# Synthesis and redox properties of trinuclear ruthenium-acetylide complexes with tri(ethynylphenyl)amine bridge

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Novel trinuclear ruthenium complexes have been prepared by using tri(4-ethynylphenyl)amine as a bridging ligand. Cyclic voltammetry of the trinuclear ruthenium complexes revealed stepwise quasireversible redox behavior of three ruthenium-acetylide species and the central triphenylamine unit, whereas the mononuclear analog showed two sequential quasi-reversible redox waves. The spectroelectrochemical UV-VIS spectral studies suggested that the 1e<sup>-</sup> oxidized triruthenium species was stable and showed a characteristic absorption at  $\lambda_{max} = 505$  nm. Chemical oxidation of the triruthenium complex with ferrocenium hexafluorophosphate led to the isolation of the 1e<sup>-</sup> oxidized complex, the near-IR spectrum of which revealed an intervalence charge transfer band due to the electronic coupling among three ruthenium species. The 1e<sup>-</sup> oxidized triruthenium complexes can be classified as class II mixed-valence compounds.

## Introduction

Organometallic complexes with  $\pi$ -conjugated bridges are versatile building blocks for carbon-rich networks that are applicable to the development of new optical materials and electronic devices.<sup>1</sup> As a model of linear multi-metallic systems, many dinuclear metalacetylide complexes have been prepared and their electrochemical behaviors studied. The dinuclear metal-acetylide complexes often show electronic interaction between metal species, which stabilizes the mixed valence state by changing the bonding mode of the bridging ligands.<sup>2,3</sup> Recently, trinuclear metal-acetylide complexes have been attracting increasing interest as a model of dendritic multi-metallic systems.<sup>4-17</sup> However, only a few examples of such complexes show strong interaction among the metal species.<sup>5,7</sup> Thus, we have decided to design a new bridging ligand that incorporates the heteroatom into the bridging unsaturated ligand, to increase the interaction among the metal species as well as the stability of the mixed valence state.

Triphenylamine derivatives have attracted considerable interest due to their unique electronic and magnetic properties.<sup>18</sup> Especially, polymeric materials containing triphenylamine units are widely used as hole transport components in optoelectronic devices.<sup>19</sup> Therefore, the acetylene compounds derived from triphenylamine may act as a bridging ligand for multinuclear organometallic complexes that have strong metal-metal interactions. However, no reports on multinuclear systems bridged by triphenvlamine derivatives are found in the literature, while only one example of a mononuclear acetylide complex having triphenylamine units is known.<sup>20</sup> We report herein the synthesis and redox properties of trinuclear ruthenium complexes bridged by tri(pethynylphenyl)amine.

# **Results and discussion**

The synthetic approach to trinuclear ruthenium complexes shown in Scheme 1 was based on known activation processes of terminal acetylenes with ruthenium complexes.<sup>6</sup> The Sonogashira coupling of tri(4-bromophenyl)amine with trimethylsilylacetylene produced tri[4-(trimethylsilylethynyl)phenyl]amine (1), which was converted to tri(4-ethynylphenyl)amine (2) by desilvlation under basic conditions.<sup>21</sup> Ruthenium moieties were introduced by reacting with cis-Ru(dppe)<sub>2</sub>Cl<sub>2</sub> (3) in the presence of KPF<sub>6</sub>, followed



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by treatment with Et<sub>3</sub>N to give the trinuclear ruthenium-acetylide complex (4) in 74% yield.<sup>22</sup> The reaction of 4 with phenylacetylene in the presence of KPF<sub>6</sub> and Et<sub>3</sub>N in refluxing THF for 24 h resulted in the formation of the ruthenium-bis(acetylide) complex (5) in 94% yield. Mononuclear ruthenium-acetylide derivatives were prepared in a similar manner as shown in Scheme 2. The Pdcatalyzed amination of 4-bromo(triisopropylsilylethynyl)benzene with diphenylamine gave a triphenylamine derivative (6) having a protected ethynyl group.<sup>23</sup> (4-Ethynylphenyl)diphenylamine (7) was obtained by deprotection of the ethynyl group of 6, and was treated with 3 to give ruthenium-acetylide complex (8) in 84% yield. Bis(acetylide)-type complex (9) was also prepared by reacting 8 with phenylacetylene in 85% yield.



As shown in Fig. 1, the cyclic voltammogram (CV) of 4 displayed four quasi-reversible waves in the region between -0.8 and +0.8 V vs. Ag/AgCl reference. The three waves at low potential ( $E_{1/2}$  = -0.17, 0.11, 0.29 V) were assignable to the stepwise Ru<sup>II</sup>-Ru<sup>III</sup> redox of the three ruthenium-acetylide units, whereas the wave at the highest potential ( $E_{1/2} = 0.60$  V) was due to the redox



Fig. 1 Cyclic voltammogram (steady state) of 4 ( $0.8 \times 10^{-3}$  M, CH<sub>2</sub>Cl<sub>2</sub>) containing 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] at room temperature with a scan rate of 50 mV s<sup>-1</sup>. The external ferrocene/ferrocenium standard was observed at 0.16 V.

of the central triphenylamine unit because 1 showed a redox wave at  $E_{1/2} = 0.77$  V. Complex 5 showed a similar CV that contained four quasi-reversible waves at  $E_{1/2} = -0.17, 0.10, 0.23$ and 0.51 V. On the other hand, complex 8 underwent two quasireversible oxidations at  $E_{1/2} = -0.03$  and 0.48 V, suggesting that the Ru<sup>II</sup> moiety acts as an strong electron-donating group. Although it has been reported that some dinuclear metal-acetylide complexes produce coupled oxidation waves due to the electronic interaction through the conjugated ligands, all ruthenium-acetylide species are coincidentally oxidized at the same potential in the trinuclear<sup>6</sup> and larger ruthenium-acetylide complexes.15 This is a rare example of a transition-metal acetylide system having electronic interaction among three metal species.5,7

The UV-VIS spectra of 8 and 9 showed the MLCT band ( $\lambda_{max} =$ 349 nm, 8:  $\varepsilon = 4.99 \times 10^4$ , 9:  $\varepsilon = 5.20 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) that is characteristic of metal-acetylide complexes (Fig. 2).24 In the spectrum of 5, the MLCT band was observed to show a significant bathochromic shift ( $\lambda_{\text{max}} = 381 \text{ nm}, \varepsilon = 1.11 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). Complex 4 also showed the MLCT band at  $\lambda_{max} = 380$  nm ( $\varepsilon =$  $6.88 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) with slightly lower absorptivity. These results suggest that 4 and 5 exhibit metal-metal interactions through the tri(p-ethynylphenyl)amine bridge.<sup>15</sup>



Fig. 2 Spectroelectrochemical UV-VIS spectra of 5 in CH<sub>2</sub>Cl<sub>2</sub> at room temperature under argon atmosphere. (a) 4e<sup>-</sup> redox reaction; (b) 1e<sup>-</sup> redox reaction.

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To examine the properties of the mixed-valence complexes, the spectroelectrochemical UV-VIS spectra were measured. When a  $CH_2Cl_2$  solution of 5 was kept at -0.05 V potential that was appropriate for 1e<sup>-</sup> oxidation, the absorption in the 300-400 nm region was decreased and new bands were noted to emerge in the 400-550 nm region, with discernible maxima at 450 and 505 nm (Fig. 2(a)). Further oxidation led to a decrease in the absorption in the 300–400 nm region and in the absorption at  $\lambda_{max} = 505$  nm, whereas the absorption at  $\lambda_{max} = 450$  nm underwent only minimal changes. The spectrum of  $5^{4+}$  was essentially the same as that of  $5^{3+}$ . These results may suggest that the interaction among three ruthenium species through the tri(p-ethynylphenyl)amine bridge in  $5^+$  is larger than those in  $5^{2+}-5^{4+}$ . When  $5^{4+}$  was reduced stepwise, the spectra reverted to the original one with slightly smaller absorbance in each oxidation state. Although a similar phenomenon was observed in the redox experiment up to the 3e<sup>-</sup> or 2e<sup>-</sup> oxidation, the 1e<sup>-</sup> redox experiment resulted in a completely reversible change of the spectra, accompanied by isosbestic points at 307 and 411 nm (Fig. 2(b)). These results suggest that 5<sup>+</sup> is stable compared to the higher oxidized species. In the spectroelectrochemical UV-VIS spectra of 9, an absorption at  $\lambda_{max} = 456$  nm, which is similar to the  $\lambda_{max}$  value found in  $5^{2+}$  $\mathbf{5}^{4+}$ , was observed for  $\mathbf{9}^+$  (Fig. 3). Although the spectra returned to the original one upon reduction, the intensity was slightly decreased. The successive redox cycles led to a gradual decrease in the intensity. An irreversible change was observed in the spectroelectrochemical UV-VIS spectra of bis(phenylethynyl)ruthenium complex (10) (Chart 1 and Fig. 4).<sup>25</sup> These results clearly suggest that not only the tri(p-ethynylphenyl)amine bridge but also the trinuclear ruthenium-acetylide skeleton plays an important role in stabilizing the 1e<sup>-</sup> oxidized species of ruthenium-acetylide complexes.







Chart 1



Fig. 4 Spectroelectrochemical UV-VIS spectra of 10 in  $CH_2Cl_2$  at room temperature under argon atmosphere.

The treatment of **5** with an equimolar amount of  $[Cp_2Fe^+][PF_6^-]$ at room temperature gave brown complex  $[5^+][PF_6^-]$  in 73% yield (Scheme 3).<sup>26</sup> Although the NMR spectra of  $[5^+][PF_6^-]$  could not be obtained because of its paramagnetic property, the UV-VIS spectrum coincided with that observed in the electrochemical 1e<sup>-</sup> oxidation of **5**. Elemental analysis also supported the structure of  $[5^+][PF_6^-]$ . The IR spectrum of  $[5^+][PF_6^-]$  showed an absorption at 1957 cm<sup>-1</sup>, which is characteristic of the allenylidene complex,<sup>27</sup> as well as a C=C absorption (2020 cm<sup>-1</sup>). As seen in Fig. 5,







Scheme

#### the near-IR spectrum of $[5^+][PF_6^-]$ showed a broad absorption at $\lambda_{\rm max}$ = 4760 cm<sup>-1</sup> with $\varepsilon$ = 6.05 × 10<sup>4</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, which is attributable to the intervalence charge transfer (ICT), whereas no absorption was detected in the near-IR region for 5. The energy levels of the ICT bands were significantly lower than those observed in the dinuclear ruthenium-acetylide system.<sup>3</sup> Although the exact value of the half-width $(\Delta v_{1/2})$ could not be determined due to the wavelength range limit of the spectrometer, the approximate value was estimated to be 3000 cm<sup>-1</sup> from the shape of the spectrum in the high-energy region, which was close to the calculated value $\Delta v_{1/2} = (2310 v_{max})^{1/2} = 3316 \text{ cm}^{-1}$ for class II mixed-valence compounds.28 Based on the data described above, $\mathbf{5}^{\scriptscriptstyle+}$ may have a structure that consists of one ruthenium-allenylidene unit stabilized by the central nitrogen atom and electronic delocalization through the ICT (Scheme 4). Although the preliminary measurement of the ESR spectrum of $[5^+]$ [PF<sub>6</sub><sup>-</sup>] was unsuccessful, we will continue further investigation to elucidate electron coupling in this system by ESR measurements under various conditions as well as MO calculations.

In summary, we have synthesized novel trinuclear ruthenium– acetylide complexes having unique redox properties and shown the electronic coupling between ruthenium species through the tri(*p*ethynylphenyl)amine bridge. As this skeleton has the potential to expand into larger molecules,<sup>15–17</sup> investigations on the synthesis of multi-redox organometallic dendrimers based on this triruthenium unit are in progress.

## Experimental

<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on JEOL JNM-LA400 and Bruker ARX-400 spectrometers using SiMe<sub>4</sub> as the internal standard for <sup>1</sup>H and <sup>13</sup>C nuclei and H<sub>3</sub>PO<sub>4</sub> as the external standard for the <sup>31</sup>P nucleus. IR and FAB mass spectra were taken on Perkin-Elmer system 2000 FT-IR and JEOL JMS-600H instruments, respectively. UV-VIS and Near-IR spectra were measured on JASCO V-560 and V-570 spectrometers, respectively. Cyclic voltammograms were recorded on an ALS 630A apparatus.

All reactions were carried out under an atmosphere of argon, and the workup was performed in air. THF was distilled over sodium benzophenone ketyl under argon, and dichloromethane, toluene and triethylamine were distilled over CaH<sub>2</sub> under argon. Other chemicals available commercially were used without further purification. *cis*-RuCl<sub>2</sub>(dppe)<sub>2</sub>,<sup>29</sup> 4-bromo(triisopropylsilylethynyl)benzene<sup>16</sup> and *trans*-Ru(C=CPh)<sub>2</sub>(dppe)<sub>2</sub> 10<sup>30</sup> were prepared by the literature methods.

#### Tri[p-(trimethylsilylethynyl)phenyl]amine (1)

To a solution of tri(p-bromophenyl)amine (1.0 g, 2.07 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (84 mg, 120 µmol) and PPh<sub>3</sub> (16 mg, 61 µmol) in triethylamine (40 mL) was added trimethylsilylacetylene (1.3 mL, 9.32 mmol) and CuI (11 mg, 58 µmol), and the reaction mixture was refluxed overnight. After removal of the solvent, the residue was dissolved in benzene and passed through a short silica gel column. The solvent was evaporated, and the residue was purified by silica gel column chromatography. The eluent was gradually changed from hexane to a mixture of hexane-benzene (1:5 v/v). Recrystallization from hexane gave pale yellow crystals (0.86 g, 80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.34 (d, J = 8.5 Hz, 6H, Ar), 6.95 (d, J = 8.8 Hz, 6H, Ar), 0.23 (s, 27H, TMS). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 146.8 (Ar), 133.2 (Ar), 123.8 (Ar), 117.8 (Ar), 104.8 (C=), 93.9 (C=). IR [KBr,  $v_{max}/cm^{-1}$ ]: 2155 (C=C). FAB MS: m/z 533 (M<sup>+</sup>). Anal. Calc. for C<sub>33</sub>H<sub>39</sub>NSi<sub>3</sub>: C, 74.23; H, 7.36; N, 2.62. Found: C, 74.33; H, 7.38; N, 2.62%.

#### Tri[p-(ethynyl)phenyl]amine (2)

To a methanol solution (500 mL) of tri[*p*-(trimethylsilylethynyl)phenyl]amine **1** (5.0 g, 9.36 mmol) was added K<sub>2</sub>CO<sub>3</sub> (3.88 g, 28.1 mmol), and the reaction mixture was stirred at room temperature for 48 h. The solvent was evaporated, and the residue was extracted with diethyl ether. The organic layer was dried over MgSO<sub>4</sub>, and the solvent was removed again. The residue was purified by silica gel column chromatography using a mixture of hexane–ethyl acetate (9 : 1, v/v) as the eluent to give a pale yellow solid (2.89 g, 97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.38 (d, *J* = 8.5 Hz, 6H, Ar), 7.01 (d, *J* = 8.8 Hz, 6H, Ar), 3.06 (s, 3H,  $\equiv$ CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  144.4 (NC), 138.8 (Ar), 124.4 (Ar), 117.3 (CC $\equiv$ ), 83.8 (*C* $\equiv$ CH), 77.5 ( $\equiv$ CH). IR [KBr,  $v_{max}$ /cm<sup>-1</sup>]: 3268 ( $\equiv$ C–H). FAB MS: *m/z* 317 (M<sup>+</sup>). Anal. Calc. for C<sub>24</sub>H<sub>15</sub>N: C, 90.82; H, 4.76; N, 4.41. Found: C, 90.95; H, 4.97; N, 4.37%.

#### $N[C_6H_4C \equiv CRu(dppe)_2Cl]_3$ (4)

*cis*-RuCl<sub>2</sub>(dppe)<sub>2</sub> **3** (2.02 g, 2.08 mmol) and tri[*p*-(ethynyl)phenyl]amine **2** (0.20 g, 0.63 mmol) were dissolved in dichloromethane (80 mL), and KPF<sub>6</sub> (1.16 g, 6.3 mmol) was added. The reaction mixture was stirred at room temperature for 17 h, and triethylamine (4 mL) was added. After stirring for 30 min, the reaction mixture was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by alumina column chromatography with benzene followed by recrystallization from THF to give a pale yellow solid (1.46 g, 74%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.67–6.92 (m, 132H, Ar), 2.58 (br, 24H, CH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 147.4–127.3 (Ar), 122.5 (qnt,  $J_{P-C} = 16$  Hz, RuC≡), 113.4 (s, RuC≡C), 31.1 (qnt, J = 12 Hz, PCH<sub>2</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ 64.3. IR [KBr,  $\nu_{max}$ /cm<sup>-1</sup>]: 2065 (C≡C). FAB MS: m/z 3114 (M<sup>+</sup> − 3). Anal. Calc. for C<sub>180</sub>H<sub>156</sub>Cl<sub>3</sub>NP<sub>12</sub>Ru<sub>3</sub>: C, 69.42; H, 5.05; N, 0.45. Found: C, 69.37; H, 5.30; N, 0.78%.

#### $N[C_6H_4C \equiv CRu(dppe)_2(CCPh)]_3$ (5)

A THF solution (30 mL) of complex 4 (0.30 g, 96 µmol), phenylacetylene (90 mg, 0.86 mmol), triethylamine (1.8 mL) and KPF<sub>6</sub> (0.12 g, 0.58 mmol) was stirred under reflux for 24 h. The reaction mixture was filtered off, and the filtrate was concentrated under reduced pressure. The residue was dissolved in benzene and passed through a short alumina column. Recrystallization from hexane– THF gave a pale yellow solid (0.30 g, 94%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 7.71–6.90 (m, 147H, Ar), 2.54 (br, 24H, CH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 147.5–126.4 (Ar), 128.5 (s, C=), 126.4 (s, C=), 120.3 (s, C=), 119.8 (s, C=), 34.7 (qnt, J = 12 Hz, PCH<sub>2</sub>CH<sub>2</sub>P). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 68.5. IR [KBr,  $v_{max}$ /cm<sup>-1</sup>]: 2059 (C=C). FAB MS: m/z 3312 (M<sup>+</sup>). Anal. Calc. for C<sub>204</sub>H<sub>171</sub>NP<sub>12</sub>Ru<sub>3</sub>: C, 73.99; H, 5.20; N, 0.42. Found: C, 73.94; H, 5.39; N, 0.42%.

#### [4-(Triisopropylsilylethynyl)phenyl]diphenylamine (6)

A toluene solution (20 mL) containing diphenylamine (0.30 g, 1.8 mmol), 4-bromo(triisopropylsilylethynyl)benzene (0.54 g, 1.6 mmol), Pd<sub>2</sub>dba<sub>3</sub>·CHCl<sub>3</sub> (23 mg, 22 µmol), di(*tert*-butyl)(2-biphenyl)phosphine (26 mg, 89 µmol), NaOBu' (0.28 g, 2.88 mmol) was stirred at 100 °C for 7 h. After diethyl ether was added, the reaction mixture was filtered with Celite and was concentrated under reduced pressure. Purification by silica gel column chromatography with hexane gave a yellow viscous oil (0.43 g, 63%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  7.37–6.92 (m, 14H, Ar), 1.13 (s, 21H, Pr<sup>*i*</sup>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  147.9 (Ar), 147.2 (Ar), 132.7 (Ar), 129.3 (Ar), 124.8 (Ar), 123.4 (Ar), 122.2 (Ar), 116.6 (Ar), 107.3 (C=), 89.3 (C=). IR [KBr,  $v_{max}$ /cm<sup>-1</sup>]: 2152 (C=C). FAB MS: *m*/*z* 426 (M<sup>+</sup> + 1). Anal. Calc. for C<sub>29</sub>H<sub>35</sub>NSi: C, 81.82; H, 8.29; N, 3.29. Found: C, 81.92; H, 8.53; N, 3.17%.

#### (4-Ethynylphenyl)diphenylamine (7)

A THF solution (30 mL) of [4-(triisopropylsilylethynyl)phenyl]diphenylamine **6** (0.95 g, 2.2 mmol) was cooled at -78 °C, and 1 M THF solution of Bu<sub>4</sub>N (2.2 mL, 2.2 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature, and was stirred for 1 h. After the solvent was evaporated, the residue was purified by silica gel column chromatography using a mixture of hexane–benzene (1 : 1 v/v) as the eluent. Recrystallization from hexane gave a pale yellow solid (0.50 g, 83%). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  7.36–6.92 (m, 14H, Ar), 3.54 (s, 1H,  $\equiv$ CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  148.8 (Ar), 147.1 (Ar), 133.5 (Ar), 129.8 (Ar), 125.5 (Ar), 124.1 (Ar), 122.5 (Ar), 115.1 (Ar), 84.3 (C $\equiv$ ), 76.6 (C $\equiv$ ). IR [KBr,  $v_{max}/cm^{-1}$ ]: 3266, ( $\equiv$ C–H). FAB MS: *m/z* 269 (M<sup>+</sup>). Anal. Calc. for C<sub>20</sub>H<sub>15</sub>N: C, 89.19; H, 5.61; N, 5.20. Found: C, 89.02; H, 5.82; N, 5.34%.

## $Ph_2N[C_6H_4C \equiv CRu(dppe)_2Cl]$ (8)

The title complex was prepared by a similar manner to that for complex 4 using cis-RuCl<sub>2</sub>(dppe)<sub>2</sub> 3 (0.72 g, 0.74 mmol) and

#### $Ph_2N[C_6H_4C\equiv CRu(dppe)_2(C\equiv CPh)]$ (9)

The title complex was prepared by a similar manner to that for complex **5** using complex **7** (0.50 g, 0.42 mmol) and phenylacetylene (85 mg, 0.83 mmol), and was isolated as a pale yellow solid (0.45 g, 85%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  7.71–6.83 (m, 59H, Ar), 2.54 (br, 8H, CH<sub>2</sub>). <sup>13</sup>C NMR ( $C_6D_6$ ):  $\delta$  149.2–123.0 (Ar), 127.0 ( $C \equiv$ ), 124.0 ( $C \equiv$ ), 117.7 ( $C \equiv$ ), 117.3 ( $C \equiv$ ), 32.3 (t, J = 11 Hz, PCH<sub>2</sub>). <sup>31</sup>P NMR ( $C_6D_6$ ):  $\delta$  68.6. IR [KBr,  $v_{max}/cm^{-1}$ ]: 2061 ( $C \equiv$ C). FAB MS: m/z 1267 (M<sup>+</sup>). Calc. for  $C_{80}H_{67}NP_4Ru$ : C, 75.82; H, 5.33; N, 1.11%. Found: C, 75.41; H, 5.67; N, 1.02%.

#### Chemical oxidation of 5

To a dichloromethane solution of **5** (50 mg, 16 µmol) was added ferrocenium hexafluorophosphate (5 mg, 16 µmol), and the reaction mixture was stirred at room temperature for 8 h. After concentration under reduced pressure, diethyl ether was added. The resulting precipitate was collected and dried under reduced pressure to give a brown solid (38 mg, 73%). Anal. IR [KBr,  $\nu_{max}/cm^{-1}$ ]: 2020 (C=C), 1957 (M=C=C=C). Calc. for C<sub>180</sub>H<sub>156</sub>Cl<sub>3</sub>F<sub>6</sub>NP<sub>13</sub>Ru<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 65.00; H, 4.76; N, 0.42. Found: C, 64.80; H, 4.92; N, 0.58%.

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