Synthesis, spectroscopic, electrochemical and computational studies of rhenium(i) dicarbonyl complexes based on meridionally-coordinated 2,2′:6′,2′′-terpyridinē:

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A homologous series of meridionally-coordinated tridentate 2,2′:6′,2′′-terpyridine Re(i) dicarbonyl complexes have been prepared and investigated. The complexes mer,cis-[Re(tpy-κ3N)(CO)2(L)]+(L = Cl− (1), OSO2CF3− (2), NCCH3 (3), CN− (4), NC5H5 (5), PMe3 (6), PEt3 (7), PPh3 (8), P(OMe)3 (9) and P(OEt)3 (10); n = 0 or +1) have been synthesized and characterized by elemental analysis, 1H NMR and infrared spectroscopy. The electrochemistry of these compounds has been studied and compared to that of other known rhenium compounds using an electrochemical parameterization model. Cyclic voltammetry measurements have shown that the first oxidation of the complexes varies systematically in potential as the ligand L is altered. Many of these one-electron oxidations occur at lower potentials compared to more familiar bidentate diimine Re(i) tricarbonyl complexes. A correlation exists between CO, a strong π-acidic ligand, and deviations of the observed reduction potentials from the calculated values. Many of the complexes absorb light throughout a significant portion of the visible spectrum. Two of these complexes, mer,cis-[Re(tpy-κ3N)(CO)2Cl (1) and mer,cis-[Re(tpy-κ3N)(CO)2CN (4), absorb light throughout the entire visible spectrum. Low temperature emission spectra were obtained for the compounds mer,cis-[Re(tpy-κ3N)(CO)2Cl (1) and mer,cis-[Re(tpy-κ3N)(CO)2(P(OEt)3);+ (10) at 77 K in a 4:1 methanol–ethanol glass matrix and give metal-to-ligand charge transfer (3MLCT) luminescence. Density functional theory (DFT) calculations of the electronic structure are in good agreement with the experimental data.

Introduction

The number of complexes based on the bidentate diimine Re(i) tricarbonyl core has grown extensively during the past few decades. These complexes attract considerable attention due to their rich photochemistry and photophysics,1–3 their potential applications in the fields of photoinduced catalysis and electrocatalysis,4,5 artificial photosynthetic materials,6–8 supramolecular systems,9–14 and diagnostic nuclear medicine.15,16 By comparison, studies of the meridionally-coordinated tridentate triimine Re(i) dicarbonyl core are rare.17–21 These complexes should offer distinct advantages over the more traditional bidentate diimine Re(i) tricarbonyl complexes. For example, Re(i) dicarbonyl complexes utilizing a meridionally-coordinated tridentate chelate, such as 2,2′:6′,2′′-terpyridine (tpy), should possess enhanced stability due to the chelate effect. Synthetic modification of the 4′-site on the tpy ligand will not result in isomeric complexes due to the existence of a two-fold axis of symmetry in the tpy-κ5N chelate. This will lead to the formation of well-defined structures where directionality is desirable, such as, surface attachment and polymerization applications. The mer,cis- [Re(tpy-κ3N)(CO)2 Re(tpy-κ5N)(CO)3 moiety is expected to be more electron rich than the fac-Re(bpy)(CO)3 fragment, due to the presence of an extra CO in the latter, resulting in lower oxidation potentials. To this end, it is important to investigate the properties of the meridionally-coordinated tridentate triimine Re(i) dicarbonyl core.

In a previous paper, we described the preparation of complexes (1), (3), (5), (7) and (8) – a new class of meridionally-coordinated tridentate 2,2′:6′,2′′-terpyridine Re(i) complexes containing two carbon monoxide co-ligands.21 The goal of this study was to prepare a homologous series of these complexes by systematic ligand substitution and investigate their properties. Structurally, the rhenium-terpyridine domain is achiral due to the C2 rotational axis that is incident on the 4′-position of tpy ligand through the Re(i) center. As result, the structure is particularly attractive as it leaves the 4′-position on
the central pyridine available for the future construction of multicomponent metal-containing systems for vectorial electron and energy transfer, and tuning emergent properties without the formation of different stereoisomers.

This paper describes the extended synthesis, electrochemistry, spectroscopic, and density functional theory (DFT) studies for a series of meridionally-coordinated tridentate terpyridine Re(i) dicarbonyl complexes. A modified synthetic procedure for the synthesis of these systems is given, and their electrochemical, spectroscopic and computational properties are discussed. The electron donating tridentate terpyridine is found to stabilize and lower oxidation potentials. Many of the complexes absorb light throughout a significant portion of the visible spectrum and are observed to be luminescent at low temperatures. Density functional theory calculations provide ample agreement with experimental data.

**Experimental section**

**Materials**

Re(CO)$_3$Cl was purchased from Strem Chemical Co. and was used without further purification. The ligands 2,2′:6′:2″-terpyridine, triphenylphosphine, pyridine, silver trifluoromethanesulfonate, triethylphosphate, trimethylphosphate, potassium cyanide were purchased commercially and used without further purification. The triphenylphosphate and trimethylphosphine were purchased as 0.1 M solutions in tetrahydrofuran and used without further purification. The fac-Re(tpy-κ$^2$N)$(CO)_3$Cl was prepared in accordance to a previous literature report.$^{16}$

All solvents for synthesis were of reagent grade and was used as received, unless otherwise specified. Dry tetrahydrofuran (THF) was distilled from Na/benzophenone.$^{22}$ For UV-vis spectroscopy and electrochemical studies HPLC grade or reagent grade solvents were used. The reagent grade acetonitrile was first dried over silica gel for a minimum of 24 hours at 120 °C. The silica gel was then filtered off and the acetonitrile was distilled over anhydrous calcium hydride.$^{22}$

**Measurements**

UV/vis spectra were recorded using a Cary 50 UV-visible spectrophotometer with a xenon flashlamp. Room temperature emission spectra were measured on a Cary Eclipse fluorosence spectrophotometer. Low temperature excitation and emission spectra were obtained with a Photon Technologies International QuantaMaster Model C-60 spectrometer equipped with a xenon flash lamp and digital emission photon multiplier tube using a band pathway of 5 nm for excitation and 2 nm for emission. IR spectra were recorded using a thin film technique$^{23}$ with a Perkin-Elmer Spectrum 400 FT-IR/FT-FIR spectrophotometer using 1 cm$^{-1}$ resolution. Volutammetry of the complexes was measured using acetonitrile as the solvent and tetra-$n$-butylammonium hexafluorophosphate (TBAH, 0.1 M) as the supporting electrolyte. The electrolyte was recrystallized in absolute ethanol and dried under vacuum in a desiccator for a minimum of 24 hours prior to use.$^{24}$ Cyclic voltammograms were recorded using a PINE WaveNow potentiostatic analyzer in a three-electrode configuration. A glassy-carbon disk working electrode (3 mm diameter), a non-aqueous Ag$^+/AgCl$ wire quasi-reference electrode, and a Pt disk counter electrode were used for all measurements. Recorded potentials were referenced using the ferrocene/ferrocnium couple (vs. SCE) as an internal standard usually added at the conclusion of the experiment.$^{25}$ $^1$H, $^13$C ($T = 40$ °C) and $^{31}$P NMR spectra were measured with a Bruker AVANCE 500 high-field superconducting NMR spectrometer. Electrospray ionization (ESI) mass spectra were obtained with an Agilent Time-of-Flight MS G1969A Series 6200 in positive ionization mode using 1 ppm of the complexes in a 50% acetonitrile–water (LC/MS) with 10 µM of acetic acid (ionization agent). Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

**Computations**

DFT calculations were carried out by using Gaussian 09, revision A.02.$^{26}$ For Gaussian calculations, Becke’s three-parameter hybrid functional with the LYP correlation functional (B3LYP)$^{27,28}$ was used with the Los Alamos effective core potential LANL2DZ$^{29-31}$ basis set. Full geometry optimizations were performed using the B3LYP functional.$^{27,28}$ A double-ζ quality basis set consisting of Hay and Wadt’s effective core potentials (LANL2DZ)$^{29-31}$ was employed for the Re(i) metal atom, and a 6-31G* basis set$^{12-36}$ was employed for the rest of the atoms. The relativistic effective core potential (ECP) replaced the inner core electrons of the Re(i) metal atom, leaving only the outer core valence electrons (6s$^2$6p$^5$3d$^4$). A vibrational frequency analysis was carried out in order to confirm the minimum-energy geometries. Molecular orbital (MO) diagrams were constructed for the fully optimized geometries in Gaussian. The Franck-Condon vertical excitation energies and oscillator strengths were obtained with time-dependent DFT (TD-DFT)$^{37}$ as implemented in Gaussian. The solvent influence was treated using conductor-like polarizable continuum model (CPCM)$^{38}$ as implemented in Gaussian.

**Synthesis**

Scheme 1 outlines the synthesis of the meridionally-coordinated 2,2′:6′:2″-terpyridine rhenium dicarbonyl complexes used in this investigation. The complexes were synthesized according to a published method.$^{21}$ Methods to prepare the precursor complexes, as well as other similar bidentate fac-Re(κ,κ-diimine)(CO)$_3$Cl complexes, are well-established.$^{16,39,40}$ The synthesis of the meridionally-coordinated tridentate mer,cis-Re(tpy-κ$^2$N)(CO)$_3$Cl (1) complex was performed by the thermal elimination of CO that was modified from a previous literature report.$^{16,21}$ The previous Carius tube method was inconvenient given the difficulty of flame sealing the tube under high vacuum and the possibility of explosion due to excessive pressure at the end of the reaction. We found that the use of a heavy-wall, low-expansion borosilicate pressure tube in conjecture with automatic control$^{41}$ greatly simplified...
the procedure. Product recovery was simplified, the reaction vessel was reusable, and the hazards associated with overpressurization were eliminated.

The removal of chloride from the mer,cis-Re(tpy-κ^N)(CO)_2Cl (1) was effectuated by use of silver triflate, Ag(CF_3SO_3), in methylene chloride, yielding mer,cis-Re(tpy-κ^N)(CO)_2(CH_2Cl_2) (2).

Reflexing this complex in acetonitrile produced mer,cis-Re(tpy-κ^N)(CO)_2(CH_3CN) (3). Subsequently, the mer,cis-Re(tpy-κ^N)(CO)_2(NCCCH_3)_2 (4) was prepared directly from mer,cis-Re(tpy-κ^N)(CO)_2Cl (1) using Ag(CF_3SO_3) in refluxing acetonitrile. Refluxing mer,cis-Re(tpy-κ^N)(CO)_2(NCCCH_3)_2 in tetrahydrofuran (THF) with an excess of the ligand L (L = NMe_2, PMe_3, PEt_3, PPh_3, P(OMe)_3, or P(OEt)_3) resulted in the displacement CH_3CN and the subsequent coordination of L. Overall yields for these reactions ranged from 86–94%.

mer,cis-Re(tpy-κ^N)(CO)_2Cl (1). To a 35 mL heavy-wall, low-expansion borepressure glass tube was added the fac-Re(tpy-κ^N)(CO)_2Cl (71 mg, 0.139 mmol). The tube was then evacuated and purged with an inert gas (nitrogen or argon) thrice before being heated to 275 °C for 4–6 hours. A black solid remained. A column of alumina (60 mm length, 30 mm width) was used to purify 1 using dichloromethane, removing any unreacted fac-Re(tpy-κ^N)(CO)_2Cl, followed by acetonitrile removing a yellow-green product (unidentified). Lastly, ethanol elution was used to isolate 1. The solvent was removed under reduced pressure from the resulting solution resulting in 1 as a black solid. Yield: 63 mg, 89%.

H NMR (DMSO-d_6): δ 8.87 (d, J = 5.6 Hz, 2H), 8.57 (d, J = 8.3 Hz, 2H), 8.53 (d, J = 8.3 Hz, 2H), 8.21 (t, J = 7.9 Hz, 1H), 8.03 (t, J = 7.8, 2H), 7.48 (t, J = 6.4, 2H).

13C NMR (DMSO-d_6): δ 157.5, 157.2 (2x), 140.1, 138.3, 129.0, 125.0, 122.7. IR (CH_2CN): ε(CO) = 1891, 1798 cm⁻¹. Anal. Calc. for C_{17}H_{11}ClN_3O_2Re: C, 39.96; H, 2.17; N, 8.22%. Found: C, 39.81; H, 2.08; N, 8.77%. Electronic absorption (CH_2CN): λ_{max} nm (ε, M⁻¹ cm⁻¹): 239 (39 501, sh.), 272 (24 456), 281 (23 756), 320 (47 126), 378 (5516), 436 (6411), 651 (1691, br.). ESI MS: m/z N/A.

mer,cis-[Re(tpy-κ^N)(CO)_{2}(CH_3CN)](CF_3SO_3) (3). An acetonitrile solution (15 mL) containing complex 2 (49 mg, 0.0078 mmol) was refluxed for 5 h under a nitrogen atmosphere. Alternatively, 3 was prepared in a one-pot synthesis by refluxing complex 1 (54 mg, 0.086 mmol) and silver trifluoromethanesulfonate (34 mg, 0.0132 mmol) in 20 mL of acetonitrile for 8 hours in the dark under a nitrogen atmosphere. In either case, the resulting solution was concentrated to a minimum volume under a reduced pressure and diethyl ether was added drop wise to the filtrate to give a green precipitate. The precipitate was collected by filtration, washed with two 20 mL portions of cold diethyl ether, and dried in vacuum. Yield: 47 mg, 90%.

H NMR (CD_3CN): δ 8.91 (d, J = 5.1 Hz, 2H), 8.34 (d, J = 8.5 Hz, 2H), 8.30 (d, J = 8.5 Hz, 2H), 8.20 (t, J = 8.3 Hz, 1H), 8.02 (td, J = 5.2 Hz, 2H), 7.45 (td, J = 5.0 Hz, 2H), 1.97 (d, J = 3.0 Hz, 3H). IR (CH_2CN): ε(CO) = 1921, 1848 cm⁻¹. Anal. Calc. for C_{18}H_{11}F_3N_3O_5ReS: C, 34.61; H, 1.78; N, 6.73%. Found: C, 34.46; H, 1.81; N, 6.74%. Electronic absorption (CH_2CN), λ_{max} nm (ε, M⁻¹ cm⁻¹): 232 (39 501, sh.), 272 (24 456), 281 (23 756), 320 (47 126), 378 (5516), 436 (6411), 651 (1691, br.). ESI MS: m/z N/A.

mer,cis-[Re(tpy-κ^N)(CO)_{2}(CH_3CN)](CF_3SO_3) (4). A THF solution (50 mL) containing complex 3 (58 mg, 0.0087 mmol) and potassium cyanide (280 mg, 4.3 mmol) was refluxed for 3 h. The solvent was removed to dryness under a reduced pressure leaving a dark green solid. 4 was purified by an alumina column using 1:1 dichloromethane-acetonitrile. The resulting solution was concentrated to a minimum volume under reduced pressure producing complex 4 as a dark green solid. The solid was collected by filtration, washed with 20 mL portions of cold diethyl ether, and dried in vacuum. Yield: 29 mg, 66%.

H NMR (CD_3CN): δ 8.60 (m, 2H), 8.02 (m, 3H), 7.90 (m, 4H), 7.21 (m, 2H). IR (CH_2CN): ε(CO) = 1902, 1835 cm⁻¹. Anal. Calc. for C_{18}H_{11}N_4O_2Re: C, 43.11; H, 2.21; N, 11.17%. Found: C, 43.09;
H, 2.14; N, 11.17%. Electronic absorption (CH$_3$CN), $\lambda_{\text{max}}$ nm ($\varepsilon$ M$^{-1}$ cm$^{-1}$): 221 (31 176, sh.), 273 (18 001), 281 (17 325), 317 (29 030), 385 (4323), 445 (3576), 661 (1421, br.). ESI MS: m/z 502 (parent peak, [M]$^+$), where M is mer, cis-Re(ppy-κN)-(CO)$_3$(N$_2$H$_3$)$_2$CN).  

**mer,cis-Re(tpy-κN)(CO)$_3$(N$_2$H$_3$)$_2$CN** (5). A THF solution (50 mL) containing complex 3 (58 mg, 0.0087 mmol) and pyridine (0.25 mL, 3.1 mmol) was refluxed for 2 h. The resulting dark green solution was concentrated to a minimum volume under a reduced pressure and diethyl ether was added drop wise to the filtrate to give a green precipitate. The precipitate was collected by filtration, washed with two 20 mL portions of cold diethyl ether, and dried in vacuum. Yield: 53 mg, 87%. 1H NMR (CD$_3$CN): $\delta$ 8.99 (d, $J = 5.6$, 2H), 8.32 (d, $J = 8.3$, 2H), 8.28 (d, $J = 8.3$, 2H), 8.17 (t, $J = 8.6$, 1H), 8.01 (m, 4H), 7.77 (m, 1H), 7.48 (m, 2H), 7.21 (m, 2H). IR (CH$_3$CN): $\nu$(CO) = 1912, 1841 cm$^{-1}$; $\nu$(CN) = 2026 cm$^{-1}$. Anal. Calc. for C$_{23}$H$_{16}$F$_3$N$_4$O$_5$ReS: C, 39.26; H, 2.29; N, 7.96%. Found: C, 39.01; H, 3.41; N, 5.57%. Electronic absorption (CH$_3$CN), $\lambda_{\text{max}}$ nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 232 (39 501, sh.), 272 (24 456), 281 (23 756), 320 (47 126), 378 (5516), 436 (6411), 651 (1691, br.). ESI MS: m/z 594 (parent peak, [M]$^+$), where [M]$^+$ is mer,cis-Re(ppy-κN)-(CO)$_3$(N$_2$H$_3$)$_2$CN). 

**mer,cis-Re(tpy-κN)(CO)$_3$(PPh$_3$)$_2$CN** (6). Complex 3 (50 mg, 0.0075 mmol) was added to THF (50 mL) and purged for 10 min. A 0.1 M solution of trimethylphosphine in THF (ca. 2.5 mL, 24 mmol) was then added to solution and refluxed for 5 h under a nitrogen atmosphere. The resulting dark green solution was concentrated to a minimum volume under a reduced pressure. Diethyl ether was added drop wise to the filtrate to give a green precipitate. The precipitate was collected by filtration, washed with two 20 mL portions of cold diethyl ether, and dried in vacuum. Yield: 48 mg, 86%. 1H NMR (CD$_3$CN): $\delta$ 8.94 (d, $J = 6.61$, 2H), 8.34 (m, 4H), 8.17 (ddt, $J = 9.7$, 2H, 7.98 (m, 1H), 7.42 (m, 2H), 1.4 (m, 2H), 0.78 (m, 6H). 31P NMR (CD$_3$CN): $\delta$ −31.27 (s, 1P). 13C NMR (DMSO-d$_6$): $\delta$ 157.5, 156.4, 156.0, 140.2, 138.7, 129.3, 125.7, 122.8, 119.5 and 10.6. IR (CH$_3$CN): $\nu$(CO) = 1919, 1848 cm$^{-1}$. Anal. Calc. for C$_{36}$H$_{26}$F$_3$N$_3$O$_5$PReC: C, 48.76; H, 2.96; N, 4.74%. Found: C, 48.95; H, 2.95; N, 4.45%. Electronic absorption (CH$_3$CN), $\lambda_{\text{max}}$ nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 228 (37 537, sh.), 273 (17 780), 319 (19 850), 371 (2321), 421 (2663), 625 (673, br.). ESI MS: m/z 738 (parent peak, [M]$^+$), where M is mer,cis-Re(tpy-κN)-(CO)$_3$(PPh$_3$)$_2$CN). 

**mer,cis-Re(tpy-κN)(CO)$_3$(P(OMe)$_3$)$_2$CN** (7). Complex 3 (54 mg, 0.0081 mmol) was added to THF (50 mL) and purged for 10 min. A 0.1 M solution of triethylphosphine in THF (ca. 2.5 mL, 26 mmol) was then added to solution and refluxed for 5 h under a nitrogen atmosphere. The resulting dark green solution was concentrated to a minimum volume under a reduced pressure. Diethyl ether was added drop wise to the filtrate to give a green precipitate. The precipitate was collected by filtration, washed with two 20 mL portions of cold diethyl ether, and dried in vacuum. Yield: 56 mg, 93%. 1H NMR (CD$_3$CN): $\delta$ 8.99 (d, $J = 5.9$, 2H), 8.36 (d, $J = 9.9$, 2H), 8.31 (d, $J = 8.9$, 2H), 8.16 (t, $J = 8.4$, 1H), 7.98 (t, $J = 7.4$, 2H), 7.41 (t, $J = 6.4$, 2H), 1.22 (m, 6H), 0.63 (m, 9H). 31P NMR (CD$_3$CN): $\delta$ −12.25 (s, 1P). 13C NMR (DMSO-d$_6$): $\delta$ 157.3, 156.1, 150.6, 139.5, 127.3, 126.2, 121.1, 120.1 and 22.7 and 11.2. IR (CH$_3$CN): $\nu$(CO) = 1927, 1855 cm$^{-1}$. Anal. Calc. for C$_{23}$H$_{16}$F$_3$N$_4$O$_5$PReC: C, 38.81; H, 3.53; N, 5.66%. Found: C, 39.01; H, 3.41; N, 5.57%. Electronic absorption (CH$_3$CN), $\lambda_{\text{max}}$ nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 232 (39 501, sh.), 272 (24 456), 281 (23 756), 320 (47 126), 378 (5516), 436 (6411), 651 (1691, br.). ESI MS: m/z 594 (parent peak, [M]$^+$), where [M]$^+$ is mer,cis-Re(tpy-κN)-(CO)$_3$(POMe)$_3$CN. 

**mer,cis-Re(tpy-κN)(CO)$_3$(P(OEt)$_3$)$_2$CN** (8). A THF solution (50 mL) containing complex 3 (55 mg, 0.0083 mmol) with triphenylphosphine (1389 mg, 5.3 mmol) was refluxed for 4 h. The resulting dark green solution was concentrated to a minimum volume under a reduced pressure and diethyl ether was added drop wise to the filtrate to give a green precipitate. A column of alumina absorbent was used to isolate the product. 100% diethyl ether was used to remove the excess triphenylphosphine followed by acetonitrile (producing a dark green band). The excess eluent solvent was concentrated under a reduced pressure. Cold hexane was added to produce a green precipitate. The precipitate was collected by filtration, washed with two 20 mL portions of cold diethyl ether, and dried in vacuum. Yield: 69 mg, 94%. 1H NMR (CD$_3$CN): $\delta$ 9.04 (d, $J = 5.5$, 2H), 7.94 (d, $J = 6.5$, 4H), 7.77 (t, $J = 7.8$, 2H), 7.35 (t, $J = 6.6$, 3H), 7.27 (t, $J = 6.5$, 3H), 7.22 (m, 6H), 7.03 (m, 6H). 31P NMR (CD$_3$CN): $\delta$ 27.32 (s, 1P). IR (CH$_3$CN): $\nu$(CO) = 1928, 1855 cm$^{-1}$. Anal. Calc. for C$_{36}$H$_{26}$F$_3$N$_3$O$_5$PReC: C, 48.76; H, 2.96; N, 4.74%. Found: C, 48.95; H, 2.95; N, 4.45%. Electronic absorption (CH$_3$CN), $\lambda_{\text{max}}$ nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 228 (37 537, sh.), 273 (17 780), 319 (19 850), 371 (2321), 421 (2663), 625 (673, br.). ESI MS: m/z 738 (parent peak, [M]$^+$), where M is mer,cis-Re(tpy-κN)(CO)$_3$(P(OEt)$_3$)CN).
and triethyl phosphate (ca. 0.35 mL, 2.0 mmol) in THF (50 mL) under a nitrogen atmosphere for 2 hours. The dark green solution was concentrated to a minimum volume under a reduced pressure. Diethyl ether was added dropwise to the concentrate giving a green solid. The green precipitate was filtered and washed with five 10 mL portions of cold diethyl ether. The solid was dried under vacuum. Yield: 51 mg, 88%. 1H NMR (CD3CN): δ 8.96 (d, J = 9.0 Hz, 2H), 8.35 (d, J = 8.1 Hz, 2H), 8.30 (dt, J = 10.2 Hz, 2H), 8.17 (m, 1H), 7.98 (m, 2H), 7.40 (m, 2H), 3.63 (p, J = 7.5 Hz, 6H), 0.84 (t, J = 14.0 Hz, 9H). 13P NMR (CD3CN): δ 105.27 (s, 1P).13C NMR (DMSO-d6): δ 158.1, 157.2, 156.6, 138.9, 129.2, 125.4, 123.3, 61.9, and 16.3. IR (CH3CN): ν(CO) = 1938, 1863 cm⁻¹. Anal. Calc. for C24H26F3N3O8PReS: C, 36.37; H, 3.33; N, 5.32%. Found: C, 36.37; H, 3.33; N, 5.32%. Electronic absorption (CH3CN), λmax, nm (ε, M⁻¹ cm⁻¹): 230 (33 868, sh.), 272 (18 682), 280 (19 779), 314 (38 948), 368 (38 948), 436 (3811), 411 (4709), 481 (1628), 530 (1504, br.), 575 (1322, br.). ESI MS: m/z 642 (parent peak, [M]⁺, where M is mer,cis-Re(tpy-xN)(CO)2(P(OEt)3)]⁺).

**Results and discussion**

**Infrared spectroscopy**

Two stretching bands were found for the complexes in the region of ca. 1795–1865 and 1890–1940 cm⁻¹. The two CO stretching modes were expected on the basis of those found for other reported rhenium(i) dicarbonyl complexes and are consistent with a mutually cis-CO geometry for all of the compounds. Ligands with greater electron accepting ability will affect the ϵ(CO) stretching band positions of metal carbonyl complexes by shifting them to higher wavenumbers. The isostructural mer,cis-Re(tpy-xN)(CO)2 complexes demonstrate this behavior with the electron acceptor ability of the ligands L showing the trend P(OEt)3 > P(OEt)2 > PMe3 > NCCH3 > NC2H5 > CF3SO3⁻ > CN⁻ > Cl⁻. Ligands P(OEt)3 and P(OEt)2 show the greatest electron accepting ability relative to the other ligands. Anionic ligands such as Cl⁻, CF3SO3⁻ and CN⁻ show the least electron accepting ability. Frequency calculations were carried out with inclusion of solvent in order to obtain the carbonyl stretching frequencies and compare them with their experimental values. The results, without any scaling, are collected in Table 1 along with their experimental counterparts. In general, the calculated frequencies represent the experimental frequencies well. The trend in electron acceptor strength is in excellent agreement with the experimental data. The only difference observed is that PPh3 and PMe3 swap positions. In addition, experimental carbonyl infrared frequencies for fac-[Re(bpy)(CO)3]L⁺ analogs are listed in Table 1. A similar trend is observed for the electron accepting ability suggesting that the ligand set similarly influences both mer,cis-[Re(tpy-xN)(CO)2(L)]⁺ and fac-[Re(bpy)-(CO)3]L⁺ type systems. As mentioned previously, ligands P(OEt)3 and P(OEt)2 show the greatest electron accepting ability relative to the other ligands. Anionic ligands such as Cl⁻, CF3SO3⁻ and CN⁻ show the least electron accepting ability.

**Table 2** Summary of electrochemical potentials for selected compounds

<table>
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<th>L</th>
<th>E (V vs. SCE)¹, ²</th>
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<tr>
<td></td>
<td>Oxidation</td>
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<td>Cl⁻</td>
<td>0.48 (65), 1.22²</td>
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<tr>
<td>CF3SO3⁻</td>
<td>0.84⁴</td>
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<tr>
<td>NCCH3</td>
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<tr>
<td>CN⁻</td>
<td>0.67, 1.25⁶</td>
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<tr>
<td>NC2H5</td>
<td>0.86, 1.35⁶</td>
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<tr>
<td>PPh3</td>
<td>0.84 (60)</td>
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<tr>
<td>PMe3</td>
<td>0.84 (75)</td>
</tr>
<tr>
<td>P(OEt)₃</td>
<td>0.92 (75), 1.30⁶</td>
</tr>
<tr>
<td>P(OEt)₂</td>
<td>0.93 (73), 1.30⁶</td>
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</table>

¹ A glassy-carbon disk working (3 mm i.d.), non-aqueous Ag⁺/AgCl wire quasi-reference and Pt-wire counter electrodes were used. Values in parentheses are peak-to-peak separations in mV. ² Scan rate 0.1 V s⁻¹. ³ Irreversible peak.
Re(bipyridine)(CO)3Cl. For several reasons, the potentials exhibit appreciable cathodic shifts and increased reversibility. The Re(II/I) couple is more electron rich than the corresponding CO ligand, which is relatively insensitive to changes in the ligand set. Based on the similarity of these potentials, we attribute these couples to ligand-centered (terpyridine) reductions.

Similar to bidentate polypyridine Re(I) tricarbonyl analogs, the meridionally-coordinated tridentate trinuclear Re(i) dicarbonyl set shows an one-electron, diffusion-controlled and chemically reversible Re(II/I) couple. However, these oxidation potentials exhibit appreciable cathodic shifts and increased reversibility. The mer,cis-Re(tpy-k^N)(CO)2 moiety is expected to be more electron rich than the fac-Re(bpy)(CO)3 fragment, due to the presence of an extra CO in the latter. The result is that the energy of the filled t_{2g} orbitals (the HOMO) is increased, resulting in a more facile oxidation of the metal center. For example, the Re(II/I) oxidation couple for mer,cis-Re(tpy-k^N)(CO)2Cl (1) is +0.85 V more reducing than fac-Re(bpy)(CO)3. For several mer,cis-[Re(tpy-k^N)-Cl2(L)]+ complexes, a second oxidation couple is observed which is relatively indifferent to the ligand. For example, the oxidation wave observed at +1.22 V for mer,cis-Re(tpy-k^N)(CO)2Cl (1) is assigned to an irreversible Re(III/II) couple due to subsequent CO ligand loss after one electron oxidation. Redox induced CO ligand loss is commonly observed for fac-Re(bpy)(CO)3 type systems due to reduced backbonding from the Re(u) center to the CO ligand. The mer,cis-[Re(tpy-k^N)(CO)2(L)]+ series of complexes behave similarly. Where the Re center is more electron rich, CO loss is less prevalent. This is observed as the Re(II/I) couple is shifted to more negative potentials (Table 3) indicating a greater electron density at the metal center, enabling a greater capacity of backbonding, resulting in greater reversibility evident in a corresponding increase in the Re(II/I) cathodic current.

Lever has demonstrated that the observed reduction potential of a transition metal complex can be estimated by a simple empirical calculation taking into account individual ligand contributions. This method provides accurate predictions of reduction potentials for octahedral complexes in most cases. The calculated values of $E$ and $\sum E_L (L)$ are given in Table S11 (ESI†). The predicted potential is based on the formula $E = S_M [\sum E_L (L)] + I_M$, where, for the Re(II/I) couple, $S_M = 0.76$ and $I_M = -0.95$ (V vs. NHE). The $\sum E_L (L)$ term is a sum based on a statistical analysis for large numbers of reversible redox couples over all the ligands around the rhenium center. The $S_M$ value is characteristic of the given redox active fragment and represents its sensitivity towards other components of the coordination sphere. $I_M$ is a constant related to the reduction potential of the relevant free ligand and the degree of interaction between the metal center and ligand. Fig. 2A shows both the observed and calculated Re(II/I) reduction potentials plotted against the corresponding $\sum E_L (L)$ values. The observed potentials are in good agreement (i.e., average difference 380 mV) with values predicted from Lever’s parameterization data.

The data shown in Fig. 2 are significant given the limited number of rhenium-terpyridine complexes present in the literature. Helberg et al. analyzed a series of rhenium-terpyridine complexes with the absence of strong $\pi$-acidic ligands using Lever’s parameters. We have included five of these rhenium-terpyridine complexes, [Re(tpy-k^N)Cl2], [Re(tpy-k^N)(PPh3)2Cl]2, [Re(tpy-k^N)(PPh3)Cl]+, [Re(tpy-k^N)(PPh3)(bpy)]+, and [Re(tpy-k^N)(PPh3)(η2-cyclohexenone)] for comparison in

Table 3: Electronic absorption maxima

<table>
<thead>
<tr>
<th>#</th>
<th>L</th>
<th>$\lambda_{\text{max}}$ (nm) $\times 10^3$ (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl$^-$</td>
<td>239 (29.1, sh.), 271 (34.0), 280 (33.9), 321 (26.5), 398 (4.0), 466 (3.6), 567 (1.4, br.), 689 (1.3, br.)</td>
</tr>
<tr>
<td>2</td>
<td>CF$_3$SO$_3^-$</td>
<td>232 (39.5, sh.), 272 (24.5), 281 (23.8), 320 (47.1), 378 (5.5), 436 (6.4), 651 (1.7, br.)</td>
</tr>
<tr>
<td>3</td>
<td>NCCH$_3$</td>
<td>231 (38.1, sh.), 273 (20.5), 280 (23.9), 318 (41.6), 427 (5.4), 652 (1.6, br.)</td>
</tr>
<tr>
<td>4</td>
<td>CN$^-$</td>
<td>221 (31.2), 273 (18.0), 281 (17.3), 317 (29.0), 385 (4.3), 445 (3.6), 661 (1.4, br.)</td>
</tr>
<tr>
<td>5</td>
<td>NC$_3$H$_6$</td>
<td>233 (16.1, sh.), 250 (9.6), 255 (9.6), 281 (5.3), 322 (6.7), 377 (1.2), 450 (1.0), 676 (0.52, br.)</td>
</tr>
<tr>
<td>6</td>
<td>PMe$_2$</td>
<td>226 (28.3, sh.), 272 (15.4), 281 (16.0), 318 (34.2), 375 (3.8), 432 (4.5), 646 (1.1, br.)</td>
</tr>
<tr>
<td>7</td>
<td>PET$_3$</td>
<td>232 (39.5, sh.), 272 (24.5), 281 (23.8), 320 (47.1), 378 (5.5), 436 (6.4), 651 (1.7, br.)</td>
</tr>
<tr>
<td>8</td>
<td>PPh$_3$</td>
<td>228 (37.5, sh.), 273 (17.8), 319 (19.9), 371 (2.3), 421 (2.7) 625 (673, br.)</td>
</tr>
<tr>
<td>9</td>
<td>P(OOMe)$_3$</td>
<td>228 (32.6, sh.), 272 (19.3), 279 (19.8), 312 (34.8), 367 (3.7), 408 (4.4), 600 (1.0, br.)</td>
</tr>
<tr>
<td>10</td>
<td>P(OEt)$_3$</td>
<td>230 (33.9, sh.), 272 (18.7), 280 (19.8), 314 (38.9), 368 (3.8), 411 (4.7), 481 (1.6), 530 (1.5, br.), 575 (1.3, br.)</td>
</tr>
</tbody>
</table>

In acetonitrile (CH$_3$CN) solvent; sh = shoulder, br = broad.
Electronic absorption

UV/vis absorption data were acquired for these complexes in acetonitrile and the prominent peaks are recorded in Table 3.

Fig. 2B. For complexes where the values of $\Sigma E_i(L)$ are large ($\geq 1.5$ V vs. NHE), the observed potentials are in good agreement with values predicted from Lever’s parameterization. Complexes where values of $\Sigma E_i(L)$ are smaller have observed potentials that deviate from the calculated potentials. Helberg et al. noted this trend and hypothesized that as the ability of a given ligand set to stabilize an electron-rich metal is sufficiently diminished, the electrochemical potential of the metal becomes considerably more sensitive to small perturbations in the $\pi$-accepting ability of the ligands. While the number of rhenium-terpyridine complexes is not sufficient to warrant any quantitative treatment, the inclusion of our complexes supports this premise. The CO, a strong $\pi$-acidic ligand, appears to stabilize an electron-rich rhenium-terpyridine complex. This result is unique because it allows a clear indication of the electron accepting ability of the ligand set through these transition(s).

Correlation of UV/vis absorption spectra with the corresponding Re(II/II) oxidation potentials shows a linear relationship. These results appear consistent with previous reports between electrochemical and spectroscopy for compounds forming MLCT exited states. It is worthy to note the transition(s) between 300–350 nm for the entire series of meridional complexes track this relationship as well. The result is unique because it allows a clear indication of the electron accepting ability of the ligand set through these transition(s).

DFT and TD-DFT calculations have been widely used in the study of metal polypyridine complexes because of their utility and relative accuracy in providing insight into the structural and electronic properties of such systems. These
calculations have been performed on the complexes. A complete listing of singlet and triplet transitions, Mulliken population analysis, and optimized structural data can be found in the ESL.† As an example, Fig. 4 illustrates the predominant molecular orbitals involved in those electronic transitions for mer,cis-Re(tpy-κ^3N)(CO)_2Cl (1).

The molecular orbitals shown in Fig. 4 provide a convenient visual descriptor for the calculated electronic transitions recorded in ESL.† For the mer,cis-Re(tpy-κ^3N)(CO)_2Cl (1), the first transition at 664.7 nm is assigned as a HOMO-to-LUMO transition with a percentage contribution to the wavefunction for the excited state at 98%. From the HOMO, it can be seen that the character of this transition is predominantly rhenium-based with an admixture of chlorine (Cl), carbon monoxide (CO), and some terpyridine. The LUMO is mostly terpyridine-based with a little contribution from the Cl and CO. It is interesting to point-out that complexes such as fac-Re(η,α-diimine)(CO)_3Cl have been shown to exhibit mixed MLCT and LLCT (ligand-to-ligand charge transfer) and, sometimes, IL (intraligand) characteristics for the Re–Cl bond of the mer,cis-Re(tpy-κ^3N)(CO)_2Cl (1) predict it to be undistorted. This is in contrast for fac-Re(α,α-diimine)(CO)_3Cl types of complexes where distortion of the Re–Cl bond has been well-established through DFT calculations and crystallography.59–64

It would appear that mer,cis-Re(tpy-κ^3N)(CO)_2Cl (1) shares some of those same properties. Indeed, the Mulliken population analysis of the HOMO shown as the MO Index in Fig. 4 is composed of 54.7% Re, 17.0% Cl, 14.8% CO, and 13.5% terpyridine. The composition of the LUMO is 89.0% terpyridine, 2.3% Cl, 4.3% CO, with the remaining 4.4% on the Re. Likewise, transitions involving the HOMO – 2 orbital, such transitions 5 and 6, are expected to contribute an admixture of MLCT, LLCT, and IL characteristics. DFT calculations for the Re–Cl bond for the mer,cis-Re(tpy-κ^3N)(CO)_2Cl (1) predict it to be undistorted. This is in contrast for fac-Re(α,α-diimine)(CO)_3Cl types of complexes where distortion of the Re–Cl bond has been well-established through DFT calculations and crystallography.59–64

In general, electronic transitions for all complexes in the region 350–800 nm are best represented as MLCT. Similarly, electronic transitions in the region 200–300 nm are predominantly ligand-based π→π* transitions and absorptions between 300–350 nm are best represented as an admixture of π→π* ligand centered and metal-to-ligand charge transfer transitions. These results are consistent with the assignments of the experimental absorption spectra described earlier. The electronic transitions by TD-DFT using the B3LYP functional with inclusion of solvent CH_3CN described by the conductor-like polarization continuum model (CPCM) correspond very well with the experimental data. As an example, the experimental UV/vis and corresponding simulated UV/vis absorption spectrum (both in acetonitrile solvent) for mer,cis-Re(tpy-κ^3N)-(CO)_3Cl (1) are shown in Fig. 5. The simulation was performed using SWizard software.66 All calculated transitions are included. Gaussian shapes of the absorption bands are assumed. The width at half-height 3000 cm^{-1} used corresponds to typical experimental bandwidths of MLCT bands.67,68 Band areas are proportional to calculated oscillator strengths. A very similar spectrum is obtained.

**Luminescence properties**

For the complexes investigated in this study, emission is not observed at room temperature in acetonitrile solution. Thus,
the following discussion is restricted to emission and excitation spectra recorded at 77 K, and variable increasing temperatures, in a 4:1 methanol–ethanol glass for compounds mer,cis-Re(tpy-κ′N)(CO)₂Cl (1) and mer,cis-[Re(tpy-κ′N)(CO)_2(P(OEt)_3)]⁺ (10).

Representative emission spectra for mer,cis-Re(tpy-κ′N)-(CO)₂Cl (1) and mer,cis-[Re(tpy-κ′N)(CO)_2(P(OEt)_3)]⁺ (10) are shown in Fig. 6. At 77 K the luminescence spectrum for mer,cis-[Re(tpy-κ′N)(CO)_2(P(OEt)_3)]⁺ (10) shows vibrational progressions with spacing of ca. 5250 cm⁻¹ with an emission maximum centered at 389 nm (λ_EX = 350 nm). In contrast, the 77 K spectrum of mer,cis-Re(tpy-κ′N)(CO)₂Cl (1) is broad and structureless, which is typical of Re-based emitters,¹²,⁶⁹–⁸¹ with an emission maximum centered at 522 nm (λ_EX = 325 nm).

For the complexes investigated, at room temperature internal conversion to the lowest energy ³MLCT excited state results in vibrational relaxation to the ground state with no emission. From our calculations this corresponds to a ³MLCT HOMO–LUMO transition centered at 715 nm for mer,cis-Re(tpy-κ′N)(CO)₂Cl (1) and 561 nm for mer,cis-[Re(tpy-κ′N)(CO)_2(P(OEt)_3)]⁺ (10) (see ESI†). Therefore, emission can not be originating from lowest energy ³MLCT excited state. The excitation spectrum at 77 K for mer,cis-Re(tpy-κ′N)(CO)₂Cl (1) (Fig. 6A) suggest that emission arises from an absorption seen as a low energy shoulder centered at 400 nm. According to TDDFT calculations, this absorption transition has a significant metal-to-ligand charge transfer component and can be described as having ¹MLCT character. The nature of the transition resulting in emission is ³MLCT. As the temperature of mer,cis-Re(tpy-κ′N)(CO)₂Cl (1) is increased, the 522 nm centered emission maximum at 77 K lowers in energy to an emission maximum centered at 548 nm (Fig. 6B) with subsequent loss of intensity. This observation is consistent with ³MLCT (Case A) type emission. We note that this emission was only observable in the 77–125 K temperature window. Likewise, the excitation spectrum at 77 K for mer,cis-[Re(tpy-κ′N)(CO)_2(P(OEt)_3)]⁺ (10) (see ESI†) shows emission arises from an absorption at 384 nm. As with mer,cis-Re(tpy-κ′N)(CO)₂Cl (1), the transition has ¹MLCT character and the nature of the transition resulting in emission is ³MLCT. For mer,cis-[Re(tpy-κ′N)(CO)_2(P(OEt)_3)]⁺ (10), the emission energy lowered as the temperature increased. The structured emission spectrum observed at 77 K became a broad, structureless emission with an emission maximum centered at 448 nm. Further emission was not observed as the temperature increased past 200 K. On close inspection (see Fig. 6C), the 77 K emission spectrum is resolved into vibronic bands. Freezing the complex in a glass restricts the vibrational motion of the excited state, thus allowing emission from higher vibrational states of the same ³MLCT excited state. At 200 K these higher vibrational states are thermally equilibrated and emission is present from the lowest vibrational state.⁸³,⁸⁴ As a result, we assign this as a ³MLCT (Case A) type emission. This can be summarized by noting at room temperature internal conversion to the lower lying ³MLCT excited states is dominant and results in complete quenching of emission. This effect is described quantitatively by the energy gap law.⁸⁵–⁹⁰ This law states that the non-radiative decay rate of a metal–ligand complex increases exponentially as the energy gap decreases.⁹¹ The fact that ³MLCT emission is observed from the electronic state at 77 K from ³MLCT located at 400 nm mer,cis-Re(tpy-κ′N)(CO)₂Cl (1) and 384 nm for mer,cis-[Re(tpy-κ′N)(CO)_2(P(OEt)_3)]⁺ (10) suggests the vibronic coupling/internal conversion to the lower lying ³MLCT states is
reduced somewhat resulting in weak $^3\text{MLCT}$ emission from the $^1\text{MLCT}$.

The mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2\text{Cl}$ (1) and mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2(P(\text{OEt}))_2$ (10) complexes exhibit different Stokes shifts at 77 K amounting to ca. 8702 and 355 cm$^{-1}$, respectively.

$$E_{\text{ABS}} - E_{\text{EM}} = E_{\text{STOKES}}$$

In the above equation $E_{\text{ABS}}$ and $E_{\text{EM}}$ are the energies corresponding to the lowest energy spectroscopic band for absorption and highest energy emission.$^{92}$ With complexes that experience a significant geometry change on excitation, or a significant reorganization of solvent, the Stokes shift will be larger. Hence, the difference in Stokes shift between the mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2\text{Cl}$ (1) and mer,cis-$\text{Re(tpy-kN)}(\text{CO})_3P(\text{OEt})_2$ (10) is mainly attributed to the fact that an $^1\text{MLCT}$ transition is accompanied by (i) a solvent rearrangement and (ii) an intramolecular rearrangement. With rigid structures for which the excited state and ground state have very similar geometries, the intramolecular rearrangement is small. So the Stokes shift primarily arises due to different solvation of the excited state relative to the ground state. An assessment of the importance of solvent reorganization may be obtained by noting that, in passing from 125 K to 77 K, the luminescence band maximum (i) for mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2\text{Cl}$ (1) moves from 548 to 522 nm, amounting to an energy difference of 909 cm$^{-1}$, and (ii) for mer,cis-$\text{Re(tpy-kN)}(\text{CO})_3P(\text{OEt})_2$ (10) moves from 448 to 402 nm, amounting to an energy difference of 831 cm$^{-1}$. The solvent reorganization for $\text{C}^-$ is greater than for $\text{P(}\text{OEt})_3$, suggesting that the MLCT luminescence level is more destabilized for mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2\text{Cl}$ (1) than that for $\text{Re(tpy-kN)}(\text{CO})_2P(\text{OEt})_2$ (10).$^{93}$

Conclusions

In conclusion, we have prepared and investigated a homologous series of meridionally-coordinated tridentate terpyridine $\text{Re(i)}$ dicarbonyl complexes. These complexes were characterized by various spectral, analytical, cyclic voltammetric, and computational methods. Reaction (via halide extraction) of mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2\text{Cl}$ (1) in the presence of a coordinating ligand (L) resulted in complexes of the type of mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2L$ (n = 0 or +1) in excellent yields. These complexes show significant absorbance across the visible spectrum. Two of these complexes absorb light across the entire visible spectrum. Absorption peaks in the visible region are consistent with metal-to-ligand charge transfer (MLCT) transitions. Results from cyclic voltammetry studies indicate that oxidation potentials for the series of complexes are lower compared to rhenium bidentate polypyridine species. Observed potentials track those values predicted from Lever’s parameterization data and correlate well with calculated potentials. Low-temperature emission spectra for the compounds mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2\text{Cl}$ (1) and mer,cis-$\text{Re(tpy-kN)}(\text{CO})_2P(\text{OEt})_2$ (10) at 77 K in a 4:1 methanol–ethanol glass matrix result in $^1\text{MLCT}$ luminescence. The Stokes shift primarily arises due to different solvation of the excited state relative to the ground state. DFT calculations represent experimental observables very well. Further studies remain to determine the coordination behaviour of the ligand, L, and how ring-substituents on the terpyridine impact the reactivity for the series of complexes.

Acknowledgements

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Notes and references

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