bacteria[12] (BChl *b*) and in green plants. Several new chlorophylls have been reported in the latter.[14,15] One of these has been proposed[15] to be part of the reaction center that initiates the electron-transport chain that fixes carbon dioxide (photosystem I).

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE-81-20891, at UCD) and the U.S. Department of Energy, Division of Chemical Sciences, under Contract DE-AC02-76CH00016 (at BNL). We are grateful to Prof. N. Pfennig for a gift of the *C. Vibrioforme* strain.

Supplementary Material Available: Positional and anisotropic thermal parameters for the non-hydrogen atoms of methyl 4-neopentyl-5-ethylbacteriopheophorbide *d* (2 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Photochemistry of Tetracarbonyl(fulvalene)diruthenium. Thermally Reversible Photoisomerization Involving Carbon-Carbon Bond Activation at a Dimetal Center

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The η^5:η^5-fulvalene ligand constitutes an attractive matrix on which to firmly affix two metal atoms in close enough proximity to enable metal-metal bonding while allowing complexes to retain dinuclear character after potential metal-metal bond fission. We report here a new synthetic approach to dimetallafulvalenes,[1] some preliminary chemistry of a diruthenium derivative, and its unexpected photoreactions.

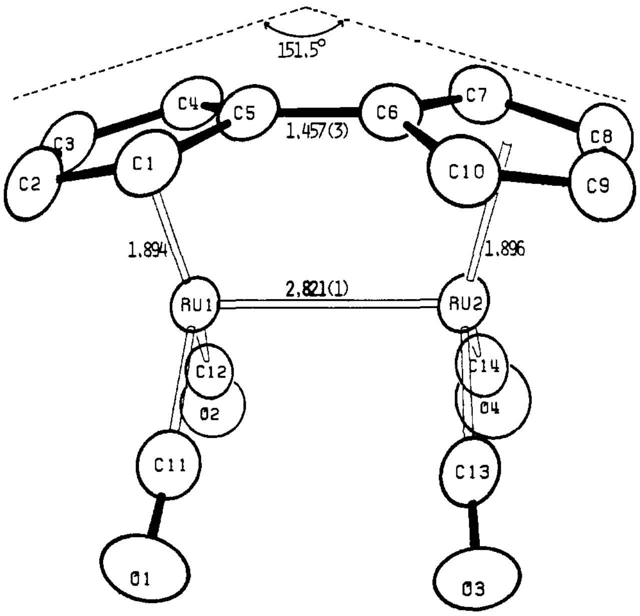


Figure 1. ORTEP drawing showing the geometry, labeling, and important bond lengths (Å) for all non-hydrogen atoms in tetracarbonyl(η^5:η^5-fulvalene)diruthenium (**2**). Ellipsoids are scaled to represent the 50% probability surface.

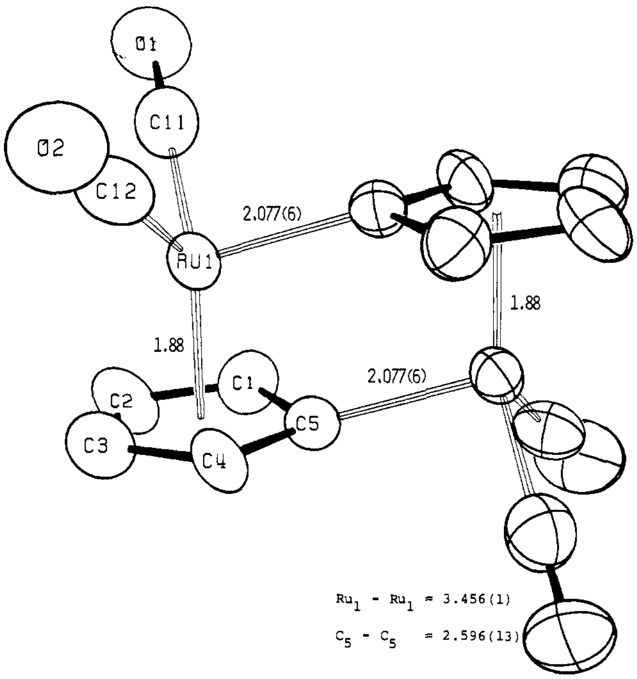
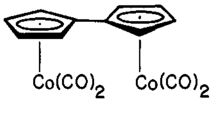


Figure 2. ORTEP drawing of **6**.

We have found that dihydrofulvalene, prepared in THF,[1a] becomes suitable for direct reaction with metal carbonyls after extraction into water-washed heptane.[2] Addition of the latter to boiling solutions of $Co_2(CO)_8$ (CH_2Cl_2) or $Ru_3(CO)_{12}$ (glyme) and/or $Mo(CO)_6$ (glyme) results in good yields of complexes **1**-**4**.[3]



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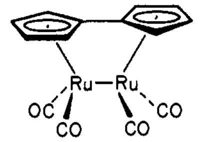

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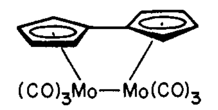

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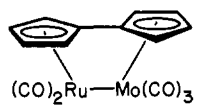

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(2) Details will be the subject of a full paper.

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The 18-electron rule requires metal–metal bonds in **2**–**4** which, if present, necessitate significant deformations of the π-ligands from planarity.[1c] A single-crystal X-ray diffraction study confirms this for **2** (Figure 1), its structure contrasting with that of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$, **5**.[4]

The chemistry of **2** (and also **3** and **4**)[2] is quite distinct from that of **5**.[5] For example, iodine cleaves the Ru–Ru bond to the diiodide, which when treated with $LiEt_3BH$ even at −60 °C gives **2** and none of the dihydride,[2] indicating the possible operation of a fast intramolecular H_2-extrusion process, not available to $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$.[6] **2**, although thermally inert, undergoes photosubstitution by alkynes (including ethyne) to give ("parallel")[7] $\mu_2\eta^2$-alkyne tricarbonyl complexes, characterized by a diruthenacyclobutene nucleus and one bridging carbonyl group.[2] In the absence of added ligands irradiation of yellow **2** in THF with 350-nm or sunlight leads to rapid formation of the new, thermally unstable, colorless compound **6**.[3] X-ray analysis (Figure 2) reveals the occurrence of a remarkable (and possibly unprecedented)[8] dinuclear oxidative addition to an sp^2–sp^2 hydrocarbon single bond.

Structures related to **6** have been postulated as precursors to (fulvalene)dimetal complexes,[1m–t] the former reacting by the thermal reverse of the **2** → **6** interconversion, although reported cases have involved metal hydride species at some stage of their formation. Nevertheless, **6** thermally reverts cleanly to **2** (THF, room temperature) following first-order kinetics ($E_a = 21.9 \pm 1.0$ kcal mol^{-1}, $\log A = 11.7$). This also occurs sharply in the crystalline state (208 °C; $\Delta G = -29.8 \pm 1.5$ kcal mol^{-1} by DSC). The **2** → **6** → **2** sequence represents a new photochemical energy storage cycle.

A crossover experiment involved a 1:1 mixture of **2** and 90% deuterated **2**.[9] The absence of any crossover was ascertained by mass spectral analyses of the resulting **6** and of subsequently regenerated **2**. This rules out the presence of monomeric (metal–carbene?)[10] intermediates in either process.

Although the exact mechanistic details of the reported reactions are not understood, it is clear that hydrides are not necessary for their occurrence. It is tempting to postulate initial photocleavage of the Ru–Ru bond,[4b] followed by rotation and rearrangement, possibly involving bridging cyclopentadienylidenes.[11] Interestingly, **2** converts to **6** in the presence of chlorinated solvents, normally excellent traps for 17-electron metal centers,[12] making this pathway less attractive. An alternative is a concerted process through a tetrahedral transition state.[1o]

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098. The crystal structure analyses were performed by Dr. F. J. Hollander, U.C. Berkeley X-ray Crystallographic Facility. K.P.C.V. is a Camille and Henry Dreyfus Teacher-Scholar (1978–1983).

Supplementary Material Available: Spectral properties of all new compounds, details of the X-ray analysis, a listing of positional and thermal parameters, and tables of bond lengths and angles of **2** and **6** (9 pages). Ordering information is given on any current masthead page.

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[3] **1**: dark red cubes, 80%; mp 97–98 °C. **2**: yellow plates, 78%; mp 288–290 °C; ^1H NMR (200 MHz, acetone-d_6) δ 5.90 (dd, 4 H, J = 2.2, 2.1 Hz), 4.40 (dd, 4 H, J = 2.1, 2.1 Hz); IR (CH_2Cl_2) ν_{CO} 2020 (vs), 1952 (vs) cm^{-1}; UV λ_{max} (THF) 243 nm (log ϵ 3.99), 273 (4.04), 329 (3.85), 388 sh (3.18). **3**: purple crystals, 60%; mp 279–280 °C (lit.[1a] mp not reported). **4**: orange flakes, 18%; mp 256–258 °C. **6**: colorless plates, 62%; mp 208 °C (isomerization point to **2**); ^1H NMR ($CDCl_3$) δ 5.39 (dd, 4 H, J = 2.1, 2.1 Hz), 4.68 (dd, 4H, J = 2.1, 2.1 Hz); IR (KBr) ν_{CO} 2000 (vs), 1960 (vs) cm^{-1}; UV λ_{max} (THF) 239 nm (log ϵ 3.90), 286 sh (3.18).

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[8] The related reaction of a fulvalene dimolybdenum dihydride might proceed through stepwise H-transfer mechanisms.[1o,p]

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Phosphine Ligands for the Construction of Polynuclear Complexes. 1. Bis(diphenylphosphinomethyl)phenylphosphine Complexes of Palladium(II) and Rhodium(I)

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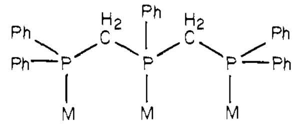
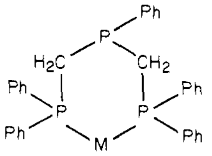
Binuclear transition-metal complexes bridged by phosphine ligands such as bis(diphenylphosphino)methane (dpm)[1] and 2-(diphenylphosphino)pyridine (Ph_2Ppy)[2] have been shown to provide a rich array of structural forms and an extensive reaction chemistry. We have become interested in obtaining complexes containing linear or nearly linear arrays of several metal atoms and have chosen to examine the coordinating properties of several polyphosphines related to dpm and Ph_2Ppy. Here we describe complexes formed from bis(diphenylphosphinomethyl)phenylphosphine (dpmp).[3] This ligand represents an elaboration of the structural elements found in dpm. It has the potential for binding three metal centers in a row, A, or forming a chelate ring about one metal ion, B. In the cases described here, the interaction of this ligand with two different d^8 metal ions, Pd(II) and Rh(I), leads to the formation of both structural types.

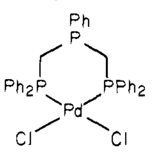


A



B

The reaction of equimolar quantities of dpmp with bis(benzonitrile)palladium(II) chloride in dichloromethane solution followed by the addition of ethyl ether yields the cream-colored crystalline complex **1** in 76% yield. The $^{31}P\{^1H\}$ NMR spectrum



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