Introduction

Multinuclear transition-metal complexes with photofunctional properties, many of which are constructed using the same repeated metal complexes, have become of interest in recent years because of their potential use in dye-sensitised solar cells and light-harvesting systems. Hetero-multinuclear metal complexes constructed using different functional units have recently been found to be efficient photocatalysts for the oxidation of water, evolution of hydrogen, and CO₂ reduction. For example, Ru(II)–Re(I) dinuclear complexes, in which the Ru(II) unit works as a photosensitiser and the Re(I) unit works as a catalytic, are effective photocatalysts for CO₂ reduction because of rapid intramolecular electron transfer from the photochemically-reduced Ru(II) unit to the Re(I) unit.10

Most of these multinuclear metal complexes have been synthesised using stepwise methods with several complexation steps. A mononuclear complex with a multidentate ligand having one chelating moiety already coordinated to the metal centre and another able to coordinate is synthesised first, which can then react with another metal centre to afford a dinuclear complex. Various multinuclear complexes have been synthesised by repeating these processes; however, there are some limitations with respect to the product selectivity achieved using this method. For example, a bridging ligand with a number of different diimine moieties can react with a metal complex (or complexes) to give a mixture of products with different numbers of metal complexes and/or with one or more metal complexes connected to different diimine moieties.

There are several reports of one-pot syntheses of hetero-multinuclear complexes using an asymmetric bridging ligand with two different coordination sites. This synthetic method requires very different rates of coordination reactions of each metal ion to each coordination site for high production selectivity of one heteronuclear complex.

Homo-coupling reactions of metal complexes have recently been applied for the synthesis of asymmetric dinuclear complexes, though the isolated yields were relatively low (5.4%–8.5%). It has also been reported that cross-coupling reactions (Sonogashira coupling and Suzuki–Miyaura coupling) were used to synthesise multinuclear complexes. In this method, each complex possessing functional groups such as a bromo group, an ethynyl group, or a boronic-acid substituent as building blocks can be connected to give a heteronuclear complex with a relatively high degree of selectivity.

Herein we report the first use of the Mizoroki–Heck reaction in a coupling reaction with different types of emissive metal complexes (Ru(II), Ir(III) and Re(I) complexes with one or more diimine ligands) to give multinuclear complexes with various photofunctional properties.

Results and discussion

Synthesis of a Re(I) dinuclear complex using the Heck reaction

![Chemical structure of the Re(I) dinuclear complex]
We chose two types of Re(i) complexes as building blocks (eqn (1)) to determine if the Mizoroki–Heck reaction is able to couple different photofunctional metal complexes. An acetonitrile (MeCN) solution (4 mL) of the two Re(i) complexes, one with a bromo group ([Re(Br,F,Et)]+, 23 μmol) and the other with a vinyl group ([Re(C=C,OEt)]+, 23 μmol), was heated in the presence of palladium acetate (Pd(OAc)2, 4.5 μmol), triphenylphosphine (PPh3, 9.2 μmol) and sodium acetate (AcONa, 140 μmol) at 75 °C under an Ar atmosphere for one day. Ar was pumped into the reaction mixture during synthesis. The solvent was evaporated once the reaction reached completion. An MeCN solution (4 mL) of Pd(OAc)2 (4.5 μmol) and PPh3 (9.2 μmol) was then added to the residue along with a small amount of air; this addition of air was needed to achieve a good yield.25 The solution was heated for one day. Electrospray ionisation mass spectrometry (ESI-MS) analysis of the crude solution was evaporated once the reaction reached completion. The solvent was acetone-d6. The red square emphasises the peak attributed to olenfin protons.

Methods, which possibly results in a mixture of four types of dinuclear complexes, i.e. two types of complexes with identical phosphine ligands in both units and two structural isomers of complexes with two different phosphine ligands in each unit.

Synthesis of various trinuclear complexes using the Heck reaction
A similar reaction could successfully be used to synthesise various trinuclear complexes. At the centre of each of these products was a Re(i) complex with a bpy ligand and two other metal complexes as substituents (eqn (2)). A Re(i) bis-carbonyl complex with two bromo groups, [Re4(4,4-dibromo-bpy)-(CO)2(PPh3)2]+ ([Re(Br,Et)]+), reacted with various photofunctional complexes possessing a vinyl group, i.e. [Re(C=C,COEt)]+, [Ru[4(bpy)2(vbpy)]2+ ([Ru(C=C,bpy)]+)2, vbpy = 4-methyl-4′-vinyl-bpy), [Ru4(dmb)(vbpy)]2+ ([Ru(C=C,dmb)]+)2, dmb = 4,4′-dimethyl-bpy) and [Ir4(ppy)(vbpy)]4+ ([Ir(C=C,ppy)]4, ppy = 2-phenyl-pyridine). This was performed under the same reaction conditions as were used to synthesise [Re(OEt)Re(Et)]24, with the exception of repeating both the heating and addition of the MeCN solution of Pd(OAc)2 and PPh3 twice, in the case of [Ru(bpy)4Re(Ph)]6+ and [Ir(ppy)3Re(Ph)]8+. The trinuclear complexes could be separated using size exclusion chromatography (SEC) or ion-exchange chromatography. The trinuclear complexes with Ru[n] or Re(i) in both edge units, i.e. [Re(OEt)2Re(Ph)]5+, [Ru(bpy)3Re(Ph)]5+ and [Ru(dmb)2Re(Ph)]5+, were obtained in 31%, 41% and 32% yields, respectively. ESI-MS analysis of the solution after the reaction between [Re4(4,4-dibromo-bpy)-(CO)2(PPh3)2]+ ([Re(Br,Et)]+) and [Ru(C=C,dmb)]2+ was performed and clearly showed that the phosphate ligands on the Re(i) unit were not substituted by the coupling reagents. The isolated yield of [Ru(dmb)2Re(Ph)]6+ was 25%. The isolated yield was relatively lower (8%) for [Ir(ppy)3Re(Ph)]8+, which had Ir[m] in both edge units, as the reaction between [Ir(C=C,ppy)]4+ and [Re(Br,Et)]+ was much slower than the other reactions; therefore, conversion of the starting complexes was low (Fig. S5, ESI†).

We chose two types of Re(i) complexes as building blocks (eqn (1)) to determine if the Mizoroki–Heck reaction is able to couple different photofunctional metal complexes. An acetonitrile (MeCN) solution (4 mL) of the two Re(i) complexes, one with a bromo group ([Re(Br,F,Et)]+, 23 μmol) and the other with a vinyl group ([Re(C=C,OEt)]+, 23 μmol), was heated in the presence of palladium acetate (Pd(OAc)2, 4.5 μmol), triphenylphosphine (PPh3, 9.2 μmol) and sodium acetate (AcONa, 140 μmol) at 75 °C under an Ar atmosphere for one day. Ar was pumped into the reaction mixture during synthesis. The solvent was evaporated once the reaction reached completion. An MeCN solution (4 mL) of Pd(OAc)2 (4.5 μmol) and PPh3 (9.2 μmol) was then added to the residue along with a small amount of air; this addition of air was needed to achieve a good yield.25 The solution was heated for one day. Electrospray ionisation mass spectrometry (ESI-MS) analysis of the crude solution was evaporated once the reaction reached completion. The solvent was acetone-d6. The red square emphasises the peak attributed to olenfin protons.

Methods, which possibly results in a mixture of four types of dinuclear complexes, i.e. two types of complexes with identical phosphine ligands in both units and two structural isomers of complexes with two different phosphine ligands in each unit.

Synthesis of various trinuclear complexes using the Heck reaction
A similar reaction could successfully be used to synthesise various trinuclear complexes. At the centre of each of these products was a Re(i) complex with a bpy ligand and two other metal complexes as substituents (eqn (2)). A Re(i) bis-carbonyl complex with two bromo groups, [Re4(4,4-dibromo-bpy)-(CO)2(PPh3)2]+ ([Re(Br,Et)]+), reacted with various photofunctional complexes possessing a vinyl group, i.e. [Re(C=C,COEt)]+, [Ru[4(bpy)2(vbpy)]2+ ([Ru(C=C,bpy)]+)2, vbpy = 4-methyl-4′-vinyl-bpy), [Ru4(dmb)(vbpy)]2+ ([Ru(C=C,dmb)]+)2, dmb = 4,4′-dimethyl-bpy) and [Ir4(ppy)(vbpy)]4+ ([Ir(C=C,ppy)]4, ppy = 2-phenyl-pyridine). This was performed under the same reaction conditions as were used to synthesise [Re(OEt)Re(Et)]24, with the exception of repeating both the heating and addition of the MeCN solution of Pd(OAc)2 and PPh3 twice, in the case of [Ru(bpy)4Re(Ph)]6+ and [Ir(ppy)3Re(Ph)]8+. The trinuclear complexes could be separated using size exclusion chromatography (SEC) or ion-exchange chromatography. The trinuclear complexes with Ru[n] or Re(i) in both edge units, i.e. [Re(OEt)2Re(Ph)]5+, [Ru(bpy)3Re(Ph)]5+ and [Ru(dmb)2Re(Ph)]5+, were obtained in 31%, 41% and 32% yields, respectively. ESI-MS analysis of the solution after the reaction between [Re4(4,4-dibromo-bpy)-(CO)2(PPh3)2]+ ([Re(Br,Et)]+) and [Ru(C=C,dmb)]2+ was performed and clearly showed that the phosphate ligands on the Re(i) unit were not substituted by the coupling reagents. The isolated yield of [Ru(dmb)2Re(Ph)]6+ was 25%. The isolated yield was relatively lower (8%) for [Ir(ppy)3Re(Ph)]8+, which had Ir[m] in both edge units, as the reaction between [Ir(C=C,ppy)]4+ and [Re(Br,Et)]+ was much slower than the other reactions; therefore, conversion of the starting complexes was low (Fig. S5, ESI†).
Attempts were also made to use the Sonogashira coupling reaction to synthesise a trinuclear complex from a Ru(II) complex with an ethynyl group at the 4-position of the bpy moiety and $\text{[Re(Br}_2\text{FPh)}]^{+}$, as shown in eqn (3). An $N,N$-dimethylformamide (DMF, 5 mL) solution containing the Ru(II) complex (38 μmol), $\text{[Re(Br}_2\text{FPh)}]^{+}$ (19 μmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.62 μmol), CuI (2.9 μmol) and diisopropylamine (1 mL) was heated at 50 °C for 12 h under Ar. The reaction mixture was analysed by SEC and ESI-MS, which indicated that the target trinuclear complex with triple bonds between the Ru(II) and Re(I) units was successfully synthesised. Unfortunately, the trinuclear complex decomposed during the SEC purification process, most likely due to instability in the mobile phase (1 : 1 (v/v) mixture of methanol and MeCN containing 0.15 M CH$_3$COONH$_4$).

As described above, the complexes that were synthesized in this research are not obtained selectively using ordinary step-wise methods because mixtures of isomers with the metals in different units are produced. Isolating the target complex from such a mixture is often difficult because of the similarities between the molecular sizes, charges, and solubility of the isomeric complexes.

Photophysical properties of the trinuclear complexes

As typical examples, UV-Vis absorption spectra of the synthesised trinuclear complexes $\text{[Ru(dmb]}_2\text{Re(Ph)}]^{5+}$, $\text{[Re(OEt)}_2\text{Re(Ph)}]^{3+}$ and $\text{[Ir(ppy)}_2\text{Re(Ph)}]^{3+}$ are shown with those of the corresponding mononuclear complexes in Fig. 3 (those of other complexes are shown in Fig. S4, ESI†). The $^1\text{MLCT}$ absorption band of $\text{[Ru(dmb]}_2\text{Re(Ph)}]^{5+}$ was observed between 370 nm and 570 nm and was red-shifted compared to the $^1\text{MLCT}$ absorption band of $\text{[Ru(C=C,dmb)]}^{2+}$. This was most likely caused by extension of the π conjugation in the bridging ligand, decreasing the energy level of the π$^*$ orbital. In addition, the molar extinction coefficient of the $^1\text{MLCT}$ absorption band was higher for $\text{[Ru(dmb]}_2\text{Re(Ph)}]^{5+}$ than for the corresponding mononuclear complexes. This suggests that the transition has more π–π$^*$ character. The π–π$^*$ absorption band of $\text{[Ru(dmb]}_2\text{Re(Ph)}]^{5+}$ with $\lambda_{\text{max}}$ = 288 nm had a shoulder at longer wavelengths, which was not observed in the summation spectra of the corresponding mononuclear complexes (a dotted line in Fig. 3a). This shoulder can be attributed to the π–π$^*$ transition in the bridging ligand with a wide π conjugation system. In the case of $\text{[Re(OEt)}_2\text{Re(Ph)}]^{3+}$ (Fig. 3b) and $\text{[Ir(ppy)}_2\text{Re(Ph)}]^{3+}$ (Fig. 3c), similar phenomena were observed, i.e. red-shifts of both the π–π$^*$ and $^1\text{MLCT}$ absorp-

Fig. 3 UV-Vis absorption spectra of trinuclear complexes obtained and corresponding mononuclear complexes. The solvent was MeCN. (a) $\text{[Ru(dmb]}_2\text{Re(Ph)}]^{5+}$ (red), $\text{[Ru(C=C,dmb)]}^{2+}$ (blue), $\text{[Re(C=C,pyp)]}^{3+}$ (green) and the 2:1 summation spectrum of $\text{[Ru(C=C,dmb)]}^{2+}$ and $\text{[Re(C=C,pyp)]}^{3+}$ (dotted line). (b) $\text{[Re(OEt)}_2\text{Re(Ph)}]^{3+}$ (red), $\text{[Re(C=C,OEt)]}^{3+}$ (blue), $\text{[Re(C=C,pyp)]}^{3+}$ (green) and the 2:1 summation spectrum of $\text{[Re(C=C,OEt)]}^{3+}$ and $\text{[Re(C=C,pyp)]}^{3+}$ (dotted line). (c) $\text{[Ir(ppy)}_2\text{Re(Ph)}]^{3+}$ (red), $\text{[Ir(C=C,pyp)]}^{3+}$ (blue), $\text{[Re(C=C,pyp)]}^{3+}$ (green) and the 2:1 summation spectrum of $\text{[Ir(C=C,pyp)]}^{3+}$ and $\text{[Re(C=C,pyp)]}^{3+}$ (dotted line).
Table 1  Photophysical properties of the trinuclear complexes and the corresponding mononuclear complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>λ&lt;sub&gt;abs&lt;/sub&gt;/nm (ε /10&lt;sup&gt;4&lt;/sup&gt; M&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt;/nm</th>
<th>Φ&lt;sub&gt;em&lt;/sub&gt;</th>
<th>τ&lt;sub&gt;r&lt;/sub&gt;/ns (A/%)</th>
<th>τ&lt;sub&gt;s&lt;/sub&gt;/ns (A/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Re(OEt)&lt;sub&gt;2&lt;/sub&gt;Re(Ph)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>406 (31.3), 476 (sh, 20.8), 299 (65.4)</td>
<td>714&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>140 (56)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>771 (44)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>[Ru(bpy)&lt;sub&gt;2&lt;/sub&gt;Re(Ph)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>481 (50.6), 341 (sh, 47.3), 287 (162)</td>
<td>710&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>674 (34)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1424 (66)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>[Ru(dmb)&lt;sub&gt;2&lt;/sub&gt;Re(Ph)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>494 (52.1), 341 (sh, 48.9), 288(150)</td>
<td>738&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.02&lt;sup&gt;b&lt;/sup&gt;</td>
<td>610 (18)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1310 (82)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>[Ir(ppy)&lt;sub&gt;2&lt;/sub&gt;Re(Ph)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>474 (14.9), 383 (35.0), 257 (120)</td>
<td>685&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>104 (82)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>784 (18)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>[Ru(dmb)&lt;sub&gt;2&lt;/sub&gt;Re(FPh)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>495 (52.3), 341 (sh, 50.7), 287 (156)</td>
<td>743&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>471 (6)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1112 (94)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>[Re(C=C,ObPy)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>376 (5.97), 290 (20.4)</td>
<td>635&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.07&lt;sup&gt;c&lt;/sup&gt;</td>
<td>326 (100)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>[Ru(C=C,ObPy)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>456 (17.0), 289 (82.1)</td>
<td>636&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1531 (100)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>[Ru(C=C,dmb)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>462 (16.3), 288 (73.1)</td>
<td>645&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1376 (100)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>[Ir(C=C,ppy)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>384 (3.26), 314 (11.5)</td>
<td>617&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>200 (100)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>[Re(C=C,Ph)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>428 (5.38), 308 (21.9)</td>
<td>647&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.08&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1561 (100)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>[Re(C=C,FPh)]&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>424 (4.29), 300 (22.2)</td>
<td>642&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.07&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1409 (100)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>—</td>
</tr>
</tbody>
</table>

a Measured in MeCN at 25 °C.  b Excitation wavelength: 456 nm.  c Excitation wavelength: 444 nm.  d Detected at each wavelength of the emission maximum.

All trinuclear complexes displayed emission (Fig. 4 and S5 (ESI†)). The emission for each trinuclear complex was red-shifted relative to the corresponding mononuclear complexes, and the emission quantum yield (Φ<sub>em</sub>) for each trinuclear complex was much lower than those of the corresponding mononuclear complexes (Table 1).

The emission decay for each trinuclear complex could be fitted using a double exponential function (Fig. S6, ESI†). The emission lifetimes (τ<sub>em</sub>) were similar to the corresponding mononuclear complexes, though the Φ<sub>em</sub> were much lower; therefore, the radiative decay of the excited states of the trinuclear complexes should be slower than those of the mononuclear complexes with respect to the following equations, which show the relationships among Φ<sub>em</sub>, τ<sub>em</sub> and the radiative and non-radiative decay constants (k<sub>r</sub> and k<sub>nr</sub>: eqn (4) and (5)).

\[
\Phi_{em} = k_r / (k_r + k_{nr}) \tag{4}
\]

\[
\tau_{em} = 1 / (k_r + k_{nr}) \tag{5}
\]

This also indicates that the lowest 3MLCT excited states of the trinuclear complexes contained higher π-π* characteristics than those of the mononuclear complexes. It has been reported that increase in π-π* character of the 3MLCT excited states of transient metal complexes induces slower radiative decay.26,29

For a more detailed investigation of the excited states of the trinuclear complexes, time-resolved emission spectra and temperature dependence of the emission decay of [Ru(dmb)<sub>2</sub>Re(Ph)]<sup>3+</sup> were measured as a typical example. Fig. 5a shows the emission decays measured at various temperatures (243–333 K) after excitation at λ<sub>ex</sub> = 456 nm, where much weaker temperature dependence was observed compared to [Ru(dmb)],<sup>3+</sup> (Fig. 5b and S7 (ESI†)). It has been reported that emission decays of many Ru(II)<sup>30</sup> trisdiimine and Re(I)<sup>31</sup> diimine phosphine complexes are strongly dependent on temperature, becoming faster at higher temperature due to thermal interconversion from the lowest 3MLCT excited state to the triplet ligand field excited state (3LF), which causes rapid nonradiative decay (Fig. 6). Therefore, the formation process of the 3LF should be suppressed in the case of [Ru(dmb)<sub>2</sub>Re(Ph)]<sup>3+</sup>, as the extension of π* conjugation in the bridging ligand lowers the energy level of the 3MLCT excited state. Suppression of this nonradiative decay process might be a reason for the long emission lifetime. Fig. 7a shows emission spectra recorded at various times after excitation at 456 nm. The shape of these time-resolved spectra gradually changed, as faster decay was observed at shorter wavelengths (Fig. 7b). This might be caused by intramolecular energy transfer between the Ru and Re units.

Since the trinuclear complex [Ru(dmb)<sub>2</sub>Re(Ph)]<sup>3+</sup> has both photosensitiser (Ru) and catalyst (Re) units for CO₂ reduction, it was reasonably expected that this complex could act as a photocatalyst for CO₂ reduction. A mixture of DMF and triethanolamine (5:1 v/v) containing 0.05 mM [Ru(dmb)<sub>2</sub>Re(Ph)]<sup>3+</sup> and 0.1 M 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]-imidazole (BHQ) was irradiated at λ<sub>ex</sub> = 600 nm for 22 h. Selective formation of CO was observed and the turnover number (TON<sub>CO</sub>) reached 115. This TON<sub>CO</sub> was higher than that found using a Ru(n)-Re(i) dinuclear complex with a N=N─CH₂─CH₂─N=N bridging ligand [N=N = 4-methyl-bpy] (TON<sub>CO</sub> = 50) under the same reaction conditions, which has been reported to be one of the most efficient supramolecular photocatalysts for the reduction of CO₂ using higher-energy light such as

Fig. 4 Emission spectra of [Ru(C=C,dmb)]<sup>3+</sup> (blue) and [Ru(dmb)<sub>2</sub>Re(Ph)]<sup>3+</sup> (red) recorded in MeCN (excitation wavelength: 456 nm).
480 nm, because the absorption at $\lambda = 600$ nm is stronger. Under these reaction conditions, most Ru(II) moieties should be mainly excited (Fig. 3a). After a reductive quenching process of the excited state of the Ru(II) unit by BIH, intramolecular electron transfer should proceed from the reduced Ru(II) unit to the Re(I) unit, followed by reduction of CO$_2$ on the reduced Re(I) unit.

Conclusions

We successfully synthesised various trinuclear complexes from photofunctional complexes possessing vinyl or bromo groups as building blocks in a single step using the Mizoroki–Heck reaction. The obtained trinuclear complexes displayed strong absorption over a wide range of visible light and a long emission lifetime. [Ru(dmb)$_2$Re(Ph)]$^{5+}$ functioned as a photocatalyst for CO$_2$ reduction, even by irradiation at 600 nm.

Experimental

General procedures

$^1$H NMR spectra were recorded using a JEOL AL400 (400 MHz) or an AL300 (300 MHz) instrument with the analyte dissolved in acetone-$d_6$, MeCN-$d_3$, or CDCl$_3$. $^{31}$P NMR spectra were recorded using a JEOL ECX400 (400 MHz) instrument with the analyte dissolved in acetone-$d_6$. IR spectra were recorded using a JASCO FT/IR-610 spectrometer with a resolution of 1 cm$^{-1}$ and with the analyte dissolved in dichloromethane. ESI mass spectrometry (MS) was performed using a Shimadzu LC-MS-2010A system, with MeCN as the mobile phase. ESI time-of-flight MS was performed using a Waters LCT Premier instrument, with MeCN as the mobile phase. Size Exclusion Chromatography (SEC) was performed using a pair of Shodex PROTEIN KW-402J columns (300 mm long, 8.0 mm i.d.) with a KW-LG guard-column (50 mm long, 6.0 mm i.d.), a JASCO 880-51 degasser, an 880-PU pump, a MD-2010 Plus UV-vis photodiode-array detector, and a Rheodyne 7125 injector. The column temperature was maintained at 40 °C using a JASCO.
Dalton Transactions

860-CO oven. The eluent was a 1:1 (v/v) mixture of methanol and MeCN containing 0.5 M CH₃COONH₄, and the flow rate was 0.2 mL min⁻¹. Separation of the trinuclear complexes was achieved using SEC with a pair of Shodex PROTEIN KW-2002.5 columns (300 mm long, 20.0 mm i.d.) with a KW-LG guard column (50 mm long, 8.0 mm i.d.) and a recycling preparative HPLC apparatus with a JASCO 870-UV detector. The eluent was a 1:1 (v/v) mixture of methanol and MeCN containing 0.15 M CH₃COONH₄, and the flow rate was 6.0 mL min⁻¹. UV-vis absorption spectra were recorded using a JASCO V-670 instrument.

Emission measurements

Each compound was dissolved in MeCN and degassed using the freeze–pump–thaw method prior to measurement. Emission spectra were recorded at 25 °C using either a JASCO FP-8600 spectrofluorometer or a Hamamatsu C9920-02 system. The absolute emission quantum yields were evaluated using the Hamamatsu C9920-02 system equipped with an integrating sphere and a multichannel photodetector (PMA-12). Emission lifetimes were obtained using a HORIBA TemPro fluorescence lifetime system with an emission monochromator. The excitation light source was a NanoLED-560 pulse lamp and the instrumental response time was less than 0.1 ns. All emission decays were fitted by single or double exponential functions determined from the difference between [Ru(4,4′-dimethyl-2,2′-bipyridine)₂]³⁺ spectra recorded with the JASCO FP-8600 spectrofluorometer and the HORIBA TemPro fluorescence lifetime system.

Photocatalytic reactions

A 4 mL aliquot of a solution in an 11 mL-cubic-quartz cell (with a light passage length of 1 cm) was irradiated with 600 nm monochromatic light obtained from a Xe lamp with a band-pass filter (FWHM = 10 nm). The incident light intensity was 4.3 × 10⁻⁸ einstein per s. The gaseous reaction products (CO and H₂) were analysed using a GC-TCD instrument (GL Science GC323). HCOOH was analysed using a capillary electrophoresis system (Otsuka Electronics Co., CAPI-3300I). Materials

N,N-Dimethylformamide (DMF) was dried over the molecular sieve 4 Å and distilled under a decreased pressure (10–20 mmHg). TEOA was distilled under a decreased pressure (<1 mmHg). The DMF and TEOA were maintained under Ar until they were used. 1,3-Dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH),³¹ 4-methyl-4′-vinyl-2,2′-bipyridine (vbpy),³² 4,4′-divinyl-2,2′-bipyridine (dvbpy),³³ Ru(N²N)₂Cl₂ (N²N = bpy or dmb),³⁴ Ru(C≡C,bpy)³⁴, ³⁵ [Ru(C≡C,dmb)]³⁴, ³⁵ [Ir(C≡C,ppy)]³⁴, ³⁶ and 4′-bromo-2,2′-bipyridine,³⁷–³⁹ Re-(CO)₅Br⁴⁰ were prepared according to the reported methods with some modifications. All of the other reagents were of reagent grade quality and were used without further purification.

Synthesis

Re(i) complexes. Re(P₆)(CO)₅Br: Re(CO)₅Br (457.9 mg, 1.127 mmol) and Et₃ alcohol solution (20 wt%, 1.63 g, 2.759 mmol) were dissolved in toluene (60 mL, degassed using Ar) and refluxed under Ar for 12 days. Upon cooling to room temperature, the solvent was evaporated and a brown oil was obtained. The oily products were separated by flash column chromatography on silica gel (eluents: toluene, first fraction).

After removing the solvent under a decreased pressure, white solids were obtained, which were recrystallized with MeOH/water, washed with water, and then dried under vacuum. Yield: 203.7 mg (30.9%). FT-IR (in CH₂Cl₂): νCO/cm⁻¹: 2044, 1940, 1888. ¹H NMR (297.60 MHz, acetone-d₆): 8/ppm, 2.12–2.02 (m, 12H, P(CH₂CH₃)₃), 1.16–1.06 (m, 18H, P(CH₂CH₃)₃).

Re(Br,bpy)(CO)₂(P₆)Br₂: Re(P₆)Br (100.0 mg, 0.1705 mmol) and silver triflate (48.5 mg, 0.189 mmol) were dissolved in THF (8 mL) and refluxed under Ar for 3 h. Precipitated AgBr was filtered with Celite. A yellow-green oil was collected after the solvent was removed under vacuum. This oil and 4-bromo-2,2′-bipyridine (Brbpy, 50.2 mg, 0.212 mmol) were dissolved in toluene (15 mL) and heated at 90 °C under Ar overnight. Brbpy (39.2 mg, 0.166 mmol) was added to the reaction mixture and heated overnight. After a second addition of Brbpy (55.6 mg, 0.233 mmol), the solution was further heated for 1 d. The solvent was evaporated to give an orange-red residue, which was purified by flash column chromatography on silica gel (collected as the second fraction using 100:0–100:5 (v/v) CH₂Cl₂/MeOH as the eluent). The obtained orange-red solid was dissolved in MeOH to which a saturated methanol solution of NH₄PF₆ and a small amount of water were added. The solution was gradually evaporated until the orange-red solid precipitated. The solid was washed with water and Et₂O and dried at 60 °C under vacuum. Yield: 112.8 mg (77.0%, over 2 steps). ESI-MS (in MeCN): m/z: 713 ([M – PF₆]⁺). FT-IR (in CH₂Cl₂): νCO/cm⁻¹: 1934, 1864. ¹H NMR (297.60 MHz, acetone-d₆): 8/ppm, 9.32 (d, J = 5.4 Hz, 1H, Brbpy-6), 9.14 (d, J = 6.0 Hz, 2H, Brbpy-6′), 9.02 (d, J = 2.2 Hz, 1H, Brbpy-3), 8.90 (dd, J = 1.4, 8.2 Hz, 1H, Brbpy-3′), 8.38 (dd, J = 6.9, 8.2 Hz, 1H, Brbpy-4), 8.03 (dd, J = 2.2, 6.0 Hz, 1H, Brbpy-5′), 7.89 (dd, J = 1.4, 5.4, 6.9 Hz, 1H, Brbpy-5′), 1.59–1.52 (m, 12H, P(CH₂CH₃)₃), 0.92–0.83 (m, 18H, P(CH₂CH₃)₃). Elemental Anal. Calcd for C₃₂H₃₁BrF₆N₃O₃P₃Re: C, 33.57; H, 4.34; N, 3.26. Found: C, 33.94; H, 4.18; N, 3.30.

Re(P(OEt)₃)₂(CO)₅Br: Re(CO)₅Br (1.17 g, 2.89 mmol) and silver triflate (1.13 g, 6.82 mmol) were dissolved in toluene (100 mL) and the solution was refluxed under Ar for 28 h. After the solvent was evaporated, the residue was separated by column chromatography on alumina (collected as a first fraction, using 100:0–0:100 (v/v) CH₂Cl₂/hexane as the eluents). The obtained white solids were dried under vacuum. Yield:
1.37 g (69.8%). FT-IR (in CH₂Cl₂) ν\_CO/cm\(^{-1}\): 2069, 2048, 1970, 1920. H NMR (297.60 MHz, acetone-d₆): δ/ppm, 4.19–4.10 (m, 12H, P(OCH\(_2\)CH\(_3\))\(_3\)). [Re(vbpy)\(_2\)P(OEt\(_3\))\(_2\)PF\(_6\)]\(^{2+}\) (δ 7.80 (d, J = 10.6 Hz, 2H, -CH=CH\(_2\)), 8.61 (dd, J = 10.6, 17.4 Hz, 2H, -CH=CH\(_2\))].

[Re\(\text{[C=C=Ph]}\)PF\(_6\)]\(^{2+}\) using dbvp as a method similar to that for the synthesis of [Re(Br,Et)]\(^{2+}\) using dbvp instead of Br₂dbpy: yield: 56.4%. ESI-MS (in MeCN) m/z: 975 ([M – PF\(_6\)]\(^{2-}\)). FT-IR (in CH₂Cl₂) ν\_CO/cm\(^{-1}\): 1937, 1867. H NMR (297.60 MHz, acetone-d₆): δ/ppm, 8.49 (d, J = 1.6 Hz, 2H, bpy-3,3'), 7.98 (d, J = 5.8 Hz, 2H, bpy-6,6'), 7.16–7.30 (m, 30H, 2PPh₃), 7.03 (dd, J = 1.6, 5.8 Hz, 2H, bpy-5,5'), 6.81 (dd, J = 10.6, 17.4 Hz, 2H, -CH=CH\(_2\)), 6.27 (d, J = 10.6 Hz, 2H, -CH=CH\(_2\) (cis)), 5.73 (d, J = 17.4 Hz, 2H, -CH=CH\(_2\) (trans)).

P(FC₄H₄)\(_3\)-dbpy-3). FT-IR (in CH₂Cl₂) ν\_CO/cm\(^{-1}\): 1920. 1H NMR (297.60 MHz, acetone-d₆): δ/ppm, 6.44 (d, J = 17.6 Hz, 1H, vbpy-CH=CH₂ (trans)), 5.76 (d, J = 10.9 Hz, 1H, vbpy-CH=CH₂ (cis)), 3.83 (m, 12H, P(O-CH₂-CH₂-CH₃)), 2.60 (s, 3H, vbpy-CH₃), 1.00 (t, J = 6.9 Hz, 18H, P(O-CH₂-CH₂-CH₃)).

[Re(Br₂bpy)(CO)\(_2\)P(OC\(_2\)H₅)\(_3\))\(PF_6\)]\(^{2+}\) using dbvp instead of Br₂bpy: yield: 50.8%. ESI-MS (in MeCN) m/z: 1189 ([Re(Br₂bpy)(CO)\(_2\)P(FC₄H₄)\(_3\)]\(^{2+}\)). FT-IR (in CH₂Cl₂) ν\_CO/cm\(^{-1}\): 1943, 1874. H NMR (297.60 MHz, acetone-d₆): δ/ppm, 8.72 (d, J = 1.8 Hz, 2H, Br₂bpy-3,3'), 8.13 (d, J = 6.0 Hz, 2H, Br₂bpy-6,6'), 7.46–7.38 (m, 14H, bpy-5,5', m-Ph), 7.14 (dd, J = 8.7, 8.7 Hz, 12H, o-Ph). Elemental Anal. Calcd for C\(_{48}\)H\(_{36}\)Br\(_6\)F\(_6\)O\(_6\)P\(_8\): C, 47.03; H, 2.96; N, 2.29. Found: C, 46.95; H, 3.03; N, 2.15.

The purification method was the same as that for [Re(Br₂bpy)\(_2\)PF\(_6\)]\(^{2+}\). Using dbvp as a method similar to that for the synthesis of [Re(Br₂bpy)\(_2\)PF\(_6\)]\(^{2+}\) using dbvp instead of Br₂bpy: yield: 56.4%. ESI-MS (in MeCN) m/z: 1083 ([M – PF\(_6\)]\(^{2-}\)). FT-IR (in CH₂Cl₂) ν\_CO/cm\(^{-1}\): 1939, 1869. H NMR (297.60 MHz, acetone-d₆): δ/ppm, 8.73 (d, J = 4.4 Hz, 1H, bpy-6), 8.62 (s, 1H, bpy-3), 8.53 (s, 1H, bpy-3'), 8.13 (d, J = 6.2 Hz, 1H, bpy-6'), 7.43–6.79 (m, 28H, 6 × P(FC₄H₄)\(_3\), bpy-5,5', 2 × -CH=CH₂), 6.29 (d, J = 17.7 Hz, 2H, 2 × -CH=CH₂ (cis)), 5.75 (d, J = 11.2 Hz, 1H, -CH=CH₂ (trans)), 6.29 (d, J = 11.2 Hz, 1H, -CH=CH₂ (trans)).

13P NMR (400 MHz, acetone-d₆): δ/ppm, 20.1 (s, 2P, P(FC₄H₄)\(_3\)), -143.6 (7, 1P, PF\(_6\)). HRMS (ESI-TOF) m/z: [M – PF\(_6\)]\(^{2-}\) Calcd for C\(_{32}\)H\(_{42}\)F\(_6\)N\(_2\)O\(_2\)P\(_8\): 1083.1718; Found: 1083.1689.
Synthesis of multinuclear complexes using the Heck reaction.

\[ \text{[Re(OTf)3Re(Ph)](PF6)2} + \text{[ReBr2(Ph)](PF6)} \] (20 mg, 0.023 mmol), \[ \text{[Re(C≡COTf)](PF6)} \] (21 mg, 0.023 mmol), Pd(OAc)2 (1.0 mg, 0.0045 mmol), PPh3 (2.4 mg, 0.0092 mmol) and AcONa (11.5 mg, 0.140 mmol) were dissolved in MeCN degassed using Ar (4 mL). The solution was refluxed at 75 °C under Ar for 14 h. An MeCN solution (4 mL) containing Pd(OAc)2 (1.0 mg, 0.0045 mmol) and PPh3 (2.4 mg, 0.0092 mmol) was added to the reaction mixture and refluxed for 20 h. The solvent was removed under vacuum to give an orange-red solid. The coupling reagents were removed by flash column chromatography on silica gel (100 : 0 v/v) and the eluents). The target complex was isolated using ion-exchange chromatography. The red portion of the eluted solution was evaporated, dissolved in MeOH and washed twice with water containing NH4PF6 (0–4 mM). The solvent was evaporated until solids were precipitated. The solid was washed with water and Et2O and dried to 60 °C under vacuum. Yield: 27.7 mg (70.2%).

1H NMR (400 MHz, acetone-\(d_6\)) \(\delta\) ppm, 9.11 (\(d, J = 5.8\) Hz, 2H, \(\beta\)-py), 8.97 (\(d, J = 5.2\) Hz, 2H, \(\alpha\)-py), 8.92 (\(s, 2H, \beta\)-py, 8.71 (\(s, 2H, \alpha\)-py), 8.57 (\(s, 2H, \gamma\)-py), 8.13 (\(d, J = 5.2\) Hz, 2H, \(\delta\)-py), 8.03 (\(d, J = 5.8\) Hz, 1H, \(\gamma\)-py), 7.93 (\(d, J = 5.2\) Hz, 2H, \(\gamma\)-py), 7.72 (\(d, J = 5.2\) Hz, 2H, \(\delta\)-py), 7.42–7.28 (m, 34H, \(–\text{CH} –\text{CH}_2 –\text{CH}_2\)), 3.95–3.88 (m, 24H, 4P(OC\(\text{H}_2\)\(\text{CH}_3\))\(\gamma\)-py, 3.88 (m, 24H, 4P(OC\(\text{H}_2\)\(\text{CH}_3\))\(\alpha\)-py, 3.87 (m, 30H, \(\delta\)-py). FT-IR (in CH2Cl2) \(\nu\) cm\(^{-1}\): 1954, 1930, 1880, 1860. ESI-MS (in MeCN) \(m/z\): 702 ([M – 2PF\(_6\)^–]). Elemental Anal. Calcld for C\(_{152}\)H\(_{178}\)N\(_4\)O\(_{10}\)P\(_6\)Re\(_2\)C, 36.05; H, 4.40; N, 3.33. HRMS (ESI-TOF) \(m/z\): [M – 2PF\(_6\)^–] was calculated for C\(_{152}\)H\(_{178}\)N\(_4\)O\(_{10}\)P\(_6\)Re\(_2\). 701.1879; Found: 701.1848.
The solution was refluxed at around 75 °C under N2 for 1 d. The solution was refluxed at around 75 °C under N2 for 1 d in dim light. An MeCN solution degassed using N2 (10 mL) containing Pd(OAc)2 (5.5 mg, 0.024 mmol), PPh3 (1.2 mg, 4.6 μmol), and AcONa (1.6 mg, 0.11 mmol) was added again and the reaction solution was refluxed for 1 d. The solvent was removed under vacuum and a small amount of water was added to the solution. After evaporation of methanol, the obtained orange solids were collected, washed with water and Et2O, and dried at 60 °C under vacuum. Yield: 2.0 mg (8.0%). 1H NMR (400 MHz, acetone-d6): δ/ppm, 8.94 (s, 2H, βpy-3), 8.71 (s, 2H, αpy-3), 8.66 (s, 8H, dmb-3,3′), 8.51 (s, 2H, γpy-3), 8.10 (d, J = 6.2 Hz, 2H, γpy-6), 8.08 (d, J = 7.3 Hz, 2H, βpy-6), 7.96 (d, J = 5.6 Hz, 2H, γpy-5), 7.86–7.82 (m, 12H, dmb-6,6′, −CH=CH−), 7.69 (d, J = 5.6 Hz, 2H, αpy-6), 7.46–7.38 (m, 24H, αpy-5, βpy-5′, dmb-5,5′, m-PH), 7.13–7.09 (m, 12 H, α-PH), 2.63 (s, 3H, α-Ch3), 2.56 (s, 24H, dmb-CH3). 31P NMR (400 MHz, acetone-d6): δ/ppm, 21.7 (s, 2P, −PPPh3), −143.5 (7, 5P, PF6−). FT-IR (in CH2Cl2) ν/cm−1: 1942, 1873. ESI-MS (in MeCN) m/z: 472 ([M − 5PF6−]3−), 626 ([M − 4PF6−]4−), 883 ([M − 3PF6−]5−). HRMS (ESI-TOF) m/z: [M − 5PF6−]3− Calcd for C112H100F12N14O2P3ReRu2 626.1226; Found: 626.1219. C, 47.82; H, 3.17; N, 6.85. Found C, 47.61; H, 3.22; N, 6.58.

Notes and references

25 Rigorously excluding air contamination in the reaction vessel dramatically decreased the yield of [Re(OEt)Re(Et)]^2+.
However, adding too much air to the reaction vessel also decreased the yield. Air contamination that occurred when the cap of the vessel was opened to allow the reagents to be added supplied a suitable amount of air for [Re(OEt)Re(Et)]^2+ to be produced. The role of air in the reaction is currently being investigated in our laboratory.
27 Various decomposition products, including several kinds of mononuclear, dinuclear, and other kinds of trinuclear complexes, were observed.