

# A facile structural rearrangement to unprecedented $\mu_2\text{-}\eta^6\text{:}\eta^6\text{-bis(cyclopentadienylidene)ethene diruthenium complexes in the oxidation of 1,2-bis(ruthenocenyl)ethynes$ †

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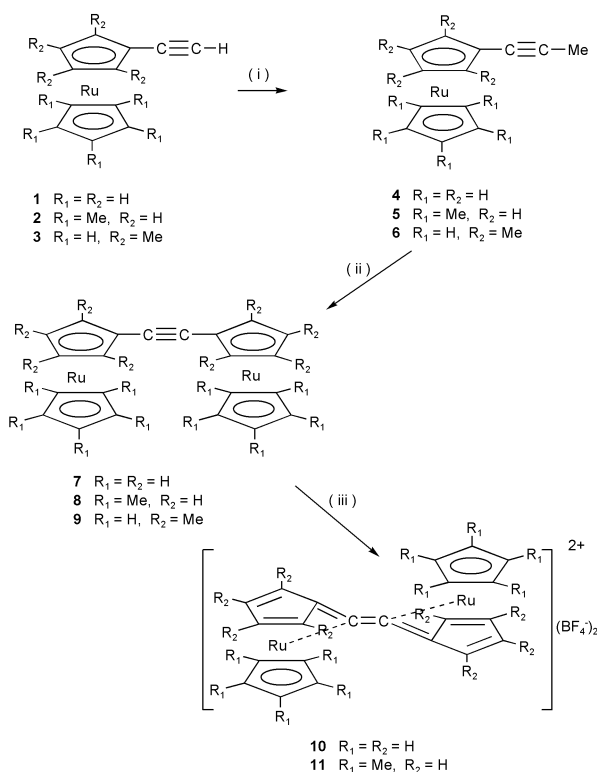
The two-electron oxidation of 1,2-bis(ruthenocenyl)ethynes and bis(1',2',3',4',5'-pentamethylruthenocenyl)ethynes, prepared from alkyne metathesis of the corresponding propynes, gave the unprecedented  $\mu_2\text{-}\eta^6\text{:}\eta^6\text{-bis(cyclopentadienylidene)ethene diruthenium complexes}$ .

There have been many investigations concerning the mixed-valence state of the one-electron oxidized species of binuclear transition-metal complexes,<sup>1</sup> while a few have reported the electronic state of two-electron oxidized species of binuclear organometallic transition-metal complexes bridged by an unsaturated hydrocarbon.<sup>2–6</sup> Two-electron oxidation of 1,2-bis(ruthenocenyl)ethenes gave bis(cyclopentadienylidene)ethane diruthenium complexes<sup>7</sup> and that of biruthenocyl afforded a ( $\mu_2\text{-}\eta^6\text{:}\eta^6\text{-fulvalene)diruthenium complex}$ .<sup>8</sup> We now report on the two-electron oxidation of 1,2-bis(ruthenocenyl)ethynes.

Ruthenocetyl- (1), 1',2',3',4',5'-pentamethylruthenocetyl- (2) and 2,3,4,5-tetramethylruthenocetyl-ethynes (3) were treated with  $\text{Bu}^n\text{Li}$  at  $-78\text{ }^\circ\text{C}$  in THF and subsequently reacted with methyl iodide to give the corresponding propyne derivatives (4–6), respectively, in good yields (Scheme 1).† Propynylruthenocene (4) was refluxed with  $\text{Mo(CO)}_6$  and  $p\text{-C}_6\text{H}_4\text{OH}$  in toluene for 2 h<sup>9</sup> to give bis(ruthenocenyl)ethyne (7) in 60% yield. A similar reaction of 5 produced bis(1',2',3',4',5'-pentamethylruthenocenyl)ethyne (8) in 20% yield, but 6 gave only a trace amount of bis(2,3,4,5-tetramethylruthenocenyl)ethyne (9).† The structure of 7 was, for example, confirmed by the  $\nu_{\text{CC}}$  frequency at  $2237\text{ cm}^{-1}$  and the carbon signal at  $\delta 65.68$ . The structure of 8 was also confirmed by X-ray diffraction.‡ The ORTEP view and selected bond distances and angles are shown in Fig. 1. The C(16)–C(17) distance [1.194(6) Å] and the bond angles C(1)–C(16)–C(17) [178.2(4)°] and C(16)–C(17)–C(18) [178.4(4)°] are typical for a triple bond. Interestingly, the ( $\eta\text{-C}_5\text{Me}_5$ )Ru moieties in 8 are on the same side of the bridging ligand and the  $\eta\text{-C}_5\text{H}_4$  rings of the ruthenocenyl moieties connected by the triple bond are not coplanar but are twisted by  $72.45(3)^\circ$  relative to each other around the linker.

Symmetrical ethynes 7, 8 and 9 showed irreversible waves in  $\text{CH}_2\text{Cl}_2$ ; single two-electron oxidation potentials ( $E_{\text{pa}}$ ) at +0.39, –0.09 and +0.14 V and single reduction potentials ( $E_{\text{pc}}$ ) at –0.02, –0.05 and –0.23 V vs.  $\text{FcH/FcH}^+$ , respectively. The  $E_{\text{pa}}$  peaks are shifted to the low-potential region by  $\Delta E_{\text{pa}} = 0.14, 0.42$  and  $0.19$  V compared with the corresponding propyne derivatives (4–6), respectively,§ suggesting that the two-electron oxidized species of these compounds may be stable since a similar low-potential shift ( $\Delta E_{\text{pa}} = 0.56$  V) was observed for 1,2-bis(ruthenocenyl)ethene which afforded a stable two-electron oxidized species.<sup>7</sup>

Symmetrical ethyne 8 was oxidized with  $p\text{-benzoquinone}$  ( $p\text{-BQ}$ ) and  $\text{BF}_3\cdot\text{OEt}_2$  in  $\text{CH}_2\text{Cl}_2$  at  $0\text{ }^\circ\text{C}$  to give red–orange microcrystals (11) in 60% yield.† A similar reaction of 7 produced the oxidized species (10) but only in low yield because of the low solubility of 7 in common organic solvents. The  $^1\text{H NMR}$  spectrum of 11 showed the  $\eta\text{-C}_5\text{H}_4$  ring protons at  $\delta 5.20$  and  $6.23$ , the position of which is similar to those of the corresponding bis(cyclopentadienylidene)ethane diruthenium complex ( $\alpha$ -protons at  $\delta 4.93$  and  $5.43$  and  $\beta$ -protons at  $\delta 5.86$  and  $5.98$ ).<sup>7</sup> In the  $^{13}\text{C NMR}$  spectrum of 11, the  $\eta\text{-C}_5\text{H}_4$  ring carbons were observed at  $\delta 82.67$  and  $97.61$ , being also near to



Scheme 1

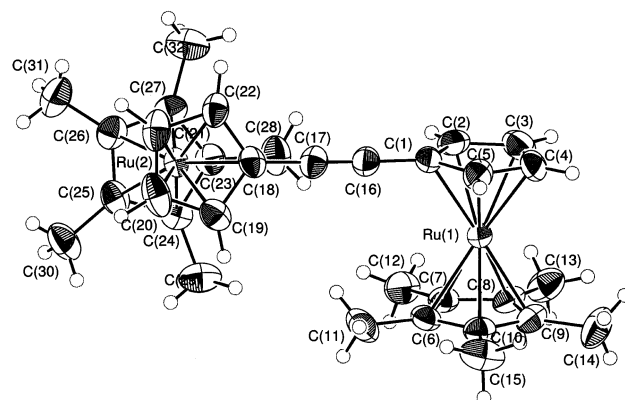
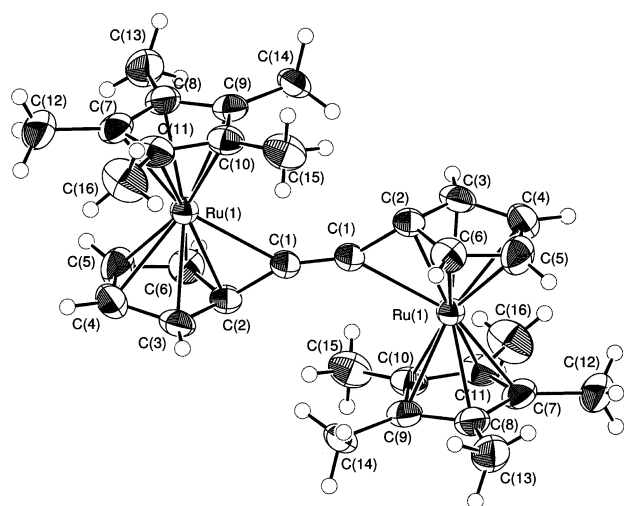


Fig. 1 ORTEP view of 8. Selected bond distances (Å) and angles (°): C(1)–C(16) 1.420(5), C(16)–C(17) 1.194(6), C(17)–C(18) 1.419(6); C(1)–C(16)–C(17) 178.2(4), C(16)–C(17)–C(18) 178.4(4).

† Electronic supplementary information (ESI) available: elemental analysis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR and Raman spectra. See <http://www.rsc.org/suppdata/cc/b2/b202811p/>

those of the corresponding bis(cyclopentadienylidene)ethane diruthenium complex ( $\alpha$ -carbons at  $\delta$  81.59 and 84.10 and  $\beta$ -carbons at  $\delta$  97.32 and 99.15).<sup>7</sup> These NMR data suggest that the  $\eta$ -C<sub>5</sub>H<sub>4</sub> ring moieties in **11** undergo structural rearrangement to the fulvene structure similar to that in the bis(cyclopentadienylidene)ethane diruthenium complex.<sup>7</sup> This is also supported from the fact that the center carbon signal of the cumulative bond appeared at  $\delta$  139.84 in the range near to that observed in the  $\beta$ -carbon atom of tetraphenylbutatriene ( $\delta$  152.03).<sup>10</sup> Complex **10** also showed NMR spectral features similar to those of **11**. The stretching vibration of the cumulative bond of **11** was observed at 2213 cm<sup>-1</sup>, the position of which was similar to that of bis(phenalenylidene)ethane (2017 cm<sup>-1</sup>).<sup>11</sup> These results suggest that the oxidized species **10** and **11** are  $\mu_2$ -bis(cyclopentadienylidene)ethene diruthenium complexes. To confirm this speculation, X-ray analysis of **11** was carried out.† A single crystal was obtained from the diffusion of diethyl ether into a solution of **11** in CH<sub>2</sub>Cl<sub>2</sub>. The ORTEP view of the cationic molecule of **11** is shown in Fig. 2, along with selected bond distances and angles. As seen in Fig. 2, the bridging ligand is coordinated in the  $\eta^6$ -mode and in an *anti* configuration by two ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru groups. The Ru(1)–C(1) distance is 2.254(3) Å, being somewhat longer than that (2.410 Å) of ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Ru( $\mu_2$ - $\eta^6$ : $\eta^6$ -C<sub>5</sub>H<sub>4</sub>CHCHC<sub>5</sub>H<sub>4</sub>)Ru( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)(BF<sub>4</sub>)<sub>2</sub><sup>7a</sup> and somewhat shorter than that (2.272(4) Å) of [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)( $\eta^6$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>)][CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>.<sup>12</sup> The C(1)–C(2) bond is folded by 41.3(3)° towards the  $\eta^4$ -C<sub>5</sub>H<sub>4</sub> ring, the value of which is similar to that of [Ru( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^6$ -C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>)]<sup>+</sup> (40.4°)<sup>13</sup> and [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)( $\eta^6$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>)]<sup>+</sup> (42.6°).<sup>12</sup> The C(1)–C(2) and C(1)–C(1) distances are 1.405(4) and 1.262(4) Å, respectively. The C(1)–C(2) bond is shortened and the C(1)–C(1) bond is elongated compared with the corresponding bonds of the neutral ethyne **8**. A clear bond alternation is observed in the  $\eta^4$ -C<sub>5</sub>H<sub>4</sub> ring of **11**. The two ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Ru moieties are in *anti*-positions relative to each other about the bridging ligand. The angle C(1)–C(1)–C(2) [153.5(3)°] is quite different from that of **8** where a linear arrangement is observed. These data confirm that the cation can be formulated as [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Ru( $\mu_2$ - $\eta^6$ : $\eta^6$ -C<sub>5</sub>H<sub>4</sub>=C=C-C<sub>5</sub>H<sub>4</sub>)Ru( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)]<sup>2+</sup>. Also, the five-membered rings in the ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Ru( $\eta^4$ -C<sub>5</sub>H<sub>4</sub>) moieties of **11** are arranged in the staggered form contrary to the ethyne **8** where an eclipsed arrangement is adopted. This is probably a result of the avoidance of the steric hindrance between the Me group of the  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> ligand and the folded bridging moiety in **11**.

In the two-electron oxidation of ethynes **7** and **8**, the first resulting radical cations on the Ru atoms are quickly coupled through spin pairing *via* the triple bond to bring about the



**Fig. 2** ORTEP view of the cation of **11**. Selected bond distances (Å) and angles (°): Ru(1)–C(1) 2.245(3), C(1)–C(1) 1.262(4), C(1)–C(2) 1.405(4), C(2)–C(3) 1.460(4), C(2)–C(6) 1.449(4), C(3)–C(4) 1.401(5), C(4)–C(5) 1.419(6), C(5)–C(6) 1.397(5); C(1)–C(1)–C(2) 153.5(3), ( $\eta^4$ -C<sub>5</sub>H<sub>4</sub> ring centroid)–C(2)–C(1) 138.7(3).

structural rearrangement producing the stable  $\mu_2$ -bis(cyclopentadienylidene)ethene ligand. An attempt to obtain the Ru(II)Ru(III) mixed valence complex of **8** was unsuccessful. Addition of a solution of **8** in CD<sub>3</sub>NO<sub>2</sub>–CD<sub>2</sub>Cl<sub>2</sub> to a solution of **11** in CD<sub>3</sub>NO<sub>2</sub>–CD<sub>2</sub>Cl<sub>2</sub> led no change of the proton signals of **11** as observed in the <sup>1</sup>H NMR spectrum although the proton signals of **8** is somewhat broadened. This is probably because the radical cation of ruthenocene is unstable if specific conditions are not satisfied.<sup>14</sup>

## Notes and references

† Crystal data for **8**: C<sub>32</sub>H<sub>38</sub>Ru<sub>2</sub>, *M* = 624.796, triclinic, space group *P* $\bar{1}$ , *a* = 8.6340(10), *b* = 11.9161(9), *c* = 13.4070(10) Å,  $\alpha$  = 86.362(7),  $\beta$  = 87.840(10),  $\gamma$  = 88.724(9)°, *V* = 1375.4(3) Å<sup>3</sup>, *T* = 298 K, *Z* = 2, *D*<sub>c</sub> = 1.509 Mg m<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 1.12 mm<sup>-1</sup>, 6742 measured reflections, 5931 unique reflections, 5931 reflections with *I*  $\geq$  3 $\sigma$ (*I*) used in refinement, empirical absorption correction (psi-scans), *R* = 0.034, *R*<sub>w</sub> = 0.165.

Crystal data for **11**: C<sub>32</sub>H<sub>38</sub>B<sub>2</sub>F<sub>8</sub>Ru<sub>2</sub>, *M* = 798.402, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 7.8670(2), *b* = 15.1480(5), *c* = 14.0120(5) Å,  $\beta$  = 103.179(2)°, *V* = 1625.82(9) Å<sup>3</sup>, *T* = 298 K, *Z* = 4, *D*<sub>c</sub> = 1.631 Mg m<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 1.99 mm<sup>-1</sup>, 3332 measured reflections, 3216 unique reflections, 3216 reflections with *I*  $\geq$  2 $\sigma$ (*I*) used in refinement, absorption correction (sortav), *R* = 0.036, *R*<sub>w</sub> = 0.110.

CCDC reference numbers 181591 and 181592. See <http://www.rsc.org/suppdata/cc/b2/b202811p/> for crystallographic data in CIF or other electronic format.

§ Cyclic voltammetry was performed in CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> under nitrogen at 25 °C, using standard three-electrode cell and an ALS60 analyzer. The potentials are relative to that of FcH/FcH<sup>+</sup> couple.

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