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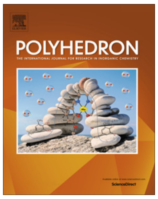

Synthesis, characterization, electrochemistry and photophysical studies of rhenium(I) tricarbonyl diimine complexes with carboxaldehyde alkynyl ligands

Siu-Tung Lam, Nianyong Zhu, Vonika Ka-Man Au, Vivian Wing-Wah Yam *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

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Dedicated to Professor Claude Lapinte for his contribution to organometallic chemistry.

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ABSTRACT

A class of rhenium(I) tricarbonyl diimine complexes with carboxaldehyde alkynyl ligands, $[Re(CO)_3(N^\wedge N)(C{\equiv}C{-}C_6H_4{-}CHO)]$ ($N^\wedge N = \alpha,\alpha'$-diimine ligand), has been successfully synthesized and characterized, and the X-ray crystal structure of one of the complexes has been determined. Electrochemical and photophysical studies have been performed to study the effect of the variation of the diimine ligand on the redox and optical properties of the rhenium(I) complexes.

1. Introduction

Materials science has become one major branch of science that has attracted immense attention over the past few decades. The constant search for new advanced materials with unique and improved properties has led to a variety of investigations into luminescent transition metal complexes. In particular, continuous attention has been drawn towards rhenium(I) tricarbonyl α,α'-diimine complexes, the first luminescence of which appeared in 1974 when the photophysical properties of $[Re(CO)_3(phen)Cl]$ were described and assigned to a metal-to-ligand charge-transfer (MLCT) excited state by Wrighton and Morse [1]. Since then, the potential use of rhenium(I) tricarbonyl diimine complexes as building blocks for luminescence and redox-active supramolecular systems has been receiving a lot of attention. Recent studies have demonstrated the successful utilization of such complexes as photoswitchable materials [2,3], DNA probes [4], photocleavage agents [5–8], biolabels [9–11], protein probes [12], cation probes [13,14], receptors for sugar molecules [15], metallogels [16,17] as well as light-emitting materials in OLEDs [18–22].

Of particular interest would be the rhenium(I) alkynyl systems. The first report of rhenium(I) alkynyl complexes dated back to the late 1960's when Bruce and co-workers reported the synthesis of $[Re(CO)_5(C{\equiv}C{-}R)]$ (R = Ph or C_6F_5) [23]. This was followed by the report of a series of mononuclear and dinuclear rhenium(I) alkynyl complexes of the type, $[Re(CO)_5(C{\equiv}C{-}R)]$ (R = CH_3, $SiMe_3$, H) and $[(CO)_5Re{-}C{\equiv}C{-}Re(CO)_5]$, by Beck and co-workers [24–26]. Subsequent work by Gladysz and co-workers demonstrated the rich photophysical and electrochemical properties of a series of rhenium(I) diynes and polyynes, $[Re(Cp)(NO)(PPh_3)\{(C{\equiv}C)_nR\}]$ [27–30]. A relatively recent work by the groups of Lapinte, Yam and co-workers has demonstrated the remarkable electro-switchable photoluminescence of a rhenium–iron mixed-metal complex, $[Re(bpy)(CO)_3{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}Fe(C_5Me_5)(dppe)]$ [31]. Yam and Halet and co-workers have also demonstrated the photophysical and electrochemical behaviors of related heterometallic rhenium–palladium branched complexes, $[1,3\text{-}\{Cl(PEt_3)_2PdC{\equiv}C\}_2\text{-}5\text{-}\{(N^\wedge N)(CO)_3ReC{\equiv}C\}C_6H_3]$ ($N^\wedge N = Me_2bpy$, bpy) [32]. In light of the rich optical, non-linear optical, redox, electronic as well as chemical behaviors of rhenium(I) alkynyls, we extend our previous work on alkynylrhenium(I) tricarbonyl diimine complexes [33–37] and report herein the synthesis and characterization of a series of rhenium(I) tricarbonyl diimine complexes with carboxaldehyde

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* Corresponding author. Tel.: +852 2859 2153; fax: +852 2857 1586.
E-mail address: wwyam@hku.hk (V.W.-W.Yam).

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alkynyl ligands, [Re(CO)$_3$(N^N)(C≡C–C$_6$H$_4$–CHO)], where N^N = 2,9-dimethyl-1,10-phenanthroline (2,9-Me$_2$phen) (**1**), 1,10-phenanthroline (phen) (**2**) and 5,6-dibromo-1,10-phenanthroline (5,6-Br$_2$phen) (**3**). Earlier studies of our group have demonstrated the successful preparation of alkynylrhenium(I) tricarbonyl diimine complexes in the presence of silver(I) triflate [35,36]. However, the yield was found to be limited by the oxidative nature of the silver(I) reagent. In the present work, thallium(I) hexafluorophosphate has been employed in place of silver(I) triflate to provide a versatile synthetic pathway with much improved yields [38,39]. Furthermore, the presence of a carboxaldehyde moiety in rhenium(I) complexes **1**–**3** would provide a reactive site to allow further functionalization of the terminal alkynyl ligand for the preparation of other novel materials. The X-ray crystal structure of **1** has been determined. The electrochemical, electronic absorption and emission properties of the rhenium(I) complexes have also been investigated in detail.

2. Experimental

2.1. Materials and reagents

4-Bromobenzaldehyde was obtained from Lancaster Synthesis Ltd. All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Anhydrous solvents were freshly distilled. THF was distilled over sodium benzophenone ketyl before use. The rhenium(I) complex precursors [40,41] and 4-ethynylbenzaldehyde [42] were synthesized according to reported procedures. Other materials and reagents were of analytical grade and were used without further purification.

2.2. Physical measurements and instrumentation

^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) or a Bruker AV400 (400 MHz) NMR spectrometer at 298 K with chemical shifts (δ, ppm) reported relative to tetramethylsilane (Me$_4$Si). Positive ion FAB mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. Infrared spectra were obtained as KBr disc, prepared by compressing the ground mixture of sample and KBr powder, on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000–400 cm^{-1}). Elemental analyses of all metal complexes were performed on a Carlo Erba 1106 elemental analyzer by the Institute of Chemistry at the Chinese Academy of Sciences in Beijing. UV–Vis spectra were obtained on a Hewlett–Packard 8452A diode array spectrophotometer. Steady-state emission and excitation spectra at room temperature and at 77 K were obtained on a Spex Fluorolog-2 Model F111 fluorescence spectrophotometer equipped with a Hamamatsu R928 PMT detector. Low-temperature solid state emission and excitation spectra were recorded with solid samples loaded in a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen. Room temperature spectra were recorded similarly but without liquid nitrogen inside the Dewar flask. Low-temperature emission and excitation of the samples in frozen glass were recorded with the same setup as for the solid state samples. For solution emission and excitation spectra, samples were degassed on a high vacuum line in a two-compartment cell consisting of a 10-ml Pyrex bulb and a 1-cm path length quartz cuvette, and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subjected to at least four freeze–pump–thaw cycles. Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355-nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser. Luminescence decay signals were detected by a Hamamatsu R928 PMT and recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope, and analyzed using a program for exponential fits. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. model CHI 600A electrochemical analyzer. The electrolytic cell used was a conventional two-compartment cell. Electrochemical measurements were performed in acetonitrile solutions with 0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$ as supporting electrolyte at room temperature. The reference electrode was a Ag/AgNO$_3$ (0.1 M in acetonitrile) electrode, and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with a platinum wire as the counter electrode. The working electrode surface was first polished with a 1-μm alumina slurry (Linde), followed by a 0.3-μm alumina slurry, on a microcloth (Buehler Co.). The ferrocenium/ferrocene couple (FeCp$_2^{+/0}$) was used as the internal reference. All solutions for electrochemical studies were deaerated with prepurified argon gas just before measurements.

2.3. Crystal structure determination

Single crystals of **1** suitable for X-ray diffraction studies were grown by layering of *n*-hexane onto a concentrated dichloromethane solution of the complex. The X-ray diffraction data were collected on a Bruker Smart CCD 1000 using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods employing the SHELXS-97 program [43]. Rhenium and many non-hydrogen atroms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least squares using program SHELXL-97 [44]. The positions of hydrogen atoms were calculated based on the riding mode with thermal parameters equal to 1.2 times those of the associated carbon atoms and participated in the calculation of final *R*-indices. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically.

2.4. Synthesis of rhenium(I) complexes

2.4.1. [Re(CO)$_3$(2,9-Me$_2$phen)Br](C≡C–C$_6$H$_4$–CHO)] (**1**)

This was prepared by modification of a previously reported procedure for related rhenium(I) diimine alkynyl complexes.[38,39] A mixture of [Re(CO)$_3$(2,9-Me$_2$phen)Br] (180 mg, 0.33 mmol), TlPF$_6$ (138 mg, 0.36 mmol) and 4-ethynylbenzaldehyde (65 mg, 0.5 mmol) in THF (100 ml) was heated under reflux in an inert atmosphere of nitrogen in the presence of Et$_3$N (5 ml) for 48 h. The yellowish orange suspension was then filtered to remove the insoluble TlBr, and the orange filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using dichloromethane as eluent. The second band, which contained the desired product, was collected and evaporated to dryness. Subsequent recrystallization by layering hexane onto a concentrated dichloromethane solution of the product gave **1** as analytically pure orange crystals. Yield: 100 mg, 50%. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, relative to Me$_4$Si): δ 3.33 (s, 6H, –CH$_3$), 6.76 (d, *J* = 8.3 Hz, 2H, –C$_6$H$_4$–), 7.41 (d, *J* = 8.3 Hz, 2H, –C$_6$H$_4$–), 7.72 (d, *J* = 8.3 Hz, 2H, 3- and 8-phenanthrolinyl H's), 7.87 (s, 2H, 5- and 6-phenanthrolinyl H's), 8.32 (d, *J* = 8.3 Hz, 2H, 4- and 7-phenanthrolinyl H's), 9.73 (s, 1H, –CHO). Positive FAB-MS: *m*/*z* 608 [M]$^+$, 580 [M–CO]$^+$. IR (KBr disc, *ν*/cm^{-1}): 1688 (s) *ν*(C=O); 1885 (s), 1909 (s), 2006 (s) *ν*(C≡O); 2088 (w) *ν*(C≡C). Elemental *Anal.* Calc. for **1**: C, 51.22; H, 2.98; N, 4.60. Found: C, 51.50; H, 3.12; N, 4.55%.

2.4.2. [Re(CO)$_3$(phen)(C≡C–C$_6$H$_4$–CHO)] (**2**)

This was prepared according to a procedure similar to that described for **1**, except that [Re(CO)$_3$(phen)Br] (190 mg, 0.33 mmol) was used in place of [Re(CO)$_3$(2,9-Me$_2$phen)Br] to give **2** as an orange microcrystalline solid. Yield: 92 mg, 48%. ^{1}H NMR

(400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 6.77 (d, J = 8.3 Hz, 2H, $-C_6H_4-$), 7.42 (d, J = 8.3 Hz, 2H, $-C_6H_4-$), 7.73 (d, J = 8.3 Hz, 2H, 3- and 8-phenanthrolinyl H's), 7.88 (s, 2H, 5- and 6-phenanthrolinyl H's), 8.33 (d, J = 8.3 Hz, 2H, 4- and 7-phenanthrolinyl H's), 9.45 (d, J = 3.9 Hz, 2H, 2- and 9-phenanthrolinyl H's), 9.74 (s, 1H, –CHO). Positive FAB-MS: *m*/*z* 580 $[M]^+$, 552 $[M-CO]^+$. IR (KBr disc, ν/cm^{-1}): 1688 (s) ν(C=O); 1886 (s), 1910 (s), 2008 (s) ν(C≡O); 2088 (w) ν(C≡C). Elemental *Anal.* Calc. for **2**·$CHCl_3$: C, 42.92; H, 2.16; N, 4.00. Found: C, 42.88; H, 2.01; N, 3.98%.

2.4.3. [Re(CO)3(5,6-Br2phen)(C≡C–C_6H_4–CHO)] (**3**)

This was prepared according to a procedure similar to that described for **1**, except that $[Re(CO)_3(5,6\text{-}Br_2\text{-}phen)Br]$ (230 mg, 0.33 mmol) was used in place of $[Re(CO)_3(2,9\text{-}Me_2phen)Br]$ to give **3** as a red microcrystalline solid. Yield: 110 mg, 45%. ^1H NMR (400 MHz, CD_3CN, 298 K, relative to Me_4Si): δ 6.92 (d, J = 8.3 Hz, 2H, $-C_6H_4-$), 7.46 (d, J = 8.3 Hz, 2H, $-C_6H_4-$), 7.96 (dd, J = 3.9 Hz and 5.1 Hz, 2H, 3- and 8-phenanthrolinyl H's), 9.00 (d, J = 5.1 Hz, 2H, 4- and 7-phenanthrolinyl H's), 9.50 (d, J = 3.9 Hz, 2H, 2- and 9-phenanthrolinyl H's), 9.77 (s, 1H, –CHO). Positive FAB-MS: *m*/*z* 738 $[M]^+$, 710 $[M-CO]^+$. IR (KBr disc, ν/cm^{-1}): 1688 (s) ν(C=O); 1888 (s), 1911 (s), 2010 (s) ν(C≡O); 2088 (w) ν(C≡C). Elemental *Anal.* Calc. for **3**: C, 43.77; H, 1.84; N, 4.26. Found: C, 43.86; H, 2.05; N, 4.12%.

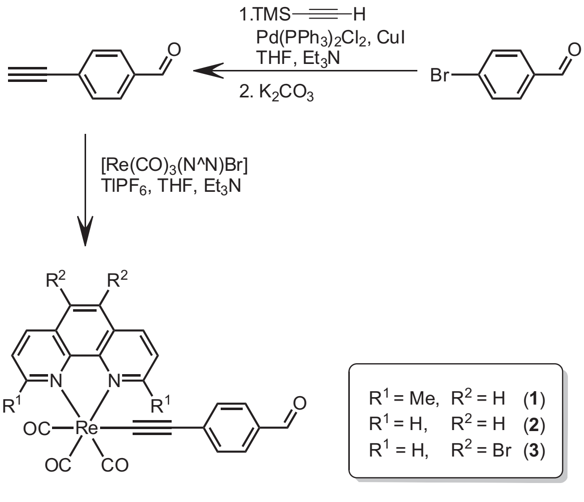
3. Results and discussion

3.1. Synthesis and characterization

Rhenium(I) tricarbonyl diimine complexes with carboxaldehyde alkynyl ligand, namely complexes **1**–**3**, were synthesized by the reaction of a mixture of $[Re(CO)_3(N\hat{}N)Br]$, thallium(I) hexafluorophosphate, triethylamine and a slight excess of the corresponding alkyne in THF under reflux conditions under an inert atmosphere of nitrogen (Scheme 1). This was followed by purification using column chromatography on silica gel and subsequent recrystallization from chloroform-hexane to afford the desired products. The identities of **1**–**3** have been confirmed by ^1H NMR, IR, FAB-MS, and satisfactory elemental analyses.

3.2. crystal structure determination

The perspective drawing of **1** with atomic numbering scheme is depicted in Fig. 1. The crystal and structure determination data are collected in Table 1 and selected bond distances and angles are summarized in Table 2. The coordination geometry at the Re atom was distorted octahedral with three carbonyl ligands arranged in a facial fashion. The N–Re–N bond angles of 74.43° were found to be less than 90°, as required by the bite distance exerted by the steric demand of the chelating diimine ligand. The C≡C bond length was 1.187(7) Å, typical of those found in other σ-bonded metal alkynyl systems.[33–37] The Re–C≡C units were essentially linear with a Re–C≡C bond angle of 170.8(4)° for **1**, similar to those found in other related Re(I) alkynyl complex systems [33–37].



Scheme 1. Synthesis of complexes **1**–**3**.

3.3. Electrochemical studies

The electrochemical behavior of the rhenium(I) diimine complexes has been investigated by cyclic voltammetry. In general, the complexes displayed irreversible oxidation waves at *ca.* +1.05 to +1.09 V and +1.42 to +1.45 V, together with a quasi-reversible oxidation couple at *ca.* +1.79 to +1.83 V and a quasi-reversible reduction couple at *ca.* −1.40 to −1.48 V versus S.C.E. in deaerated acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$). The electrochemical data of **1**–**3** are summarized in Table 3, and the representative cyclic voltammograms of **1** and **2** are shown in Fig. 2.

With reference to the electrochemical studies on related rhenium(I) diimine alkynyl complexes [33–37], the first irreversible oxidation wave that occurred at *ca.* +1.05 to +1.09 V versus S.C.E. was tentatively assigned as the Re(I) → Re(II) oxidation, though a mixing of an alkynyl ligand-centered character would also be possible. All of the complexes showed a less positive potential for their first oxidation wave than their bromo counterparts, $[Re(CO)_3(N\hat{}N)Br]$ (*ca.* +1.22 V), consistent with the better σ- and π-donating ability of the alkynyl ligand than the bromo group, rendering the rhenium(I) metal center more electron-rich and hence increased its ease of oxidation. Given the similar values of the complexes, the second oxidation wave at +1.42 to +1.45 V was tentatively assigned to a ligand-centered oxidation of the electron-rich arylalkynyl ligand.

In addition, the oxidation wave, which occurred at *ca.* +1.8 V versus S.C.E., was found to vary with the nature of the diimine ligands. An EC mechanism was proposed for this oxidation wave, in which a weakening of the metal–carbon bond between the rhenium center and the alkynyl ligand occurred after the first oxidation (Scheme 2). This resulted in the loss of an alkynyl radical to give the coordinative-unsaturated intermediate, $[Re(CO)_3(N\hat{}N)]^+$, which then readily picked up an acetonitrile molecule from the solvent to form the corresponding solvent complex, $[Re(CO)_3(N\hat{}N)(MeCN)]^+$. Therefore, this oxidation process of these rhenium(I) alkynyl complexes was tentatively assigned to the oxidation of Re(I) → Re(II) of the corresponding solvento analogues, $[Re(CO)_3(N\hat{}N)(MeCN)]^+$, in acetonitrile. The observation that complex **1**, with the 2,9-Me_2phen ligand, showed the least positive potential for this oxidation wave compared to complex **2** bearing the unsubstituted phen ligand and complex **3** bearing the 5,6-Br_2phen ligand, was in line with the presence of the most electron-rich and least π-accepting 2,9-Me_2phen ligand, which would make the Re(I) in **1** more easily to be oxidized than in **2** and **3**. The assignment could be supported by the observation of a similar oxidation wave at +1.77 V (vs. S.S.C.E.) for a related complex, $[Re(CO)_3(bpy)(MeCN)]PF_6$, in acetonitrile solution [45].

The quasi-reversible reduction couple reduction couple at −0.86 to −1.50 V versus S.C.E., which was found to vary with the nature of the diimine ligand, was tentatively assigned as a diimine ligand-centered reduction. The observation that **1** (−1.50 V versus S.C.E.) showed a more negative reduction potential than **3** (−1.0 V versus S.C.E.) was in line with the attachment of the electron-donating methyl substituents on the diimine ligand, which would render the diimine ligand more electron-rich and less π-accepting,

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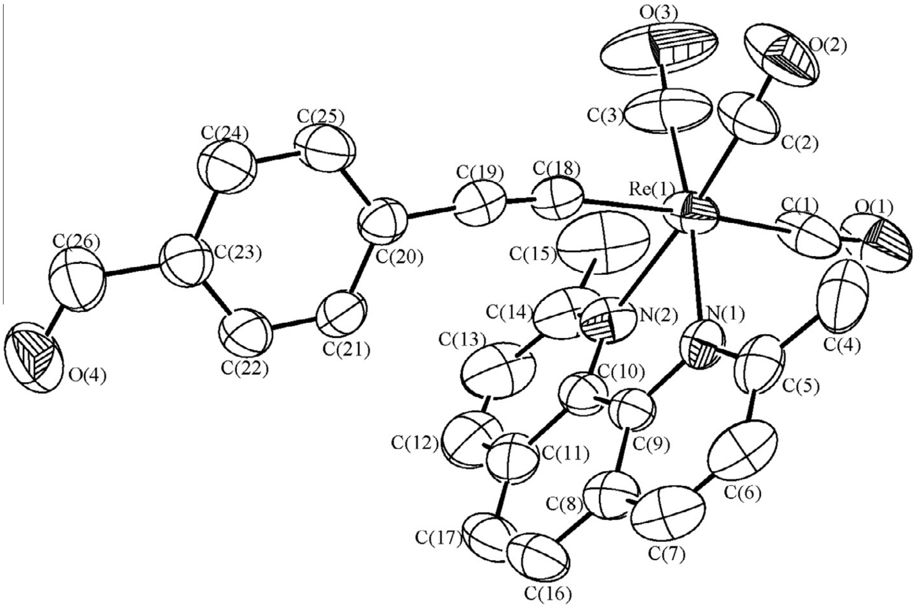

Fig. 1. Perspective drawing of **1** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 30% probability level.

thus decreased its ease of reduction. On the other hand, the electron-withdrawing bromo substituents would make the 5,6-Br_2phen ligand in **3** more π-accepting, rendering **3** easier to be reduced.

Table 1
Crystal and structure determination data for **1**.

	[Re(CO)$_3$(2,9-Me_2phen)(C≡C–C_6H_4–CHO)] (**1**)
Empirical formula	$C_{26}H_{17}N_2O_4Re$
Formula weight	607.62
T (K)	301(2)
Wavelength (Å)	0.71073
Crystal structure	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	10.0527(7)
b (Å)	10.3952(8)
c (Å)	11.6816(9)
α (°)	103.74(1)
β (°)	96.39(1)
γ (°)	92.57(1)
V (Å^3)	1175.19(15)
Z	2
Density (g cm^{-3})	1.717
Absorption coefficient (mm^{-1})	5.204
F(000)	588
Crystal size (mm^3)	0.32 × 0.31 × 0.09
θ Range for data collection (°)	1.81–25.68
Index ranges	$-12 \leqslant h \leqslant 12$; $-12 \leqslant k \leqslant 12$, $-14 \leqslant l \leqslant 14$
Reflections collected	11847
Independent reflections (R_{int})	4453 (0.0218)
Completeness to $\theta = 71.64°$	99.7%
Absorption correction	empirical
Maximum and minimum transmission	1.000000 and 0.585659
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4453/0/300
Goodness-of-fit (GOF) on F^2	1.079
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0285$, $wR_2 = 0.0683$[a]
R indices (all data)	$R_1 = 0.0423$, $wR_2 = 0.0757$[a]
Largest difference in peak and hole (e Å^{-3})	1.042 and −0.7114

[a] $w = 1/[\sigma^2(F_o^2) + (0.0330P)^2 + 0.9336P]$, where P is $(F_o^2 + 2F_c^2)/3$.

3.4. Electronic absorption spectroscopy

All complexes were found to show moderately intense to intense absorptions in the visible region. The data for electronic absorption studies are summarized in Table 4, and the representative electronic absorption spectrum of **2** is shown in Fig. 3. In general, the electronic absorption spectra of complexes **1–3** in THF at room temperature showed intense absorptions in the high energy region at *ca.* 268–354 nm, with extinction coefficients in the order of 10^4 dm^3 mol^{-1} cm^{-1}. The intense absorption bands were tentatively assigned to the mixture of intraligand IL π–π* transitions of the diimine and the alkynyl ligands. In addition, moderately intense low-energy absorption bands with extinction coefficients in the order of 10^3 dm^3 mol^{-1} cm^{-1} at *ca.* 410–429 nm were also observed. The energies of these low energy absorption bands were found to vary with the nature of the diimine ligands. The absorption energies were in the order of **1** (410 nm) > **2** (420 nm) > **3** (429 nm), consistent with the energies of the π* orbitals of the diimine ligands, *i.e.* 2,9-Me_2phen > phen > 5,6-Br_2phen, resulting from the fact that the π-accepting abilities of the diimine ligands were in the order of 2,9-Me_2phen < phen < 5,6-Br_2phen. This observation together with previous spectroscopic works on the rhenium(I) tricarbonyl diimine alkynyl complexes were suggestive of an assignment of MLCT [dπ(Re) → π*(diimine)] transition, probably with some mixing of an alkynyl-to-diimine ligand-to-ligand charge transfer LLCT [π(C≡CR) → π*(diimine)] character.

3.5. Emission spectroscopy

Excitation of the rhenium(I) tricarbonyl diimine alkynyl complexes **1–3** in both the solid state and in fluid solution at $\lambda > 350$ nm resulted in intense photoluminescence. The emission data and lifetimes of the complexes are summarized in Table 4.

In tetrahydrofuran solution at room temperature, the complexes were found to show structureless emission bands with peak maxima at 630–672 nm, as shown in Fig. 4. While in the solid state, the complexes were found to emit at *ca.* 550–600 nm. The relatively long luminescence lifetime, in the sub-microsecond to microsecond range, measured for all the complexes at low and ambient temperatures suggested the triplet parentage of the

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Table 2
Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1**.

Selected bond distances (Å)			
Re(1)–C(1)	1.955(6)	C(1)–O(1)	1.150(7)
Re(1)–C(2)	1.898(6)	C(2)–O(2)	1.146(7)
Re(1)–C(3)	1.889(7)	C(3)–O(3)	1.135(8)
Re(1)–C(4)	2.132(5)	C(4)–C(5)	1.187(7)
Re(1)–N(1)	2.215(4)	Re(1)–N(2)	2.230(4)
Selected bond angles (°)			
O(1)–C(1)–Re(1)	176.5(5)	N(2)–Re(1)–N(1)	74.43(15)
O(2)–C(2)–Re(1)	176.5(7)	C(2)–Re(1)–C(3)	83.4(4)
O(3)–C(3)–Re(1)	175.9(11)	C(2)–Re(1)–C(1)	91.7(2)
C(19)–C(18)–Re(1)	170.8(4)	C(3)–Re(1)–N(2)	99.9(3)
C(18)–C(19)–C(20)	173.0(5)	C(1)–Re(1)–N(2)	97.0(2)

Table 3
Electrochemical data[a] of **1**–**3**.

Complex	Oxidation $E_{1/2}$/V vs. S.C.E.[b] (ΔE_p/mV)	Reduction $E_{1/2}$/V vs. S.C.E.[b] (ΔE_p/mV)
1	+1.05 (69)	−1.48 (140)
	+1.43 (108)	
	+1.79 (137)	
2	+1.06 (103)	−1.40 (110)
	+1.42 (92)	
	+1.81 (151)	
3	+1.09 (100)	−0.86[c]
	+1.45 (82)	
	+1.83 (88)	−1.46[c]

[a] Working electrode: glassy carbon; scan rate 100 mV s^{-1}.
[b] $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively.
[c] Irreversible reduction wave. The potential refers to E_{pc} which is the cathodic peak potential.

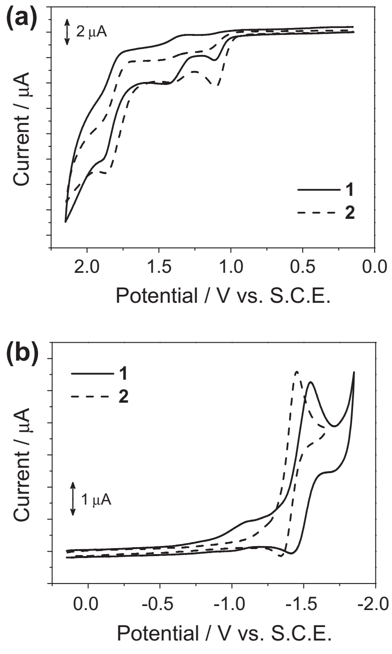
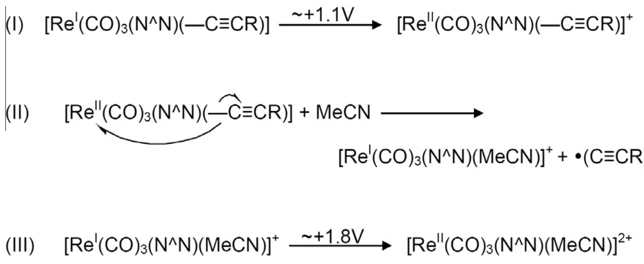


Fig. 2. Cyclic voltammograms showing the (a) oxidative and (b) reductive scans of **1** and **2** in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$).



Scheme 2. The proposed EC mechanism for the oxidation of the Re(I) alkynyl complexes in acetonitrile.

Table 4
Photophysical data of **1**–**3**.

Complex	Medium (T/K)	Absorption λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	Emission λ_{em}/nm (τ_0/µs)	Φ_{lum}[a]
1	THF (298)	268 (53950), 302 (34860), 354 (43865), 410sh (4870)	630 (<0.1)	2 × 10^{-3}
	Solid (298)		560 (0.2)	
	Solid (77)		550 (5.3)	
	Glass (77)[b]		520 (7.7)	
2	THF (298)	268 (56675), 297 (23960), 354 (3735), 420sh (5690)	640 (<0.1)	3 × 10^{-3}
	Solid (298)		580 (0.9)	
	Solid (77)		565 (7.2)	
	Glass (77)[b]		550 (14.6)	
3	THF (298)	277 (53700), 317 (27920), 354 (37825), 429 (5260)	672 (<0.1)	6 × 10^{-4}
	Solid (298)		600 (<0.1)	
	Solid (77)		580 (2.0)	
	Glass (77)[b]		570 (4.4)	

[a] The luminescence quantum yield was measured at 298 K using [Ru(bpy)$_3$]Cl$_2$ as the standard.
[b] Measured in EtOH–MeOH (4:1 v/v).

emissive states. These emission bands were assigned to be derived from ^{3}MLCT [dπ(Re) → π*(diimine)] origin. Similar to the low-energy absorption bands observed in the electronic absorption spectra, the emission energies of complexes **1–3** were found to be affected significantly by the variation of the diimine ligands. With the same alkynyl ligand, the emission energy dependence, **1** (630 nm) > **2** (640 nm) > **3** (672 nm), was found to be inversely related to the π-accepting ability of the diimine ligands, 5,6-Br$_2$-phen > phen > 2,9-Me$_2$phen, and in agreement with such a ^{3}MLCT origin. The MLCT emission energy of **3** was found to be the lowest amongst these complexes, and was in accordance with the strongest π-accepting ability of 5,6-Br$_2$phen in **3**. Similarly, with the poorer π-accepting diimine ligand, 2,9-Me$_2$phen in **1**, higher energy emission bands were observed. Complexes **1–3** also displayed strong photoluminescence in EtOH–MeOH (4:1 v/v) glass at 77 K. These emissions were tentatively assigned as the ^{3}MLCT phosphorescence as similar emission energy trends have been observed.

The incorporation of the ancillary alkynyl ligand has been demonstrated to enhance the photoluminescence of the Re(I) complexes by raising the energies of the metal-centered d–d states and thus improving the population of the emissive MLCT state. In particular, the presence of the moderately electron-withdrawing carboxaldehyde groups in the alkynyl moiety has resulted in a relatively red-shifted emission band (630–672 nm in THF), when compared to related Re(I) compounds of the same phenanthroline ligands but electron-rich trialkoxyphenylalkynyls in the literature (602–640 nm in THF),[16] suggestive of some mixing of an alkynyl-to-diimine ligand-to-ligand charge transfer LLCT [π(C≡CR) → π*(diimine)] character in the structureless emission band. It could be observed that variation of the substituents on the alkynyl ligands could enable the fine tuning of the photoluminescence energy, which would be exceptionally important in the realization of supramolecular electron- and energy-transfer systems.

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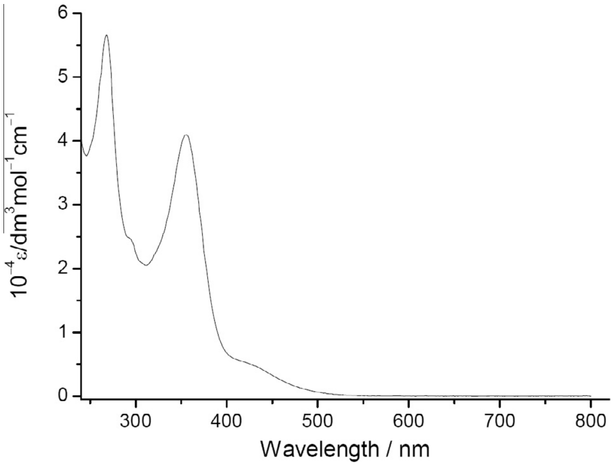

Fig. 3. Electronic absorption spectrum of **2** in THF at 298 K.

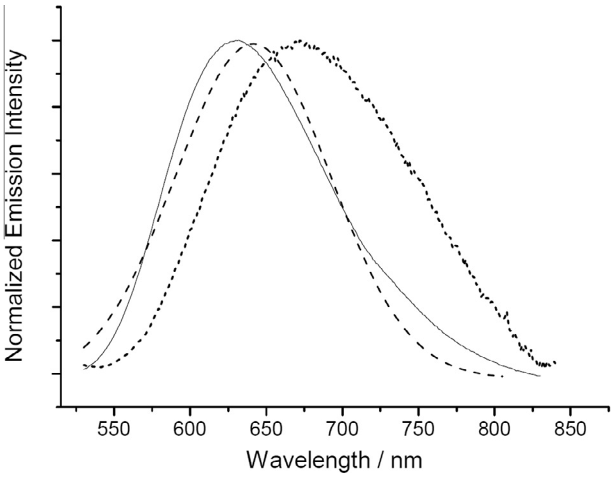

Fig. 4. Normalized emission spectra of **1** (–), **2** (—) and **3** (···) in THF at 298 K.

4. Conclusion

A series of rhenium(I) tricarbonyl diimine complexes of carboxaldehyde alkynyl have been successfully synthesized and characterized. Cyclic voltammetry showed that these complexes exhibited oxidative waves at *ca.* +1.1 and +1.8 V, which could be assigned to Re(I) → Re(II) oxidation. In addition, diimine ligand-centered reductive waves were observed at −1.40 to −1.48 V. The rhenium(I) complexes were found to show higher-energy absorption bands at 268–354 nm and lower-energy absorption bands at 410–429 nm, which could respectively be assigned to intraligand and MLCT transitions. Emission studies showed that the complexes exhibited structureless emission bands at 630–672 nm in the solution state at room temperature, attributed to a ^{3}MLCT origin. The present study has demonstrated the rich redox and photophysical behaviors of the alkynylrhenium(I) tricarbonyl diimine system, and it is anticipated that such complexes could be exploited for applications as functional materials.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

CCDC-985729 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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