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Rhenium(I) Tricarbonyl Complexes with Peripheral *N*-Coordination Sites: a Foundation for Heterotrimetallic Nonlinear Optical Chromophores

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ABSTRACT: The compounds 4,4'-dicyano-2,2'-bipyridyl (dcbpy), 4,4'-bis(4-cyanophenyl)-2,2'-bipyridyl (bcpbpy), 4,4'-bis[(*E*)-2-(4-cyanophenyl)vinyl]-2,2'-bipyridyl (bcpvbpy) and 4,4'-bis[(*E*)-2-(4-pyridyl)vinyl]-2,2'-bipyridyl (bpvbpy) are used to prepare 9 new complexes with $fac\text{-}\{Re^I(CO)_3(L)\}^{n+}$ ($L = Cl^-$, MeCN, pyridine (py) or 4-cyanopyridine (cpy)) centers. The cationic complexes are isolated as their OTf^- salts. These new monometallic species are studied together with the known $fac\text{-}Re^I Cl(CO)_3(qpy)$ ($qpy = 4,4':2',2'':4'',4'''$ -quaterpyridyl) (de Wolf, P.; et al. *Inorg. Chim. Acta* **2003**, 355, 280–285). Coordination of $\{Ru^{II}(NH_3)_5\}^{2+}$ centers to the peripheral N atoms of $fac\text{-}Re^I Cl(CO)_3(qpy)$ and $fac\text{-}[Re^I(CO)_3(bcpbpy)(py)]^+$ affords heterotrimetallic complexes which are isolated as their PF_6^- salts. Single crystal X-ray structures are reported for the solvates $fac\text{-}Re^I Cl(CO)_3(dcbpy) \cdot Me_2CO$, $fac\text{-}[Re^I(CO)_3(dcbpy)(MeCN)]OTf \cdot PhMe$, $fac\text{-}[Re^I(CO)_3(dcbpy)(py)]OTf \cdot 0.5PhMe$, $fac\text{-}[Re^I(CO)_3(dcbpy)(cpy)]OTf \cdot 0.5Me_2CO$, $fac\text{-}Re^I Cl(CO)_3(bcpbpy) \cdot 0.5PhMe$ and $fac\text{-}[Re^I(CO)_3(bcpbpy)(MeCN)]OTf \cdot MeCN$. Cyclic voltammetry reveals irreversible $Re^{II/I}$ processes in all cases, while the trimetallic compounds show a reversible 2-electron $Ru^{III/II}$ oxidation wave. Ligand-based reductions are generally irreversible, but reversible waves are observed for the dcbpy complexes. Electronic absorption spectra show strong $d \rightarrow \pi^*$ metal-to-ligand charge-transfer (MLCT) and intraligand $\pi \rightarrow \pi^*$ absorptions. The Ru^{II} -based MLCT bands have lower energies and higher intensities than the Re^I -based ones. The monometallic species emit weakly in the red/NIR region ($\lambda_{em} = 594\text{--}732$ nm; $\phi = 0.6\text{--}8.1\%$) when excited at 350–520 nm. Molecular first hyperpolarizabilities β for the trimetallic complex salts are measured in MeCN solutions via the hyper-Rayleigh scattering technique at 1064 nm. Stark (electroabsorption) spectroscopic studies on the low energy MLCT bands in frozen PrCN allow the indirect estimation of static first hyperpolarizabilities β_0 . The trimetallic complexes have relatively large β_0 values, ca. 500×10^{-30} esu or more, which are substantially greater than those of the monometallic species.

INTRODUCTION

Organotransition metal complexes often have very interesting electronic and optical properties which may prove useful in various applications.¹ Areas currently attracting major attention include the use of luminescence in organic light-emitting diodes (OLEDs),² photoinduced charge-transfer in dye-sensitized solar cells,³ and nonlinear optics which allows the manipulation of laser light beams.⁴ In most cases, the valuable properties derive from the presence of low energy and long-lived metal-to-ligand charge-transfer (MLCT) excited states. Complexes of various metals have been studied intensively, particularly the heavy d^6 ions Ru^{II} , Re^I or Ir^{III} in an octahedral coordination with polypyridyl ligands. In the case of Re , the chromophores typically have the structure $fac-[Re^I(CO)_3(L-L)(L)]^{n+}$ where $L-L$ is an α -diimine such as 2,2'-bipyridyl (bpy) or its derivatives, and L is an anionic or charge-neutral monodentate ligand (and therefore $n = 0$ or 1 , respectively).⁵ Especially recent publications on such complexes include fundamental studies of charge-transfer photoexcitation behavior,⁶ electrocatalytic CO_2 reduction,^{7,8} and potential anticancer drugs with both therapeutic and imaging capabilities.⁹

An attractive prospect to enhance properties and/or impart multifunctionality is to create polymetallic complexes by using bridging ligands. For $fac-[Re^I(CO)_3(L-L)(L)]^{n+}$ systems, either L and/or $L-L$ can be used to attach additional metal centers. The complex $fac-Re^I Cl(CO)_3(qpy)$ (**10**, $qpy = 4,4':2',2'':4'',4'''$ -quaterpyridyl) has been reported,¹⁰ but apparently not used to assemble polymetallic species as yet. While using pendent pyridyl units is appealing, incorporating nitrile substituents provides an alternative approach. However, $fac-\{Re^I(CO)_3\}^+$ complexes of nitrile-functionalized $L-L$ ligands were apparently unknown when we commenced our investigations. We report here the synthesis and full characterization of a series of such new complexes, along with another bearing pyridyl substituents. **10** together with a complex of the ligand 4,4'-bis(4-cyanophenyl)-2,2'-bipyridyl (bcpbpy) are used to prepare heterotrimetallic species with two $\{Ru^{II}(NH_3)_5\}^{2+}$ centers. We have studied previously the nonlinear optical (NLO) properties of a range of transition metal complexes, especially Ru^{II} ammines,¹¹ and also a few bimetallic Ru^{II}/Re^I complexes

containing bis(4-pyridyl) bridging ligands.¹² Therefore, the characterization of the new trimetallic compounds includes both direct and indirect measurements of NLO responses, revealing some promising results.

EXPERIMENTAL SECTION

Materials and Procedures. The compounds 4,4'-bis[(diethoxyphosphinyl)methyl]-2,2'-bipyridyl,¹³ 4,4'-dicyano-2,2'-bipyridyl (dcbpy),¹⁴ 4,4'-bis[(*E*)-2-(4-pyridyl)vinyl]-2,2'-bipyridyl (bpvbp),¹⁵ *fac*-Re^ICl(CO)₃(qpy) (**10**)¹⁰ and [Ru^{II}(NH₃)₅(H₂O)](PF₆)₂¹⁶ were prepared by following published procedures. Products were dried at room temperature overnight in a vacuum desiccator (silica gel) or by direct attachment to a high vacuum line for several hours before characterization. All other reagents were obtained commercially and used as supplied.

General Physical Measurements. ¹H NMR spectra were recorded on Bruker UltraShield 500 or AV-400 spectrometers, with all shifts referenced to residual solvent signals and quoted with respect to TMS. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester, and UV-vis absorption spectra were obtained by using a Shimadzu UV-2401 PC spectrophotometer. UV-vis spectra for the spectroelectrochemical measurements were recorded in 0.1 M [N(C₄H₉-*n*)₄]⁺PF₆⁻ (Fluka, electrochemical grade) in MeCN in a BASi optically transparent thin layer electrochemical (OTTLE) cell. Steady-state emission and excitation spectra were recorded on an Edinburgh Instruments FP920 Phosphorescence Lifetime Spectrometer equipped with a 5 W microsecond pulsed Xe flashlamp. Lifetime data were recorded following excitation with an EPL 375 picosecond pulsed diode laser (Edinburgh Instruments), using time-correlated single photon counting (PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fitting on the data obtained, or by a reconvolution fit using a solution of Ludox® in the scatterer, and the quality of fit judged by minimization of reduced chi-squared and residuals squared. Quantum yields were measured upon excitation at 420 nm by using a SM4 Integrating Sphere mounted on an Edinburgh Instruments FP920 Phosphorescence Lifetime Spectrometer.

IR spectroscopy was performed on solid samples by using an Excalibur BioRad FT-IR spectrometer, and mass spectra were recorded by using MALDI on a Micromass Tof Spec 2e or +electrospray on a Micromass Platform II spectrometer. Cyclic voltammetric

measurements were performed by using an Ivium CompactStat. A single-compartment cell was used with a silver/silver chloride reference electrode (3 M NaCl, saturated AgCl) separated by a salt bridge from a 3 mm disk glassy-carbon working electrode and Pt wire auxiliary electrode. MeCN was used as supplied from Sigma-Aldrich (HPLC grade), and $[N(C_4H_9-n)_4]PF_6$ was used as the supporting electrolyte. Solutions containing ca. 10^{-3} M analyte (0.1 M $[N(C_4H_9-n)_4]PF_6$) were deaerated by purging with N_2 . All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 100 mV s^{-1} .

Synthesis of 4,4'-bis(4-cyanophenyl)-2,2'-bipyridyl (bcpbpy). Aqueous Na_2CO_3 (2 M, 14 mL) was added to a solution of 4,4'-dibromo-2,2'-bipyridyl (300 mg, 0.955 mmol) in toluene (20 mL), and the biphasic mixture purged with Ar. $[Pd(PPh_3)_4]$ (55 mg, 5 mol%) was added under Ar, followed by an Ar-purged solution of 4-cyanophenylboronic acid pinacol ester (670 mg, 2.92 mmol) in ethanol (10 mL). The reaction was heated at $110^\circ C$ for 48 h. After cooling, the mixture was diluted with water (30 mL) and toluene (30 mL), the ethanol removed in vacuo and $CHCl_3$ added (30 mL). The phases were separated, the aqueous phase extracted with $CHCl_3$ ($2 \times 20 \text{ mL}$) and the combined extracts washed with saturated aqueous NaCl ($2 \times 20 \text{ mL}$) and dried over anhydrous $MgSO_4$. The latter was filtered off and washed with $CHCl_3$ to dissolve any beige precipitate. Removal of the solvents in vacuo was followed by column chromatography on silica gel eluting with CH_2Cl_2 /methanol (0–10%). The final beige band was collected and concentrated under vacuum. Methanol (10 mL) was added to the residue and the beige solid filtered off, washed with methanol (10 mL) then diethyl ether (10 mL) and dried in vacuum: 170 mg, 43%; δ_H (500 MHz, $CDCl_3$) 8.81 (2 H, d, $J = 5.0 \text{ Hz}$, $C_5H_3N-H^6$), 8.76 (2 H, d, $J = 1.5 \text{ Hz}$, $C_5H_3N-H^3$), 7.89 (4 H, d, $J = 8.5 \text{ Hz}$, C_6H_4), 7.82 (4 H, d, $J = 8.5 \text{ Hz}$, C_6H_4), 7.57 (2 H, d, $J = 5.0, 2.0 \text{ Hz}$, $C_5H_3N-H^5$). $\nu(C\equiv N)$ 2225 m cm^{-1} . Anal. Calcd (%) for $C_{24}H_{14}N_4 \cdot 0.6CH_2Cl_2$: C, 72.2; H, 3.7; N, 13.7. Found: C, 72.2; H, 3.9; N, 14.0.

Synthesis of 4,4'-bis[(E)-2-(4-cyanophenyl)vinyl]-2,2'-bipyridyl (bcpvbpy). KO^tBu (295 mg, 2.63 mmol) was added to a solution of 4-cyanobenzaldehyde (316 mg, 2.41 mmol) and 4,4'-bis[(diethoxyphosphinyl)methyl]-2,2'-bipyridyl (500 mg, 1.11 mmol) in THF (25 mL). The mixture was stirred at room temperature in the dark for 1 h, then quenched by the addition of water (60 mL). The cream-colored precipitate was filtered off, washed with water

and diethyl ether and dried in vacuo: 375 mg, 81%; δ_{H} (400 MHz, CDCl_3) 8.72 (2 H, d, $J = 5.6$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^6$), 8.60 (2 H, s, $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 7.68 (4 H, d, $J = 8.4$ Hz, C_6H_4), 7.65 (4 H, d, $J = 8.4$ Hz, C_6H_4), 7.48–7.42 (4 H, $\text{C}_5\text{H}_3\text{N}-\text{H}^5 + \text{CH}$), 7.25 (2 H, d, $J = 16.0$ Hz, CH). $\nu(\text{C}\equiv\text{N})$ 2225 m cm^{-1} . Anal. Calcd (%) for $\text{C}_{28}\text{H}_{18}\text{N}_4 \cdot 0.5\text{H}_2\text{O}$: C, 80.2; H, 4.6; N, 13.4. Found: C, 80.2; H, 4.4; N, 13.0. ES-MS: $m/z = 433$ ($[\text{M} + \text{Na}]^+$).

Synthesis of *fac*- $\text{Re}^{\text{I}}\text{Cl}(\text{CO})_3(\text{dcbpy})$ (1). $\text{Re}^{\text{I}}\text{Cl}(\text{CO})_5$ (175 mg, 0.484 mmol) and dcbpy (100 mg, 0.485 mmol) in an Ar-degassed mixture of toluene (10 mL) and CHCl_3 (3 mL) were protected from the light and heated under reflux for 7 h. After cooling to room temperature, toluene (20 mL) was added to the solution. The orange solid was filtered off, washed with CHCl_3 (5 mL) and dried: 210 mg, 79%; δ_{H} (500 MHz, $(\text{CD}_3)_2\text{CO}$) 9.42 (2 H, dd, $J = 5.8, 0.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^6$), 9.29 (2 H, d, $J = 1.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 8.25 (2 H, dd, $J = 5.8, 1.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^5$). $\nu(\text{C}\equiv\text{N})$ 2240 w, $\nu(\text{C}\equiv\text{O})$ 2014 st, $\nu(\text{C}\equiv\text{O})$ 1899 br cm^{-1} . Anal. Calcd (%) for $\text{C}_{15}\text{H}_6\text{ClN}_4\text{O}_3\text{Re} \cdot 0.4\text{PhMe}$: C, 39.0; H, 1.7; N, 10.2. Found: C, 39.2; H, 1.8; N, 9.9. MALDI-MS: $m/z = 512$ ($[\text{M}]^+$). The filtrate was allowed to evaporate slowly overnight yielding further product as dark orange needles: 30 mg, 11%. Crystals suitable for X-ray diffraction were grown by slow evaporation of an acetone/ethanol solution.

Synthesis of *fac*- $[\text{Re}^{\text{I}}(\text{CO})_3(\text{dcbpy})(\text{MeCN})]\text{OTf}$ (2). $1 \cdot 0.4\text{PhMe}$ (50 mg, 0.091 mmol) and AgCF_3SO_3 (28 mg, 0.109 mmol) were dissolved in Ar-degassed MeCN (10 mL), protected from the light and heated under reflux for 16 h. The mixture was cooled to room temperature and filtered through Celite to remove AgCl. The filtrate was concentrated in vacuo and toluene was added to precipitate an orange microcrystalline solid: 58 mg, 91%; δ_{H} (500 MHz, CD_3CN) 9.22 (2 H, dd, $J = 5.8, 0.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^6$), 8.81 (2 H, d, $J = 1.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 8.06 (2 H, dd, $J = 5.8, 1.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 2.05 (3 H, s, MeCN). $\nu(\text{C}\equiv\text{N})$ 2306 w, $\nu(\text{C}\equiv\text{N})$ 2245 w, $\nu(\text{C}\equiv\text{O})$ 2038 st, $\nu(\text{C}\equiv\text{O})$ 1929 st cm^{-1} . Anal. Calcd (%) for $\text{C}_{18}\text{H}_9\text{F}_3\text{N}_5\text{O}_6\text{ReS} \cdot 0.4\text{PhMe}$: C, 35.5; H, 1.8; N, 10.0. Found: C, 35.6; H, 1.9; N, 9.7. MALDI-MS: $m/z = 518$ ($[\text{M} - \text{OTf}]^+$). Crystals suitable for X-ray diffraction were grown by slow evaporation of an MeCN/toluene solution.

Synthesis of *fac*- $[\text{Re}^{\text{I}}(\text{CO})_3(\text{dcbpy})(\text{py})]\text{OTf}$ (3). $1 \cdot 0.4\text{PhMe}$ (51 mg, 0.093 mmol) and AgCF_3SO_3 (33 mg, 0.128 mmol) were placed in Ar-degassed acetone (10 mL) with

pyridine (a few drops). The mixture was protected from the light and heated to reflux under Ar for 6 h. The mixture was cooled to room temperature and filtered through Celite to remove AgCl. The volatiles were removed in vacuo to leave an orange solid which was exposed to visible light for ca. 24 h to decompose any remaining silver salt. Acetone was added and the mixture filtered through Celite. Toluene was added to the filtrate and the solution was allowed to evaporate slowly at room temperature, yielding orange crystals suitable for X-ray diffraction: 60 mg, 86%; δ_{H} (500 MHz, $(\text{CD}_3)_2\text{CO}$) 9.83 (2 H, dd, $J = 5.8, 0.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^6$), 9.30 (2 H, d, $J = 1.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 8.62 (2 H, d, $J = 5.0$ Hz, $\text{py}-\text{H}^{2,6}$), 8.47 (2 H, dd, $J = 5.5, 1.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 8.04 (1 H, t, $J = 7.8$ Hz, $\text{py}-\text{H}^4$), 7.49 (2 H, t, $J = 7.0$ Hz, $\text{py}-\text{H}^{3,5}$). $\nu(\text{C}\equiv\text{N})$ 2242 vw, $\nu(\text{C}=\text{O})$ 2028 st, $\nu(\text{C}=\text{O})$ 1922 st cm^{-1} . Anal. Calcd (%) for $\text{C}_{21}\text{H}_{11}\text{F}_3\text{N}_5\text{O}_6\text{ReS}\cdot 0.5\text{PhMe}$: C, 39.2; H, 2.0; N, 9.3. Found: C, 39.2; H, 2.1; N, 9.2. MALDI-MS: $m/z = 556$ ($[\text{M} - \text{OTf}]^+$).

Synthesis of *fac*-[Re^I(CO)₃(dcbpy)(cpy)]OTf (4). This compound was prepared and purified in a manner similar to **3** by using **1**·0.4PhMe (65 mg, 0.118 mmol), AgCF₃SO₃ (44 mg, 0.171 mmol) and 4-cyanopyridine (19 mg, 0.182 mmol) instead of pyridine. Yellow/orange crystals suitable for X-ray diffraction were obtained: 74 mg, 83%; δ_{H} (500 MHz, CD_3CN) 9.39 (2 H, dd, $J = 5.8, 0.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^6$), 8.72 (2 H, d, $J = 1.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 8.39 (2 H, d, $J = 6.5$ Hz, $\text{C}_5\text{H}_4\text{N}$), 8.13 (2 H, dd, $J = 5.8, 1.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 7.62 (2 H, d, $J = 6.5$ Hz, $\text{C}_5\text{H}_4\text{N}$). $\nu(\text{C}\equiv\text{N})$ 2256 vw, $\nu(\text{C}=\text{O})$ 2037 st, $\nu(\text{C}=\text{O})$ 1907 st cm^{-1} . Anal. Calcd (%) for $\text{C}_{22}\text{H}_{10}\text{F}_3\text{N}_6\text{O}_6\text{ReS}\cdot 0.5\text{Me}_2\text{CO}$: C, 37.2; H, 1.7; N, 11.1. Found: C, 37.1; H, 1.9; N, 10.8. MALDI-MS: $m/z = 728$ ($[\text{M}]^+$), 582 ($[\text{M} - \text{OTf} + \text{H}]^+$).

Synthesis of *fac*-Re^ICl(CO)₃(bcpbpy) (5). This compound was synthesized in a manner similar to **1** by using bcpbpy·0.6CH₂Cl₂ (48 mg, 0.117 mmol) instead of dcbpy, and Re^ICl(CO)₅ (43 mg, 0.119 mmol) in an Ar-degassed mixture of toluene (10 mL) and CHCl₃ (3 mL). After cooling to room temperature, toluene was added and the solution was allowed to slowly evaporate at room temperature, yielding an orange microcrystalline solid: 72 mg, 90%; δ_{H} (500 MHz, $(\text{CD}_3)_2\text{CO}$) 9.29 (2 H, d, $J = 2.0$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 9.22 (2 H, dd, $J = 7.5, 0.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^6$), 8.27 (4 H, d, $J = 8.5$ Hz, C_6H_4), 8.17 (2 H, dd, $J = 7.0, 2.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 8.07 (4 H, d, $J = 8.5$ Hz, C_6H_4). $\nu(\text{C}\equiv\text{N})$ 2229 w, $\nu(\text{C}=\text{O})$ 2024 st, $\nu(\text{C}=\text{O})$ 1929 st, $\nu(\text{C}=\text{O})$ 1879 st

cm^{-1} . Anal. Calcd (%) for $\text{C}_{27}\text{H}_{14}\text{ClN}_4\text{O}_3\text{Re}\cdot\text{H}_2\text{O}$: C, 47.5; H, 2.4; N, 8.2. Found: C, 47.8; H, 2.2; N, 8.0. MALDI-MS: $m/z = 664$ ($[\text{M}]^+$).

Synthesis of *fac*-[Re^I(CO)₃(bcpbpy)(MeCN)]OTf (6). This compound was prepared in a manner similar to **2** by using **5**·H₂O (36 mg, 0.053 mmol) in place of **1**·0.4PhMe, and AgCF₃SO₃ (19 mg, 0.074 mmol). The work-up was as for **3**, except that MeCN was used in the second filtration through Celite. Yellow crystals suitable for X-ray diffraction were obtained: 35 mg, 79%; δ_{H} (500 MHz, CD₃CN) 9.11 (2 H, dd, $J = 7.3, 0.5$ Hz, C₅H₃N–H⁶), 8.89 (2 H, d, $J = 2.0$ Hz, C₅H₃N–H³), 8.13 (4 H, d, $J = 8.5$ Hz, C₆H₄), 8.03–7.99 (6 H, C₅H₃N–H⁵ + C₆H₄), 2.07 (3 H, s, MeCN). $\nu(\text{C}\equiv\text{N})$ 2227 w, $\nu(\text{C}\equiv\text{N})$ 2167 w, $\nu(\text{C}\equiv\text{O})$ 2030 st, $\nu(\text{C}\equiv\text{O})$ 1926 st, $\nu(\text{C}\equiv\text{O})$ 1897 st cm^{-1} . Anal. Calcd (%) for $\text{C}_{30}\text{H}_{17}\text{F}_3\text{N}_5\text{O}_6\text{ReS}\cdot\text{H}_2\text{O}$: C, 43.1; H, 2.3; N, 8.4. Found: C, 43.3; H, 2.1; N, 7.9. MALDI-MS: $m/z = 670$ ($[\text{M} - \text{OTf}]^+$).

Synthesis of *fac*-[Re^I(CO)₃(bcpbpy)(py)]OTf (7). This compound was prepared and purified in a manner similar to **3** by using **5**·H₂O (45 mg, 0.066 mmol) instead of **1**·0.4PhMe, and AgCF₃SO₃ (20 mg, 0.078 mmol). A yellow microcrystalline solid was obtained: 36 mg, 63%; δ_{H} (500 MHz, (CD₃)₂CO) 9.62 (2 H, dd, $J = 7.5, 0.5$ Hz, C₅H₃N–H⁶), 9.36 (2 H, d, $J = 1.5$ Hz, C₅H₃N–H³), 8.68 (2 H, d, $J = 6.5$ Hz, py–H^{2,6}), 8.40 (2 H, dd, $J = 7.0, 2.5$ Hz, C₅H₃N–H⁵), 8.27 (4 H, d, $J = 8.5$ Hz, C₆H₄), 8.05 (4 H, d, $J = 8.5$ Hz, C₆H₄), 8.03 (1 H, t, $J = 7.8$ Hz, py–H⁴), 7.50 (2 H, d, $J = 7.0$ Hz, py–H^{3,5}). $\nu(\text{C}\equiv\text{N})$ 2223 m, $\nu(\text{C}\equiv\text{O})$ 2029 st, $\nu(\text{C}\equiv\text{O})$ 1932 st, $\nu(\text{C}\equiv\text{O})$ 1905 st cm^{-1} . Anal. Calcd (%) for $\text{C}_{33}\text{H}_{19}\text{F}_3\text{N}_5\text{O}_6\text{ReS}\cdot 0.8\text{H}_2\text{O}$: C, 45.5; H, 2.4; N, 8.0. Found: C, 45.9; H, 2.6; N, 7.6. MALDI-MS: $m/z = 708$ ($[\text{M} - \text{OTf}]^+$). Prior to reaction with [Ru^{II}(NH₃)₅(H₂O)](PF₆)₂ (see below), **7**·0.8H₂O was converted into its PF₆[−] salt by precipitation from an acetone solution with aqueous NH₄PF₆; δ_{H} (500 MHz, (CD₃)₂CO) 9.64 (2 H, d, $J = 5.8$ Hz, C₅H₃N–H⁶), 9.36 (2 H, d, $J = 1.6$ Hz, C₅H₃N–H³), 8.68 (2 H, d, $J = 6.5$ Hz, py–H^{2,6}), 8.41 (2 H, dd, $J = 5.9, 1.9$ Hz, C₅H₃N–H⁵), 8.25 (4 H, d, $J = 8.6$ Hz, C₆H₄), 8.07 (4 H, d, $J = 8.6$ Hz, C₆H₄), 8.05 (1 H, t, $J = 7.7$ Hz, py–H⁴), 7.52 (2 H, d, $J = 6.6$ Hz, py–H^{3,5}).

Synthesis of *fac*-Re^ICl(CO)₃(bcpvbpy) (8). Re^ICl(CO)₅ (52 mg, 0.144 mmol) and bcpvbpy·0.5H₂O (64 mg, 0.154 mmol) in an Ar-degassed mixture of toluene (10 mL) and CHCl₃ (3 mL) were protected from the light and heated under reflux for 16 h. The solution was cooled to room temperature and the orange precipitate filtered off and washed thoroughly

with CHCl_3 : 86 mg, 81%; the lack of solubility in organic solvents precludes characterization by NMR spectroscopy or mass spectrometry. $\nu(\text{C}\equiv\text{N})$ 2226 w, $\nu(\text{C}\equiv\text{O})$ 2014 st, $\nu(\text{C}\equiv\text{O})$ 1908 st, $\nu(\text{C}\equiv\text{O})$ 1871 st cm^{-1} . Anal. Calcd (%) for $\text{C}_{31}\text{H}_{18}\text{ClN}_4\text{O}_3\text{Re}\cdot\text{H}_2\text{O}$: C, 50.7; H, 2.7; N, 7.6. Found: C, 50.4; H, 2.6; N, 7.4.

Synthesis of *fac*- $\text{Re}^{\text{I}}\text{Cl}(\text{bpvbp})_3(\text{CO})_3$ (9**).** This compound was prepared in a manner similar to **8** by using $\text{bpvbp}\cdot 0.5\text{H}_2\text{O}$ (147 mg, 0.396 mmol) in place of $\text{bcpvbp}\cdot 0.5\text{H}_2\text{O}$, and $\text{Re}^{\text{I}}\text{Cl}(\text{CO})_5$ (142 mg, 0.393 mmol) to give an orange solid: 243 mg, 82%; the lack of solubility in organic solvents precludes characterization by NMR spectroscopy or mass spectrometry. $\nu(\text{C}\equiv\text{O})$ 2016 st, $\nu(\text{C}\equiv\text{O})$ 1911 st, $\nu(\text{C}\equiv\text{O})$ 1889 st cm^{-1} . Anal. Calcd (%) for $\text{C}_{27}\text{H}_{18}\text{ClN}_4\text{O}_3\text{Re}\cdot 0.7\text{CHCl}_3$: C, 44.3; H, 2.5; N, 7.5. Found: C, 44.3; H, 2.8; N, 7.2.

Synthesis of *fac*- $[\text{Re}^{\text{I}}\text{Cl}(\text{CO})_3(\text{qpy})\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}_2](\text{PF}_6)_4$ (11**).** A solution of **10** (21 mg, 0.034 mmol) and $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ (67 mg, 0.136 mmol) in Ar-degassed acetone (10 mL), was protected from the light and stirred at room temperature for 24 h. Addition of aqueous NH_4PF_6 produced a precipitate that was filtered off, washed with water and dried. Purification was effected by sequential precipitations from acetone/ CHCl_3 to afford a dark red solid: 31 mg, 56%; δ_{H} (500 MHz, CD_3CN) 9.22 (2 H, d, $J = 1.6$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^6$), 9.17 (2 H, d, $J = 5.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 9.04 (4 H, dd, $J = 4.4, 1.6$ Hz, $\text{C}_5\text{H}_4\text{N}$), 8.22 (2 H, d, $J = 5.8$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 8.04 (4 H, d, $J = 5.8$ Hz, $\text{C}_5\text{H}_4\text{N}$), 3.40 (6 H, s, NH_3), 2.51 (24 H, s, NH_3). $\nu(\text{C}\equiv\text{O})$ 2022 st, $\nu(\text{C}\equiv\text{O})$ 1973 st cm^{-1} . Anal. Calcd (%) for $\text{C}_{23}\text{H}_{44}\text{ClF}_{24}\text{N}_{14}\text{O}_3\text{P}_4\text{ReRu}_2\cdot 3.5\text{H}_2\text{O}$: C, 16.9; H, 3.1; N, 12.0. Found: C, 17.0; H, 2.7; N, 11.6. ES-MS: $m/z = 641$ ($[\text{M} - 2\text{PF}_6]^{2+}$).

Synthesis of *fac*- $[\text{Re}^{\text{I}}(\text{CO})_3(\text{py})(\text{bcpbpy})\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}_2](\text{PF}_6)_5$ (12**).** This compound was prepared and purified in a manner similar to **11** by using *fac*- $[\text{Re}^{\text{I}}(\text{CO})_3(\text{bcpbpy})(\text{py})]\text{PF}_6$ (50 mg, 0.059 mmol) in place of **10**, and $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ (116 mg, 0.235 mmol) to afford a dark red solid: 32 mg, 29%; δ_{H} (500 MHz, CD_3CN) 9.57 (2 H, d, $J = 1.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^6$), 9.51 (2 H, s, $\text{C}_5\text{H}_3\text{N}-\text{H}^3$), 8.69 (2 H, d, $J = 6.5$ Hz, $\text{py}-\text{H}^{2,6}$), 8.47 (4 H, d, $J = 8.0$, $\text{C}_5\text{H}_4\text{N}$), 8.44 (2 H, d, $J = 1.5$ Hz, $\text{C}_5\text{H}_3\text{N}-\text{H}^5$), 8.10–8.05 (5 H, $\text{C}_5\text{H}_4\text{N} + \text{py}-\text{H}^4$), 7.61 (2 H, pseudo-t, $J = 6.5$, $\text{py}-\text{H}^{3,5}$), 3.44 (6 H, s, NH_3), 2.51 (24 H, s, NH_3). $\nu(\text{C}\equiv\text{O})$ 2028 st, $\nu(\text{C}\equiv\text{O})$

1977 cm^{-1} . Anal. Calcd (%) for $\text{C}_{32}\text{H}_{49}\text{F}_{30}\text{N}_{15}\text{O}_3\text{P}_4\text{ReRu}_2\cdot 3\text{H}_2\text{O}$: C, 20.7; H, 3.0; N, 11.3. Found: C, 20.4; H, 2.6; N, 10.9.

X-Ray Structural Determinations. The data for **1**·Me₂CO, **2**·PhMe, **3**·0.5PhMe, **4**·0.5Me₂CO, **5**·0.5PhMe and **6**·MeCN were collected on an Oxford diffraction XCalibur 2 or an Agilent SuperNova diffractometer by using Mo K α radiation ($\lambda = 0.71073$ Å). Data processing was carried out by using APEX2, and semi-empirical absorption corrections were applied by using SADABS.¹⁷ The structures were solved by direct methods or by the superflip structure solution program¹⁸ using the charge-flipping algorithm. They were refined by full-matrix least-squares on all F_o^2 data using SHELXS-97¹⁹ and SHELXL-97.^{20,21} All non-H atoms were refined anisotropically, with H atoms bonded to C or N included in calculated positions by using the riding method. The solvent molecules in **3**·0.5PhMe, **4**·0.5Me₂CO and **5**·0.5PhMe are disordered and were modelled over two positions in each case. The hydrogens were omitted from the acetone molecule in **4**·0.5Me₂CO because of the high disorder. In **3**·0.5PhMe and **5**·0.5PhMe, the position of the methyl group in the PhMe molecules was restrained using the DFIX command. The displacement parameters for the PhMe and pyridine ring in **3**·0.5PhMe and PhMe, CO and bcpbpy fragments in **5**·0.5PhMe were refined by using the SIMU, FLAT, EADP or RIGU commands. All other calculations were carried out by using the OLEX2 software package.²² Crystallographic data and refinement details are presented in the Supporting Information (Table S1).

Hyper-Rayleigh Scattering. General details of the HRS experiment have been discussed elsewhere,²³ and these measurements were carried out in MeCN. Dilute solutions (ca. 10^{-4} M) of complex salts **11** and **12** were used, and after applying a small Lambert-Beer correction for reabsorption of the second-harmonic generated light, a linear relationship was obtained between signal and concentration. A fundamental wavelength of 1064 nm was provided by a Spectra-Physics InSight® DS+ laser (1 W average power, < 100 fs pulses, 80 MHz). The collection optics were coupled to a spectrograph (model Bruker 500is/sm) and an EMCCD camera (Andor Solis model iXon Ultra 897). The MeCN solvent was used as an internal reference ($\beta_{\text{HRS},1064} = 0.258 \times 10^{-30}$ esu; $\beta_{\text{zzz},1064} = 0.623 \times 10^{-30}$ esu).²⁴ Although the spectral deconvolution between weak multiphoton-induced luminescence and HRS did result

in accurate, luminescence-free β values, accurate depolarization ratios²⁵ for these V-shaped 2D complexes could not be obtained.

Stark Spectroscopy. The Stark apparatus, experimental methods and data collection procedure were as previously reported,²⁶ except that a Xe arc lamp was used as the light source instead of a W filament bulb. The Stark spectrum for each compound was measured at least twice. The data analysis was carried out as previously described,²⁶ by using the zeroth, first and second derivatives of the absorption spectrum for analysis of the Stark $\Delta\epsilon(\nu)$ spectrum in terms of the Liptay treatment.²⁷ The dipole-moment change, $\Delta\mu_{12} = \mu_e - \mu_g$, where μ_e and μ_g are the respective excited and ground-state dipole moments, was then calculated from the coefficient of the second derivative component. PrCN was used as the glassing medium, for which the local field correction f_{int} is estimated as 1.33.²⁶ A two-state analysis of the MLCT transitions gives

$$\Delta\mu_{\text{ab}}^2 = \Delta\mu_{12}^2 + 4\mu_{12}^2 \quad (1)$$

where $\Delta\mu_{\text{ab}}$ is the dipole-moment change between the diabatic states and $\Delta\mu_{12}$ is the observed (adiabatic) dipole-moment change. The value of the transition dipole-moment μ_{12} is determined from the oscillator strength f_{os} of the transition by

$$|\mu_{12}| = \left(\frac{f_{\text{os}}}{1.08 \times 10^{-5} E_{\text{max}}} \right)^{1/2} \quad (2)$$

where E_{max} is the energy of the MLCT maximum (in wavenumbers) and μ_{12} is in eÅ. The latter is converted into Debye units on multiplying by 4.803. The degree of delocalization c_b^2 and electronic coupling matrix element H_{ab} for the diabatic states are given by

$$c_b^2 = \frac{1}{2} \left[1 - \left(\frac{\Delta\mu_{12}^2}{\Delta\mu_{12}^2 + 4\mu_{12}^2} \right)^{1/2} \right] \quad (3)$$

$$|H_{ab}| = \left| \frac{E_{\max}(\mu_{12})}{\Delta\mu_{ab}} \right| \quad (4)$$

If the hyperpolarizability β_0 tensor has only nonzero elements along the MLCT direction, then this quantity is given by

$$\beta_0 = \frac{3\Delta\mu_{12}(\mu_{12})^2}{(E_{\max})^2} \quad (5)$$

A relative error of $\pm 20\%$ is estimated for the β_0 values derived from the Stark data and using eq 5, while experimental errors of $\pm 10\%$ are estimated for μ_{12} , $\Delta\mu_{12}$ and $\Delta\mu_{ab}$, $\pm 15\%$ for H_{ab} and $\pm 50\%$ for c_b ². Note that the $\pm 20\%$ uncertainty for the β_0 values is merely statistical and does not account for any errors introduced by two-state extrapolation.

RESULTS AND DISCUSSION

Figure 1. Chemical structures of the proligands dcbpy, bcpbpy, bcpvbpy and bpvbpy.

Figure 2. Chemical structures of the monometallic Re^{I} complexes and complex salts investigated.

Synthesis. The compound 4,4'-dicyano-2,2'-bipyridyl (dcbpy, Figure 1) has been reported,^{14,28} and complexed with the transition metals Cr, Fe, Co, Cu, Mo, Ru, W and Ir. However, at the outset of this work, complexes of this ligand with Re were apparently unknown.²⁹ Therefore, we prepared the family of four new complexes/complex salts **1–4** (Figure 2) by using standard methods starting from $\text{Re}^{\text{I}}\text{Cl}(\text{CO})_5$. Very recently, Clark et al. reported complex **1** for use in the electrocatalytic reduction of CO_2 .³⁰ The related

benzonitrile-functionalized compound 4,4'-bis(4-cyanophenyl)-2,2'-bipyridyl (bcpbpy, Figure 1) has been prepared by Han et al.³¹ via a Suzuki-Miyaura cross-coupling reaction. These authors have also reported the only complex of bcpbpy known to date (containing Ru^{II}).³¹ Unfortunately, we were unable to reproduce the published procedure to make this proligand, but found success using a similar approach, using the 4-cyanophenylboronic acid pinacol ester as opposed to the boronic acid. The new complexes/complex salts **5–7** (Figure 2) were thus prepared.

We used also the proligands 4,4'-bis[(*E*)-2-(4-cyanophenyl)vinyl]-2,2'-bipyridyl (bcpvbpy) and 4,4'-bis[(*E*)-2-(4-pyridyl)vinyl]-2,2'-bipyridyl (bpvbpy) (Figure 1),¹⁵ to synthesize their *fac*-Re^ICl(CO)₃ complexes **8** and **9** (Figure 2). However, the solubility of the latter proved to be too low to allow the preparation of further derivatives by chloride ligand substitutions. The compound bcpvbpy has been reported previously,³² but was prepared via a method different to ours, involving a Perkin-type condensation reaction between 4,4'-dimethyl-2,2'-bipyridyl and 4-cyanobenzaldehyde. A lower yield of 53% was achieved, and the homogeneity/purity of the product was not confirmed via microanalyses.

Figure 3. Chemical structures of the trimetallic Ru^{II}-Re^I complex salts investigated. {R} = {Ru^{II}(NH₃)₅}²⁺.

The heterotrimetallic complex salts **11** and **12** (Figure 3) were prepared by treating complex **10** and the PF₆⁻ salt of **7**, respectively, with 4 equivalents of [Ru^{II}(NH₃)₅(H₂O)][PF₆]₂¹⁶ in acetone. Both of the products were purified by several precipitations from acetone/CHCl₃ and moderate-to-good yields (56% for **11**, 29% for **12**) of hydrated materials were obtained. It is worth noting that attempts to prepare a related

trimetallic complex from **1** incorporating the dcbpy ligand afforded significant contamination by the bimetallic complex which could not be removed satisfactorily via chromatography or reprecipitation.²⁹ However, Mecchia Ortiz et al. have used the ligand 4-methyl-4'-cyano-2,2'-bipyridyl (mcbpy) to prepare a heterobimetallic complex featuring *fac*-{Re^I(CO)₃(MeCN)}⁺ and {Ru^{II}(NH₃)₅}²⁺ centers.³³

The identities and purities of all the new complexes and complex salts are confirmed by ¹H NMR spectroscopy, and representative spectra are included in the Supporting Information (Figures S1 and S2). MALDI mass spectra were obtained for all compounds except **8** and **9**, due to their extremely poor solubilities. The molecular ion peaks for the trimetallic complex salts **11** and **12** could not be found in MALDI or ES+ spectra, but signals corresponding to [M – 2PF₆]²⁺ are observed for **11**. IR spectra reveal characteristic $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}\equiv\text{O})$ stretching bands. Comparing the spectra of the pairs **1/2** and **5/6** indicates that the MeCN ligand is responsible for the relatively weak bands at 2306 cm⁻¹ in **2** and 2167 cm⁻¹ in **6**, while the uncoordinated nitrile substituents of the bpy ligands give absorptions at ca. 2240–50 cm⁻¹ (dcbpy) and ca. 2230 cm⁻¹ (bcbpy). The bands due to the CO ligands are much stronger, and either two or three distinct peaks are observed in the region ca. 2040–1880 cm⁻¹, as is typical of *fac*-{Re^I(CO)₃}⁺ complexes. In most cases, crystalline products were isolated and CHN elemental analyses all fit satisfactorily for variable levels of solvation/hydration.

X-Ray Crystallography. Single crystal X-ray structures have been obtained for the monometallic solvated compounds **1**·Me₂CO, **2**·PhMe, **3**·0.5PhMe, **4**·0.5Me₂CO, **5**·0.5PhMe and **6**·MeCN. Representations of their molecular structures are shown in Figures 4–9, and selected bond distances and angles are listed in Table 1. Clark et al. have reported the structure of **1**·CH₂Cl₂ very recently.³⁰

In all six structures, the Re^I center exhibits the expected facial arrangement of the CO ligands and a distorted octahedral coordination, with geometric parameters typical for such complexes. The three Re–C distances are indistinguishable for **2**·PhMe, **3**·0.5PhMe and **6**·MeCN, but the axial distance differs significantly from the equatorial ones in the other compounds, showing a relative lengthening in **1**·Me₂CO and **4**·0.5Me₂CO, but a shortening in **5**·0.5PhMe (Table 1). It is worth noting that while the structures are broadly similar, there are

some significant differences between $1 \cdot \text{Me}_2\text{CO}$ and $1 \cdot \text{CH}_2\text{Cl}_2$ reported by Clark et al.³⁰ For example, the axial bond distances determined for $1 \cdot \text{CH}_2\text{Cl}_2$ are $\text{Re}-\text{C} = 1.928(3) \text{ \AA}$ and $\text{Re}-\text{Cl} = 2.4698(7) \text{ \AA}$,³⁰ respectively shorter and longer compared with $1 \cdot \text{Me}_2\text{CO}$ (Table 1). The angle $\text{Cl}-\text{Re}-\text{C}_{\text{ax}}$ is $178.36(8)^\circ$ for $1 \cdot \text{CH}_2\text{Cl}_2$, larger than that for $1 \cdot \text{Me}_2\text{CO}$. These differences are attributable to packing effects; the arrangements of the four complex units within the unit cell are quite different, and $1 \cdot \text{CH}_2\text{Cl}_2$ also shows a short contact between the O atom of the axial CO ligand and a Cl atom of the CH_2Cl_2 solvent molecule.

Figure 4. Representation of the molecular structure of $1 \cdot \text{Me}_2\text{CO}$ with the acetone molecule and H atoms omitted for clarity (50% probability ellipsoids).

In $2 \cdot \text{PhMe}$, the MeCN ligand is bonded in an almost linear fashion, with a $\text{Re}-\text{N}-\text{C}$ angle of $177.3(4)^\circ$. The corresponding angle in $fac\text{-}[\text{Re}^{\text{I}}(\text{CO})_3(\text{MeCN})(\text{mcbpy})]\text{PF}_6 \cdot \text{PhMe}$ reported by Mecchia Ortiz et al. is similar at ca. 175.9° ,³³ while a value of ca. 175.5° is found in $fac\text{-}[\text{Re}^{\text{I}}(\text{CO})_3(\text{MeCN})(\text{bpy})]\text{ClO}_4$.³⁴ In contrast, significant bending is observed at the coordinated N-atom in $6 \cdot \text{MeCN}$, with an angle of $168.6(9)^\circ$. The $\text{Re}-\text{N}(\text{MeCN})$ distances of ca. $2.13 \text{ \AA}$ in $2 \cdot \text{PhMe}$ and $6 \cdot \text{MeCN}$ are similar to those in $fac\text{-}[\text{Re}^{\text{I}}(\text{CO})_3(\text{MeCN})(\text{mcbpy})]\text{PF}_6 \cdot \text{PhMe}$ ($2.138(3) \text{ \AA}$)³³ and $fac\text{-}[\text{Re}^{\text{I}}(\text{CO})_3(\text{MeCN})(\text{bpy})]\text{ClO}_4$ ($2.140(3) \text{ \AA}$).³⁴ These distances are all substantially longer than that in $trans\text{-}\text{Re}^{\text{I}}\text{Cl}(\text{CO})_2(\text{bpy})(\text{MeCN})$ ($2.043(4) \text{ \AA}$)³⁵ due to the structural trans effect of the CO ligand on the competing π -acceptor MeCN.³⁶ Comparison between $3 \cdot 0.5\text{PhMe}$ and $4 \cdot 0.5\text{Me}_2\text{CO}$ shows

that both the axial Re–C and Re–N distances are significantly elongated when a 4-cyano substituent is added to the pyridine ligand (Table 1). A number of the bond angles also show small differences between these two related compounds. The bcbbpy ligands show variable degrees of twisting between the phenyl and pyridyl ring planes, with dihedral angles of ca. 29.9 and 23.2° in **5**·0.5PhMe and ca. 14.2 and 26.6° in **6**·MeCN. The bpy units are generally almost planar, but dihedral angles of ca. 6.0 and 11.1° are found in **4**·0.5Me₂CO and **5**·0.5PhMe, respectively.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for Solvates of 1–6^a

	1·Me ₂ CO	2·PhMe	3·0.5PhMe	4·0.5Me ₂ CO	5·0.5PhMe	6·MeCN
Re–C(trans-bpy)	1.91(1)	1.923(5)	1.928(9)	1.908(8)	1.90(1)	1.94(1)
Re–C(trans-bpy)	1.92(1)	1.921(5)	1.924(9)	1.916(8)	1.94(1)	1.93(1)
Re–C(trans-L)	2.00(1)	1.932(5)	1.91(1)	1.951(9)	1.86(1)	1.944(9)
Re–N(bpy)	2.177(8)	2.171(4)	2.180(6)	2.166(5)	2.15(1)	2.181(7)
Re–N(bpy)	2.182(8)	2.160(4)	2.165(6)	2.171(5)	2.18(1)	2.167(7)
Re–Cl/N(L)	2.452(3)	2.125(4)	2.163(8)	2.207(6)	2.483(3)	2.131(8)
N(bpy)–Re–N(bpy)	75.4(3)	74.9(2)	74.8(2)	75.0(2)	74.7(4)	75.1(3)
N(bpy)–Re–C _{eq}	95.9(4)	99.1(2)	99.0(3)	97.5(2)	97.7(4)	95.6(3)
N(bpy)–Re–C _{ax}	92.1(4)	93.4(2)	92.9(3)	93.2(3)	93.7(5)	96.7(3)
N(bpy)–Re–C _{eq}	176.2(4)	172.6(2)	172.4(3)	176.0(3)	173.3(5)	172.0(3)
N(bpy)–Re–C _{eq}	100.9(4)	98.1(2)	97.8(3)	101.0(3)	98.8(5)	100.7(3)
N(bpy)–Re–C _{ax}	92.2(4)	94.9(2)	93.3(3)	94.9(3)	96.9(5)	92.6(3)
N(bpy)–Re–C _{eq}	170.7(4)	172.6(2)	173.5(3)	171.6(2)	170.8(4)	170.4(3)
N(bpy)–Re–Cl/N(L)	83.9(2)	84.7(2)	84.3(2)	84.6(2)	84.8(2)	85.1(3)
N(bpy)–Re–Cl/N(L)	83.0(2)	85.0(2)	85.5(2)	85.9(2)	82.6(2)	82.1(3)
Cl/N(L)–Re–C _{eq}	92.9(3)	90.2(2)	92.1(3)	93.8(3)	91.7(4)	95.4(4)
Cl/N(L)–Re–C _{ax}	174.4(3)	178.0(2)	177.2(3)	179.0(2)	178.5(4)	173.8(3)
Cl/N(L)–Re–C _{eq}	94.8(3)	92.5(2)	93.6(3)	91.1(3)	92.5(4)	87.6(3)
C _{eq} –Re–C _{eq}	87.7(4)	87.8(2)	88.4(3)	86.4(3)	88.6(5)	88.4(4)
C _{eq} –Re–C _{ax}	91.4(4)	89.7(2)	88.8(4)	87.1(3)	88.7(6)	90.3(4)
C _{eq} –Re–C _{ax}	88.9(4)	89.5(2)	89.1(4)	89.4(3)	89.0(6)	90.2(4)

^a L = axial ligand; eq = equatorial; ax = axial.

Figure 5. Representation of the molecular structure of **2**·PhMe with the toluene molecule and H atoms removed for clarity (50% probability ellipsoids).

Figure 6. Representation of the molecular structure of **3**·0.5PhMe with the toluene molecule and H atoms removed for clarity (50% probability ellipsoids).

Figure 7. Representation of the molecular structure of 4·0.5Me₂CO with the acetone molecule and H atoms omitted for clarity (50% probability ellipsoids).

Figure 8. Representation of the molecular structure of 5·0.5PhMe with the toluene molecule and H atoms omitted for clarity (50% probability ellipsoids).

Figure 9. Representation of the molecular structure of **6**·MeCN with the MeCN molecule and H atoms omitted for clarity (50% probability ellipsoids).

Electrochemistry and Spectroelectrochemistry. Cyclic voltammetric data for **1–7** and **10–12** are included in Table 2, and representative voltammograms are shown in the Supporting Information (Figures S3–S6). All potentials are quoted with respect to the Ag–AgCl reference electrode.

The neutral complexes **1**, **5** and **10** show an irreversible oxidation at ca 1.5 V corresponding to the $\text{Re}^{\text{II/I}}$ couple (Supporting Information, Figure S3), while this process is observed at a more anodic potential for the cationic complexes in **2–4**, **6** and **7** (Supporting Information, Figure S4). The trimetallic complex salts show a reversible oxidation process assigned to the two Ru centers (Supporting Information, Figures S5 and S6). The observation of only single waves is unsurprising, and consistent with an absence of any significant mutual electronic coupling via the qpy or bcpbpy linkage. The $\text{Ru}^{\text{III/II}}$ $E_{1/2}$ value is lower for the qpy complex in **11** (0.48 V cf. 0.58 V for **12**), due to the increased electron richness of the pyridyl-coordinated Ru^{II} centers. The $\text{Re}^{\text{II/I}}$ wave is observed at similar values for **10** and its ruthenated counterpart **11** (1.49 and 1.46 V, respectively), but the value for **12** is somewhat lower than that for **7** (1.72 cf. 1.89 V). The assignment of the first wave to the $\text{Ru}^{\text{III/II}}$ couple is confirmed by UV–vis spectroelectrochemistry studies with **11** (Supporting Information, Figure S7). Stepwise oxidation causes the gradual disappearance of the low energy band assigned to Ru^{II} -based MLCT (*vide infra*), while this absorption is restored on re-reduction.

Electronic Spectroscopy.

Absorption. Electronic absorption spectral data for the compounds **1–7** and **10–12** recorded in MeCN are displayed in Table 2. Representative spectra for **1–4** are shown in Figure 10, while those for **5–7** are included in the Supporting Information (Figure S8).

For **1–7**, the relatively low energy bands above ca. 320 nm are assigned to Re^{I} -based MLCT excitations involving both the mono- and bidentate *N*-donor ligands, while higher energy absorptions are due to intraligand $\pi \rightarrow \pi^*$ transitions.^{37–40}

Table 2. UV-vis Absorption, Emission and Electrochemical Data for Compounds 1–7 and 10–12

compd	$\lambda_{\max}$, nm ^a (ϵ , 10 ³ M ⁻¹ cm ⁻¹)	$E_{\max}$ (eV)	assignment	$\lambda_{\text{em}}^b / \lambda_{\text{exc}}$ (nm)	τ (μ s)	ϕ (%)	E , V vs Ag–AgCl ^c (ΔE_p , mV)		
							ligand-based	Ru ^{II} I/II	Re ^{III}
1	432 (5.9)	2.87	d(Re ^I) $\rightarrow$ π^* (dcbpy)				–0.70		1.55 ^e
	313 (24.3)	3.96	$\pi \rightarrow \pi^*$				–1.05		
	246 (28.5)	5.04	$\pi \rightarrow \pi^*$				–1.17 ^d		
2	381 (6.5)	3.25	d(Re ^I) $\rightarrow$ π^* (dcbpy)	668 / 350–460	1.2	2.3	–0.60		1.95 ^e
	335 (14.3)	3.70	d(Re ^I) $\rightarrow$ π^* (MeCN)				–1.02		
	316sh (15.5)	3.92	$\pi \rightarrow \pi^*$						
	298 (20.0)	4.16	$\pi \rightarrow \pi^*$						
	247sh (19.8)	5.02	$\pi \rightarrow \pi^*$						
3	397 (6.3)	3.12	d(Re ^I) $\rightarrow$ π^* (dcbpy)	732 / 350–460	1.4	0.6	–0.56		2.01 ^e
	333 (12.5)	3.72	d(Re ^I) $\rightarrow$ π^* (py)				–1.04		
	302 (21.5)	4.11	$\pi \rightarrow \pi^*$						
	250 (21.8)	4.96	$\pi \rightarrow \pi^*$						
4	390 (5.3)	3.18	d(Re ^I) $\rightarrow$ π^* (dcbpy)	678–688 / 350–520	1.5	0.6	–0.59		2.02 ^e
	323sh (16.6)	3.84	d(Re ^I) $\rightarrow$ π^* (cpy)				–1.02		
	303 (19.4)	4.09	$\pi \rightarrow \pi^*$				–1.58 ^d		
5	393 (2.6)	3.16	d(Re ^I) $\rightarrow$ π^* (bcbppy)	678–684 / 350–470	2.0	3.6	–1.12 ^d		1.45 ^e
	290sh (14.1)	4.28	$\pi \rightarrow \pi^*$				–1.22 ^d		
	260 (18.8)	4.77	$\pi \rightarrow \pi^*$				–1.69 ^d		
6	353sh (9.2)	3.51	d(Re ^I) $\rightarrow$ π^* (bcbppy)	594 / 350–450	1.2	8.1	–1.86 ^d		
	329 (18.5)	3.77	d(Re ^I) $\rightarrow$ π^* (MeCN)				–0.80 ^d		1.87 ^e
	282 (40.2)	4.40	$\pi \rightarrow \pi^*$				–0.98 ^d		
							–1.13 ^d		
7	364 (9.1)	3.41	d(Re ^I) $\rightarrow$ π^* (bcbppy)	615 / 340–470	0.8	5.0	–1.50 ^d		
	327 (18.9)	3.79	d(Re ^I) $\rightarrow$ π^* (py)				–0.94 ^d		1.89 ^e
	285 (44.6)	4.35	$\pi \rightarrow \pi^*$				–1.20 ^d		
10^f	389sh	3.19	d(Re ^I) $\rightarrow$ π^* (qpy)	642 / 385	4.7	1.0	–1.36 ^d		
	306 (13.1)	4.05	$\pi \rightarrow \pi^*$				–1.09 ^d		1.49 ^e
	247 (25.9)	5.02	$\pi \rightarrow \pi^*$				–1.39 ^d		
11	527 (19.3)	2.35	d(Ru ^{II}) $\rightarrow$ π^* (qpy)				–1.70 ^d		
	404 (12.4)	3.07	d(Re ^I) $\rightarrow$ π^* (qpy)				–0.73 ^d	0.48	1.46 ^e
	339 (23.7)	3.66	$\pi \rightarrow \pi^*$				–1.21 ^d	(80)	
	311 (24.9)	3.99	$\pi \rightarrow \pi^*$				–1.63 ^d		
	257 (48.2)	4.82	$\pi \rightarrow \pi^*$				–1.88 ^d		
	223 (65.1)	5.56	$\pi \rightarrow \pi^*$						
12	465 (18.7)	2.67	d(Ru ^{II}) $\rightarrow$ π^* (bcbppy)				–0.52 ^d	0.58	1.72 ^e
	381 (13.5)	3.25	d(Re ^I) $\rightarrow$ π^* (bcbppy)				–1.02 ^d	(90)	
	332 (21.4)	3.73	$\pi \rightarrow \pi^*$				–1.59 ^d		
	244 (61.2)	5.08	$\pi \rightarrow \pi^*$						

^a MeCN solutions ca. 1–4 $\times 10^{-5}$ M. ^b In MeCN at 293 K. ^c MeCN solutions ca. 1.5 $\times 10^{-4}$ M in analyte and 0.1 M in [N(C₄H₉-*n*)₄]PF₆ at a 3 mm disk glassy-carbon working electrode with a scan rate of 100 mV s⁻¹. Ferrocene internal standard $E_{1/2}$ = 0.44 V, ΔE_p = 70–90 mV. ^d E_{pc} for an irreversible reduction process. ^e E_{pa} for an irreversible oxidation process. ^f Absorption and emission wavelengths taken from Ref 10.

The dcbpy-containing series **1–4** illustrates the effects of changing the axial ligand (Figure 10). The lowest energy band assigned to d(Re^I) $\rightarrow$ π^* (dcbpy) MLCT is relatively red-

shifted when L is chloride (in **1**) because this ligand is the most effective electron donor, causing destabilization of the Re-based HOMO. The MLCT energy increases markedly when L is the less electron-donating MeCN (in **2**), with a shift in the band maximum of ca. 0.4 eV. The bands for the py and cpy complexes show intermediate energies, with that for **4** being blue-shifted slightly when compared with **3** due to the electron-withdrawing influence of the cyano substituent. The high energy bands at ca. 320–335 nm in **2–4** are attributable to MLCT involving L. The spectra of the bcbpy complexes **5–7** show the same trend for the energies of the low energy bands, but the spectral profiles are generally less well resolved than those of their dc bpy analogues (Supporting Information, Figure S8).

Figure 10. UV-vis absorption spectra of **1** (black), **2** (red), **3** (green), **4** (blue) in MeCN at 293 K.

In the trimetallic complexes, both the Re^I and Ru^{II} centers have π -electron donating abilities, but the latter are stronger donors as evidenced by the electrochemical data (see above). Ruthenation appears to cause red-shifts of the Re^I-based MLCT band; 364 $\rightarrow$ 381 nm for **7** and **12** (Supporting Information, Figure S9); ca. 389 $\rightarrow$ 404 nm for **10** and **11**. These

shifts are consistent with the observation of decreased Re^{III} potentials via cyclic voltammetry, with the more pronounced change for the bcbpy complexes. However, given the uncertainties about the actual band positions in most cases, firm conclusions cannot be drawn. The visible regions for **11** and **12** are dominated by the Ru^{II} -based MLCT bands which have especially high absorptivity due in part to the involvement of two metal centers. These bands are strongly overlapped with the Re^{I} -based ones (Supporting Information, Figure S10).

Luminescence. Electronic emission spectral data for **2–7** and **10** in MeCN solutions are collected in Table 2, while representative spectra are included in the Supporting Information (Figures S11–S14). Due to low solubility, **8** and **9** could not be studied, while the emission properties of **10** have been reported previously.¹⁰

All of the complexes show low emission intensities ($\phi = 0.6\text{--}8.1\%$, Table 2), except **1** for which no detectable emission was observed. **2–7** and **10** exhibit a broad featureless emission band in the low energy region with maxima in the range 594–732 nm, characteristic of a $\text{Re}^{\text{I}}/\alpha\text{-diimine } ^3\text{MLCT}$ state.^{5a,41,42} For **4** and **5**, small red-shifts of ca. 10 nm are observed on increasing the excitation wavelength, as reported previously for low temperature emissions in related complexes.⁴³ The $^3\text{MLCT}$ assignment is supported also by the radiative lifetimes in the low microsecond range ($\tau = 0.8\text{--}4.7 \mu\text{s}$).

The value of λ_{em} within the series **2–4** (dcbpy ligand, Figures S11) and **5–7** (bcbpy ligand, Figures S12) increases with the electron-donating nature of L, i.e. $\text{MeCN} < \text{cpy} < \text{py}$, and $\text{MeCN} < \text{py} < \text{Cl}$. With both $\alpha\text{-diimine}$ ligands, as previously observed for related complexes,^{5a,44} the quantum yields are larger when L is MeCN as opposed to py ($\phi = 2.3\%$ for **2**, cf. 0.6% for **3**; $\phi = 8.1\%$ for **6**, cf. 5.0% for **7**), and the chloride complex **5** displays the lowest intensity ($\phi = 3.6\%$) of the bcbpy species. Extending the π -conjugation by replacing dcnbpy with bcbpy causes blue-shifting of the emission (Figures S13 and S14, e.g. $\lambda_{\text{em}} = 732 \text{ nm}$ for **3**, cf. 615 nm for **7**) and increased quantum yields.

Hyper-Rayleigh Scattering. The β values of complex salts **11** and **12** have been measured in MeCN solutions at 293 K by using the HRS technique with a laser wavelength of 1064 nm,²³ and the results are shown in Table 3. Due to their low NLO activity and emissive nature, no HRS data could be obtained for compounds **1–10**. Both trimetallic complexes show

relatively large β values, with an apparent increase for the qpy complex in **11** when compared with **12**. However, the observed difference is attributable at least in part to resonance enhancement, because $\lambda_{\max}$ of the low energy MLCT band is very close to the second harmonic wavelength of 532 nm.

Table 3. Visible MLCT absorption and HRS data for complex salts **11 and **12** in MeCN**

complex salt	$\lambda_{\max}$ (nm)	$\sqrt{\langle \beta_{HRS}^2 \rangle}^a$ (10^{-30} esu)
11	535	225 ± 22
12	481	135 ± 14

^a The total molecular HRS response irrespective of symmetry or contributing tensor elements, measured by using a 1064 nm laser. The quoted cgs units (esu) can be converted into SI units ($C^3 m^3 J^{-2}$) by dividing by 2.693×10^{20} , or into atomic units by dividing by 0.8640×10^{-32} .

Figure 11. Spectra and calculated fits for the complex salts **7**, **11** and **12** in PrCN at 77 K. Top panel: absorption spectrum; middle panel: electroabsorption spectrum, experimental (blue) and fits (green) according to the Liptay equation;^{27a} bottom panel: contribution of 0th (blue), 1st (green) and 2nd (red) derivatives of the absorption spectrum to the calculated fits.

Stark Spectroscopy. The compounds **1**, **3**, **7**, **11** and **12** have been investigated by Stark spectroscopy^{26,27} in PrCN at 77 K, and the results are shown in Table 4. Unfortunately, the complex **10** is inadequately soluble under the required conditions, so could not be studied, precluding comparisons with the ruthenated complex in **12**. Representative absorption and electroabsorption spectra for **7**, **11** and **12** are shown in Figure 11, while those for **1** and **3** are in the Supporting Information (Figure S15). All the data obtained by Stark spectroscopy must be treated with caution since low solubility in PrCN (especially for **1**, **3** and **7**) increases the already significant experimental errors.

For **1** and **7**, the visible band maxima show respective small blue or red-shifts (ca. 0.1 eV) on going from MeCN solution to PrCN glass, while **3** shows no change (Tables 2 and 4). In contrast, the Re^I/Ru^{II} complexes in **11** and **12** show substantial red-shifts of ca. 0.2–0.3 eV, as observed in previous studies with Ru^{II} ammine species.²⁶ The values of f_{os} and μ_{12} (Table 4) confirm that the band absorptivity increases substantially on replacing L = Cl[−] with py (**1** vs **3**) and on coordinating {Ru^{II}(NH₃)₅}²⁺ centers (**7** vs **12**). The parameters $\Delta\mu_{12}$, r_{12} , $\Delta\mu_{ab}$, and r_{ab} are of similar magnitude for the dc bpy complexes **1** and **3**, while **7** shows somewhat smaller values. All of these parameters are clearly increased when the structure of **7** is extended by Ru^{II} complexation to give **12**. The degree of delocalization (represented by c_b^2) and the matrix element H_{ab} that quantifies the strength of π -electronic coupling are quite similar for all of the compounds.

The traditional two-state model (i.e., eq 5, corresponding with the “perturbation series” convention)⁴⁵ has been used to estimate β_0 values, and the results are included in Table 4. This approach is only rather approximate because the chromophores are not one-dimensional. Furthermore, it is likely that higher energy excitations with charge-transfer character will also contribute to the overall NLO responses, so the β_0 values reported here for the MLCT bands alone correspond with lower limits only for **1**, **3** and **7**. For **11** and **12**, the analysis focuses on the Ru^{II}-based MLCT absorptions, making the assumption that those will dominate the NLO responses because the directionally opposed Re^I-based MLCT transitions are weaker and at relatively high energy. These limitations notwithstanding, using Stark-derived data provides a valuable alternative to the direct determination of β values via HRS,

avoiding any complications due to resonance effects. The dcby complexes **1** and **3** have similar β_0 responses, while the decrease on moving to **7** with the extended ligand bcby is attributable to its increased $E_{\max}$ and decreased $\Delta\mu_{12}$. As expected, much larger β_0 values are found for the ruthenated complexes in **11** and **12**, with a ca. 5-fold increase on moving from **7** to **12**. This large enhancement is associated with a combination of increased μ_{12} and $\Delta\mu_{12}$, and decreased $E_{\max}$ (Table 4).

Unfortunately, the gaps in the available data preclude further comparisons, but it is notable that both the Stark and HRS results reveal substantial NLO responses for the trimetallic complex salts, with the largest being for **11** (Tables 3 and 4). Furthermore, the cyclic voltammetric data show that these novel Ru^{II} ammine chromophores have potential for redox-switching of optical properties at readily accessible potentials.⁴⁶

CONCLUSION

We have synthesized and characterized a series of new monometallic *fac*-{Re^I(CO)₃}⁺ complexes with pendent *N*-coordination sites. One of these, and also the known *fac*-Re^ICl(CO)₃(qpy) have been used to create heterotrimetallic complexes with two {Ru^{II}(NH₃)₅}²⁺ centers. The structures of six of the monometallic species are confirmed by single-crystal X-ray crystallography. The UV–vis absorption spectra of these compounds show bands ascribed to Re^I-based MLCT at wavelengths above ca. 320 nm and intraligand $\pi \rightarrow \pi^*$ transitions at higher energies, while the trimetallic complexes absorb much more strongly in the visible region due to Ru^{II}-based MLCT bands. Weak red/NIR emission is observed for all of the monometallic compounds that show sufficient solubility in organic solvents, except for the chloride complex **1**. Ruthenation quenches the luminescence. Cyclic voltammograms show irreversible Re^{III/I} processes in the range ca. 1.5–2.0 V vs Ag–AgCl for all of the complexes, with reversible 2-electron Ru^{III/II} oxidation waves at ca. 0.5–0.6 V for the trimetallic compounds. Ligand-based reductions vary from being irreversible and ill-defined to reversible for the dcby-containing compounds. Both HRS and Stark spectroscopic measurements indicate that the trimetallic complexes show relatively large β responses,

enhanced markedly when compared with their monometallic counterparts due to the combined effects of increasing μ_{12} and $\Delta\mu_{12}$, and decreasing $E_{\max}$.

Table 4. Absorption and Stark Spectroscopic Data for Complex Salts 1, 3, 7, 11 and 12 in PrCN at 77 K

compd	λ_{max} (nm)	E_{max} (eV)	f_{os}^a	μ_{12}^b (D)	$\Delta\mu_{12}^c$ (D)	$\Delta\mu_{\text{ab}}^d$ (D)	r_{12}^e (Å)	r_{ab}^f (Å)	c_{b}^{2g}	H_{ab}^h (10^3 cm^{-1})	β_0^i (10^{-30} esu)
1 ^j	420	2.95	0.39	5.9	12.9	17.5	2.7	3.6	0.13	7.8	64
3 ^j	397	3.12	0.60	7.1	11.7	18.4	2.4	3.8	0.18	8.9	85
7 ^j	371	3.34	0.33	5.1	8.3	13.1	1.7	2.7	0.18	8.9	31
11	596	2.08	1.59	14.2	17.4	33.3	3.6	6.9	0.24	9.8	506
12	514	2.41	0.51	7.4	21.2	25.9	4.4	5.4	0.09	6.6	169

^a Obtained from $(4.32 \times 10^{-9} \text{ M cm}^2)A$ where A is the numerically integrated area under the absorption peak. ^b Calculated from eq 2. ^c Calculated from $f_{\text{int}}\Delta\mu_{12}$ using $f_{\text{int}} = 1.33$. ^d Calculated from eq 1. ^e Delocalized electron-transfer distance calculated from $\Delta\mu_{12}/e$. ^f Effective (localized) electron-transfer distance calculated from $\Delta\mu_{\text{ab}}/e$. ^g Calculated from eq 3. ^h Calculated from eq 4. ⁱ Calculated from eq 5. ^j Due to the low solubility in PrCN, and the consequent noisy absorption spectra, these data should be viewed with caution.

ASSOCIATED CONTENT

Supporting Information

Structures of **1**·Me₂CO, **2**·PhMe, **3**·0.5PhMe, **4**·0.5Me₂CO, **5**·0.5PhMe and **6**·MeCN, additional cyclic voltammetric and spectroscopic figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Graphical Abstract