). The resulting solution was refluxed overnight under an inert atmosphere of nitrogen. After removal of the solvent under reduced pressure, the residue was redissolved in methanol (0.5 mL). Subsequent metathesis reaction with a saturated methanolic ammonium hexafluorophosphate solution gave the target complex as a PF_6^- salt. After column chromatography on silica gel using CH_2Cl_2 as the eluent, the complex was further purified by recrystallisation by the slow diffusion of diethyl ether vapour into a concentrated dichloromethane solution of the complexes to yield **1** as an analytically pure yellow crystalline solid. Yield: 71 mg, 0.068 mmol; 50%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 1.47 (s, 18H; ^{t}Bu), 2.91 (s, 12H, NCH_3), 6.61 (d, 4H, J = 8.9 Hz, phenyl protons at 2,2′,6,6′ positions), 6.95 (d, 4H, J = 8.9 Hz, phenyl protons at 3,3′,5,5′ positions), 7.33 (dd, 2H, J = 5.3, 1.5 Hz, pyridyl protons at 3,5 positions), 7.66 (dd, 2H, J = 5.9, 1.8 Hz, bipyridyl protons at 5,5′ positions), 8.15 (dd, 2H, J = 5.3, 1.5 Hz, pyridyl protons at 2,6 positions), 8.37 (d, 2H, J = 1.8 Hz, bipyridyl protons at 3,3′ positions), 8.89 (d, 2H, J = 5.9 Hz, bipyridyl protons at 6,6′ positions); positive-ion ESI-MS: m/z: 895 $[M–PF_6]^+$; IR (KBr disc): ν/cm^{-1}: 2035, 1940, 1925 (C≡O); 835 (P–F); elemental analyses calcd (%) for $C_{44}H_{48}N_6O_3RePF_6$ (1040.06): C 50.81 H 4.65 N 8.08; found: C 50.89 H 4.51 N 8.08.

$[Re(CO)_3(phen)(L1)](PF_6)$ (2). The title complex was synthesised according to a procedure similar to that of **1**, except that $[Re(CO)_3(phen)(CH_3CN)](CF_3SO_3)$ (88 mg, 0.14 mmol) was used in place of $[Re(CO)_3(^tBu_2bpy)(CH_3CN)](CF_3SO_3)$ in the substitution reaction. Yield: 53 mg, 0.063 mmol; 40%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 2.90 (s, 12H, NCH_3), 6.57 (d, 4H, J = 8.9 Hz, phenyl protons at 3,3′,5,5′ positions), 6.86 (d, 4H, J = 8.9 Hz, phenyl protons at 2,2′,6,6′ positions), 7.22 (dd, 2H, J = 5.3, 1.5 Hz, pyridyl protons at 3,5 positions), 8.11 (dd, 2H, J = 5.3, 1.5 Hz, pyridyl protons at 2,6 positions), 8.15 (dd, 2H, J = 8.3, 5.2 Hz, phenanthrolinyl protons at 3,8 positions), 8.21 (s, 2H, phenanthrolinyl protons at 5,6 positions), 8.83 (dd, 2H, J = 8.3, 1.3 Hz, phenanthrolinyl protons at 4,7 positions), 9.50 (dd, 2H, J = 5.2, 1.3 Hz, phenanthrolinyl protons at 2,9 positions); positive-ion ESI-MS: m/z: 806.9 $[M–PF_6]^+$; IR (KBr disc): ν/cm^{-1}: 2035, 1930, 1920 (C≡O); 840 (P–F); elemental analyses calcd (%) for $C_{38}H_{32}N_6O_3RePF_6$ (951.87): C 47.95 H 3.39 N 8.83; found: C 47.67 H 3.63 N 8.71.

$[Re(CO)_3(Br_2phen)(L1)](CF_3SO_3)$ (3). The title complex was synthesised according to a procedure similar to that of **1**, except that $[Re(CO)_3(Br_2phen)(CH_3CN)](CF_3SO_3)$ (110 mg, 0.14 mmol) was used in place of $[Re(CO)_3(^tBu_2bpy)(CH_3CN)](CF_3SO_3)$ in the substitution reaction, and the complex was obtained as a $CF_3SO_3^-$ salt. Yield: 91 mg, 0.082 mmol; 60%. ^1H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 2.91 (s, 12H, NCH_3), 6.50 (d, 4H, J = 9.0 Hz, phenyl protons at 2,2′,6,6′ positions), 6.87 (d, 4H, J = 9.0 Hz, phenyl protons at 3,3′,5,5′ positions), 7.23 (dd, 2H, J = 5.2, 1.7 Hz, pyridyl protons at 3,5 positions), 8.32 (dd, 2H, J = 5.2, 1.7 Hz, pyridyl protons at 2,6 positions), 8.35 (dd, 2H, J = 8.7, 5.1 Hz, phenanthrolinyl protons at 3,8 positions), 9.17 (dd, 2H, J = 8.7, 1.3 Hz, phenanthrolinyl protons at 4,7 positions), 9.68 (dd, 2H, J = 5.1, 1.3 Hz, phenanthrolinyl protons at 2,9 positions); positive-ion ESI-MS: m/z: 964.7 $[M–CF_3SO_3]^+$; IR (KBr disc): ν/cm^{-1}: 2035, 1940, 1920 (C≡O); elemental analyses calcd (%) for $C_{38}H_{30}Br_2N_6O_3ReCF_3SO_3{\cdot}0.5CH_2Cl_2$ (1156.23): C 41.03 H 2.70 N 7.27; found: C 41.28 H 2.74 N 7.46.

$[Re(CO)_3(NO_2phen)(L1)](PF_6)$ (4). The title complex was synthesised according to a procedure similar to that of **1**, except that $[Re(CO)_3(NO_2phen)(CH_3CN)](CF_3SO_3)$ (94 mg, 0.14 mmol) was used in place of $[Re(CO)_3({}^tBu_2bpy)(CH_3CN)](CF_3SO_3)$ in the substitution reaction. Yield: 60 mg, 0.060 mmol; 44%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 2.88 (d, 12H, J = 4.5 Hz, NCH_3), 6.56 (d, 4H, J = 6.8 Hz, phenyl protons 2,2′,6,6′ positions), 6.88 (d, 4H, J = 6.8 Hz, phenyl protons at 3,3′,5,5′ positions), 7.28 (dd, 2H, J = 5.3, 1.5 Hz, pyridyl protons at 3,5 positions), 8.13 (dd, 2H J = 5.3, 1.5 Hz, pyridyl protons at 2,6 positions), 8.26 (dd, 1H, J = 8.0, 5.1 Hz, phenanthrolinyl proton at 8 position), 8.28 (dd, 1H, J = 8.0, 5.2 Hz, phenanthrolinyl proton at 3 position), 8.98 (dd, 1H, J = 8.0, 1.3 Hz, phenanthrolinyl proton at 7 position), 9.08 (s, 1H, phenanthrolinyl proton at 6 position), 9.55 (dd, 1H, J = 8.0, 1.4 Hz, phenanthrolinyl proton at 4 position), 9.59 (dd, 1H, J = 5.1, 1.3 Hz, phenanthrolinyl proton at 9 position), 9.65 (dd, 1H, J = 5.2, 1.4 Hz, phenanthrolinyl proton at 2 position); positive-ion ESI-MS: m/z: 851.9 $[M–PF_6]^+$; IR (KBr disc): ν/cm^{-1}: 2035, 1935, 1920 (C≡O); 840 (P–F); elemental analyses calcd (%) for $C_{38}H_{31}N_7O_5RePF_6{\cdot}0.5CH_2Cl_2$ (1039.33): C 44.49 H 3.10 N 9.43; found: C 44.42 H 3.30 N 9.71.

$[Re(CO)_3(L2)Br]$ (5). Complex **5** was synthesised by refluxing a suspension of $[Re(CO)_5Br]$ (100 mg, 0.25 mmol) and **L2** (129.6 mg, 0.3 mmol) in benzene (40 mL) for 5 h under an inert atmosphere of argon. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using dichloromethane–acetone (9 : 1 v/v) as the eluent. Slow diffusion of diethyl ether vapour into a concentrated CH_2Cl_2 solution of the complex gave a yellowish orange crystalline solid of **5**. Yield: 98 mg, 0.12 mmol; 50%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, TMS): δ 2.55 (s, 1H, bipyridyl CH_3), 2.97 (d, 12H, J = 1.3 Hz, NCH_3), 6.68 (m, 4H, phenyl protons at 2,2′,6,6′ positions), 7.13 (m, 4H, phenyl protons at 3,3′,5,5′ positions), 7.29 (d, 1H, J = 5.4 Hz, bipyridyl proton at 5′ position), 7.35 (dd, 1H, J = 5.8, 1.7 Hz, bipyridyl H at 5 position), 7.96 (s, 1H, bipyridyl proton at 3′ position), 8.44 (d, 1H, J = 1.7 Hz, bipyridyl proton at 3 position), 8.76 (d, 1H, J = 5.4 Hz, bipyridyl H at 6′ position); 8.88 (d, 1H, J = 5.8 Hz, bipyridyl H at 6 position); positive-ion ESI-MS: m/z: 708.8 $[M–Br]^+$; IR (KBr disc): ν/cm^{-1}: 2015, 1910, 1890 (C≡O); elemental analyses calcd (%) for $C_{31}H_{30}N_4O_4ReBr$ (788.71): C 47.21, H 3.83, N 7.10; found: C 47.37, H 4.12, N 6.99.

Physical measurements and instrumentation

^{1}H NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane (Me_4Si). All positive-ion ESI mass spectra were recorded on a PE-SCIEX API 300 triple quadrupole mass spectrometer. Elemental analyses of all the compounds were performed on an Elementar Vario EL III elemental analyser.

Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer or a Shimadzu UV-1700 spectrophotometer. Photoexcitation was carried out using a 500 W ozone-free Orieal Hg(Xe) lamp, and monochromatic light was obtained by passing the light through an Oriel 77200 1/4m monochromator. Steady-state emission and excitation spectra at room temperature and at 77 K were recorded on a Horiba Jobin Yvon FluoroMax-4 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 diluted EtOH–MeOH sample solutions contained in a quartz tube inside a liquid nitrogen filled quartz optical Dewar flask. Luminescence quantum yields were determined using the method described by Demas and Crosby[6] with aqueous solution of $[Ru(bpy)_3]Cl_2$ (ϕ_{em} = 0.042[7] with 436-nm excitation) as reference. Luminescence lifetimes of the samples were measured using time-correlated single photon counting (TCSPC) technique on the TCSPC spectrofluorometer in a Fast MCS mode with a NanoLED-375LH excitation source, which has its excitation peak wavelength at 375 nm and pulse width shorter than 750 ps.

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. Model CHI 620 Electrochemical Analyzer. Electrochemical measurements were performed in acetonitrile solutions with 0.1 M $^nBu_4NPF_6$ as the supporting electrolyte at room temperature. The reference electrode was 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 pre-purified argon gas prior to measurements.

Crystal structure determination†

Experimental details for the crystal structure determinations are summarised in Table 1. Crystals of **2** and **3** suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether vapour into a dichloromethane solution of the complexes. Crystals of **2** and **3** mounted in glass capillaries were used for data collection on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer using graphite monochromatised Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods employing the SHELXL-97 program[8] on a PC. Re and many non-H atoms were located according to the direct methods. The positions of other non-H atoms were found after successful refinement by full-matrix least-squares using the SHELXL-97 program[8] on a PC. In the final stage of least-squares refinement, all non-H atoms were refined anisotropically. H atoms were generated by the SHELXL-97 program.[8] The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of the final R-indices. A conventional index R_1 based on observed F values larger than $4\sigma(F_o)$ is given (corresponding to intensity $\geq 2\sigma(I)$). $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$, The Goodness of Fit is always based on

Table 1 Crystal and structure determination data for complexes **2** and **3**

	2	**3**
Formula	$C_{38}H_{32}N_6O_3RePF_6$	$C_{39}H_{30}Br_2F_3N_6O_6ReS$
Mr	951.88	1113.77
T/K	293 (2)	298 (2)
A/Å	16.7916 (4)	17.4444 (3)
b/Å	11.0807 (3)	11.1975 (2)
c/Å	26.4430 (7)	20.8885 (4)
α/°	90.00	90.00
β/°	128.189 (2)	91.2079 (15)
γ/°	90.00	90.00
V/$Å^3$	3867.04 (17)	4079.32 (13)
Crystal colour	Orange	Red
Crystal system	Monoclinic	Monoclinic
Space group	*P*2/*c*	*P*2/*n*
Z	4	4
F(000)	1880	2168
D_c/g cm^{-3}	1.635	1.813
Crystal dimensions/mm	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20
λ/Å (graphite monochromated, Mo-Kα)	0.71073	0.71073
μ/mm^{-1}	3.257	5.056
Collection range/°	$3.15 \le \theta \le 25.00$ *h*: −19 to 19 *k*: −8 to 13 *l*: −21 to 31	$3.07 \le \theta \le 25.00$ *h*: −20 to 20 *k*: −13 to 13 *l*: −24 to 24
Completeness to theta (%)	96.7	99.5
No. of data collected	13 037	62 975
No. of unique data	6579	7169
No. of data used in refinement, *m*	3976	4632
No. of parameters refined, *p*	498	599
R^a	0.0371	0.0390
wR^a	0.0776	0.0796
Goodness-of-fit, *S*	0.846	0.917
Maximum shift, $(\Delta/\sigma)_{max}$	0.002	0.001
Residual extrema in final difference map/e $Å^{-3}$	+1.479, −0.895	+1.505, −0.984

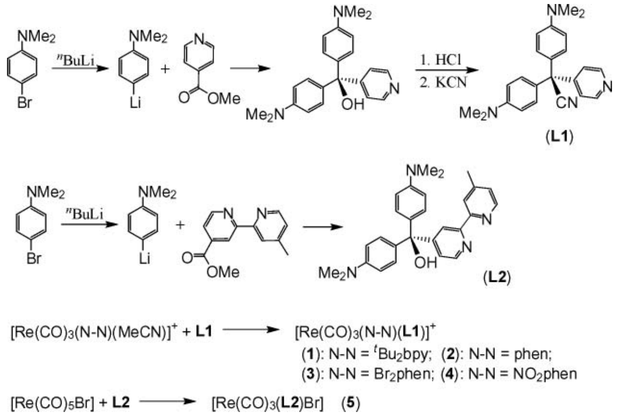
[a] $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bP]$, where $P = [2F_c^2 + \max(F_o^2,0)]/3$.

F^2: GooF $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined. The weighting scheme is: $w = 1/[\sigma^2(F_o^2) + (\alpha P)^2 + bP]$, where *P* is $[2F_c^2 + \max(F_o^2,0)]/3$.

Results and discussion

Synthesis and characterisation

The synthetic routes for the formation of the leucotriarylmethane-containing ligands are summarised in Scheme 1. Reaction of lithiated 4-dimethylaminobenzene with methyl isonicotinate or methyl 4′-methyl-2,2′-bipyridine-4-carboxylate, which was prepared by the esterification of 4-4-carboxyl-4′-methyl-2,2′-bipyridine[4b] with methanol using H_2SO_4 as catalyst, gave **L1OH** and **L2**, respectively. Acidification of **L1OH** with hydrochloric acid, which generates the triarylmethane cation, followed by cyanation with potassium cyanide afforded pyridine-containing leucotriarylmethane nitrile (**L1**). Substitution of $[Re(CO)_3(N–N)(MeCN)](CF_3SO_3)$ with **L1** gave complexes **1–4** that, after purification by column chromatography using silica gel and subsequent recrystallisation from $CH_2Cl_2–Et_2O$, were isolated as yellow to orange crystalline solids, depending on the nature of the diimine ligands. Substitution reactions of $Re(CO)_5Br$ with **L2** in anhydrous benzene under reflux conditions afforded complex **5**. The identities of the ligands **L1**, **L2** and their rhenium complexes **1–5** were confirmed by satisfactory elemental analyses, ^1H NMR, IR spectroscopy and ESI mass spectrometry, and for complexes **2** and **3**, by X-ray crystallography.



Scheme 1 Synthetic routes for **L1**, **L2** and their rhenium(I) complexes.

X-Ray crystal structures

Fig. 1 depicts the perspective drawings of the complex cations of **2** and **3**. The experimental details for the crystal structure determinations and selected bond distances and bond angles

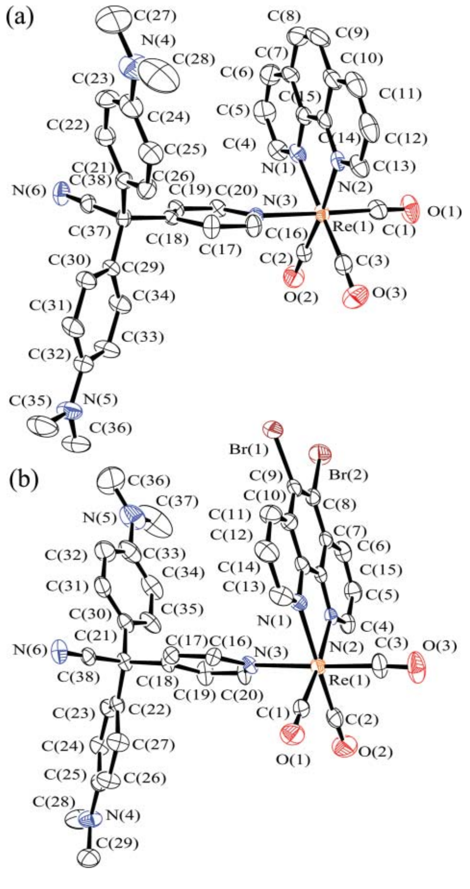


Fig. 1 Perspective drawing of complex cations of (a) **2** and (b) **3** with atomic numbering. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Table 2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for **2** and **3**

2	Re(1)–C(1)	1.922(9)	Re(1)–N(3)	2.202(5)
	Re(1)–C(2)	1.888(8)	C(1)–O(1)	1.144(8)
	Re(1)–C(3)	1.913(9)	C(2)–O(2)	1.166(8)
	Re(1)–N(1)	2.168(5)	C(3)–O(3)	1.151(8)
	Re(1)–N(2)	2.177(5)	C(38)–N(6)	1.130(7)
	N(1)–Re(1)–N(2)	75.5(2)	Re(1)–C(1)—O(1)	177.3(7)
	Re(1)–C(2)–O(2)	179.0(6)	Re(1)–C(3)—O(3)	177.6(7)
	C(1)–Re(1)–C(2)	88.8(3)	C(1)–Re(1)—C(3)	88.3(3)
	C(2)–Re(1)–C(3)	86.1(3)	C(37)–C(38)–N(6)	179.4(9)
3	Re(1)–C(1)	1.932(8)	Re(1)–N(3)	2.224(4)
	Re(1)–C(2)	1.933(9)	C(1)–O(1)	1.139(8)
	Re(1)–C(3)	1.931(7)	C(2)–O(2)	1.143(8)
	Re(1)–N(1)	2.182(5)	C(3)–O(3)	1.126(7)
	Re(1)–N(2)	2.174(5)	C(38)–N(6)	1.121(7)
	N(1)–Re(1)–N(2)	75.13(18)	Re(1)–C(1)—O(1)	178.1(6)
	Re(1)–C(2)–O(2)	177.2(7)	Re(1)–C(3)—O(3)	176.9(7)
	C(1)–Re(1)–C(2)	87.1(3)	C(1)–Re(1)—C(3)	88.4(3)
	C(2)–Re(1)–C(3)	87.7(3)	C(21)–C(38)–N(6)	178.1(7)

are summarised in Tables 1 and 2, respectively. The rhenium metal centres of both structures adopted a distorted octahedral geometry, with angles subtended by the nitrogen atoms of phenanthroline at the rhenium centre of complexes **2** and **3**, N(1)–Re(1)–N(2), of 75.5° and 75.13°, respectively, which are much smaller than the ideal angle of 90° in a regular octahedral geometry. The deviation from the ideal angle of 90° is due to the steric requirements of the chelating phenanthroline ligands, which is commonly observed in other related systems.[5,9] The Re–C, C≡O, Re–N (pyridine) bond lengths in these complexes are in the range of 1.888–1.933 Å, 1.126–1.166 Å and 2.202–2.224 Å, respectively. These bonding parameters are similar to those reported for other related rhenium(I) tricarbonyl diimine pyridine complexes.[5,9] In these structures, the phenyl and pyridyl rings of the **L1** moiety are all connected through an sp^3 carbon, which is in a tetrahedral geometry with bond angles in the range of 106–116°. The non-coplanarity of these rings suggested that there is no π-conjugation between these rings in this form.

Photophysical and photochromic properties

The electronic absorption data of the ligands and their rhenium complexes in CH_2Cl_2 solution at 298 K are collected in Table 3. The absorption spectra of the ligands in CH_2Cl_2 showed very intense absorption bands from 250–320 nm, with molar extinction coefficients on the order of 10^4 dm^3 mol^{-1} cm^{-1}, which was tentatively assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the bipyridine, pyridine and N,N-dimethylamino benzene moieties. Complexes **1**–**5**, in addition to the very intense IL $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorptions at 250–360 nm, had a moderately intense shoulder *ca.* 400–450 nm in their electronic absorption spectra. This absorption shoulder with molar extinction coefficients in the order of 10^3 dm^3 mol^{-1} cm^{-1} was ascribed to the metal-to-ligand charge transfer (MLCT) [dπ(Re) → π*(diimine)] transition that is typical of rhenium(I) tricarbonyl diimine systems,[5,9] probably with some mixing of a ligand-centred character. With the same leucotriarylmethane-containing pyridine ancillary ligand, an absorption energy dependence of this band of **1** > **2** > **3** > **4**, which is inversely related to the π-accepting ability of the diimine ligands (^{t}Bu$_2$bpy < phen < Br$_2$phen < NO$_2$phen), was observed, in agreement with the MLCT assignments.

Except for complex **4**, all complexes in CH_2Cl_2 solution displayed luminescence (Fig. 2) with λ_{em} in the range of 540–591 nm and emission lifetime in the range of 0.2–0.7 μs, which is in the typical range for room temperature MLCT phosphorescence of the rhenium complexes,[5,9] upon excitation at $\lambda = 355$ nm. These emissions showed a similar energy dependence on the π-accepting ability of the diimine ligands as the lowest energy absorption shoulder. With reference to the previous spectroscopic work on related complexes[5,9,10] and the observed emission energy dependence on the diimine ligands, these emissions were also assigned as being derived from MLCT phosphorescence. The luminescence quantum yields of these emissions were also determined to be in the range of 1.5–5.7 × 10^{-3} with 436-nm excitation. The absence of the ^{3}MLCT phosphorescence of **4** can be explained by the non-radiative deactivation pathway to the lower-lying ^{3}IL state associated with the NO$_2$phen ligands.[10d]

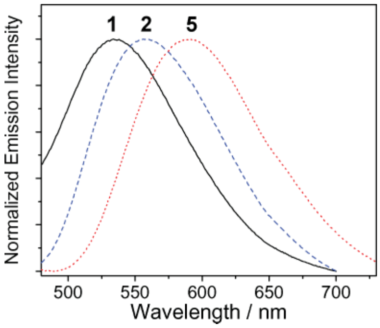
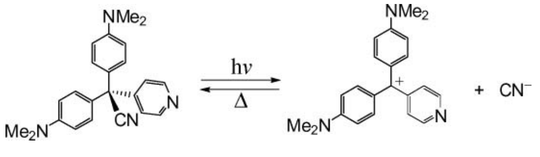


Fig. 2 Overlaid emission spectra of complexes **1**, **2** and **5** in degassed dichloromethane solution at 298 K.

All complexes displayed strong luminescence in EtOH–MeOH 4 : 1 glass at 77 K. These emissions followed the same emission energy trends as the solution emissions, but they were blue shifted. They were also assigned as being derived from ^{3}MLCT origin. The blue shift in emission energy in the glass medium relative to the solution state is attributed to the increased rigidity in the glass medium, which is commonly observed in other related systems.[11] The sub-microsecond excited state lifetime observed in glass medium at 77 K is also supportive of the phosphorescence assignment.

Upon prolonged irradiation at 313 nm, all ligands and complexes in CH_2Cl_2 and DMF solution displayed photochromic behaviour with the formation of new absorption bands peaking *ca.* 420 and 640 nm (Fig. 3), corresponding to the generation of the triarylmethane cation (Scheme 2).[1] The slight red shift of the absorption bands of the triarylmethane cation in **5** (420 and 668 nm) *versus* that in free ligand **L2** (410 and 637 nm) is attributed to perturbation of the transitions by the metal centre in the metal complex. In CH_2Cl_2 solution, the backward reaction rate is very slow, as reflected by the new absorptions remaining unchanged on prolonged standing. The observation of the very well-defined



Scheme 2 Photochromism of **L1**.

Table 3 Photophysical data for the ligands and their rhenium(I) complexes

Compound	Medium (T/K)	Emission λ_{em}/nm (τ_o/μs)	$\Phi_{em}/10^{-3}$	Absorption[a] λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})
L1	CH_2Cl_2(298)	460 (< 0.1)	62.3	266(44 830), 274(49 600), 300(12 640), 341(770)
	Glass[b](77)	420 (< 0.1)		
L1c[c]	CH_2Cl_2(298)	—[d]		312, 418, 640
L2	CH_2Cl_2(298)	515 (< 0.1)	146	252(27 485), 270(38 550), 284(26 630), 312(7580), 345(8105)
	Glass[b](77)	459 (< 0.1)		
L2c[c]	CH_2Cl_2(298)	—[d]		300, 410, 637
1	CH_2Cl_2(298)	540 (0.5)	1.47	254(34 755), 274(51 180), 303(23 085), 317(19 745), 345(8105), 405(1725)
	Glass[b](77)	479 (5.2)		
1c[c]	CH_2Cl_2(298)	—[d]		318, 422, 647
2	CH_2Cl_2(298)	558 (0.7)	1.70	229(41 075), 275(60 240), 310(16 940), 355(7070), 414(1735)
	Glass[b](77)	490 (13.4)		
2c[c]	CH_2Cl_2(298)	—[d]		420, 647
3	CH_2Cl_2(298)	567 (0.5)	1.89	250(42 920), 275(53 950), 286(46 475), 313(17 355), 348(8305), 438(1340)
	Glass[b](77)	520 (9.3)		
3c[c]	CH_2Cl_2(298)	—[d]		416, 646
4	CH_2Cl_2(298)	—[d]		272(77 465), 315(19 660), 358(9760), 442(1540)
	Glass[b](77)	530 (0.2)		
4c[c]	CH_2Cl_2(298)	—[d]		418, 644
5	CH_2Cl_2(298)	591 (0.6)	5.72	257(39 000), 269(44 340), 293(27 305), 313(16 515), 386(5195), 450(1275)
	Glass[b](77)	530 (5.7)		
5c[c]	CH_2Cl_2(298)	—[d]		420, 668

[a] In CH_2Cl_2 at 298 K. [b] EtOH–MeOH (4 : 1 v/v). [c] Triarylmethane cation form. [d] Non-emissive.

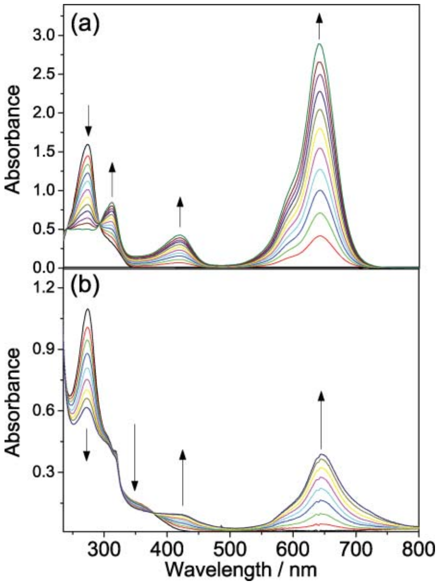


Fig. 3 UV-vis absorption spectral changes of (a) **L1** and (b) **1** in CH_2Cl_2 solution at room temperature upon excitation at 313 nm.

isosbestic points in these UV-vis absorption spectral changes (Fig. 3), and the close resemblance of the absorption spectral changes for all complexes and their free ligands are suggestive of a clean conversion process for the generation of the triarylmethane cations. In DMF solution, these new absorptions decreased in intensity, indicative of the reversibility of the photochromic reaction. The significant difference in the backward reaction rate in CH_2Cl_2 solution is attributed to the formation of the relatively stable chloride salt of the triarylmethane cation.[12] This has been commonly observed in other leucotriarylmethanes.[1,12]

The identities of the triarylmethane cationic form were also further confirmed by the ESI-mass spectrometry. The ESI-mass spectra of **5** in CH_2Cl_2 after photo-irradiation are depicted in Fig. 4. Except for the free ligand **L1**, in which the half-life of the first order decay of triarylmethane cation in DMF solution was determined to be 360 s at 16 °C (Fig. 5), the half-lives of the triarylmethane cation form of **L2** and all rhenium complexes in DMF solutions were too short to be determined with certainty by monitoring the UV-vis absorption changes. The much shorter lifetimes for these cations in the metal complexes can be attributed to the electron-withdrawing effect of the metal centres, as well as the overall positive charge on the metal complexes, both of which render nucleophilic attack on the triarylmethane cation more likely.[1,13] These photochromic processes can be recycled a number of times without significant decomposition, as exemplified in the time dependence of the

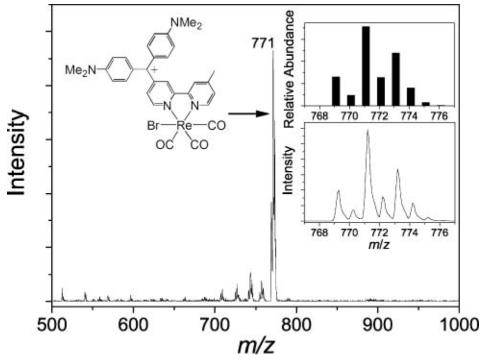


Fig. 4 ESI-mass spectrum of a CH_2Cl_2 solution of **5** after photoirradiation. The inserts show the simulated isotope pattern for the triarylmethane cation form of **5** (top) and the expanded ion cluster from the parent peak of the ESI-mass spectrum (bottom).

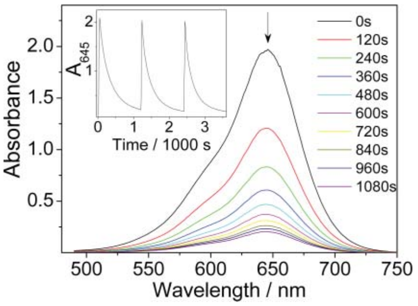


Fig. 5 UV-vis absorption spectral changes of **L1** in DMF solution at 16 °C after excitation at 313 nm. The insert shows the UV-vis absorption changes of **L1** at 645 nm with 313-nm excitation and the subsequent decay trace in the dark over 3 cycles.

absorption spectral changes at 645 nm of **L1** in DMF solution with alternating UV excitation and thermal decolouration cycles (Fig. 5, insert).

Apart from the change in the absorption properties, the emission intensity of all complexes was found to decrease upon excitation into the isosbestic absorption point during the conversion to the triarylmethane cation form in CH_2Cl_2 solution. This is probably attributed to the quenching of the emissive excited state by the lowly lying excited state associated with the triarylmethane cation as reflected by the characteristic low-energy absorption at *ca.* 647 nm.

Electrochemical studies

Complexes **1–5** displayed two quasi-reversible oxidation couples at +0.67 to +0.88 V and +1.72 to +1.81 V in the oxidative scan of the cyclic voltammograms in acetonitrile (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$), while one quasi-reversible reduction couple and one to two irreversible reduction waves at –0.58 to –1.78 V *vs.* SCE were observed in the reductive scan. Complex **5** also showed an irreversible oxidation wave at *ca.* +0.96 V. The electrochemical data for the free ligands and their rhenium(I) complexes are summarised in Table 4, and the representative cyclic voltammograms of **1** are shown in Fig. 6.

The insensitivity of the change of the diimine ligands of the first oxidative couple in complexes **1–4**, as well as the close resemblance of the potential of the first irreversible oxidation wave with that of the free ligands, suggested that the first oxidative couple of **1–4** be assigned to oxidation of the **L1** moiety, probably arising from the removal of a lone pair electron on the nitrogen atom of the dimethylamino moiety.

Table 4 Electrochemical data for ligands and their complexes[a] in acetonitrile solution (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$) at 298 K

Compound	Oxidation[b] $E_{\frac{1}{2}}$/V *vs.* SCE (E_{pa}/V *vs.* SCE)	Reduction[b] $E_{\frac{1}{2}}$/V *vs.* SCE (E_{pc}/V *vs.* SCE)
L1	(+0.99)	(–2.49)
L2	(+0.76), (+0.97)	(–2.29)
1	+0.88, +1.72	–1.26, (–1.60)
2	+0.88, +1.75	–1.15, (–1.52), (–1.78)
3	+0.88, +1.80	–0.97, (–1.57)
4	+0.88, +1.81	–0.58, –1.13
5	+0.67, (+0.96), +1.81	–0.97, (–1.57)

[a] Working electrode, glassy carbon; scan rate, 100 mVs^{-1}. [b] $E_{\frac{1}{2}}$ is estimated from (E_{pa} + E_{pc})/2; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.

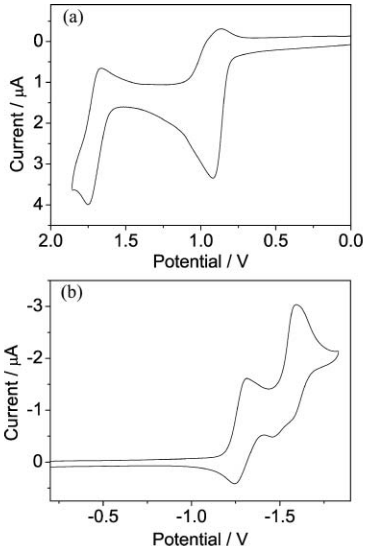


Fig. 6 Cyclic voltammograms of (a) the oxidative scan and (b) reductive scan of **1** in MeCN (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$).

The close resemblance of the first two oxidations of complex **5** and the free ligand **L2** are also suggestive of ligand-centred oxidations of the **L2** moiety.

The second quasi-reversible oxidation couple in the rhenium complexes at *ca.* +1.72 to +1.81 V was found to be dependent on the nature of the diimine ligand and was assigned to the metal-centred oxidation of Re(I) to Re(II). The potential for the oxidation was found to follow the order: **4** (+1.81 V) ≈ **3** (+1.80 V) > **2** (+1.75 V) > **1** (+1.72 V), in line with the π-accepting ability of the diimine ligands: NO_2phen ≥ Br_2phen > phen > $^{t}Bu_2$bpy. In general, the better the π-accepting ability of the diimine ligand, the more stable the dπ(Re) orbital is, and hence, the more difficult the oxidation process becomes. Similar oxidation couples ascribed to a Re(I)/Re(II) oxidation have been reported in other related systems, such as $[Re(CO)_3(N–N)(py)]$.[14]

The first two reductions were tentatively assigned to diimine ligand-centred reductions, as they are commonly observed in related systems.[14] The trends of these reduction potentials are also in line with the electron-richness and π-accepting ability of the diimine ligands as discussed above, but with a much stronger dependence when compared to the metal-centred oxidation.

Conclusion

A series of photochromic leucotriarylmethane-containing ligands and their rhenium(I) tricarbonyl diimine complexes were successfully synthesised, and their photophysical and photochromic properties were studied. Except for **4**, all complexes displayed MLCT phosphorescence in CH_2Cl_2 solution and in a 77 K EtOH–MeOH glass medium. Upon UV excitation at 313 nm, all of the ligands and complexes underwent photo-ionisation in CH_2Cl_2 solution. In DMF solution, the triarylmethane cations of all of the ligands and complexes underwent the thermal backward reaction. The half-life of the first order decay of the triarylmethane cation of **L1** in DMF solution was found to be 360 s at 16 °C. The electrochemistry of these ligands and complexes was also studied.

Acknowledgements

The work described in this paper was supported by a RGC GRF grant from the Research Grants Council of the Hong Kong (Project No. CityU 101008), the Special Equipment Grant from the University Grants Committee of the Hong Kong (SEG_City U02) and a grant from City University of Hong Kong (Project No. 7002307). H. Feng acknowledges the receipt of a Postgraduate studentship from City University of Hong Kong.

Notes and references

1 (*a*) R. C. Bertelson, *Photochromism, Techniques in Chemistry*, ed. G. H. Brown, Wiley Interscience, New York, 1971; (*b*) *Chemistry and Applications of Leuco Dyes*, ed. R. Muthyala, Plenum Press, New York, 1997.

2 (*a*) K. Kimura, R. Mizutani, M. Yokoyama, R. Arakawa, G. Matsubayashi, M. Okamoto and H. Doe, *J. Am. Chem. Soc.*, 1997, **119**, 2062; (*b*) K. Kimura, R. Mizutani, M. Yokoyama, R. Arakawa and Y. Sakurai, *J. Am. Chem. Soc.*, 2000, **122**, 5448; (*c*) Y. Jiang, Y. Wang, N. Ma, Z. Wang, M. Smet and X. Zhang, *Langmuir*, 2007, **23**, 4029.

3 (*a*) H. Nishihara, *Coord. Chem. Rev.*, 2005, **249**, 1468; (*b*) S. Kume and H. Nishihara, *Dalton Trans.*, 2008, 3260; (*c*) C.-C. Ko and V. W.-W. Yam, *J. Mater. Chem.*, 2010, **20**, 2063; (*d*) C.-C. Ko, L.-X. Wu, K. M.-C. Wong, N. Zhu and V. W.-W. Yam, *Chem.–Eur. J.*, 2004, **10**, 766; (*e*) V. W.-W. Yam, C.-C. Ko and N. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 12734; (*f*) C.-C. Ko, W.-M. Kwok, V. W.-W. Yam and D. L. Phillips, *Chem.–Eur. J.*, 2006, **12**, 5840; (*g*) J. K.-W. Lee, C.-C. Ko, K. M.-C. Wong, N. Zhu and V. W.-W. Yam, *Organometallics*, 2007, **26**, 12; (*h*) T.-W. Ngan, C.-C. Ko, N. Zhu and V. W.-W. Yam, *Inorg. Chem.*, 2007, **46**, 1144; (*i*) Z. Bao, K.-Y. Ng, V. W.-W. Yam, C.-C. Ko, N. Zhu and L.-X. Wu, *Inorg. Chem.*, 2008, **47**, 8912; (*j*) R. T. F. Jukes, B. Bozic, F. Hartl, P. Belser and L. De Cola, *Inorg. Chem.*, 2006, **45**, 8326; (*k*) R. T. F. Jukes, B. Bozic, P. Belser, L. De Cola and F. Hartl, *Inorg. Chem.*, 2009, **48**, 1711; (*l*) J. D. Lewis, R. N. Pertuz and J. N. Moore, *Chem. Commun.*, 2000, 1865; (*m*) S.-S. Sun and A. J. Lees, *Organometallics*, 2002, **21**, 39; (*n*) O. S. Wenger, L. M. Henling, M. W. Day, J. R. Winkler and H. B. Gray, *Inorg. Chem.*, 2004, **43**, 2043; (*o*) M. Busby, P. Matousek, M. Towrie and A. Vlček, Jr., *J. Phys. Chem. A*, 2005, **109**, 3000; (*p*) M. T. Indelli, S. Carli, M. Ghirotti, C. Chiorboli, M. Ravaglia, M. Garavelli and F. Scandola, *J. Am. Chem. Soc.*, 2008, **130**, 7286; (*q*) R. T. F. Jukes, V. Adamo, F. Hartl, P. Belser and L. De Cola, *Inorg. Chem.*, 2004, **43**, 2779.

4 (*a*) J. Mlochowski, *J. Rocz. Chem.*, 1974, **48**, 2145; (*b*) D. G. McCafferty, B. M. Bishop, C. G. Wall and S. G. Hughes, *Tetrahedron*, 1995, **51**, 1093.

5 (*a*) R. Lin, Y. Fu, C. P. Brock and T. F. Guarr, *Inorg. Chem.*, 1992, **31**, 4346; (*b*) G. Tapolsky, R. Duesing and T. J. Meyer, *Inorg. Chem.*, 1990, **29**, 2285; (*c*) V. W.-W. Yam, C.-C. Ko, L.-X. Wu, K. M.-C. Wong and K. K. Cheung, *Organometallics*, 2000, **19**, 1820.

6 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

7 J. van Houten and R. J. Watts, *J. Am. Chem. Soc.*, 1976, **98**, 4853.

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

9 (*a*) E. Horn and M. R. Snow, *Aust. J. Chem.*, 1980, **33**, 2369; (*b*) P. Chen, M. Curry and T. J. Meyer, *Inorg. Chem.*, 1989, **28**, 2271; (*c*) V. W.-W. Yam, V. C.-Y. Lau and K.-K. Cheung, *J. Chem. Soc., Chem. Commun.*, 1995, 259; (*d*) V. W.-W. Yam, S. H.-F. Chong, C.-C. Ko and K. K. Cheung, *Organometallics*, 2000, **19**, 5092; (*e*) C.-O. Ng, L. T.-L. Lo, S.-M. Ng, C.-C. Ko and N. Zhu, *Inorg. Chem.*, 2008, **47**, 7447.

10 (*a*) M. S. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998; (*b*) K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 2401; (*c*) R. A. Kirgan, B. P. Sullvan and D. P. Rillema, *Top. Curr. Chem.*, 2007, **281**, 45; (*d*) A. Gabrielsson, P. Matousek, M. Towrie, F. Hartl, S. Zalis and A. Vlcek, Jr, *J. Phys. Chem. A*, 2005, **109**, 6147.

11 (*a*) P. J. Giordano and M. S. Wrighton, *J. Am. Chem. Soc.*, 1979, **101**, 2888; (*b*) A. J. Lees, *Chem. Rev.*, 1987, **87**, 711; (*c*) T. G. Kotch, A. J. Lees, S. J. Fuerniss, K. I. Papathomas and R. W. Snyder, *Inorg. Chem.*, 1993, **32**, 2570; (*d*) H. Kunkely and A. Vogler, *Mater. Chem. Phys.*, 2008, **109**, 506.

12 (*a*) K. Bobrowski, G. Dzierzkowska, J. Grodkowski, Stuglik, Z. P. Zagorski and W. L. McLaughlin, *J. Phys. Chem.*, 1985, **89**, 4358; (*b*) P. K. Das, *Chem. Rev.*, 1993, **93**, 119; (*c*) V. V. Jarikov and D. C. Neckers, *J. Org. Chem.*, 2001, **66**, 659.

13 (*a*) M. L. Herz, *J. Am. Chem. Soc.*, 1975, **97**, 6777; (*b*) V. V. Jarikov and D. C. Neckers, *Adv. Photochem.*, 2001, 1.

14 (*a*) J. C. Luong, L. Nadjo and M. S. Wrighton, *J. Am. Chem. Soc.*, 1978, **100**, 5790; (*b*) C. Kutal, M. A. Weber, G. Ferraudi and D. Geiger, *Organometallics*, 1985, **4**, 2161; (*c*) L. Sacksteder, A. P. Zipp, E. A. Brown, J. Streich, J. N. Demas and B. A. Degraff, *Inorg. Chem.*, 1990, **29**, 4335; (*d*) V. W.-W. Yam, V. C.-Y. Lau and L.-X. Wu, *J. Chem. Soc., Dalton Trans.*, 1998, 1461.