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# Luminescent rhenium(I)–gold(I) hetero organometallics linked by ethynylphenanthrolines

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## Abstract

The first luminescent rhenium(I)–gold(I) hetero organometallics, Re{phen—≡—Au(PPh$_3$)}(CO)$_3$Cl (**3**) and Re{(PPh$_3$)Au—≡—phen—≡—Au(PPh$_3$)}(CO)$_3$Cl (**4**), have been prepared using the gold(I) complex AuCl(PPh$_3$) (PPh$_3$ = triphenylphosphine) and the novel rhenium(I) complexes Re(phen—≡—H)(CO)$_3$Cl (**5**) (phen—≡—H = 3-ethynyl-1,10-phenanthroline) or Re(H—≡—phen—≡—H)(CO)$_3$Cl (**6**) (H—≡—phen—≡—H = 3,8-bis(ethynyl)-1,10-phenanthroline). All the present rhenium(I) complexes **3**–**6** were revealed to possess a facial configuration (*fac*-isomer) with respect to the three carbonyl ligands. The main frameworks for these new gold(I) organometallics were constructed by the Au–C σ-bonding (with the η$^1$-type coordination) between the ethynylphenanthrolines and the Au(I) phosphine unit. Re(I)–Au(I) heterometallics **3** and **4** have shown single phosphorescence from the $^3$MLCT excited state and this observation can be interpreted in terms of the efficient intramolecular energy transfer from the Au(I) unit to the Re(I) unit.
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## 1. Introduction

There has been a growing interest in the design of multinuclear systems built-up by the photoactive d$^6$ transition-metal complexes owing to the development of photonic nano-devices [1]. Rhenium(I) tricarbonyl diimine complexes, Re(L–L)(CO)$_3$X, have been particularly intriguing not only because of their unique photophysical properties, but also because of a possible synthon for the photoactive supramolecular system [2]. Recent studies have exhibited many types of rhenium tectonics such as molecular wires, squares, and triangles based on Re(CO)$_3$ units with respect to the diversities of the supramolecular structures [3–5]. However, photophysical explorations so far done for the heteronuclear Re–M (M = Ru, Os, Zn, Fe, etc.) complexes have demonstrated only several examples of the specific energy transfer from the other metal unit to the rhenium carbonyl unit [6–8]. On the other hand, interesting luminescent properties have been revealed for gold(I) acetylide organometallics which have been investigated for the past decade. Che and coworkers [9] have reported a tantalizing phosphorescence for novel gold(I) ethynylarene organometallics and suggested the potential applications of these complexes to opt-electronic materials. In addition, our recent communication on the gold(I) ethynylphenanthroline organometallics, phen—≡—Au(PPh$_3$) (**1**) and (PPh$_3$)Au—≡—Phen—≡—Au(PPh$_3$) (**2**), revealed the intense phosphorescence even at an ambient

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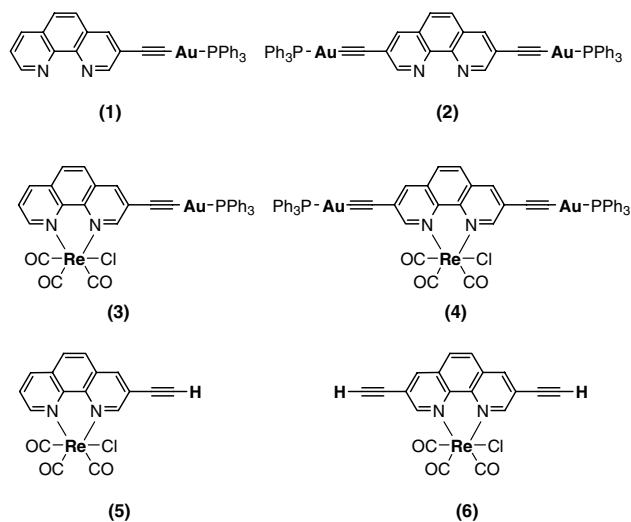*E-mail address:* michito@nitech.ac.jp (M. Shiotsuka).

Chart 1.

temperature (Chart 1) [10]. To the best of our knowledge, there is no report on the synthesis of Re(I)–Au(I) organometallics containing rhenium tricarbonyl diimine unit and the luminescent gold(I) unit. Thus, we were tempted to the synthesis of Re(I)–Au(I) organometallics, each unit of which has a characteristic luminescent property. In the present paper, we report on the synthesis and the unique photophysical properties of the first hetero organometallics which are constructed from the luminescent rhenium(I) tricarbonyl unit and the luminescent gold(I) phosphine unit; both units are connected by ethynylphenanthrolines as a π-conjugated ligand. The new entries to this heterometallic systems are Re{phen─≡─Au(PPh$_3$)}(CO)$_3$Cl (3) and Re-{(PPh$_3$)Au─≡─phen─≡─Au(PPh$_3$)}(CO)$_3$Cl (4) and the synthesis of relevant novel precursor rhenium(I) complexes, Re(phen─≡─H)(CO)$_3$Cl (5) and Re-(H─≡─phen─≡─H)(CO)$_3$Cl (6) is also described (Chart 1).

## 2. Results and discussion

### 2.1. Synthesis and structural study

The precursor rhenium complexes, Re(phen─≡─H)-(CO)$_3$Cl (5) and Re(H─≡─phen─≡─H)(CO)$_3$Cl (6), were first prepared by modifying the literature method [11]. The ligand 3-ethynylphenanthroline, Phen─≡─H (7), or 3,8-bis(ethynyl)phenanthroline, H─≡─Phen ─≡─H (8), and Re(CO)$_5$Cl were heated together in benzene at 60 °C for several hours. The solvent was partially removed from the reaction mixture and to this was added *n*-pentane resulting in precipitation of the yellow powder 5 or orange solid 6, respectively, in good yields. Re(I)–Au(I) hetero organometallics, Re{phen─≡─

Au(PPh$_3$)}(CO)$_3$Cl (3) and Re{(PPh$_3$)Au─≡─ phen─≡─Au(PPh$_3$)}(CO)$_3$Cl (4), were synthesized from the rhenium complexes 5 or 6 and AuCl(PPh$_3$) (PPh$_3$ = triphenylphosphine) with a 1:1 or 1:2 mol ratio in THF by adding an excess of amine as a base. Re(I)–Au(I) organometallics 3 and 4 were obtained in reasonable yields. These novel rhenium complexes 3–6 have been characterized by ^{1}H NMR, IR, UV–Vis spectroscopies, and elemental analysis.

The C≡O, C≡C, and H–C(≡C) stretching frequencies are collated in Table 1 for 1–8. The IR spectra of Re(I)–Au(I) and Au(I) organometallics 1–4 showed the characteristic weak *v*(C≡C) band in the region of 2080–2120 cm$^{-1}$, which is typical for the η$^1$ coordination of alkynylgold(I) organometallics [2,9,12]. However, gold(I) compounds 1–4 lack the *v*(H–C(≡C)) bands. On the contrary, the precursor rhenium(I) complexes and the phenanthroline ligands 5–8 exhibit the *v*(H–C(≡C)) stretches in the area of 3140–3190 cm$^{-1}$. These data clearly demonstrate the existence of the Au–C σ-bonding with the η$^1$ type coordination between the ethynylphenanthrolines and Au(I) phosphine complex. Further, the data of rhenium(I) compounds 3–6 in Table 1 show three strong *v*(CO) bands in the range between 1860 and 2030 cm$^{-1}$. The *v*(CO) pattern of these complexes suggests that the present rhenium(I) derivatives have a "C$_{3v}$" symmetry with respect to the three carbonyl ligands, which indicates a facial configuration around the rhenium center [1,13,14]. Previous studies on all rhenium(I) diimine tricarbonyl halides, Re(CO)$_3$(L–L)X, have been reported to have a facial configuration as far as we know (confirmed by NMR and X-ray crystallography) [14,15]. The structural characteristics for the present rhenium(I) compounds, including the Au–C σ-bonding with respect to the ethynylphenanthrolines for all gold(I) compounds, are further supported by the ^{1}H NMR measurements discussed below.

The ^{1}H NMR spectra of 1–6 exhibit well defined signals with the required numeral aromatic protons for the phenanthrolines in the range of $\delta = 7.60–9.50$ ppm. The phenyl proton signals on the gold(I) compounds 1–4 are observed as multiplets with an exact integration in the region between 7.40 and 7.70 ppm, while the singlet

Table 1
The collected stretching frequencies for compounds 1–8

| Compounds | $v_{CO}$ (cm$^{-1}$) | $v_{C≡C}$ (cm$^{-1}$) | $v_{H-C(≡C)}$ (cm$^{-1}$) |
|---|---|---|---|
| 1 | | 2108(w) | |
| 2 | | 2105(w) | |
| 3 | 2002(s), 1907(s), 1891(s) | 2088(w) | |
| 4 | 2019(s), 1914(s), 1895(s) | 2113(w) | |
| 5 | 2022(s), 1908(s), 1870(sh) | 2105(w) | 3182(m) |
| 6 | 2021(s), 1905(s), 1861(sh) | 2113(w) | 3188(m) |
| 7 | | 2090(w) | 3146(m) |
| 8 | | 2097(w) | 3175(m) |

signal assignable to the terminal ethynyl proton disappears. However, this type of proton signals for **5–8** are clearly observed in the range of $\delta = 3.37$–3.59 ppm.

The aromatic proton signals of the phenanthroline ligands shift to the lower field by the coordination with the present rhenium(I) carbonyl unit. For example, three sets of signals (H-2,9, H-4,7, and H-5,6) observed at $\delta$ 9.27, 8.28, and 7.68 for **2** cause the downfield shift ($\delta$ 9.40, 8.42, and 7.81 ppm) for **4**. Similar downfield shifts upon coordination of the rhenium(I) carbonyl unit are observed for all the sets of compounds between **8** and **6** or **1** and **3** or **7** and **5** as shown in Table 2. This phenomenon is generally interpreted in terms of the $\sigma$ donation of the phenanthroline ligand [14]. However, the upfield shifts are triggered by the coordination of the gold(I) phosphine unit to the ethynylphenanthroline–Re(CO)$_3$Cl moiety. For instance, three sets of signals at $\delta$ 9.41, 8.60, and 8.00 for **6** move to $\delta$ 9.40, 8.42, 7.81 ppm for **4**. Similar upfield shifts upon coordination of the gold(I) unit are displayed for almost all the sets of compounds between **8** and **2** or **7** and **1** or **5** and **3**, although the signals assignable to H-2 and H-2,9 proton show slight downfield shifts. The upfield shift is interpreted in terms of the $\pi$ back donation from Au(I) center to the ethynylphenanthroline ligands. Further, these $^1$H NMR data definitely support the "C$_{3v}$" symmetry

around the Re center (the facial configuration) because only three sets of signals are observed for the symmetrical diethynylphenanthroline ligand in the rhenium compounds **4** and **6**; the signals of the meridional isomer should show six sets of aromatic proton signals in the phenanthroline ligand because of the different *trans* influence between carbonyl and chloride ligands.

## 2.2. Photophysical properties

Table 3 culls the numerical data and the quantum yields for the UV–Vis and emission spectra on the complexes **1–6**. The UV–Vis absorption spectra for **1**, **3**, and **5** which contain an ethynyl ligand exhibit a new intense absorption band assignable to $\pi$–$\pi^*$(C≡C) absorption in the 300–370 nm region compared with the spectra of Re(phen)(CO)$_3$Cl although weak absorption for MLCT transition should overlap in this region (Fig. 1). Fig. 2 clearly shows quite similar intense $\pi$–$\pi^*$(C≡C) absorption band for **2**, **4**, and **6** in which the two ethynyl groups are attached to the phenanthroline skeleton in the 320–390 nm. Further, the assignment of $\pi$–$\pi^*$(C≡C) transition for these intense bands is supported by the fact that these bands observed on **1–6** are almost intact upon changing the solvent from DMF to CH$_2$Cl$_2$ because the solvatochromic

Table 2
The $^1$H NMR data for compounds **1–8**

| Compounds | Chemical shift (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | H-2 | H-9 | H-4 | H-7 | H-5 | H-6 | H-3 | H–C(≡C) |
| **1** | 9.28 | 9.16 | 8.32 | 8.24 | 7.79 | 7.72 | 7.63 | |
| **3** | 9.44 | 9.35 | 8.49 | 8.47 | 7.94 | 7.90 | 7.80 | |
| **5** | 9.42 | 9.42 | 8.61 | 8.56 | 8.05 | 7.99 | 7.90 | 3.57 |
| **7** | 9.23 | 9.21 | 8.36 | 8.25 | 7.82 | 7.75 | 7.65 | 3.37 |
| | H-2,9 | | H-4,7 | | H-5,6 | | | H–C(≡C) |
| **2** | 9.27 | | 8.28 | | 7.68 | | | |
| **4** | 9.40 | | 8.42 | | 7.81 | | | |
| **6** | 9.41 | | 8.60 | | 8.00 | | | 3.59 |
| **8** | 9.24 | | 8.37 | | 7.80 | | | 3.39 |

Table 3
The photophysical data for compounds **1–6**[a]

| Compounds | UV–Vis absorption | | | | | Emission[b] |
|---|---|---|---|---|---|---|
| | $\lambda_{abs}$ (nm) ($\varepsilon$, $10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$) | | | | | $\lambda_{em}$ (nm) ($\Phi_{em}$, $10^{-3}$) |
| **1** | | 328 (3.9), | 315 (3.5), | 279 (5.1), | 269 (4.5) | 470, 505 |
| **2** | | 357 (7.5), | 337 (6.1), | 286 (5.9), | 276 (5.5) | 501, 543 |
| **3** | | 349 (2.3), | 334 (2.2), | 284 (2.9), | 268 (2.5) | 637 (3.2) |
| **4** | | 379 (3.7), | 358 (3.3), | 294 (4.3), | 276 (4.1),   269 (4.0) | 644 (1.8) |
| **5** | 388 (0.4), | | 316 (1.8), | 279 (3.9), | | 655 (2.6) |
| **6** | 414 (0.3), | 335 (1.9), | 326 (1.9), | 283 (2.9), | 272 (2.8) | 673 (0.8) |

[a] UV–Vis and emission spectra were measured in a degassed dichloromethane at room temperature.
[b] The quantum yields were determined upon excitation at 450 nm and calculated relative to Re(bpy)Cl(CO)$_3$ ($\Phi_{em} = 0.0031$ in CH$_2$Cl$_2$) as a standard.
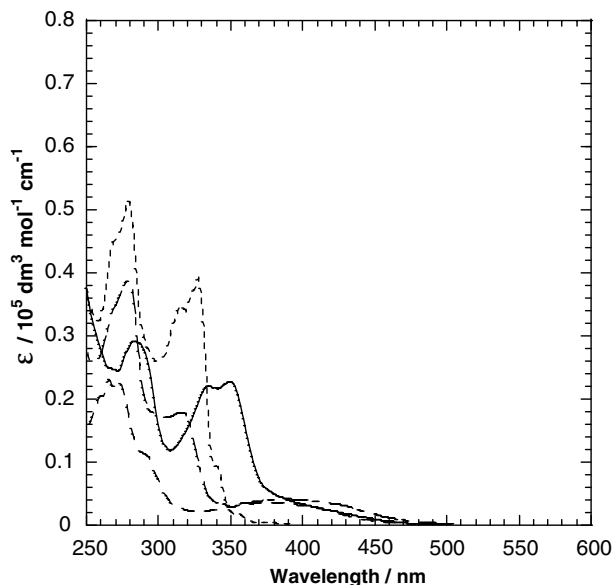
Fig. 1. UV–Vis absorption spectra of **1** (---), **3** (—), **5** (–·–) and Re(phen)(CO)$_3$Cl (––) in the degassed CH$_2$Cl$_2$ solution at room temperature.
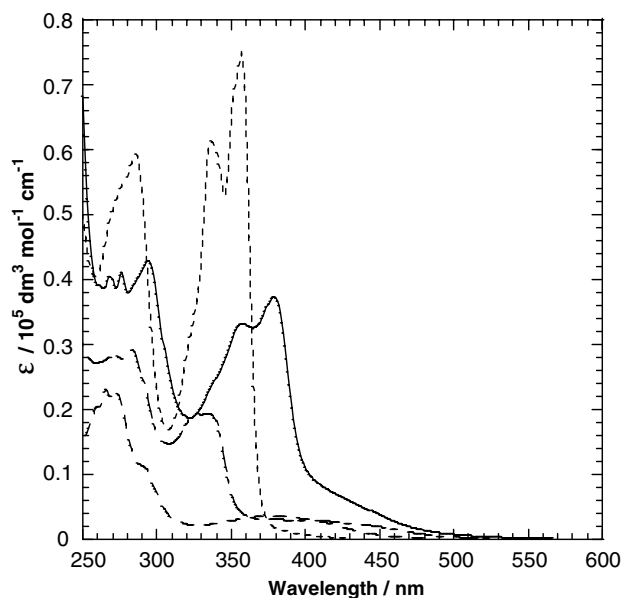


Fig. 2. UV–Vis absorption spectra of **2** (---), **4** (—), **6** (–·–) and Re(phen)(CO)$_3$Cl (––) in the degassed CH$_2$Cl$_2$ solution at room temperature.

shift of MLCT band on rhenium diimine complexes is generally observed [16]. The molar extinction coefficients for the π–π$^*$ bands in the Re(I)–Au(I) hetero complex **4** are almost twice as those of **3** due to the doubled number of the Au(I)–ethynyl units. The result is consistent with our recent communication on the gold(I) complexes **2** and **1** [10]. Each of the present rhenium(I) complexes **3–6** has a broad band at approximately 400 nm with a tail extending to the 500–550

nm region and this band is characteristic of the Re($\delta$)→L(π$^*$) MLCT transition which has been extensively studied for many kinds of rhenium(I) diimine tricarbonyl complexes [16–18]. These MLCT bands for the diethynyl compounds **4** and **6** tailed to a longer wavelength area compared with the ethynyl compounds **3** and **5**. This tailing should be accounted for in terms of the more extended electronic delocalization between the phenanthroline ligands. In addition, the π–π$^*$ transition bands have been red-shifted upon coordination of the rhenium(I) carbonyl group. For example, the absorption bands assignable to the π–π$^*$ transitions for **3** at 351, 334 nm shift to 328, 315 nm for **1**. Similar red-shifts are observed for the pair of **4** and **2** as shown in Fig. 2. These red-shifts in π–π$^*$ absorptions are due to the electronic modification of the phenanthroline ligands, which is induced by the rhenium(I) carbonyl coordination; ^{1}H NMR study discussed above supports the interpretation.

Luminescence spectra of the present rhenium(I) complexes **3–6** were observed as a broad emission around 650 nm in the CH$_2$Cl$_2$ solution at room temperature as shown in Fig. 3. This type of luminescence is typical for the phosphorescence from the dπ(Re)–π$^*$ (diimine) [3]MLCT excited state, which has been reported in many rhenium(I) diimine tricarbonyl complexes [16–18]. Interestingly, the Re(I)–Au(I) organometallics **3** and **4** do not emit such a structured band assignable to the [3][π–π$^*$(C≡C-phen)] transition originated from the Au(I) ethynylphenanthroline excited state [10]. The excitation spectra of these hetero organometallics are in accordance with the absorption spectra, including the π–π$^*$(C≡C) absorption bands for respective derivatives. These results indicate that the present Re(I)–Au(I)
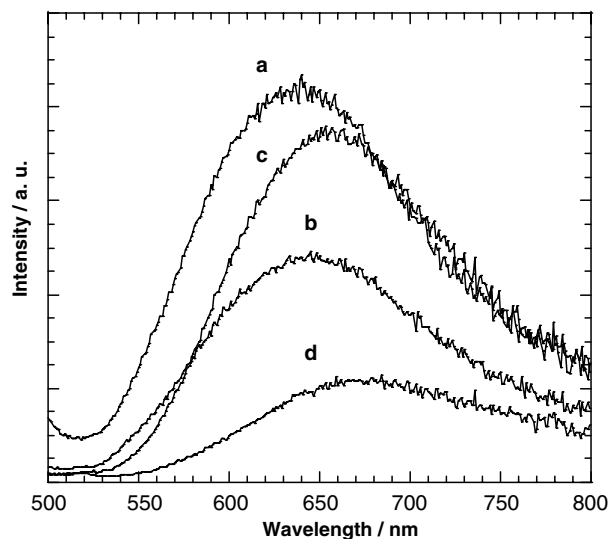


Fig. 3. Emission spectra of **3** (a), **4** (b), **5** (c) and **6** (d) in the degassed CH$_2$Cl$_2$ solution at room temperature. These spectra were detected upon excitation at 450 nm.

organometallics are susceptible to the efficient intramolecular energy transfer from the Au(I) ethynylphenanthroline units to the Re(I) diimine tricarbonyl unit. Furthermore, the increase of the luminescence quantum yield between Re(I)–Au(I) organometallics **3** or **4** and the precursor Re(I) complexes **5** or **6** has been observed, respectively (Fig. 3). The quantum yield is increased more than 200% in **4** compared with that of **6**, while the relative intensification for **3** is about 120% against **5** (Table 3). This difference might be investigated by using the energy gap law, because the wavelength of emission maxima ($\lambda_{em}$) for Re(I)–Au(I) organometallics **3** and **4** is observed at high energy relative to that of these precursor complexes **5** and **6**, respectively (Table 3).

## 3. Conclusion

The first luminescent rhenium(I)–gold(I) organometallics have been successfully synthesized by linking the luminescent rhenium(I) tricarbonyl complex unit and the luminescent gold(I) phosphine complex unit via ethynylphenanthrolines as a π-conjugated ligand. These Re(I)–Au(I) organometallics and novel rhenium(I) complexes have a facial configuration with respect to the three carbonyl ligands, and all gold(I) compounds possess a linear two-coordination around the Au(I) center. Re(I)–Au(I) organometallics have shown the single phosphorescence from the dπ(Re)–π* (diimine) $^3$MLCT excited state. However, the structured emission from the $^3[\pi–\pi^*(C\equiv Cphen)]$ excited state on Au(I) ethynylphenanthroline unit was not observed. These spectral characteristics are interpreted in terms of the efficient intramolecular energy transfer from the Au(I) unit to the Re(I) unit. These heterometallics should be a versatile luminescent scaffolding and a building block for constructing multimetallic arrays, which have the potential applications to further develop into opt-electronic devices by appropriate design and modification. These studies are underway in our laboratory.

## 4. Experimental

### 4.1. Materials and general measurements

All reactions were carried out under an argon atmosphere. Solvents were freshly distilled according to standard procedure. The starting materials were purchased from Sigma–Aldrich and used without further purification. The rhenium complex ReCl(CO)$_5$ was prepared according to the literature method [19]. The 3-ethynyl-1,10-phenanthroline (Phen—$\equiv$—H) (**7**) and 3,8-bis(ethynyl)-1,10-phenanthroline (H—$\equiv$—phen—$\equiv$—H) (**8**) were synthesized by the method of Tor et al. [20]. The charac-

terization of the novel complexes has been done by $^1$H NMR, IR, ESI-MS spectroscopy, and elemental analyses. The $^1$H NMR spectra were recorded with a Bruker AVANCE NMR spectrometer (200 and 600 MHz) at room temperature and the chemical shifts were referenced to TMS. IR spectra were obtained on a JASCO FT/IR 460 spectrometer using the KBr-pellet method. Elemental analyses were carried out at the Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Sciences, Kyoto University. UV–Vis spectra were recorded on a JASCO V-750 UV/VIS/NIR spectrophotometer and the emission spectra were recorded on an OTSUKA Electronics PTI-5100S spectrophotometer in a degassed dichloromethane (spectroscopic grade) at room temperature. The quantum yields on the present rhenium(I) complexes were determined upon the excitation at 450 nm and calculated relative to Re(bpy)Cl(CO)$_3$ ($\Phi_{em} = 0.0031$ in CH$_2$Cl$_2$) as a standard [21].

### 4.2. Preparation of phen—$\equiv$—Au(PPh$_3$) (**1**)

The methanol solution (10 ml) of sodium methoxide (45 mg, 0.8 mmol) was added to the methanol solution (20 ml) of AuCl(PPh$_3$) (PPh$_3$ = triphenylphosphine) (247 mg, 0.5 mmol) and Phen—$\equiv$—H (102 mg, 0.5 mmol) under Ar. After the mixture was stirred at room temperature for 1 h, the white precipitate was collected by filtration with a suction filter and washed with MeOH, H$_2$O, and ether successively. The powder was dried at 30 °C under vacuum for 12 h. Yield: 84% (278 mg). Anal. Calc. for C$_{32}$H$_{22}$N$_2$P$_1$Au$_1$H$_2$O: C, 56.48; H, 3.55; N, 4.12. Found C, 56.23; H, 3.45; N, 3.90%. IR (cm$^{-1}$) ν(C$\equiv$C): 2108. $^1$H NMR (CDCl$_3$): δ = 9.28 (d, J = 1.9 Hz, 1H, H-2), 9.16 (dd, J = 4.3, 1.6 Hz, 1H, H-9), 8.32 (d, J = 1.9 Hz, 1H, H-4), 8.24 (dd, J = 7.6, 1.6 Hz, 1H, H-7), 7.79 (d, J = 8.9 Hz, 1H, H-5), 7.72 (d, J = 8.9 Hz, 1H, H-6), 7.65–7.40 (m, 16H, H-8 and phenyl-H).

### 4.3. Preparation of (PPh$_3$)Au—$\equiv$—phen—$\equiv$—Au-(PPh$_3$) (**2**)

Fifty-seven mg of H—$\equiv$—phen—$\equiv$—H (0.25 mmol) was dissolved in an anhydrous methanol (30 ml) under argon. This solution was added to the dry THF solution (30 ml) of AuCl(PPh$_3$) (248 mg, 0.50 mmol) and the mixture was stirred at room temperature. The methanol solution (8 ml) of KOH (157 mg, 2.8 mmol) was added dropwise to the mixture. After 10 min, a pale-yellow precipitate appeared in the solution. The precipitate was collected by filtration with a suction filter and washed with MeOH, H$_2$O, and ether successively. The powder was dried at 30 °C under vacuum for 5 h. Yield: 88% (252 mg). IR (cm$^{-1}$) ν(C$\equiv$C): 2109. Anal. Calc. for C$_{52}$H$_{36}$N$_2$P$_2$Au$_2$2H$_2$O: C, 52.89; H, 3.41; N, 2.37. Found C, 53.25; H, 3.23; N, 2.36%. $^1$H NMR (CDCl$_3$): δ = 9.27

(d, $J = 1.9$ Hz, 2H, H-2,9), 8.28 (d, $J = 1.9$ Hz, 2H, H-4,7), 7.68 (s, 2H, H-5,6), 7.65–7.40 (m, 15H, phenyl-H).

### 4.4. Preparation of fac-Re(phen—≡—H)(CO)₃Cl (5) and fac-Re(H—≡—phen—≡—H)(CO)₃Cl (6)

Precursor Re(I) complexes **5** and **6** were synthesized by the modification of general literature methods on Re(L–L)(CO)₃Cl (L–L = bpy, phen) from the reaction of Re(CO)₅Cl with L–L. The chelating ligands Phen—≡—H (163 mg, 0.8 mmol) and Re(CO)₅Cl (180 mg, 0.5 mmol) in benzene were heated at 60 °C for several hours. The solution was concentrated and then 30 mL of *n*-pentane was added to redissolve the excess ligand. The yellow precipitate of **5** was filtered off and dried under vacuum. Yield: 94% (240 mg). IR (cm⁻¹) $v$(C≡C): 2105(w), $v$(CO): 2022(s), 1908(s), 1870(sh), $v$(H–C(≡C)): 3182(m). ¹H NMR (CDCl₃): $\delta$ 9.42 (d, $J = 1.6$ Hz, 1H, H-2), 9.42 (dd, $J = 4.9$, 1.3 Hz, 1H, H-9), 8.61 (d, $J = 1.6$Hz, 1H, H-4), 8.56 (dd, $J = 8.2$, 1.3 Hz, 1H, H-7), 8.05 (d, $J = 8.8$ Hz, 1H, H-5), 7.99 (d, $J = 8.8$ Hz, 1H, H-6), 7.90 (dd, $J = 8.2$, 4.9 Hz, 1H, H-8), 3.57 (s, 1H, H–C(≡C)).

A similar procedure was adopted for **6** using H—≡—phen—≡—H (182 mg, 0.8 mmol) to give orange powders. Yield: 90% (223 mg). IR (cm⁻¹) $v$(C≡C): 2113(w), $v$(CO): 2021(s), 1905(s), 1861(sh), $v$(H–C(≡C)): 3188(m). ¹H NMR (CDCl₃) $\delta$ 9.41 (d, $J = 1.6$Hz, 2H, H-2,9), 8.60 (d, $J = 1.6$Hz, 2H, H-4,7), 8.00 (s, 2H, H-5,6), 3.59 (s, 2H, H–C(≡C)).

### 4.5. Preparation of Re{phen—≡—Au(PPh₃)}(CO)₃Cl (3)

AuPPh₃Cl (149 mg, 0.3 mmol) and **5** (153 mg, 0.3 mmol) were dissolved in anhydrous THF (50 ml). An excess of diisopropylamine (0.35 ml) was added to the solution and stirred at room temperature for 1 day. The solvent and excess amine were removed under reduced pressure and the residue was washed with ethanol and then acetonitrile. After drying at 30 °C under vacuum, **3** was obtained as light yellow powders. Yield: 73% (210 mg). IR (cm⁻¹) $v$(C≡C): 2088(w), $v$(CO): 2002(s), 1907(s), 1891(s). Anal. Calc. for C₃₅H₂₂N₂O₃Cl₁-P₁Au₁Re₁·H₂O: C, 42.63; H, 2.45; N, 2.84. Found C, 42.78; H, 2.78; N, 2.32%. ¹H NMR (CDCl₃): $\delta = 9.44$ (d, $J = 1.7$ Hz, 1H, H-2), 9.35 (dd, $J = 5.1$, 1.3 Hz, 1H, H-9), 8.49 (dd, $J = 8.2$, 1.3 Hz, 1H, H-7), 8.47 (d, $J = 1.7$ Hz, 1H, H-4), 7.94 (d, $J = 8.9$ Hz, 1H, H-5), 7.90 (d, $J = 8.9$ Hz, 1H, H-6), 7.80 (dd, $J = 8.2$, 5.1 Hz, 1H, H-8), 7.65–7.40 (m, 15H, phenyl-H).

### 4.6. Preparation of Re{(PPh₃)Au—≡—phen—≡—Au-(PPh₃)}(CO)₃Cl (4)

AuPPh₃Cl (297 mg, 0.6 mmol) and **6** (160 mg, 0.3 mmol) were dissolved in 80 ml of THF. An excess of diisopropylamine (0.70 ml) was added to the solution and stirred at room temperature for 1 day. The solvent was distilled off under reduced pressure and the residue was washed with acetonitrile. After drying under vacuum, **4** was obtained as orange powders. Yield: 80% (348 mg). IR (cm⁻¹) $v$(C≡C): 2113(w), $v$(CO): 2019(s), 1914(s), 1895(s). Anal. Calc. for C₃₅H₂₂N₂O₃Cl₁-P₂Au₂Re₁: C, 45.54; H, 2.50; N, 1.93. Found C, 45.12; H, 2.61; N, 2.28%. ¹H NMR (CDCl₃): $\delta = 9.40$ (d, $J = 1.7$ Hz, 2H, H-2,9), 8.42 (d, $J = 1.7$ Hz, 2H, H-4,7), 7.81 (s, 2H, H-5,6), 7.60–7.40 (m, 30H, phenyl-H).

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