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# Photosubstitution of (Fulvalene)tetracarbonyldiruthenium by Alkenes and Alkynes: First Observation of Alkyne Coupling on Fulvalene Dimetals and Synthesis of a (Fulvalene)dimetallacyclopentadiene(alkene) Complex

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Irradiation ($\lambda_{max} = 300-375$ nm) of $FvRu_2(CO)_4$ (**1**, Fv = $\eta^5$:$\eta^5$-bicyclopentadienyl) or ($\mu_2$-$\eta^1$:$\eta^5$-cyclopentadienyl)$_2$$Ru_2(CO)_4$ (**2**) with dimethyl *cis*- or *trans*-butenedioate resulted in $FvRu_2$($\eta^2$-*trans*-CHR═CHR)$(CO)_3$ (**3**, R = $CO_2CH_3$). Prolonged irradiation of **1**−**3** provided $FvRu_2$($\eta^2$-*trans*-CHR═CHR)$_2$$(CO)_2$ (**4a**, R = $CO_2CH_3$) and $FvRu_2$($\eta^2$-*cis*-CHR═CHR)($\eta^2$-*trans*-CHR═CHR)$(CO)_2$ (**4b**, R = $CO_2CH_3$). Photocatalytic isomerization of cis to trans alkene occurred in the presence of **1**−**4**. Irradiation of **1**−**3** with dimethyl butynedioate produced $FvRu_2$($\mu_2$-$\eta^2$-dimethyl butynedioate)$(CO)_3$ (**5**). Prolonged irradiation of **1**−**5** with the alkyne afforded $FvRu_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$(CO) (**6**, R = $CO_2CH_3$). Irradiation of a THF solution of **6** generated $FvRu_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$(THF) (**7**, R = $CO_2CH_3$). Photochemical alkyne cyclotrimerization was observed in the presence of **1**−**7**. In the presence of CO, **7** reverted to **6** thermally. Heating **7** in the presence of dimethyl *cis*-butenedioate, thiophene, $PPh_3$, or dimethyl sulfoxide (DMSO) afforded $FvRu_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$(L) (**8**, R = $CO_2CH_3$, L = *cis*-CHR═CHR; **9**, L = thiophene; **10**, L = $PPh_3$; **11**, L = DMSO). Irradiation (300 nm) of a THF solution of **8**, **9**, or **11** provided **7**, while **10** was inert. Thermal conversion of **8** to **10** or **11** was effected only at relatively high temperatures. Treatment of **9** with dimethyl *cis*-butenedioate, $PPh_3$, or DMSO yielded **8**, **10**, and **11**, respectively. Heating **11** at 210 °C in molten $PPh_3$ afforded slowly **10**. Kinetic experiments on the conversion of **9** to **10** point to dissociative substitution, $E_a = 30.5$ kcal mol$^{-1}$. Complexes **3**−**8** have been characterized by X-ray crystal analyses.

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## Introduction

In the general context of the burgeoning area of binuclear transition metal mediated transformations of organic substances,[1] we have focused on the fulvalene ligand as a means to maximize the potential for synergism.[2] The present study was undertaken because (1) ruthenium has a rich catalytic chemistry involving C−C $\pi$ bonds;[3] (2) (fulvalene)tetracarbonyldiruthenium [$FvRu_2(CO)_4$] (**1**) displays unique photochemistry, highlighted by the thermally reversible photoisomerization **1** $\rightleftharpoons$ **2** (Scheme 1), which stores 30 kcal mol$^{-1}$ in energy;[4,5] (3) remarkably, there are no examples of Fv(M−M)(monoalkene) complexes in the literature;[6,7] (4) while a few Fv(M−M)(alkyne) complexes have been reported, alkyne coupling has never been observed.[4a,8] The system **1**/**2** thus seemed a suitable choice on which to probe the potential of the $FvM_2$ core to effect C−C bond formation of unsaturated substrates. We report the photochemis-

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(1) For recent reviews, see: (a) Wheatley, N.; Kalck, P. *Chem. Rev.* **1999**, *99*, 3379. (b) Van den Beuken, E. K.; Feringa, B. L. Tetrahedron **1998**, *54*, 12985. (c) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998.

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(3) For recent reviews, see: (a) Mitsudo, T.; Kondo, T. *Synlett* **2001**, 309. (b) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901. (c) Yi, C. S.; Liu, N. *Synlett* **1999**, 281. (d) Dixneuf, P.; Bruneau, C. In *Transition Metal Catalysed Reactions*; Murahashi, S.-I., Davies, S. G., Eds.; Blackwell: Oxford, 1999. (e) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599. (f) Trost, B. *Chem. Ber.* **1996**, *129*, 1313.

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(5) For topologically partly related reactions which may or may not be mechanistically distinct, see: (a) Burger, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1917. (b) Bitterwolf, T. E. *Coord. Chem. Rev.* **2000**, *206*−*207*, 419, and references therein.

(6) On the basis of electronic and manual searches (SciFinder Scholar listed 182 references under “fulvalene complexes” on 8.23.01) of 237 papers dealing with $FvM_2$ compounds.

(7) However, nonmetal−metal bonded simple $FvM_2$(alkene) complexes are known: (a) Green, M. L. H.; Mtetwa, V. S. B.; Sella, A.; Chernega, A. N. *J. Chem. Soc., Dalton Trans.* **1994**, 201. (b) Kreiter, C. G.; Conrad, W. *Z. Naturforsch.* **1994**, *49b*, 383. (c) Kreiter, C. G.; Conrad, W.; Exner, R. *Z. Naturforsch.* **1993**, *48b*, 1635. (d) Rausch, M. D.; Spink, W. C.; Conway, B. G.; Rogers, R. D.; Atwood, J. L. *J. Organomet. Chem.* **1990**, *383*, 227. (e) Kahn, A. P.; Newman, D. A.; Vollhardt, K. P. C. *Synlett* **1990**, 141. (f) Herrmann, W. A.; Andrejewski, D.; Herdtweck, E. *J. Organomet. Chem.* **1987**, *319*, 183.

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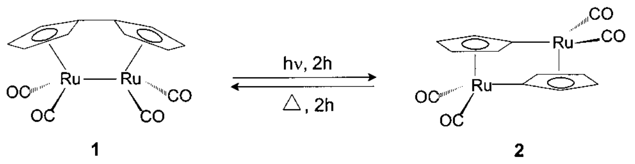
**Scheme 1**



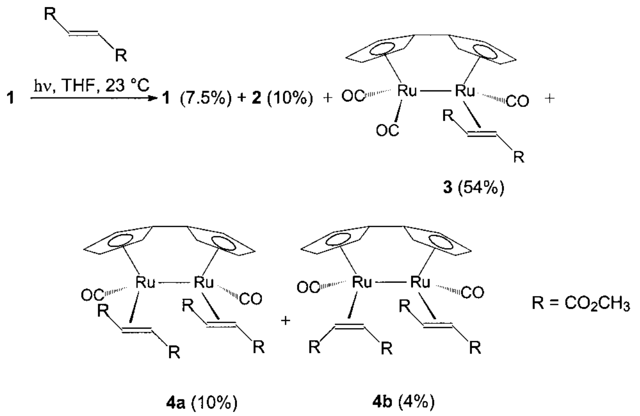
try of **1** (and **2**) with dimethyl *cis*- and *trans*-butenedioate and dimethyl butynedioate, which has filled the voids indicated in points 3 and 4 above by the synthesis of complexes **3**−**11**, including the X-ray crystal structure determination of **3**−**8**. Compound **8** constitutes a rare example of a dimetallacyclopentadiene(alkene), a potential intermediate in [2+2+2] cycloadditions of two alkynes with an alkene to give cyclohexadienes.[9]

## Results and Discussion

**Syntheses and Structures of ($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\eta^2$-*trans*-CHR=CHR)(CO)$_3$ (3), ($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\eta^2$-*trans*-CHR=CHR)$_2$(CO)$_2$ (4a), and ($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\eta^2$-*cis*-CHR=CHR)($\eta^2$-*trans*-CHR=CHR)(CO)$_2$ (4b) (R = CO$_2$CH$_3$).** Irradiation of a solution of **1** and dimethyl *trans*-butenedioate (5−15 equiv) in THF purged with N$_2$ with 350 nm UV light (Rayonet reactor) at 23 °C resulted in rapid establishment of the photoequilibrium **1** $\rightleftharpoons$ **2**[4a] and only very sluggish (but measurable) conversion to **3**. Assuming that the latter was due to photodissociation effected by the high-energy range of the lamps,[4a] the photoreactor was outfitted with both 350 and 300 nm bulbs. Under these conditions (used for all subsequent reactions), starting from either pure **1** or **2** or the photostationary mixture of both, yellow monoalkene complex **3** was generated in 41% yield (>60% by NMR) after 6 h, in addition to recovered **1** (30%) and **2** (9%). Prolonged irradiation of **1** (48 h) and the trans-alkene gave rise to **3** (54%) and four additional new compounds, only two of which, yellow **4a** (10%) and yellow **4b** (4%) (Scheme 2), are structurally certain, while the remaining two (generated in comparable amounts) are not (vide infra and Experimental Section). In an attempt to increase the yield of **4**, **3** was exposed to the trans-alkene (10 equiv) and light (12 h), providing **1**, **2**, **3**, and **4** in a ratio of 5:1:20:4, indicating the occurrence of ligand scrambling. Indeed, this took place simply starting with **3** (*hν*, 6 h), leading to **1**, **2**, and **3** in a ratio of 2:1:5 (NMR) and some decomposition.

Attempts to achieve the observed ligand substitution of **1** or **2** thermally (100 °C) led to either unchanged starting material or rapid conversion of **2** to **1**,[4a] respectively, and no other products. A similar experiment with **3** gave no trace of **4** (NMR). Ethylene and curiously (considering the obtention of **4b**) butenedioic anhydride failed to provide analogous products on photolysis of **1** or **2**, but led only to decomposition (>90%, 24 h).

**Scheme 2**



The gross structural assignment of **3** was evident on the basis of the spectral data. The yellow color ($\lambda_{max}$ 410 sh) suggested retention of the Ru−Ru bond.[2c,4a] Elemental and mass spectral analysis established the exchange of one CO for an alkene ligand, in agreement with the integrated peak values in the $^1$H NMR spectrum, ascertaining a Fv-to-alkene ratio of 1:1. The dissymmetrization of **1** was indicated by the presence of eight Fv hydrogen signals, in addition to two doublets at $\delta$ 4.19 and 3.90 ppm, $J$ = 7.2 Hz, and two methoxycarbonyl singlets, arising from the alkene groups. Similarly, there are 10 Fv and six alkene carbon peaks; among the latter two absorptions at 37.0 and 36.2 ppm are characteristic of a complexed alkene group. The data are comparable to those found for related Ru complexes[10] and indicate undetectable alkene rotation on the NMR time scale.[11] They are, however, not sufficient to pinpoint the stereochemistry of the alkene ligand itself (i.e., cis versus trans) and with respect to the stereogenic ruthenium center. For these reasons and because of the novelty of the complex, an X-ray crystal structure analysis was executed.

As shown in Figure 1, **3** crystallizes in the form of two rotamers with respect to the mutual orientation of the methoxycarbonyl functions, syn and anti. However, it is clearly only one diastereomer in which the trans

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[8] (a) El Amouri, H.; Besace, Y. *Organometallics* **1996**, *15*, 1514. (b) El Amouri, H.; Besace, Y.; Vaissermann, J.; Jaouen, G.; McGlinchey, M. J. *Organometallics* **1994**, *13*, 4426. (c) El Amouri, H.; Vaissermann, J.; Besace, Y.; Vollhardt, K. P. C.; Ball, G. E. *Organometallics* **1993**, *12*, 605. (d) Boese, R.; Huffman, M. A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1463. (e) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280. (f) Drage, J. S.; Tilset, M.; Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 812.

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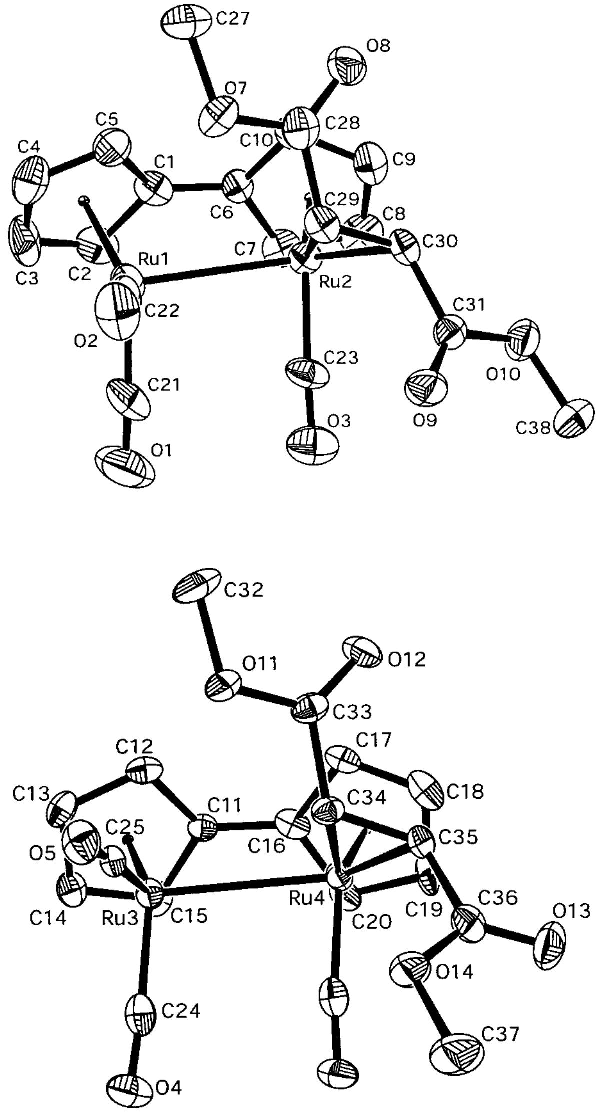

**Figure 1.** ORTEP diagram of the two rotamers of **3** in the unit cell (50% probability surface). The bottom structure is shown as the mirror image of the actual neighbor of the top form, for comparative viewing.

stereochemistry of the starting ligand is retained and the position of the R group proximal to the second Ru atom is syn with respect to the Fv frame. Selected bond lengths and angles are listed in Table 1.

The $\eta^2$-bound butenedioate carbons exhibit average bond lengths to Ru2 of 2.179 Å and to Ru4 of 2.158 Å, in accord with similar values for related assemblies in the literature.[10d,e,f] The two Ru−Ru distances are 2.8761(6) and 2.9031(6) and 2.9031(6) Å, slightly longer than that in **1**, 2.821 (1) Å. Similarly, the Fv bond angle (between the planes of the two Cp rings) averages to 28.9° and the corresponding twist (dihedral angle $Cp1_{centroid}-Ru1-Ru2-Cp2_{centroid}$) to 12.8°. The corresponding values in **1** are 28.5° and 4.3°, respectively.

Having established the completely diastereoselective incorporation of one molecule of trans-alkene into **1**,[12] the structures of potentially disubstituted products became of interest. Even assuming stereochemical integrity of the double bond under the reaction conditions (an assumption that proved incorrect), there are a number of diastereomeric Fv regioisomers (i.e., syn or anti with respect to the $FvRu_2$ frame) or metal locoisomers, giving rise to a total of nine bis(trans-alkene) isomers that could be formed. In the event, a second molecule of dimethyl *trans*-butenedioate entered **3** with remarkable stereo-, regio-, locoselectivity to give yellow **4a**. Apart from the mass spectrum and elemental analysis, the gross structure was clearly indicated by the presence of two pairs of doublets in the $^1H$ NMR spectrum at $\delta$ 4.47/4.31 and 4.57/4.30 ppm ($J = 9.6$, 9.9 Hz) for the complexed alkene hydrogens and a corresponding set of four peaks in the $^{13}C$ NMR spectrum. The dissymmetry of the Fv ligand was equally evident. The final structural determination had to again rely on an X-ray crystal analysis (Figure 2, Table 1).

Taking **3** as a reference, the second alkene unit has entered the diruthenium moiety from the same side to give a chiral molecule, the methoxycarbonyl substituents alternating up−down−up−down relative to the Fv ligand, as opposed to either of two possible meso arrangements, which would presumably be sterically more congested. The Ru−alkene carbon distances are quite similar within the molecule and in comparison to **3**, the "inside" bonds (Ru1−C16 and Ru2−C21) being slightly longer (average 2.200 Å) than their "outside" counterparts (Ru1−C15 and R2−C22; average 2.157 Å). The Ru1−Ru2 separation is 2.9730(7) Å, consistent with steric congestion, a feature that is also reflected in a considerable Fv twist of 28.3° to relieve eclipsing. The Fv bend angle of 32.5° is similar to that in **3**.

The proof of the structure of yellow **4b** ended in a surprise, namely, the discovery of cis−trans isomerization of the alkene during the reaction. Spectral and analytical criteria initially pointed toward the presence of one of the other possible bis-trans unsymmetrical isomers of **4a**. Thus, NMR spectroscopy showed pairs of alkene hydrogen doublets of $\delta$ 4.45/4.36 and 4.15/4.11 ppm ($J = 9.5$, 11.2 Hz) and the same multiplicity of the other hydrogen and carbon signals as that observed for **4a**. The value of X-ray crystallography is evident in Figure 3 (Table 1). Without implying a mechanism, **4b** is formally derived from **4a** by rotating the unique "outside" alkene carbon that points its methoxycarbonyl substituent toward the FvCp into the cis configuration. Both $\eta^2$-bound alkenes have the same average bond distance of 2.16 Å, the metal−metal bond length is 2.968(2) Å, the Fv twist angle is again considerable, 26.7°, and the corresponding bend angle is 31.0°.

As mentioned earlier, two other products were isolable from the reaction mixture that produced the above alkene complexes. On the basis of the spectral data (see Experimental Section), they appear to be additional isomers of **4**. In the absence of X-ray analyses due to poor crystal quality, we cannot formulate detailed structures, however.

**Catalytic Cis−Trans Photoisomerization of Dimethyl *cis*-Butenedioate.** The observation of a cis-ligand in **4b** suggested a number of experiments involving dimethyl *cis*-butenedioate as a substrate. Thus, photolysis of the cis-alkene on its own (6 h) revealed unchanged starting material (NMR). However, adding

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[12] Such stereoselective alkene ligation is important in future potential synthetic organic applications. See: Halterman, R. L. In *Metallocenes. Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1, p 455, and references therein.

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**Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 3, 4a, 4b, 5, 6, 7, and 8[a]**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **3** | | | | | | | |
| Ru1−Ru2 | 2.8761(6) | Ru1−C21 | 1.877(7) | Ru2−Ru1−C21 | 97.1(2) | Ru2−Ru1−C22 | 94.5(7) |
| Ru1−C22 | 1.892(6) | Ru2−C23 | 1.844(6) | Ru1−Ru2−C23 | 82.3(2) | Ru1−Ru2−C29 | 90.9(1) |
| Ru2−C29 | 2.198(5) | Ru2−C30 | 2.160(5) | Ru1−Ru2−C30 | 127.0(1) | Ru2−Ru1−Cp1 | 104.41(2) |
| Ru1−Cp1 | 1.8943(5) | Ru2−Cp2 | 1.8852(4) | Ru1−Ru2−Cp2 | 102.94(2) | C21−Ru1−C22 | 91.3(3) |
| C5−C6 | 1.436(7) | C29−C30 | 1.431(7) | C21−Ru1−Cp1 | 128.3(2) | C22−Ru1−Cp1 | 132.0(2) |
| C28−C29 | 1.478(8) | C28−O8 | 1.213(6) | C29−Ru2−C30 | 38.3(2) | C23−Ru2−C29 | 96.2(2) |
| C30−C31 | 1.489(7) | C31−O9 | 1.185(6) | C23−Ru2−C30 | 88.6(2) | C29−Ru2−Cp2 | 133.5(1) |
| Ru3−Ru4 | 2.9031(6) | Ru4−C34 | 2.173(5) | C30−Ru2−Cp2 | 122.2(1) | Ru2−C29−C30 | 69.4(3) |
| Ru4−C35 | 2.142(5) | C34−C35 | 1.429(6) | Ru2−C30−C29 | 72.3(3) | C28−C29−C30 | 119.1(5) |
| C1−C6 | 1.436(7) | C11−C16 | 1.450(7) | C29−C30−C31 | 119.0(5) | C14−Ru2−Cp2 | 132.9 |
| **4a** | | | | | | | |
| Ru1−Ru2 | 2.9730(7) | Ru1−C12 | 1.858(6) | Ru2−Ru1−C12 | 85.2(2) | Ru1−Ru2−C11 | 89.6(2) |
| Ru1−C16 | 2.208(5) | Ru1−C15 | 2.173(6) | Ru2−Ru1−C15 | 128.2(2) | Ru1−Ru2−C21 | 93.8(1) |
| Ru2−C11 | 1.846(6) | Ru2−C21 | 2.192(5) | Ru2−Ru1−C16 | 90.3(1) | Ru1−Ru2−C22 | 131.2(2) |
| Ru2−C22 | 2.141(5) | C15−C16 | 1.436(8) | Cp1−Ru1−C12 | 130.9(2) | Cp2−Ru2−C11 | 124.7(2) |
| C21−C22 | 1.406(7) | Ru1−Cp1 | 1.8829(5) | Cp1−Ru1−C15 | 117.1(1) | Cp2−Ru2−C21 | 139.7(2) |
| Ru2−Cp2 | 1.9143(4) | C5−C6 | 1.442(8) | Cp1−Ru1−C16 | 132.8(1) | Cp2−Ru2−C22 | 121.5(1) |
| | | | | C15−Ru1−C16 | 38.3(2) | C21−Ru2−C22 | 37.8(2) |
| | | | | Ru1−C15−C16 | 72.2(3) | Ru2−C21−C22 | 69.1(3) |
| | | | | C12−Ru1−C15 | 91.8(2) | C11−Ru2−C21 | 93.2(2) |
| | | | | C12−Ru1−C16 | 94.9(2) | C11−Ru2−C22 | 88.0(2) |
| **4b** | | | | | | | |
| Ru1−Ru2 | 2.968(2) | Ru1−C11 | 1.86(2) | Ru2−Ru1−C11 | 88.3(6) | Ru1−Ru2−C12 | 85.7(5) |
| Ru1−C13 | 2.17(2) | Ru1−C14 | 2.14(2) | Ru2−Ru1−C13 | 89.1(4) | Ru1−Ru2−C21 | 95.6(5) |
| Ru2−C12 | 1.85(2) | Ru2−C21 | 2.21(2) | Ru2−Ru1−C14 | 126.9(4) | Ru1−Ru2−C22 | 134.4(5) |
| Ru2−C22 | 2.11(2) | C13−C14 | 1.40(2) | Cp1−Ru1−C11 | 129.3(5) | Cp2−Ru2−C12 | 126.4(6) |
| C21−C22 | 1.44(2) | Ru1−Cp1 | 1.90 | Cp1−Ru1−C13 | 134.9(5) | Cp2−Ru2−C21 | 137.9(5) |
| Ru2−Cp2 | 1.90 | C5−C6 | 1.44(2) | Cp1−Ru1−C14 | 119.0(4) | Cp2−Ru2−C22 | 116.1(5) |
| | | | | C13−Ru1−C14 | 38.0(5) | C21−Ru2−C22 | 38.9(6) |
| | | | | Ru1−C13−C14 | 69.8(9) | Ru2−C21−C22 | 67(1) |
| | | | | C11−Ru1−C13 | 94.5(7) | C12−Ru2−C21 | 92.9(8) |
| | | | | C11−Ru1−C14 | 91.4(7) | C12−Ru2−C22 | 92.0(8) |
| **5** | | | | | | | |
| Ru1−Ru2 | 2.7392(1) | Ru1−C11 | 2.082(3) | Ru2−Ru1−C11 | 70.30(8) | Ru2−Ru1−C17 | 117.48(9) |
| Ru1−C17 | 1.855(3) | Ru1−C19 | 2.052(3) | Ru2−Ru1−C19 | 48.59(9) | Ru2−Ru1−Cp1 | 105.97(1) |
| Ru1−Cp1 | 1.9125(2) | Ru2−C12 | 2.074(3) | C11−Ru1−C17 | 85.5(1) | C11−Ru1−C19 | 100.1(1) |
| Ru2−C18 | 1.871(3) | Ru2−C19 | 2.068(3) | Cp1-Ru1−C11 | 120.25(8) | Cp1-Ru1−C17 | 135.33(9) |
| Ru2−Cp2 | 1.8997(2) | C11−C12 | 1.324(4) | Cp1-Ru1−C19 | 121.83(8) | C17−Ru1−C19 | 83.3(1) |
| C5−C6 | 1.457(4) | | | Ru1−Ru2−C12 | 69.85(8) | Ru1−Ru2−C18 | 117.22(9) |
| | | | | Ru1−Ru2−C19 | 48.09(8) | Ru1−Ru2−Cp2 | 106.47(1) |
| | | | | C12−Ru2−Cp2 | 121.07(8) | C18−Ru2−C19 | 84.1(1) |
| | | | | C18−Ru2−Cp2 | 134.92(10) | C19−Ru2−Cp2 | 120.63(8) |
| **6** | | | | | | | |
| Ru1−Ru2 | 2.5750(6) | Ru1−C11 | 2.086(5) | Ru2−Ru1−C12 | 77.8(1) | Ru2−Ru1−C11 | 51.5(1) |
| Ru1−C12 | 2.195(5) | Ru1−C13 | 2.204(5) | Ru2−Ru1−C13 | 77.7(1) | Ru2−Ru1−C14 | 51.9(1) |
| Ru1−C14 | 2.092(5) | Ru1−Cp1 | 1.8301(4) | Ru2−Ru1−Cp1 | 114.94(2) | C11−Ru1−C12 | 38.3(2) |
| Ru2−C11 | 2.073(5) | Ru2−C14 | 2.088(5) | C11−Ru1−C13 | 67.3(2) | C11−Ru1−C14 | 75.8(2) |
| Ru2−C23 | 1.877(6) | Ru2−Cp2 | 1.9013(4) | Cp1-Ru1−C11 | 134.4(1) | C12−Ru1−C13 | 38.3(2) |
| O9−C23 | 1.144(5) | C5−C6 | 1.457(7) | C12−Ru1−C14 | 68.1(2) | C12−Ru1−Cp1 | 156.8(1) |
| C11−C12 | 1.408(7) | C11−C15 | 1.505(7) | C13−Ru1−C14 | 38.7(2) | C13−Ru1−Cp1 | 158.3(1) |
| C12−C13 | 1.445(6) | C13−C14 | 1.426(7) | C14−Ru1−Cp1 | 135.1(1) | Ru1−Ru2−C11 | 52.0(1) |
| C14−C21 | 1.490(7) | | | Ru1−Ru2−C14 | 52.1(1) | Ru1−Ru2−C23 | 126.4(2) |
| | | | | Ru1−Ru2−Cp2 | 103.96(2) | C11−Ru2−C14 | 76.2(2) |
| | | | | C11−Ru2−C23 | 89.0(2) | C11−Ru2−Cp2 | 127.8(1) |
| | | | | C14−Ru2−C23 | 87.7(2) | C14−Ru2−Cp2 | 129.5(1) |
| | | | | C23−Ru2−Cp2 | 129.6(2) | Ru1−C11−Ru2 | 76.5(2) |
| | | | | Ru2−C11−C12 | 118.4(4) | C11−C12−C13 | 113.1(5) |
| | | | | C12−C13−C14 | 113.6(4) | C13−C14−Ru2 | 116.8(3) |
| **7** | | | | | | | |
| Ru1−Ru2 | 2.5603(6) | Ru1−C11 | 2.100(7) | Ru2−Ru1−C12 | 78.8(2) | Ru2−Ru1−C11 | 51.5(2) |
| Ru1−C12 | 2.189(8) | Ru1−C13 | 2.180(7) | Ru2−Ru1−C13 | 78.5(2) | Ru2−Ru1−C14 | 51.0(2) |
| Ru1−C14 | 2.120(6) | Ru1−Cp1 | 1.8370(6) | Ru2−Ru1−Cp1 | 114.57(3) | C11−Ru1−C12 | 39.2(2) |
| Ru2−C11 | 2.068(7) | Ru2−C14 | 2.053(7) | C11−Ru1−C13 | 67.8(3) | C11−Ru1−C14 | 74.1(3) |
| Ru2−O9 | 2.131(5) | Ru2−Cp2 | 1.8819(6) | Cp1-Ru1−C11 | 135.6(2) | C12−Ru1−C13 | 38.3(2) |
| C11−C12 | 1.440(9) | C5−C6 | 1.486(10) | C12−Ru1−C14 | 67.1(3) | C12−Ru1−Cp1 | 157.9(2) |
| C12−C13 | 1.434(9) | C11−C15 | 1.494(9) | C13−Ru1−C14 | 38.5(2) | C13−Ru1−Cp1 | 156.6(2) |
| C14−C21 | 1.483(9) | C13−C14 | 1.420(9) | C14−Ru1−Cp1 | 135.0(2) | Ru1−Ru2−C11 | 52.7(2) |
| | | | | Ru1−Ru2−O9 | 134.8(1) | O9−Ru2−C11 | 92.4(2) |
| | | | | Ru1−Ru2−C14 | 53.3(2) | C11−Ru2−C14 | 76.2(3) |
| | | | | Ru1−Ru2−Cp2 | 105.06(3) | C11−Ru2−Cp2 | 129.3(2) |
| | | | | C11−Ru2−O9 | 92.4(2) | C14−Ru2−Cp2 | 129.3(2) |
| | | | | C14−Ru2−O9 | 95.0(2) | Ru1−C11−Ru2 | 75.8(2) |
| | | | | O9−Ru2−Cp2 | 120.1(1) | C11−C12−C13 | 112.4(7) |
| | | | | Ru2−C11−C12 | 118.2(5) | C13−C14−Ru2 | 119.2(5) |
| | | | | C12−C13−C14 | 113.2(7) | | |

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**Table 1 (Continued)**

**8**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ru1−Ru2 | 2.5947 (9) | Ru1−C11 | 2.081 (7) | Ru2−Ru1−C12 | 78.5 (2) | Ru2−Ru1−C11 | 52.0 (2) |
| Ru1−C12 | 2.177 (7) | Ru1−C13 | 2.181 (7) | Ru2−Ru1−C13 | 77.6 (2) | Ru2−Ru1−C14 | 50.8 (2) |
| Ru1−C14 | 2.151 (8) | Ru1−Cp1 | 1.8086 (6) | Ru2−Ru1−Cp1 | 118.56 (3) | C11−Ru1−C12 | 39.1 (3) |
| Ru2−C11 | 2.102 (7) | Ru2−C14 | 2.074 (7) | C11−Ru1−C13 | 68.2 (3) | C11−Ru1−C14 | 75.1 (3) |
| Ru2−C23 | 2.180 (7) | Ru2−C24 | 2.188 (7) | Cp1-Ru1−C11 | 137.0 (2) | C12−Ru1−C13 | 38.8 (2) |
| Ru2−Cp2 | 1.9384 (6) | C11−C12 | 1.428 (10) | C12−Ru1−C14 | 67.5 (3) | C12−Ru1−Cp1 | 155.6 (2) |
| C5−C6 | 1.49 (1) | C12−C13 | 1.45 (1) | C13−Ru1−C14 | 38.1 (2) | C13−Ru1−Cp1 | 154.6 (2) |
| C11−C15 | 1.48 (1) | C14−C21 | 1.48 (1) | C14−Ru1−Cp1 | 136.5 (2) | Ru1−Ru2−C11 | 51.3 (2) |
| C13−C14 | 1.41 (1) | C23−C24 | 1.41 (1) | Ru1−Ru2−C23 | 124.3 (2) | Ru1−Ru2−C24 | 135.4 (2) |
| | | | | C23−Ru2−C11 | 78.3 (3) | Ru1−Ru2−Cp2 | 100.06 (3) |
| | | | | Ru1−Ru2−C14 | 53.5 (2) | C11−Ru2−C14 | 76.3 (3) |
| | | | | C23−Ru2−C24 | 37.6 (3) | C11−Ru2−Cp2 | 125.1 (2) |
| | | | | C11−Ru2−C23 | 97.5 (2) | C14−Ru2−Cp2 | 128.0 (2) |
| | | | | C14−Ru2−C24 | 84.9 (3) | Ru1−C11−Ru2 | 76.7 (2) |
| | | | | C24−Ru2−Cp2 | 120.2 (1) | C11−C12−C13 | 112.5 (6) |
| | | | | Ru2−C11−C12 | 117.4 (5) | C13−C14−Ru2 | 118.1 (5) |
| | | | | C12−C13−C14 | 114.4 (7) | | |

[a] Cp stands for the centroid of the ligand.

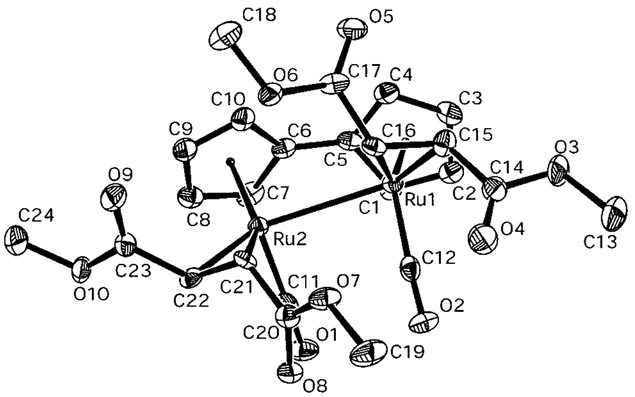

**Figure 2.** ORTEP diagram of **4a** (50% probability surface).

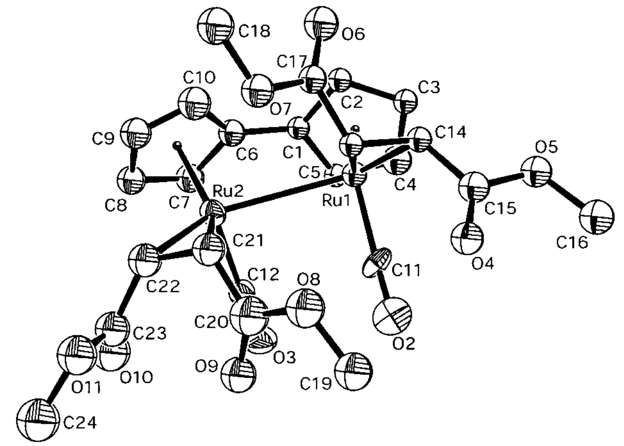

**Figure 3.** ORTEP diagram of **4b** (50% probability surface).

**1** (or **2** and **3**) under the conditions used in the preparation of **3** and **4** using trans-alkene (10 equiv) gave an identical product mixture, in particular, recovered alkene in the trans form (>20:1 trans:cis, NMR),[13] pointing to rapid metal-catalyzed cis−trans isomerization. Light is necessary for this, as in its absence there was no change. Because of the low yield of **4b** and the sensitivity of all alkene complexes to air and light, no mechanistic experiments were attempted. Cis−trans isomerizations of alkenes by ruthenium complexes are precedented, and a number of mechanisms have been proposed. For alkene esters in the absence of Ru−H species, most plausible appears electron transfer from the metal to generate conformationally labile zwitterions or ion pairs.[10d,e,14] In our system, the relative stability of the cis-alkene ligand in **4b** seems to render unlikely simple isomerization pathways in the coordination sphere of the intact $FvRu_2L_4$ core.

**Syntheses and Structures of ($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\mu^2$-$\eta^2$:$\eta^4$-CRCRCRCR)(CO) (6) and ($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\mu^2$-$\eta^2$:$\eta^4$-CRCRCRCR)(THF) (7) (R = $CO_2CH_3$).** While the previous section established the feasibility of attaching alkene ligands in close proximity to a supporting $FvM_2$ scaffold, no evidence was obtained for C−C bond formation, such as to or via intermediate ruthenacyclopentanes.[15] As a consequence, and with the knowledge that the coupling of alkenes with alkynes to metallacyclopentenes is much more readily achieved,[3e,16] **3** was photolyzed (40 h) with dimethyl butynedioate, resulting in the expulsion of the alkene ligand and products **5** and **6** (8:5 by NMR; 83%). These were more readily accessed starting directly from **1**. Thus, irradiation of **1** and the alkyne (14 equiv) in THF purged with $N_2$ for 5 days furnished yellow alkyne complex **5** (25%)[4a] and orange-red dimetallacyclopentadiene **6** (58%) (Scheme 3).

Compound **5** was formed almost quantitatively from **1** after 4 h irradiation and, when reacted further (after isolation), slowly transformed to **6** (50% conversion, 36 h). Remarkably, **6** lost its last CO ligand on further exposure to light in THF, providing the very air sensitive, orange-red THF complex **7** (78%). The same results were recorded regardless of the identity of the starting

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(13) While relevant thermochemical data are not available for the methyl esters, in the corresponding diethyl butenedioates the trans is more stable than the cis isomer by 4−5 kcal mol$^{-1}$ (on the basis of measured heats of hydrogenation): *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, November 1998, National Institute of Standards and Technology; Gaithersburg, MD 20899 (http://webbook.nist.gov).

(14) (a) Borowski, A. F.; Sabo-Etienne, S.; Christ, M. L.; Donnadieu, B.; Chaudret, B. *Organometallics* **1996**, *15*, 1427. (b) Johnson, K. A.; Gladtfelter, W. L. *Organometallics* **1991**, *10*, 376. (c) For a compilation of earlier references, see: Cabeza, J. A.; Del Rio, I.; Garcia-Granda, S.; Lavigne, G.; Lugan, N.; Moreno, M.; Nombel, P.; Perez-Priede, M.; Riera, V.; Rodriguez, A.; Suarez, M.; Van der Maelen, J. F. *Chem. Eur. J.* **2001**, *7*, 2370.

(15) For catalytic intermediates, see: (a) Yamamoto, Y.; Nakagai, Y.; Ohkoshi, N.; Itoh, K. *J. Am. Chem. Soc.* **2001**, *123*, 6372, and references therein. For two rare isolable examples of the products of oxidative coupling of alkenes, see ref 11c and: (b) Kuwae, R.; Kawakami, K.; Tanaka, T. *Inorg. Chim. Acta* **1977**, *22*, 39.

(16) For a compilation of references, see: Amarasinghe, K. K. D.; Chowdhury, S. K.; Heeg, M. J.; Montgomery, J. *Organometallics* **2001**, *20*, 370.

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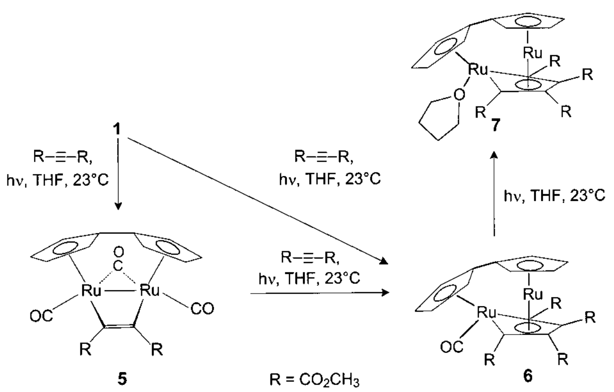
**Scheme 3**



material (**1**−**5**). Again, in the absence of light, no such chemistry was evident, even on heating (130 °C).

The structure of **5** had been ascertained previously on the basis of spectral data,[4a] but an X-ray crystallographic analysis was deemed useful for the purpose of comparison with the other structures in this series. The results are presented in Figure 4 and Table 1.

As in the case of the parent ethyne complex,[4a] the molecule exhibits the parallel alkyne bonding mode[17] and has quite similar structural features (comparison data in parentheses): the Ru−alkyne carbon distances average to 2.08 Å (2.09 Å), those of the Ru atoms to their respective Cp centroids are 1.91 Å (1.92 Å) and 1.90 Å (1.90 Å), and the Ru−Ru bond length is 2.7392(1) Å [2.719(1) Å]. The Fv twist angle is minimal for both (2°), and the corresponding bend is 30.9° (31.6°). The Cp−Cp connection (C5−C6) is identical [1.457(4) Å] to that in **1** [1.457(3) Å].[4a] The only noticeable difference is the larger alkyne carbon (C11−C12) separation of 1.324(4) Å [1.268(4) Å], a consequence of the difference in the ligands' back-bonding ability, but a value within the expected range.[18]

For compound **6**, mass spectral and analytical data indicated the incorporation of an additional alkyne unit and loss of two CO ligands, compared to **5**. IR spectroscopy revealed the remaining CO as ligated terminally ($\tilde{\nu}$ = 1986 $cm^{-1}$), and NMR data established some symmetry by the observation of only four sets of Fv hydrogen signals. In the $^{13}C$ NMR spectrum, the low-field region showed an additional peak to those for the three carbonyl carbons at $\delta = 146.0$ ppm, diagnostic of the α-carbon in a di(cyclopentadienylruthena)cyclopentadiene.[19] The presence of the corresponding $\beta$-carbon is indicated by an additional peak (to the expected six) in the Fv region. An X-ray crystal structure analysis confirmed the suspected connectivity of the precursor alkynes (Figure 5, Table 1). The metallacyclopentadiene is characterized by marginal puckering into an envelope conformation, Ru2 bending slightly away from Ru1 (e.g., torsion angle Ru2−C11−C12−C13 9.8°) and a nearly planar diene portion (C11−C12−C13−C14 1.1°) in what amounts to a distorted ruthenocene fragment bridged by Cp (C6−C10).[18c,19,20] Accordingly, the diene unit exhibits only slight bond alternation (Table 1). The Fv twist (0.6°) and bend angles (33.8°) are comparable to those in **5** and **1**.[4a] Most striking is the short Ru−Ru distance, 2.5750(6) Å, considerably shorter than those in any of the crystallographically scrutinized $FvRu_2$ systems and, while not required by the 18-electron rule, in the regime of a double bond. A Cambridge Crystallographic Data Centre search of "typical" Ru−Ru single and double bonds reveals medium values for the former of 2.848 Å and for the latter of 2.287 Å, with considerable scatter between. Some constitutionally close relatives to **6** in which electron counting suggests the necessity for the formulation of Ru=Ru links are found in the structures of (Ru−Ru bond length in brackets) $(Cp^*Ru)_2(\mu\text{-}CH_2)(SiMe_3)\mu\text{-}Cl$ [2.527(1) Å],[21] $(Cp^*Ru)_2(\mu\text{-}SiPhOMe)(\mu\text{-}OMe)$ ($\mu$-H) [2.569(5) Å],[22] $(Cp^*Ru)_2(\mu\text{-}$

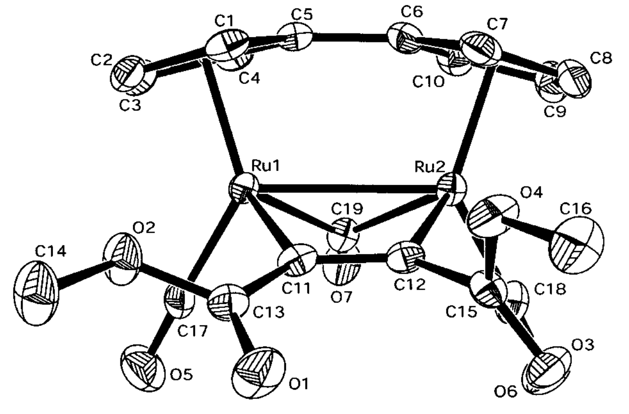


**Figure 4.** ORTEP diagram of **5** (50% probability surface).

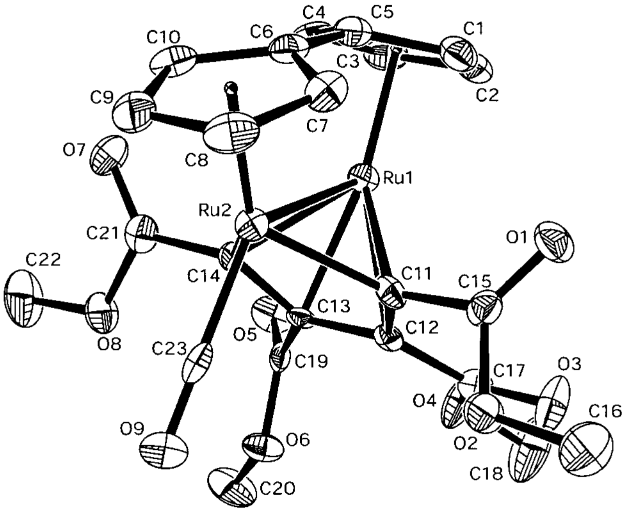


**Figure 5.** ORTEP diagram of **6** (50% probability surface).

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[18] See, inter alia: (a) Casey, C. P.; Cariño, R. S.; Hayashi, R. K.; Schladetzky, K. D. *J. Am. Chem. Soc.* **1996**, *118*, 1617, and references therein. For some examples of crystallographically analyzed methyl diruthenacyclobutenecarboxylates, see: (b) Mirza, H. A.; Vittal, J. J.; Puddephatt, R. J. *J. Coord. Chem.* **1996**, *37*, 131. (c) Muller, F.; van Koten, G.; Polm, L. H.; Vrieze, K.; Zoutberg, M. C. *Organometallics* **1989**, *8*, 1340. (d) Muller, F.; van Koten, G.; Kraakman, M. J. A.; Vrieze, K.; Zoet, R.; Duineveld, K. A. A.; Heijdenrijk, D.; Stam, C. H.; Zoutberg, M. C. *Organometallics* **1989**, *8*, 982.

[19] For example, see: (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1990**, *9*, 1106. (b) Omori, H.; Suzuki, H.; Moro-oka, Y. *Organometallics* **1989**, *8*, 1576.

[20] See also other selected related $(CpRu)_2$ structures: (a) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Tanase, T.; Hidai, M. *Organometallics* **1994**, *13*, 4214. (b) Brady, L. A.; Dyke, A. F.; Garner, S. E.; Knox, S. A. R.; Irving, A.; Nicholls, S. M.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 487. (c) He, X. D.; Chaudret, G.; Dahan, F.; Huang, Y.-S. *Organometallics* **1991**, *10*, 970. For a related (tetramethoxycarbonyl)-$Ru_2(CO)_6$ complex: (d) Bruce, M. I.; Matisons, J. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1983**, *251*, 249.

[21] Lin, W.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 2309.

[22] Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1992**, *11*, 3918.

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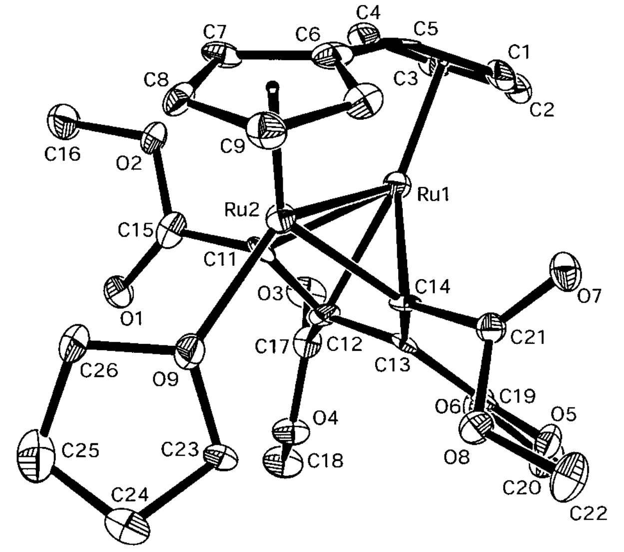

**Figure 6.** ORTEP diagram of **7** (50% probability surface).

$H)_2(\mu$-PhCCPh) [2.552(1) Å],[23] and $(CpRu)_2(\mu$-CO)($\mu$-PhCCPh) [2.505(1) Å ].[24] While these data seem to suggest a metal−metal double bond for **6**, there are other structures in which short single bonds in the same range occur, their occurrence rationalized by the bidentate effect of short bridges present.[25] In **6**, compared to its $(CpRu)_2$ metallacyclopentadiene relatives, the Fv strain effect[2c] would be expected to lengthen the Ru−Ru bond, an expectation at odds with reality. An explanation for this discrepancy might be based on electronic considerations. Thus, analysis of the bonding picture for the $Ru_2(\mu_2\text{-}\eta^2\text{:}\eta^4\text{-}C_4R_4)$ core[26] reveals significant delocalization, stabilizing the intermetallic overlap. Attaching the delocalized Fv ligand would have the same electronic effect on the M−M bond,[2a,c] the two reinforcing each other and resulting in the observed short distance. An illustrative resonance structure would be one involving a dipolar Fv bridge in which a (Ru1) ruthenocenium fragment is attached to a $[CpRu_2(CO)(R_2)]^-$ anion. As we shall see, the $FvRu_2(C_4Ru_4)$ core in **6** and its derivatives is extraordinarily robust.

The structure of **7** was already strongly implicated on comparison of its spectral data with those of **6**. In particular, the IR peak for the metal-bound CO ligand disappeared, and the NMR spectra showed peaks for coordinated THF at $\delta = 1.67$, 3.46 ($^1$H NMR) and 24.9, 49.4 ppm ($^{13}$C NMR), respectively. X-ray diffraction analysis resulted in the data in Figure 6 and Table 1. The structural details are very similar to those of **6**. Thus, the Ru2−C11−C12−C13 torsion angle is 8.0°, that corresponding to C11−C12−C13−C14 is 1.8°, the Fv twist is 0.9°, the Fv bend is 33.0°, and many related atomic separations are almost identical. The Ru−Ru bond is again unusually short, 2.5603(6) Å. The THF ligand is attached to Ru2 fairly normally.[27]

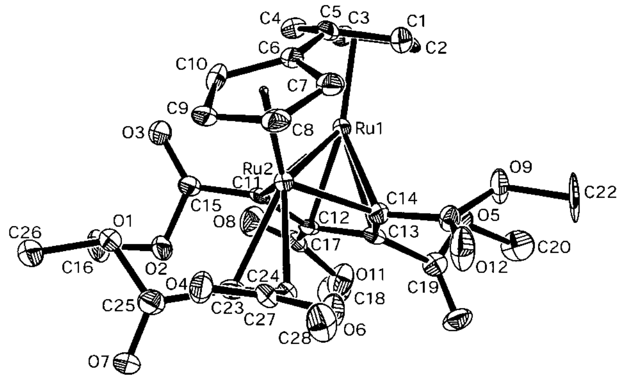

**Figure 7.** ORTEP diagram of **8** (50% probability surface).

**Alkyne Cyclotrimerizations.** The formation of **6** and **7** by alkyne oxidative coupling is unprecedented for $FvM_2$ complexes. In an effort to observe further alkyne "stitching" along the lines documented in other dinuclear complexes of Ru[19a,20b,28] (and other metals),[28d,29] **6** or **7** was treated with excess (15−30 equiv) dimethyl butynedioate and either heated or photolyzed, but no new organometallic complexes were evident in the resulting solutions. Under thermal conditions (135 °C) there was either no reaction (**6**, 72 h) or decomposition (**7**, 2.5 h) accompanied by ca. 15% conversion of the alkyne to hexamethyl benzenehexacarboxylate. On irradiation (23 °C), both **6** and **7** exhibited some limited ability to cyclotrimerize the alkyne (20% conversion, 4 days). A brief experimental scan of other alkynes, such as ethynylbenzene, (phenylethynyl)benzene, and bis(trimethylsilyl)acetylene, failed to produce any isolable organometallic or organic compounds. Similar limited results were obtained with **1**−**5**, at best 50% conversion of dimethyl butynedioate to cyclotrimer recorded after days of irradiation in THF at 23 °C. Typically, **6** and **7** could be detected by $^1$H NMR in the resulting crude reaction mixtures. These results are disappointing and surprising in light of the rich ligand exchange chemistry of **7** (vide infra). Steric hindrance may be the culprit, if weak coordination prevents sufficient alkyne bending.[30]

**Thermal and Photochemical Ligand Exchange in $FvRu_2(C_4R_4)L$ ($R = CO_2CH_3$).** The lability of the ligated THF in **7** was readily established by treatment with CO (1 atm, THF, 75 °C, 4 days), which regenerated **6** (95%). Encouraged by this result, other potential ligands were explored (Scheme 4). Thus, heating **7** with dimethyl *cis*-2-butenedioate (THF, 85 °C) smoothly provided red and air stable compound **8** in 83% yield (quantitative by NMR). The ligand exchange was evi-

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[26] Astier, A.; Daran, J.-C.; Jeannin, Y.; Rigault, C. *J. Organomet. Chem.* **1983**, *241*, 53.

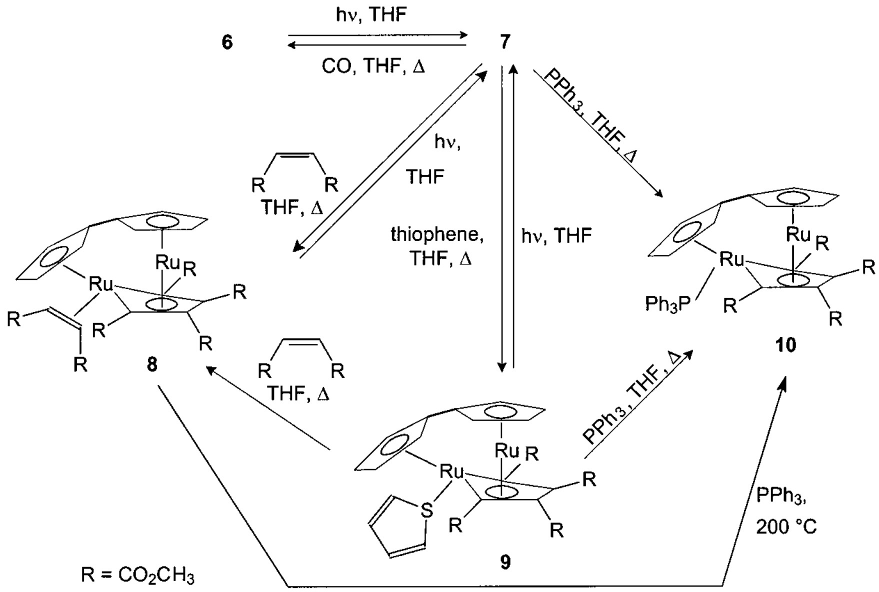
[27] $(Ru-O)_{av} = 2.15$ Å. See: Han, S.-H.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 2561.

[28] See, inter alia: (a) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem.* **2000**, *53*, 99. (b) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem.* **1989**, *52*, 413. (c) Pertici, P.; Verrazzani, A.; Vitulli, G.; Baldwin, R.; Bennett, M. A. *J. Organomet. Chem.* **1998**, *551*, 37. (d) Knox, S. A. R. *J. Organomet. Chem.* **1990**, *400*, 255.

[29] For a sampling of references, see: (a) Baxter, R. J.; Knox, G. R.; Moir, J. H.; Pauson, P. L.; Spicer, M. D. *Organometallics* **1999**, *18*, 206. (b) Bartlett, I. M.; Connelly, N. G.; Legge, M. S.; Martín, A. J.; Metz, B.; Orpen, A. G. *Chem. Commun.* **1996**, 1877. (c) Giordano, R.; Sappa, E.; Predieri, G. *Inorg. Chim. Acta* **1995**, *228*, 139. (d) Gervasio, G.; Sappa, E.; Markó, L. *J. Organomet. Chem.* **1993**, *444*, 203. (e) Chisholm, M. H.; Clark, D. L.; Hampden-Smith, M. J.; Hoffman, D. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 432. (f) Green, M.; Kale, P. A.; Mercer, R. J. *J. Chem. Soc., Chem. Commun.* **1987**, 375. (g) Brammer, L.; Green, M.; Orpen, A. G.; Paddick, K. E.; Saunders, D. R. *J. Chem. Soc., Dalton Trans.* **1986**, 657.

[30] For a compilation of data, see: Gervasio, G.; Rosetti, R.; Stanghellini, P. L. *Organometallics* **1985**, *4*, 1612.

**Scheme 4**



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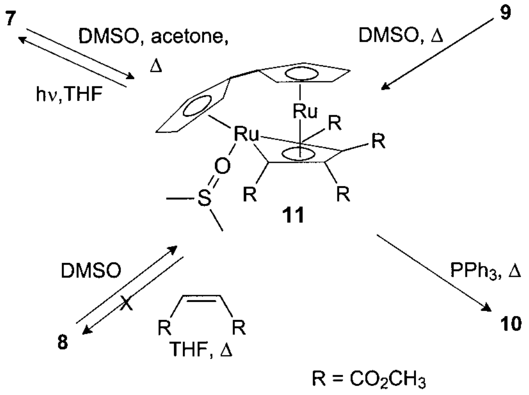
dent in the NMR spectra, in which the signals for THF had disappeared and new ones, characteristic of an $\eta^2$-alkenedioate, had appeared ($\delta_H = 3.18$ ppm, $\delta_C = 48.2$ ppm). An X-ray crystal structure determination confirmed this assignment and established the (less hindered) exo-configuration of the new alkene moiety (Figure 7, Table 1). The Ru2−C11−C12−C13 torsion angle is 9.8°, that for C11−C12−C13−14 is 2.3°, the Fv twist is 1.8°, and the corresponding bend angle is 32.2°. The bound butenedioate carbons are at unexceptional distances from Ru2 (average value 2.184 Å). The Ru−Ru bond is again short, 2.5947(9) Å.

Complex **8** is intriguing, inasmuch as it is an extremely rare example of a dimetallacyclopentadiene(alkene) complex,[31] a species that seems an attractive intermediate in a potential dinuclear metal complex mediated [2+2+2] cycloaddition of two alkynes and an alkene.[9,16] Unfortunately, **8** could not be induced (yet) to proceed in a detectable way along such a pathway. Thus, for example, heating in the presence of excess butenoate was ineffective, as was the same treatment with dimethyl butynedioate, attesting to the stability of the system. Eventually, heating **8** in molten $PPh_3$ to 200 °C for 1 h converted it to **10** (90%)! Irradiation in THF for 5 days merely regenerated **7** (78%).

Compound **10** was much more readily made directly from **7** ($PPh_3$, THF, 85 °C, 78%), and its structural assignment rests on spectral and analytical measurements. Similarly, thiophene in THF at 85 °C displaced THF from **7** to give brown, air sensitive **9** (72%). The formulation as an $\mu^1$(S) complex is suggested by the presence of an AA′ BB′ multiplet centered at $\delta = 7.02$ and 7.27 ppm in the $^1$H NMR spectrum and corresponding carbon resonances at $\delta = 128.5$ and 140.2 ppm.[32] Stable $\mu^1$(S) complexes of thiophene are rare, and most contain a positively charged metal nucleus.[33] Dinuclear ruthenium activation of thiophene is known to cause C−S bond cleavage,[34] but none was observed here. Rather, heating **9** (THF, 65 °C) with the appropriate ligands led to **8** (82%) and **10** (85%), respectively. The kinetics of the second process (vide infra) suggest an appreciable thiophene−Ru bond strength of perhaps 30 kcal mol$^{-1}$. Again, irradiation of **9** in THF reconstituted the original relay complex **7** (80%), but the same protocol for **10** left unchanged starting material. Indeed, **10** seems to be most stable in this series, recovered unchanged when irradiated or heated in the presence of dimethyl *cis*-butenedioate or butynedioate. Another ligand exchange manifold was established with the dimethyl sulfoxide complex **11** at its center (Scheme 5). This compound could be made by heating **7** in acetone in the presence of excess DMSO (90%), a process that is reversible with light (THF, 23 °C, 1 h, **7**:**11** = 4:1). Alternatively, **8** and **9** can function as thermal precursors of **11**, the former (DMSO, 210 °C, 30 min, **11**:**8** = 5.5:1) being much more sluggish than the latter (DMSO, 100 °C, 2 h, **11**:**9** = 9:1).

**Scheme 5**



Red compound **11** decomposed on column chromatography and could not be obtained analytically pure. Its

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(31) For two other examples, see: (a) Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fuku-shima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129. (b) Noda, I.; Yasuda, H.; Nakamura, A. *Organometallics* **1983**, *2*, 1207.

(32) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436.

(33) Angelici, R. J. *Organometallics* **2001**, *20*, 1259, and references therein.

(34) (a) Jones, W. D.; Chin, R. M.; Hoaglin, C. L. *Organometallics* **1999**, *18*, 1786. (b) Koczaja Dailey K. M.; Rauchfuss, T. B.; Rheingold, A. L.; Yap, G. P. A. *J. Am. Chem. Soc.* **1995**, *117*, 6396.

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structure rests on spectral data, in particular mass and NMR spectroscopy. In the IR spectrum, a band at $\tilde{\nu}$ = 1030 cm$^{-1}$ is consistent with (but does not prove) O−Ru bonding.[35] The complex is thermally quite robust, surviving unchanged heating in neat dimethyl butenedioate at 200 °C for 12 h. On the other hand, while heating with $PPh_3$ in acetone (100 °C, sealed tube, 1.5 h) left **11** intact, switching to neat $PPh_3$ (200 °C, 12 h) gave **10**, admixed with **11** (2:1). The combined results point to the following trend in bonding ability to the $FvRu_2(C_4R_4)$ fragment of the ligands investigated: THF < thiophene < dimethyl *cis*-butenedioate < DMSO < $PPh_3$.

**Kinetics of Ligand Exchange.** The mechanism of the thermal reactions described in the preceding section was of interest fundamentally and, if proceeding via rate-determining ligand dissociation, might provide some estimate of ligand−metal bond strengths. The conversion of **9** to **10** was chosen to probe this issue kinetically, as it was particularly clean, took place in a convenient temperature range, and featured thiophene as the leaving entity, a ligand receiving much current attention in connection with model studies of catalytic hydrodesulfurization.[33] Phosphine-independent rates were established by measurement of the disappearance of **9** (and appearance of **10**) in $C_6D_6$ at 86 °C using 1, 2, and 4 equiv of $PPh_3$, $k_{obs} = 7.4 \times 10^{-5}$ s$^{-1}$. For comparison, the neutral $CpRe(CO)_2$(thiophene) shows similar behavior at 80 °C, $k_{obs} = 3.0 \times 10^{-4}$ s$^{-1}$.[36] Further experiments were carried out in a similar fashion (4 equiv of $PPh_3$) at 69, 76, 86, and 96 °C, yielding clean first-order kinetics, $E_a = 30.5$ kcal mol$^{-1}$, $\Delta H^\ddagger = 29.7$ kcal mol$^{-1}$, $\Delta S^\ddagger = 5.1$ eu, $\Delta G^\ddagger(298\text{ K}) = 28.2$ kcal mol$^{-1}$. The mechanism of exchange thus appears to be dissociative[37] and the Ru−S bond appreciably strong.

## Conclusions

$FvRu_2(CO)_4$ (**1**), on photoirradiation, has been shown to bind one and two alkene moieties, in the form of the dimethyl butenedioates, with remarkable diastereoselectivity to give complexes **3** and **4**. While C−C bond formation from these compounds could not be achieved, their isolation demonstrates the potential utility of the Fv(M−M) motif for the activation of alkenes. In this connection, a report of ethylene polymerization with Fv[CpZr($\mu$-Cl)]$_2$ is noteworthy.[38] In contrast, alkyne coupling is observed with dimethyl butynedioate to furnish the diruthenacyclopentadienes $FvRu_2(\mu_2\text{-}\eta^2\text{:}\eta^4\text{-}C_4R_4)L$, **6**−**11**, in which L can be exchanged thermally (by a dissociative mechanism) or photolytically. As such, the resulting (and, indeed, in some cases novel) complexes appear ideally suited to enter into further reactions by incorporating L into the metallacyclic frame, but so far, this has not occurred. The shortening of the Ru−Ru bond explicitly measured for **5**−**8** is interpreted to be another manifestation of the "Fv effect", namely, extensive delocalization through the Fv ligand.

## Experimental Section

**General Procedures.** Unless otherwise indicated, all manipulations were conducted under purified $N_2$ either in a Vacuum Atmospheres Inc. glovebox or using standard Schlenk/vacuum line techniques. Tetrahydrofuran (THF), dimethoxyethane (DME), and diethyl ether ($Et_2O$) were distilled from either potassium or sodium benzophenone ketyl immediately prior to use. Diethylene glycol dimethyl ether (diglyme), decane, and acetonitrile were distilled from liquid sodium, lithium aluminum hydride, or calcium hydride, respectively. Chromatography solvents were deoxygenated by purging with a stream of $N_2$. $FvRu_2(CO)_4$ (**1**)[4a] was prepared by literature methods. Crystals of **3**−**8** suitable for analysis by X-ray diffraction were obtained by slow diffusion of hexanes into a saturated methylene chloride or tetrahydrofuran solution at 0 °C or room temperature. All other chemicals were obtained from commercial suppliers and used without further purification.

Photoreactions were performed in Pyrex vessels employing a Rayonet Model RPR 100 photochemical reactor charged with eight light rods of primary output at 350 nm and another eight at 300 nm. Thermal reactions executed above the boiling point of solvent took place in sealed tubes.

$^1$H NMR spectra were recorded on UC Berkeley (UCB) AMX-300, Bruker AM-400, or DRX-500 MHz instruments equipped with Cryomagnets Inc. superconducting magnets and Nicolet Model 1180 or 1280 data collection systems. $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra were measured on the Bruker AM-400 or DRX-500 instruments. $^1$H and $^{13}$C{$^1$H} NMR spectra are reported in ppm downfield from tetramethylsilane and are referenced to the resonances of the deuterated solvent. IR spectra were obtained on a Perkin-Elmer Model 681 spectrophotometer and UV−vis absorptions on a Hewlett-Packard Model 8450A UV−visible diode array system. Mass spectral data were provided by the UCB Mass Spectrometry Laboratory and collected on either an AEI-MS12 mass spectrometer at 70 eV or a Finnigan 4000 instrument. Chemical ionization (CI) techniques used methane, whereas fast atom bombardment (FAB) studies relied on glycerol, nitrobenzyl alcohol (NBA), or tetramethylenesulfone (TMES) matrixes. Because the natural isotopic distribution of Ru resulted in broad peak envelopes, only the major peak for each fragment is reported. All peak patterns were accurately reproduced by calculation. Elemental analyses were carried out by the UCB Microanalytical Laboratory. HPLC used HP series 1100 equipment on normal phase Microsorb-Si. Melting points were observed in sealed glass capillaries under $N_2$ on a Büchi melting point apparatus and are uncorrected.

**($\eta^5$:$\eta^5$-Fulvalene)$Ru_2$($\eta^2$-*trans*-CHR=CHR)$(CO)_3$ (R = $CO_2CH_3$) (3).** A solution of **1** (0.100 g, 0.226 mmol) and dimethyl *trans*-butenedioate (0.50 g, 3.47 mmol) in THF (100 mL) was placed in a Pyrex tube and irradiated for 6 h, while being purged with $N_2$. The content was concentrated to saturation by vacuum transfer and chromatographed on alumina (II), using pentane. First to be eluted was crystalline **2** (9 mg, 9%). Switching solvent to $CH_2Cl_2$ produced a yellow band containing unreacted **1** (30 mg, 30%). Finally, ethyl acetate/methylene chloride (1:4) separated yellow crystals of **3** (52 mg, 41%): mp 175−176 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.88 (m, 1H), 5.85 (m, 1H), 5.68 (m, 1H), 5.66 (m, 1H) 4.19 (m, 1H), 4.19 (d, $J$ = 6.9 Hz, 1H), 3.90 (d, $J$ = 7.2 Hz, 1H), 3.78 (m, 1H), 3.73 (s, 3H), 3.62 (m, 1H), 3.51 (m, 1H), 3.37 (s, 3H); $^{13}$C{$^1$H} NMR ($CDCl_3$) $\delta$ 203.3, 203.1, 202.2, 176.3, 175.8, 102.2, 92.35, 91.20, 89.65, 88.70, 88.23, 79.47, 78.48, 77.26, 76.17, 51.14, 50.65, 36.98, 36.16; IR (film) $\tilde{\nu}_{CO}$ 2005, 1951, 1692 cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 255 sh ($\epsilon$ 9900), 280 sh (9000), 305 (8600), 340 sh (5200), 410 sh (2400) nm; EI-MS *m/z* (rel intensity) 559(1), 531(52), 503(18), 475(4), 388(100), 357(70), 330(46), 178(44); HRMS calcd for $C_{19}H_{16}O_7\,{}^{99}Ru\,{}^{104}Ru$ 558.9010, found 558.9020. Anal. Calcd for $C_{19}H_{16}O_7Ru_2$: C, 40.86; H, 2.89. Found: C, 40.65; H, 2.58.

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[35] (a) Alessio, E.; Balducci, G.; Calligaris, M.; Costa, G.; Attia, W. M.; Mestroni, G. *Inorg. Chem.* **1991**, *30*, 609. (b) For an S-bound Ru(II)(DMSO) complex, see: Jazzar, R. F. R.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2001**, *20*, 3745.

[36] Choi, M.-G.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 1417.

[37] Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

[38] Hamura, S. *Kyushu Daigaku Kino Busshitsu Kagaku Kenkyusho Hokoku* **1999**, *13*, 13.

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**Other Routes to 3. Method a.** From **2**: A THF-$d_8$ (0.5 mL) solution of **2** (5 mg, 0.011 mmol) and the trans-alkene (10 mg, 0.069 mmol) was irradiated as described above. After 15 h, an $^1$H NMR spectrum indicated the formation of **3** in 60% yield, in addition to **1** (20%) and **2** (7%). The ratio of trans to cis alkene was 20:1.

**Method b.** From **1** with cis-alkene: A THF-$d_8$ (0.5 mL) solution of **1** (5 mg, 0.011 mmol) and the alkene (7 mg, 0.05 mmol) was irradiated as described above. After 6 h, an $^1$H NMR spectrum indicated the formation of **3** in 48% yield, in addition to **1** (30%) and **2** (10%). The ratio of trans to cis alkene was >20:1.

**Typical Catalytic Isomerization of Dimethyl *cis*-Butenedioate by 3.** A THF-$d_8$ (0.5 mL) solution of **3** (5.5 mg, 0.010 mmol) and cis-alkene (15 mg, 0.10 mmol) was irradiated with 300 nm light. After 12 h, an $^1$H NMR spectrum indicated the formation of the mixture of **1**, **2**, and **3** in the ratio 3:1:5. The ratio of trans to cis alkene was >20:1.

**Irradiation of 3.** A THF-$d_8$ (0.5 mL) solution of **3** (5.5 mg, 0.010 mmol) was irradiated for 6 h. An $^1$H NMR spectrum indicated the formation of a mixture of **1**, **2**, and **3** in the ratio 2:1:5.

**($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\eta^2$-*trans*-CHR═CHR)$_2$(CO)$_2$ (4a) and ($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\eta^2$-*cis*-CHR═CHR)($\eta^2$-*trans*-CHR═CHR)(CO)$_2$ (R = CO$_2$CH$_3$) (4b).** A solution of **1** (100 mg, 0.23 mmol) and the trans-alkene (450 mg, 3.13 mmol) in THF (50 mL) was irradiated as in the preparation of **3** but for 48 h, while being slowly purged with argon. Chromatography as above gave **2** (5 mg, 5%), then unreacted **1** (7.7 mg, 8%). Further elution (ethyl acetate/methylene chloride, 1:4) separated **3** (69 mg, 54%) and then a red band containing an unknown complex (15 mg). A third yellow band consisted of **4a** (16 mg, 10%). Changing the solvent ratio from 1:4 to 1:2 produced a fourth yellow band of **4b** and another unknown (12 mg). They were separated by preparative HPLC (ethyl acetate/methylene chloride, 4:1) to give pure **4b** (6 mg, 4%) and then the yellow unknown (4 mg).

**Red unknown:** red crystals, mp 250−253 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.75 (m, 1H), 5.68 (m, 1H), 5.52 (d, $J = 9.4$ Hz, 1H), 5.32 (m, 1H), 5.24 (m, 1H), 4.58 (m, 1H), 3.87 (m, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.59 (s, 3H), 3.52 (m, 1H), 3.48 (s, 3H), 3.43 (d, $J = 9.6$ Hz, 1H), 3.27 (d, $J = 9.6$ Hz, 1H), 2.86 (d, $J = 9.6$ Hz, 1H), 2.51 (m, 1H); $^{13}$C{$^1$H} NMR (500 MHz, CDCl$_3$) $\delta$ 203.1, 180.7, 176.8, 176.3, 175.4, 133.4, 102.3, 90.94, 88.13, 86.80, 84.94, 83.18, 77.33, 76.63, 76.55, 52.31, 51.59, 51.45, 50.52, 47.71, 46.76, 37.57, 31.09; IR (KBr) $\tilde{\nu}_{CO}$ 1932, 1702 cm$^{-1}$; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 285 sh, 366, 486; EI-MS $m/z$ (rel intensity) 648(6), 531(4), 503(7), 443(5), 113(100). Anal. Calcd for C$_{24}$H$_{24}$O$_{10}$Ru$_2$: C, 42.73; H, 3.59. Found: C, 44.19; H, 4.49.

**Complex 4a:** yellow crystals, mp 212−213 °C; $^1$H NMR (300 MHz, acetone-$d_6$) $\delta$ 6.70 (m, 1H), 6.08 (m, 1H), 5.71 (m, 1H), 5.38 (m, 1H), 4.57 (d, $J = 9.9$ Hz, 1H), 4.47 (d, $J = 9.6$ Hz, 1H), 4.31 (d, $J = 9.6$ Hz, 1H), 4.31 (m, 1H), 4.30 (d, $J = 9.9$ Hz, 1H), 4.06 (m, 1H), 3.94 (m, 1H), 3.89 (m, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.64 (s, 3H), 3.33 (s, 3H); $^{13}$C{$^1$H} NMR (CDCl$_3$) $\delta$ 201.2, 197.5, 178.2, 176.7, 176.1, 174.7, 106.6, 105.7, 90.84, 88.18, 87.36, 84.91, 81.33, 81.27, 79.69, 75.20, 51.82, 51.44, 51.41, 50.79, 45.29, 44.31, 44.10, 42.88; IR (film) $\tilde{\nu}_{CO}$ 1982, 1946, 1693 cm$^{-1}$; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 290 sh ($\epsilon$ 7000), 307 sh (6000), 327 sh (5000), 373 (4800) nm; FAB-MS $m/z$ 677; FAB-HRMS calcd for (C$_{24}$H$_{24}$O$_{10}$$^{101}$Ru$^{104}$Ru)H$^+$ 677.9553, found 677. 9558. Anal. Calcd for C$_{24}$H$_{24}$O$_{10}$Ru$_2$: C, 42.73; H, 3.59. Found: C, 42.34; H, 3.31.

**Complex 4b:** yellow crystals, mp 182−185 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.36 (m, 1H), 6.15 (m, 1H), 5.56 (m, 1H), 4.99 (m, 1H), 4.86 (m, 1H), 4.45 (d, $J = 9.5$ Hz, 1H), 4.36 (d, $J = 9.5$ Hz, 1H), 4.15 (d, $J = 11.2$ Hz, 1H), 4.11 (d, $J = 11.2$ Hz, 1H), 3.93 (m, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 3.72 (m, 1H), 3.59 (m, 1H) 3.29 (s, 3H); $^{13}$C{$^1$H} NMR (500 MHz, CDCl$_3$) $\delta$ 202.9, 199.0, 176.3, 175.2, 174.4, 173.1, 129.6, 105.1, 90.64, 87.01, 85.30, 81.14, 80.60, 75.42, 52.57, 51.79, 51.36, 50.63, 41.69, 41.60, 40.86, 34.17, 30.88, 29.75; IR (KBr, $\tilde{\nu}_{CO}$ 2003, 1942, 1706, 1687; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 255 sh ($\epsilon$ 4500), 297 sh (4000), 381 (3500) nm; FAB-MS $m/z$ 663; EI-MS $m/z$ (rel intensity) 531(22), 503(11), 475(4), 457(3), 443(7), 416(10), 388(30), 357(20) 331(12) 113 (100). Anal. Calcd for C$_{24}$H$_{24}$O$_{10}$Ru$_2$: C, 42.73; H, 3.59. Found: C, 42.43; H, 3.41.

**Yellow unknown:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.12 (br s, 1H), 5.75 (br s, 1H), 5.43 (br s, 1H), 4.69 (br s, 1H), 4.68 (br s, 1H), 4.45 (br s, 1H), 4.45 (br s, 1H), 4.06 (br s, 1H), 3.92 (br s, 1H), 3.75 (br s, 1H), 3.75 (s, 9H), 3.57 (br s, 1H), 3.55 (br s, 1H), 3.39 (s, 3H); $^{13}$C{$^1$H} NMR (500 MHz, CDCl$_3$) $\delta$ 198.4, 198.3, 176.7, 175.5, 107.7, 103.3, 88.53, 86.46, 85.68, 82.84, 82.67, 80.43, 80.25, 79.05, 51.48, 51.11, 50.92, 44.81, 43.61, 41.94 (two carbonyl carbons could not be located); IR (KBr) $\tilde{\nu}_{CO}$ 1964, 1950, 1699 cm$^{-1}$; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 259 sh, 297 sh, 347 sh, 417 sh nm; FAB-MS $m/z$ 663; EI-MS $m/z$ (rel intensity) 531(22), 503(12), 475(4), 444(7), 415(10), 388(36), 357(26), 331(15), 113(100).

**($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$(CO) (R = CO$_2$CH$_3$) (6).** A solution of **1** (0.221 g, 0.500 mmol) and dimethyl butynedioate (1.00 g, 7.04 mmol) in THF (200 mL) was irradiated for 5 days, while being slowly purged with N$_2$. The content was concentrated by vacuum transfer and chromatographed on silical gel using ethyl acetate/methylene chloride (1:4) as eluent to collect the major red band. Removal of solvent under reduced pressure and recrystallization of the red residue at ambient temperature yielded orange-red **6** (186 mg, 58%). Subsequent elution furnished a yellow band containing **5** (67 mg, 25%). Complex **6**: mp 214−215 °C; $^1$H NMR (300 MHz, acetone-$d_6$) $\delta$ 5.83 (m, 2H), 5.46 (m, 2H), 4.81 (m, 2H), 4.33 (m, 2H); 3.66 (s, 6H), 3.50 (s, 6H); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.60 (m, 2H), 5.51 (m, 2H), 4.78 (m, 2H), 4.26 (m, 2H), 3.75 (s, 6H), 3.59 (s, 6H); $^{13}$C{$^1$H} NMR (CDCl$_3$) $\delta$ 198.8, 174.9, 168.7, 146.0, 100.8, 90.57, 90.35, 84.73, 84.11, 81.51, 78.28, 52.72, 52.15; IR (film) $\tilde{\nu}_{CO}$ 1986, 1724, 1711 cm$^{-1}$; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 233 ($\epsilon$ 22 000), 287 sh (6100), 470 (1550) nm; EI-MS $m/z$ (rel intensity) 644 (100), 614 (6), 556 (12), 381 (60), 357 (40). Anal. Calcd for C$_{23}$H$_{20}$O$_9$Ru$_2$: C, 42.99; H, 3.14. Found: C, 43.31; H, 2.83.

**Typical Photochemical Cyclotrimerizations of Dimethyl Butynedioate. Method a.** A THF-$d_8$ (0.5 mL) solution of **1** (5 mg, 0.01 mmol) and the alkyne (21 mg, 0.15 mmol) was irradiated for 20 days. An $^1$H NMR spectrum showed a mixture of alkyne and hexamethyl benzenehexacarboxylate in the ratio 2.6:1, in addition to **6** and **7** (1:1).

**Method b.** A THF-$d_8$ (0.5 mL) solution of **3** (5.5 mg, 0.01 mmol) and the alkyne (40 mg, 0.28 mmol) was irradiated for 20 days. An $^1$H NMR spectrum revealed a mixture of alkyne and cyclotrimer in the ratio 5:2.

**Method c.** An acetone-$d_6$ (0.5 mL) solution of **5** (5.5 mg, 0.01 mmol) and the alkyne (40 mg, 0.28 mmol) was irradiated for 4 days. An $^1$H NMR spectrum showed a 1:1 ratio of alkyne to cyclotrimer.

**Method d.** A THF-$d_8$ (0.5 mL) solution of **6** (3 mg, 0.005 mmol) and the alkyne (20 mg, 0.14 mmol) was irradiated for 11 days. An $^1$H NMR spectrum indicated a 6:1 ratio of alkyne to cyclotrimer and traces of **7**.

**($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$(C$_4$H$_8$O) (R = CO$_2$CH$_3$) (7).** A solution of **6** (0.321 g, 0.50 mmol) in THF (300 mL) was irradiated for 7 days, while being purged with N$_2$. The content was concentrated by vacuum transfer and crystallized by diffusion of hexanes into the dark brown THF solution at ambient temperature to yield orange-red **7** (267 mg, 78%): mp 230−231 °C; $^1$H NMR (300 MHz, THF-$d_8$) $\delta$ 5.70 (m, 2H), 5.29 (m, 2H), 4.45 (m, 2H), 4.16 (m, 2H), 3.62 (s, 6H), 3.50 (s, 6H), 3.48 (m, 4H), 1.62 (m, 4H); $^1$H NMR (300 MHz, acetone-$d_6$) $\delta$ 5.80 (m, 2H), 5.26 (m, 2H), 4.44 (m, 2H), 4.19 (m, 2H), 3.64 (s, 6H), 3.54 (s, 6H), 3.49 (m, 4H), 1.64 (m, 4H); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.63 (m, 2H), 5.43 (m, 2H), 4.48 (m, 2H), 4.20 (m, 2H), 3.77 (s, 6H), 3.63 (s, 6H), 3.46 (m, 4H), 1.67 (m, 4H); $^{13}$C{$^1$H} NMR (THF-$d_8$) $\delta$ 174.7, 168.3, 145.3, 99.82, 84.78, 84.57, 82.07, 80.79, 79.83, 73.18, 70.49, 49.95,

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**Table 2. Summary of Crystal and Data Collection Parameters for 3−8**

| | **3** | **4a** | **4b** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|
| empirical formula | $C_{38}H_{32}Ru_4O_{14}$ | $C_{24}H_{24}O_{10}Ru_2$ | $C_{24}H_{24}O_{10}Ru_2$ | $C_{19}H_{14}O_7Ru_2$ | $C_{23}H_{20}O_9Ru_2$ | $C_{26}H_{28}O_9Ru_2$ | $C_{28}H_{28}O_{12}Ru_2$ |
| fw | 1116.94 | 674.59 | 674.59 | 556.46 | 642.55 | 686.64 | 758.66 |
| cryst size (mm) | 0.32 × 0.21 × 0.05 | 0.26 × 0.14 × 0.07 | 0.19 × 0.12 × 0.04 | 0.36 × 0.15 × 0.07 | 0.15 × 0.05 × 0.05 | 0.21 × 0.03 × 0.06 | 0.21 × 0.29 × 0.03 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic | triclinic | monoclinic | orthorhombic |
| lattice type | primitive | primitive | primitive | primitive | primitive | primitive | primitive |
| no. reflns used for unit cell determination | 6433 | 3800 | 1541 | 6055 | 2412 | 1974 | 6282 |
| $2\theta$ range (deg) | 3−52.1 | 3−52.0 | 3−52.3 | 3−52.0 | 3−52.2 | 3−52.3 | 3−52.4 |
| $a$ (Å) | 14.8258(4) | 9.8473(1) | 11.443(1) | 7.9009(5) | 8.5872(3) | 10.5575(4) | 14.305(4) |
| $b$ (Å) | 17.5445(5) | 18.5092(1) | 13.274(1) | 14.6035(9) | 10.9541(4) | 12.9868(5) | 14.149(6) |
| $c$ (Å) | 15.6526(3) | 13.9317(3) | 15.811(1) | 16.076(1) | 13.7158(5) | 18.4548(3) | 26.896(9) |
| $\alpha$ (deg) | | | | | 88.442(1) | | |
| $\beta$ (deg) | 112.552(1) | 106.250(1) | 92.237(2) | 96.973(1) | 86.365(1) | 95.954(2) | |
| $\gamma$ (deg) | | | | | 67.168(1) | | |
| $V$ (Å$^3$) | 3760.1(2) | 2437.83(5) | 2399.6(3) | 1841.2(2) | 1186.69(7) | 2516.7(1) | 5443(5) |
| space group | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ | $Pbca$ (no. 61) |
| $Z$ | 4 | 4 | 4 | 4 | 2 | 4 | 8 |
| $D_{calc}$, g/cm$^3$ | 1.973 | 1.838 | 1.867 | 2.007 | 1.859 | 1.812 | 1.851 |
| $F_{000}$ | 2192.00 | 1344.00 | 1344.00 | 1088.00 | 636.00 | 1376.00 | 3040.00 |
| $\mu$, cm$^{-1}$ | 16.46 | 12.96 | 13.17 | 16.81 | 13.68 | 12.54 | 11.77 |
| temp, °C | −110 | −147 | −130 | −100 | −104 | −134 | −100 |
| scan rate (s) | 10 | 10 | 10 | 10 | 10 | 10 | 20 |
| $T_{max}$, $T_{min}$ | 0.934, 0.701 | 0.921, 0.810 | 0.920, 0.717 | 0.884, 0.634 | 0.920, 0.813 | 0.801, 0.576 | 0.996, 0.732 |
| no. of total rflns | 18 252 | 11 788 | 11 661 | 8934 | 3930 | 12 259 | 20 625 |
| no. of unique rflns | 6927 | 4489 | 4463 | 3427 | 3930 | 4705 | 5477 |
| no. of obsd rflns[a] | 11602 | 2540 | 1358 | 2745 | 2512 | 2008 | 2935 |
| no. of variables | 505 | 325 | 174 | 253 | 307 | 329 | 379 |
| refln to param ratio | 22.97 | 7.82 | 7.8 | 10.85 | 8.18 | 6.10 | 7.74 |
| $R$ | 0.041 | 0.029 | 0.055 | 0.022 | 0.031 | 0.030[b] | 0.037 |
| $R_w$ | 0.041 | 0.031 | 0.054 | 0.029 | 0.026 | 0.027 | 0.046 |
| $R_{all}$ | 0.078 | 0.071 | 0.188 | 0.031 | 0.073 | 0.106 | 0.052 |
| GOF | 1.43 | 0.86 | 1.19 | 1.08 | 1.20 | 0.76 | 1.35 |
| max. peak in final diff map (e$^-$/Å$^3$) | 2.39 | 0.60 | 0.74 | 0.31 | 0.62 | 0.43 | 1.87 |
| min. peak in final diff map (e$^-$/Å$^3$) | −0.83 | −0.62 | −1.47 | −0.73 | −0.54 | −0.41 | −1.03 |

[a] $I > 3.00\sigma(I)$. [b] One carbon was refined isotropically.

49.40, 24.86; IR (film) $\tilde{\nu}_{CO}$ 1710, 1694 cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 239 ($\epsilon$ 17 000), 287 (8200), 390 sh (1300), 450 sh (1020) nm; FAB-MS *m*/*z* 687. Anal. Calcd for $C_{26}H_{28}O_9Ru_2$: C, 45.48; H, 4.11. Found: C, 45.47; H, 4.55.

**Reaction of 7 with CO.** A THF-$d_8$ (0.5 mL) solution of **7** (6 mg, 0.01 mmol) was charged with CO (1 atm) and placed in a 75 °C oil bath. After 4 days, an $^1$H NMR spectrum indicated the formation of **6** in 95% yield.

**($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$($\eta^2$-*cis*-CHR=CHR) (R = CO$_2$CH$_3$) (8).** A solution of **7** (100 mg, 0.146 mmol) and dimethyl *cis*-butenedioate (500 mg, 3.47 mmol) in THF (50 mL) was placed in an 85 °C oil bath for 12 h. The contents were concentrated and chromatographed on silical gel using ethyl acetate/methylene chloride (1:4) as eluent to collect a red band. Concentration under reduced pressure produced red crystalline **8** (92 mg, 83%): mp 215−216 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.54 (m, 2H), 5.11 (m, 2H), 5.08 (m, 2H), 4.58 (m, 2H), 3.70 (s, 6H), 3.69 (s, 6H), 3.60 (s, 6H), 3.18 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 174.3, 172.9, 168.5, 155.5, 99.09, 98.42, 92.48, 89.17, 86.38, 83.06, 74.22, 52.66, 52.07, 51.96, 48.18; IR (film) $\tilde{\nu}_{CO}$ 1736, 1711 cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 230 ($\epsilon$ 37 000), 290 sh (11 400), 465 (1560) nm; FAB-MS *m*/*z* 760; HRMS calcd for $C_{28}H_{28}O_{12}Ru^{100}Ru^{104}$ 759.9677, found 759.9702. Anal. Calcd for $C_{28}H_{28}O_{12}Ru_2$: C, 44.33; H, 3.72. Found: C, 44.52; H, 3.81.

**Thermal Conversions of 8 to 7, 10, and 11. Method a.** A THF-$d_8$ (0.5 mL) solution of **8** (6 mg, 0.079 mmol) and dimethyl butynedioate (15 mg, 0.10 mmol) was monitored for 2 days by $^1$H NMR. There was no change. Subsequent photolysis for 2 h indicated the formation of **7** in 30% yield, without detectable formation of any new complex.

**Method b.** A solid mixture of **8** (7.0 mg, 0.009 mmol) and PPh$_3$ (21 mg, 0.080 mmol) in an NMR tube was heated in a sand bath at 200−230 °C for 1 h. After adding THF-$d_8$, an $^1$H NMR spectrum indicated the formation of **10** (>90%). The ratio of *trans*-butenedioate to the cis isomer was >20:1.

**Method c.** A DMSO (0.2 mL) solution of **8** (6 mg, 0.008 mmol) was heated to 210 °C (sand bath) for 30 min. The $^1$H NMR spectrum showed the presence of **11** and **8** (5.5:1).

**Photochemical Conversion of 8 to 7.** A THF-$d_8$ (0.5 mL) solution of **8** (6 mg, 0.008 mmol) was irradiated for 5 days. An $^1$H NMR spectrum indicated the presence of **7** in 78% yield.

**($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$(C$_4$H$_4$S) (R = CO$_2$CH$_3$) (9).** A sealed solution of **7** (100 mg, 0.146 mmol) and thiophene (500 mg, 5.95 mmol) in THF (50 mL) was placed in an oil bath at 85 °C for 12 h. The solvent was removed and the residue chromatographed on silical gel using ethyl acetate/methylene chloride (1:4) as eluent to furnish a red band. Removal of solvent under reduced pressure and crystallization of the residue at ambient temperature yielded red-brown crystalline **9** (74 mg, 72%): mp 173−174 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.27 (m, 2H), 7.02 (m, 2H), 5.46 (m, 2H), 4.80 (m, 2H), 4.69 (m, 2H), 4.13 (m, 2H), 3.74 (s, 6H), 3.65 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 176.2, 169.8, 147.8, 140.2, 128.5, 99.24, 86.00, 84.75, 83.81, 82.74, 80.57, 74.68, 52.42, 51.65; IR (film) $\tilde{\nu}_{CO}$ 1709 cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 230 ($\epsilon$ 38 000), 290 sh (14 100), 430 (1820) nm; FAB-MS *m*/*z* 700; HRMS calcd for $C_{26}H_{24}O_8Ru^{102}Ru^{104}S$ 700.9302, found 700.9310. Anal. Calcd for $C_{26}H_{24}O_8Ru_2S$: C, 44.70; H, 3.46. Found: C, 44.99; H, 3.59.

**Thermal Conversion of 9 to 8 and 10.** A THF-$d_8$ (0.5 mL) solution of **9** (6 mg, 0.086 mmol) and either dimethyl *cis*-butenedioate (15 mg, 0.10 mmol) or PPh$_3$ (14 mg, 0.05 mol) was placed in an oil bath at 85 °C for 12 h. $^1$H NMR spectroscopy recorded the formation of **8** (82%) and **10** (85%), respectively.

**Photochemical Conversion of 9 to 7.** A THF-$d_8$ (0.5 mL) solution of **9** (6 mg, 0.086 mmol) was irradiated for 3 days to produce ($^1$H NMR) **7** (80%).

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**($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$(PPh$_3$) (R = CO$_2$CH$_3$) (10).** A sealed solution of **7** (100 mg, 0.146 mmol) and PPh$_3$ (260 mg, 1.00 mmol) in THF (50 mL) was placed in an oil bath at 85 °C for 12 h. The contents were concentrated and chromatographed on silica gel using ethylene acetate/methylene chloride (1:4) as eluent to collect a red band. Removal of the solvent under reduced pressure until crystallization yielded orange-red crystalline **10** (100 mg, 78%): mp 319−320 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.25−7.34 (m, 15H), 5.38 (m, 2H), 4.62 (m, 2H), 4.49 (m, 2H), 4.32 (m, 2H), 3.58 (s, 6H), 3.33 (s, 6H); $^{13}$C{$^1$H} NMR (CDCl$_3$) $\delta$ 176.6, 170.1, 146.9 (d, $J$ = 10.8 Hz, Ru-C), 135.7 (br d), $J$ = 49.7 Hz, PPh$_3$), 133.9 (d, $J$ = 10.5 Hz, PPh$_3$), 129.4, 127.4 (d, $J$ = 10.4 Hz, PPh$_3$), 98.59, 87.46 (d, $J$ = 3.2 Hz), 86.12, 85.70, 83.31, 80.62, 76.43, 51.91, 50.80; $^{31}$P{$^1$H} NMR (CDCl$_3$) $\delta$ 46.82(s); IR (film) $\tilde{\nu}_{CO}$ 1712, 1696 cm$^{-1}$; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 235 ($\epsilon$ 47 500), 455 (1292) nm; HRMS calcd for $C_{40}H_{35}O_8\,Ru^{104}{}_2P$ 878.0170, found 878.0200. Anal. Calcd for $C_{40}H_{35}O_8Ru_2P$: C, 54.79; H, 4.02. Found: C, 54.79; H, 3.92.

**($\eta^5$:$\eta^5$-Fulvalene)Ru$_2$($\mu_2$-$\eta^2$:$\eta^4$-CRCRCRCR)$_2$(DMSO-*d*$_6$) (R = CO$_2$CH$_3$) (11).** A solution of **7** (7.0 mg, 0.010 mmol) and DMSO-*d*$_6$ (20 mg, 0.26 mmol) in acetone-*d*$_6$ (0.5 mL) was placed in an oil bath at 105 °C for 1.5 h. NMR indicated the formation of a new complex in greater than 90% yield. The volatiles were removed under high vacuum to give a red oil of **11-d$_6$**: $^1$H NMR (300 MHz, acetone-*d*$_6$) $\delta$ 5.58 (m, 2H), 5.36 (m, 2H), 4.62 (m, 2H), 4.24 (m, 2H), 3.64 (s, 6H), 3.51 (s, 6H), 2.48 (m, $CH_xD_{3-x}$). Adding a trace of DMSO to this sample gave rise to an additional peak at 2.48 ppm. $^1$H NMR (400 MHz, DMSO-*d*$_6$) $\delta$ 5.60 (m, 2H), 5.41 (m, 2H), 4.74 (m, 2H), 4.56 (m, 2H), 3.63 (s, 6H), 3.48 (s, 6H); $^{13}$C{$^1$H} NMR (DMSO-*d*$_6$) $\delta$ 174.9, 169.0, 146.1, 99.61, 87.03, 86.06, 83.44, 83.20, 80.45, 77.01, 52.12, 51.44. IR (film) $\tilde{\nu}_{CO}$ 1658, 1641, 1025 cm$^{-1}$; UV (CH$_2$Cl$_2$) $\lambda_{max}$ 290 sh, 465 nm; FAB-MS *m*/*z* 700; HRMS calcd for $C_{24}H_{20}D_6O_9Ru^{102}Ru^{104}S$ 700.9784, found 700.9799.

**Synthesis of 11 from 8 and 9.** A DMSO (0.2 mL) solution of **8** (6 mg, 0.01 mmol) was placed in an oil bath at 210 °C for 30 min. $^1$H NMR showed the presence of **11** and **8** (5.5:1). A similar experiment but using **9** (35 mg, 0.05 mmol) at 100 °C for 2 h revealed the generation of **11** in >90% yield.

**Thermal Conversion of 11 to 10.** A neat mixture of **11** (7 mg, 0.01 mmol) and PPh$_3$ (40 mg, 0.15 mmol) was heated in a sand bath at 200−230 °C for 12 h. An $^1$H NMR spectrum of the crude product showed **10** and **11** (2:1).

**Photochemical Reaction of 11 to 7.** A THF-*d*$_8$ (0.5 mL) solution of **11** (7 mg, 0.01 mmol) was irradiated for 1 h to give **7** and **11** (4:1) by $^1$H NMR.

**Kinetic Experiments of the Conversion of 9 to 10.** Measurements were carried out by dissolving **9** (7.0 mg, 0.01 mmol) and 1, 2, or 4 equiv of PPh$_3$ (2.6 mg, 0.01 mmol; 5.2 mg, 0.02 mmol; 10 mg, 0.04 mmol, respectively) in dry benzene-*d*$_6$ (0.5 mL) in 5 mm thick-wall NMR tubes. Each solution was then degassed three times by freeze−pump−thawing and sealed under vacuum. For each run, the entire NMR tube was wrapped in aluminum foil and then completely immersed in a constant-temperature oil bath. The samples were placed in 0 °C water immediately after removal from the heated area. The progress of the reaction was followed most conveniently by measuring the change in the fulvalene hydrogen signal at $\delta$ 4.2 ppm over a period of two to three half-lives at four different temperatures, 69, 76, 86, and 96 °C.

**X-ray Crystallography.** Crystallographic information and numerical data of the structure analyses are listed in Table 2. For further general experimental details, see the Supporting Information.

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**Supporting Information Available:** Complete information on data collection, atomic coordinates, thermal parameters, and structural tables for **3**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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