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SYNTHESIS, STRUCTURE, AND PHOTOCHEMISTRY OF FULVALENE DIRUTHENIUM TETRACARBONYL. THERMALLY REVERSIBLE PHOTOISOMERIZATION INVOLVING CARBON-CARBON BOND ACTIVATION AT A DIMETAL CENTER

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K. Peter C. Vollhardt and Timothy W. Weidman

January 1983

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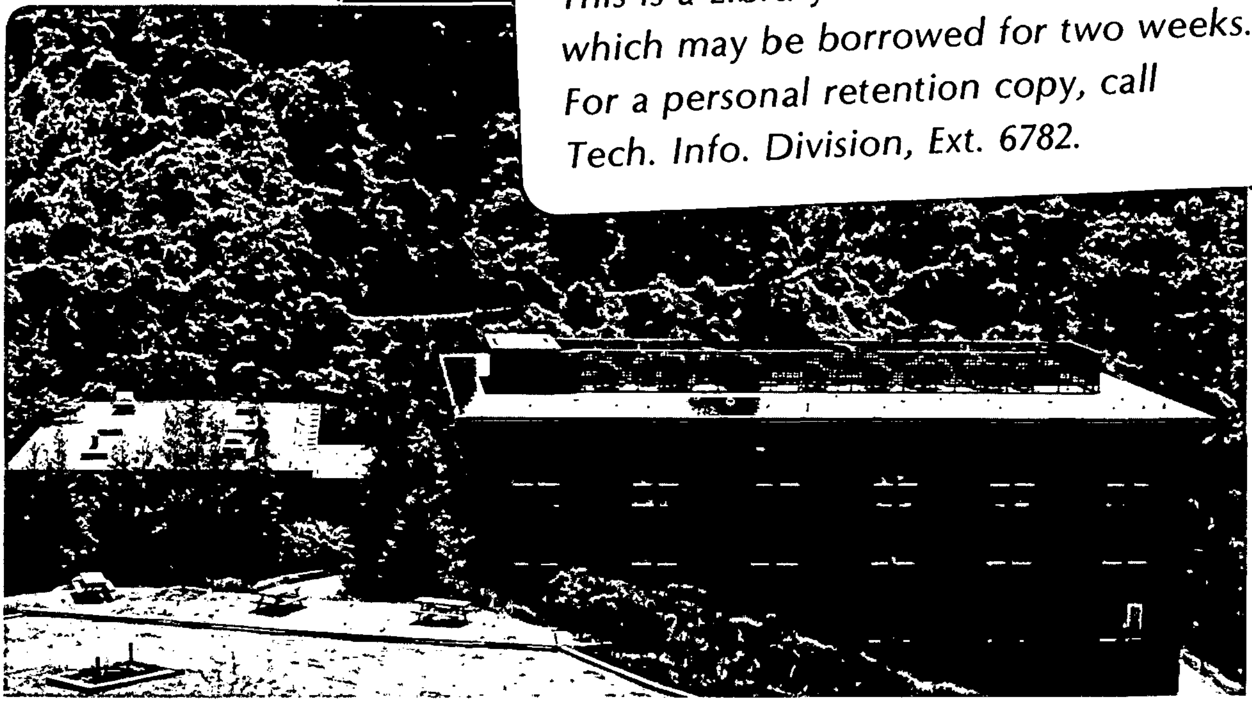

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Synthesis, Structure, and Photochemistry of Fulvalene Diruthenium Tetracarbonyl. Thermally Reversible Photoisomerization Involving Carbon-Carbon Bond Activation at a Dimetal Center

K. Peter C. Vollhardt* and Timothy W. Weidman

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Berkeley, California 94720.

Abstract

The synthesis of several new fulvalene dimetal complexes has been accomplished by direct reaction of dihydrofulvalene with metal carbonyls. The X-ray structure of $\eta^5:\eta^5$-fulvalene diruthenium tetracarbonyl exhibits a bent π-ligand with a Ru-Ru bond length of 2.821(1)Å and four terminally bound carbonyl ligands. The complex undergoes a variety of substitution reactions. Upon irradiation at 350 nm it rearranges via cleavage of the Ru-Ru and carbon-carbon single bond to form an isomeric $\eta^1:\eta^5$-C_5H_4 bridged complex. Upon heating this species reverts to starting material. Crossover experiments verify the intramolecularity of both the photochemical and thermal isomerizations.

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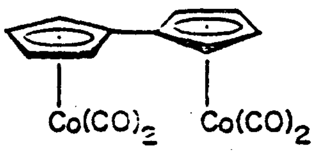
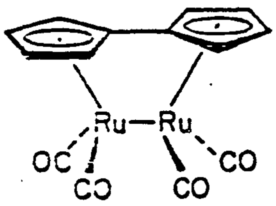
The η^5:η^5-fulvalene ligand constitutes an attractive matrix on which to firmly affix two metal atoms in close enough proximity to enable metal-metal bonding while allowing complexes to retain dinuclear character after potential metal-metal bond fission. We report here a new synthetic approach to dimetallafulvalenes,[1]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

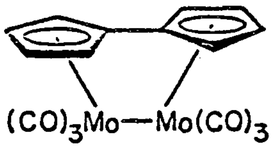
We have found that dihydrofulvalene, prepared in THF,[1a] becomes suitable for direct reaction with metal carbonyls after extraction into water washed heptane.[2] Addition of the latter to boiling solutions of $Co_2(CO)_8$ (CH_2Cl_2), or $Ru_3(CO)_{12}$ (glyme), and/or $Mo(CO)_6$ (glyme) results in good yields of complexes 1-4.[3] The 18e-rule requires metal-metal bonds in



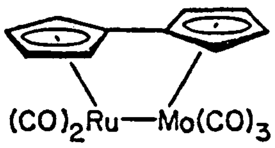
1



2



3



4

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 that of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$, 5.[4]

Figure 1

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 $(\eta^5-C_5H_5)Ru(CO)_2H$.[6] Complex 2, although thermally inert, undergoes photosubstitution by alkynes (including ethyne) to give ("parallel")[7] $\mu_2\eta^2$-alkyne tricarbonyl complexes, characterized by a dirutheniacyclobutene nucleus and one bridging carbonyl group.[2] In the absence of added ligands irradiation of yellow 2 in THF with 350 nm or sun light leads to rapid formation of a 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.

<u>Figure 2</u>

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, RT) following first order kinetics ($Ea = 21.9 \pm 1.0$ kcal mole^{-1}, $\log A = 11.7$). This also occurs sharply in the crystalline state (208°C; $\Delta G = -29.8 \pm 1.5$ kcal mole^{-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 cross-over 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 17e metal centers,[12] making this pathway less attractive. An alternative is a concerted process through a tetrahedral transition state.[1o]

Acknowledgement. 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 NO. 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 (10 pages). Ordering information is given on any current masthead page.

(1) For alternative approaches from fulvalene dianion, see:

(a) Smart, J.C.; Curtis, C.J. *Inorg. Chem.* 1977, *16*, 1788. (b) Davison, A.; Smart, J.C. *J. Organomet. Chem.* 1973, *49*, C43. (c) Smart, J.C.; Curtis, C.J. *J. Am. Chem. Soc.* 1977, *99*, 3518. (d) Smart, J.C.; Pinsky, B.L.; Fredrich, M.F.; Day, V.W. *J. Am. Chem. Soc.* 1979, *101*, 4369. (e) McKinney, R.J. *J. Chem. Soc., Chem. Commun.* 1980, 603. (f) Köhler, F.H.; Doll, K.H.; Proßdorf, W.; Müller, J. *Angew. Chem.* 1982, *94*, 154; *Angew. Chem., Int. Ed. Engl.* 1982, *21*, 151; *Angew. Chem. Suppl.* 1982, 283.

From η^5-halocyclopentadienyl complexes by Ullmann type coupling, see:

(g) Hedberg, F.L.; Rosenburg, H. *J. Am. Chem. Soc.* 1969, *91*, 1258.

(h) Rausch, M.D.; Kovar, R.F.; Kraihanzel, C.S. *J. Am. Chem. Soc.* 1969, *91*, 1259. (i) Rausch, M.D.; Genetti, R.A. *J. Org. Chem.* 1970, 35, 3888. (j) Neuse, E.W.; Loonat, M.S. *Transition Met. Chem.* 1981, *6*, 260. (k) Bednarik, L.; Neuse, E.W. *J. Org. Chem.* 1980, *45*, 2032.

(l) Nesmeyanov, A.N.; Sedova, N.N.; Moiseev, S.K.; Sazonova, V.A. *Izv. Akad. Nauk., Ser. Khim.* 1980, 1171.

From η^5-cyclopentadienyl complexes by reductive coupling see:

(m) Antropiusová, H.; Dosedlová, A.; Hanuš, V.; Mach, K. *Transition Met. Chem.* 1981, *6*, 90. (n) Gell, K.I.; Harris, T.V.; Schwartz, J. *Inorg. Chem.* 1981, *20*, 481. (o) Berry, M.; Cooper, J.; Green, M.L.H.; Simpson, S.J. *J. Chem. Soc., Dalton Trans.* 1980, 29. (p) Barral, M.C.; Green, M.L.H.; Jimenez, R. *ibid.* 1982, 2495. (q) Pez, G.P. *Adv.*

Organomet. Chem. 1981, 19, 1. (r) Pez, G.P.; Apgar, P.; Crissey, R.K. J. Am. Chem. Soc. 1982, 104, 482. (s) Pez, G.P. J. Am. Chem. Soc. 1981, 103, 8072. (t) Lemenovskii, D.A.; Konde, S.A.; Perevalova, E.G. J. Organomet. Chem. 1982, 226, 223, and the references therein.

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

(3) Compound 1: dark red cubes, 80%; mp 97-98°C. 2: yellow plates, 78%; mp 288-290°C; ^{1}H NMR (200 MHz, acetone-d_6): δ 5.90 (dd, 4H, $J = 2.2$, 2.1), 4.40 (dd, 4H, $J = 2.1$, 2.1); IR (CH_2Cl_2) ν_{CO}: 2020 (vs), 1952 (vs) cm^{-1}; UV λmax (THF) 243 (lg $\varepsilon = 3.99$), 273 (4.04), 329 (3.85), 388 sh (3.18) nm. 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); ^{1}H-NMR ($CDCl_3$): δ 5.39 (dd, 4H, $J = 2.1$, 2.1), 4.68 (dd, 4H, $J = 2.1$, 2.1); IR (KBr) ν_{CO} 2000 (vs), 1960 (vs) cm^{-1}; UV λmax (THF) 239 (lg $\varepsilon = 3.90$), 286 sh (3.18).

(4) (a) Mills, O.S.; Nice, J.P. J. Organomet. Chem. 1967, 9, 339; see also: Bailey, N.A.; Radford, S.L.; Sanderson, J.A.; Tabatabaian, K.; White, C.; Worthington, J.M. J. Organomet. Chem. 1978, 154, 343. (b) Abrahamson, H.B.; Palazzotto, M.C.; Reichel, C.L.; Wrighton, M.S. J. Am. Chem. Soc. 1979, 101, 4123.

(5) See: Dyke, A.F.; Knox, S.A.R.; Naish, P.J.; Taylor, G.E. J. Chem. Soc., Dalton Trans. 1982, 1297; Davies, D.L.; Dyke, A.F.; Knox, S.A.R.; Morris, M.J. J. Organomet. Chem. 1981, 215, C30.

(6) Humphries, A.P.; Knox, S.A.R. J. Chem. Soc., Dalton Trans. 1975, 1710.

(7) Hoffman, D.M.; Hoffmann, R.; Fisel, C.R. J. Am. Chem. Soc. 1982, 104,

3858.

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

(9) From 90% C_5D_6, modified from McLean, S.; Webster, C.J.; Rutherford, R.J.D. *Can*. *J*. *Chem*. 1969, 1557.

(10) Baker, E.C.; Raymond, K.N.; Marks, T.J.; Wachter, W.A. *J*. *Am*. *Chem*. *Soc*. 1974, *96*, 7586.

(11) Herrmann, W.A.; Kriechbaum, G.; Bauer, C.; Guggolz, E.; Ziegler, M.L. *Angew*. *Chem*. 1981, *93*, 838; *Angew*. *Chem*., *Int*. *Ed*. *Engl*. 1981, *20*, 815.

(12) Eisenstadt, A.; Tannenbaum, R.; Efraty, A. *J*. *Organomet*. *Chem*. 1981, *221*, 317; Caspar, J.V.; Meyer, T.J. *J*. *Am*. *Chem*. *Soc*. 1980, *102* 7794.

Figure Captions

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

Figure 2. ORTEP drawing of 6.

Figure 1

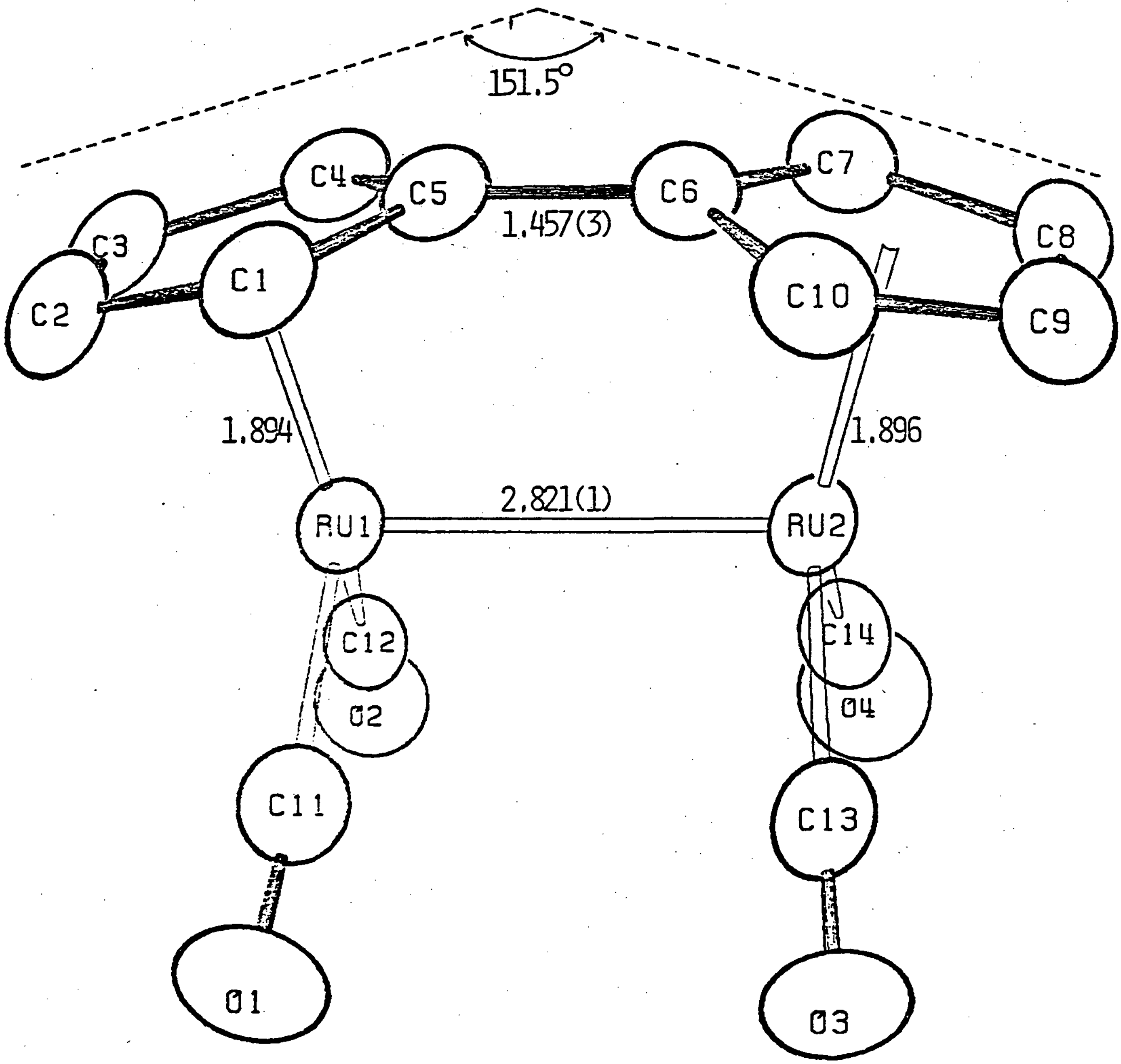
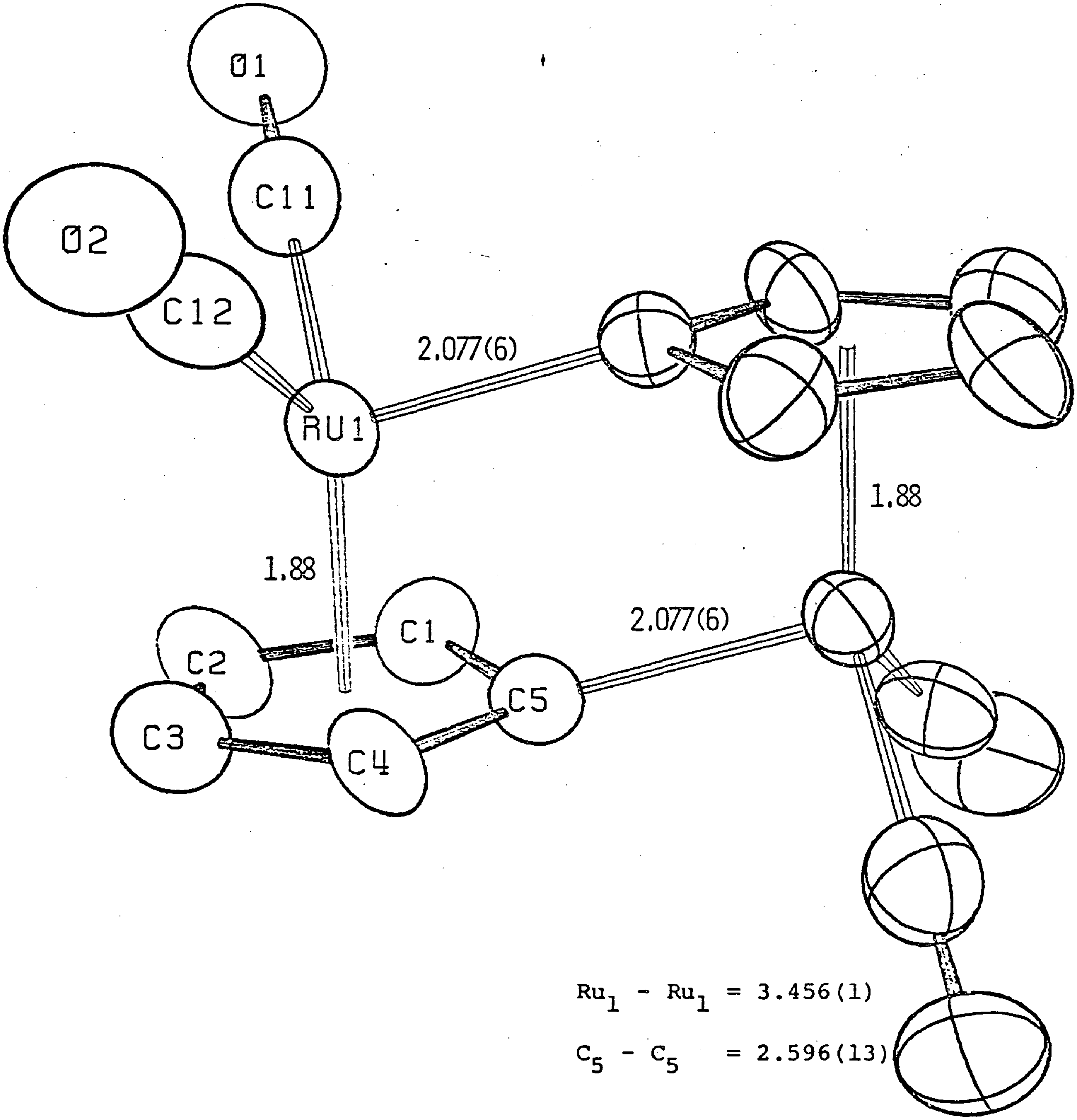

151.5°
C4
C5
C6
C7
C3
C8
1.457(3)
C1
C2
C10
C9
1.894
1.896
2.821(1)
RU1
RU2
C12
C14
O2
O4
C11
C13
O1
O3

Figure 2



$Ru_1 - Ru_1 = 3.456(1)$

$C_5 - C_5 = 2.596(13)$

Synthesis, Structure, and Photochemistry of Fulvalene Diruthenium Tetracarbonyl. Thermally Reversible Photoisomerization Involving Carbon-Carbon Bond Activation at a Dimetal Center

K. Peter C. Vollhardt* and Timothy W. Weidman

Supplemental Material

Compound 1: dark red cubes, 80%; mp 97-98^{o}C; ^{1}H NMR (250 MH$_z$, C_6D_6): δ 4.69 (dd, 4H, J = 2.5, 2.5), 4.35 (dd, 4H, J = 2.5, 2.5); IR (CH_2Cl_2)ν_{CO}: 2024 (vs), 1965 (vs) cm^{-1}; m/e (70 ev) 358 (M$^+$, 0.32%), 330 (M-CO, 75.8%), 302 (M-2CO, 59.5%), 274 (M-3CO, 84.5%), 246 (M-4CO, 96.6%), 59 (100%). 2: yellow plates, 78%; mp 288-290^{o}C; ^{1}H NMR (200 MH$_z$, acetone-d$_6$): δ 5.90 (dd, 4H, J = 2.2, 2.1), 4.40 (dd, 4H, J = 2.1, 2.1); IR (CH_2Cl_2) ν_{CO}: 2020 (vs), 1952 (vs) cm^{-1}; UV λmax (THF) 243 (lg ε = 3.99), 273 (4.04), 329 (3.85), 388 sh (3.18) nm; m/e (20 ev, major peaks in isotope envelopes) 443 (M$^+$, 92.0%), 432 (M-CO, 1.6%), 415 (M-2CO, 63.1%), 387 (M-3CO, 85.8%), 359 (M-4CO, 100%). 3: purple crystals, 60%; mp 279-280^{o}C (lit.[1a] mp not reported). 4: orange flakes, 18% (from the reaction of $Ru_3(CO)_{12}$ and $Mo(CO)_6$, 1:1; isolated from a 1:1:2 mixture of 2, 3, and 4); mp 256-258^{o}C; ^{1}H NMR (250 MH$_z$, acetone-d$_6$): δ 5.88 (dd, 2H, J = 2.2, 2.1), 5.53 (dd, 2H, J = 2.3, 2.3), 4.79 (2H, J= 2.4, 2.3), 4.42 (2H, J = 2.2, 2.1); IR (KBr) ν_{CO} 2020(s), 1942(s), 1935(s), 1868(s); m/e (70ev, major peaks in isotope envelopes) 465 (M$^+$, 19.6%), 438 (M$^+$-CO, 15.9%), 411 (M$^+$-2CO, 7.0%), 381 (M$^+$-3CO, 71.0%), 352 (M$^+$-4CO, 16.2%), 324 (M$^+$-5CO), 100%). 6: colorless plates, 62%; mp 208^{o}C (isomerization point to 2, then mp 288-290^{o}C); ^{1}H-NMR ($CDCl_3$): δ 5.39 (dd, 4H, J = 2.1, 2.1), 4.68 (dd, 4H, J= 2.1, 2.1); IR (KBr) ν_{CO} 2000 (vs), 1960 (vs) cm^{-1}; UV λmax (THF) 239 (lg ε = 3.90), 286 sh (3.18); m/e (20 eV, major peaks in isotope envelopes) 443 (M$^+$, 81.4%), 415 (M$^+$-CO, 83.2%), 387 (M$^+$-2CO, 74.7%), 359 (M$^+$-3CO, 100%), 331 (M$^+$-4CO, 31.7%). All new compounds gave satisfactory elemental analyses.

Compound 2: crystal size 0.12 x 0.25 x 0.35 mm; monoclinic Laue symmetry;

space group $P2_1/n$; $\underline{a}$ = 12.7489(5)Å, $\underline{b}$ = 6.9816(5)Å, $\underline{c}$ = 15.8212(12)Å, $\underline{\beta}$ = 112.360(5)°; $\underline{V}$ = 1302.4(3)$Å^3$ at 25°C, μ_{calc} = 22.7 cm^{-1}; radiation = graphite monochromatized MoKα; scan range = 3° ≤ 2θ ≤ 45°; reflections collected = 1958, 1702 unique with $F^2 > 3\sigma(F^2)$, R = 0.0176, Rw = 0.0320. 6: crystal size 0.13 x 0.14 x 0.28 mm; triclinic; space group P1; $\underline{a}$ = 7.0874(20)Å, $\underline{b}$ = 8.5705(17)Å, $\underline{c}$ = 12.8038(21)Å, $\underline{\alpha}$ = 71.909(15), $\underline{\beta}$ = 79.752(18), $\underline{\gamma}$ = 64.418(19); $\underline{V}$ = 665.9(3)$Å^3$ at 25°C; $\underline{Z}$ = 2; μ_{calc} = 22.3 cm^{-1}; radiation = graphite monochromatized Mokα; scan range 3° ≤ 2θ ≤ 45°; reflections collected: 1734, unique = 1473 with $F^2 > 3\sigma(F^2)$, R = 0.0573, Rw = 0.0746. The unit cell contains two chemically identical, crystallographically distinct molecules with very similar bond lengths and angles.

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS.

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
RU1	0.27193(2)	0.04899(3)	0.09500(1)	0.00460(1)	0.01343(5)	0.00236(1)	-0.00055(4)	0.00283(2)	-0.00038(3)
RU2	0.23167(2)	0.14210(3)	-0.00825(1)	0.00501(1)	0.01420(5)	0.00246(1)	-0.00123(4)	0.00332(2)	-0.00050(3)
O1	0.4510(2)	-0.2476(3)	0.1143(2)	0.0071(2)	0.0211(5)	0.0071(1)	0.0064(5)	0.0055(2)	0.0021(4)
O2	0.0064(2)	-0.2463(3)	0.0450(1)	0.0067(1)	0.0180(5)	0.0054(1)	-0.0071(4)	0.0045(2)	-0.0010(4)
O3	0.3920(2)	-0.1572(3)	-0.1040(2)	0.0105(1)	0.0227(5)	0.0074(1)	0.0102(5)	0.0118(2)	0.0018(4)
O4	0.0345(2)	-0.1305(3)	-0.1666(2)	0.0076(2)	0.0262(6)	0.0061(1)	-0.0129(5)	0.0017(2)	-0.0041(5)
C1	0.3787(2)	0.3104(4)	0.1544(2)	0.0063(2)	0.0176(6)	0.0034(1)	-0.0030(6)	0.0025(2)	-0.0042(5)
C2	0.3538(2)	0.2193(5)	0.2261(2)	0.0067(2)	0.0232(7)	0.0026(1)	-0.0021(7)	0.0025(2)	-0.0038(5)
C3	0.2362(2)	0.2246(4)	0.2003(2)	0.0075(2)	0.0200(7)	0.0031(1)	-0.0019(7)	0.0051(2)	-0.0045(5)
C4	0.1858(2)	0.3140(4)	0.1146(2)	0.0053(2)	0.0153(6)	0.0036(1)	0.0008(6)	0.0035(2)	-0.0039(5)
C5	0.2733(2)	0.3665(4)	0.0847(2)	0.0052(2)	0.0135(6)	0.0030(1)	-0.0003(5)	0.0022(2)	-0.0036(4)
C6	0.2503(2)	0.4157(3)	-0.0087(2)	0.0061(2)	0.0116(5)	0.0035(1)	-0.0006(6)	0.0037(2)	-0.0005(5)
C7	0.1514(2)	0.4254(4)	-0.0832(2)	0.0068(2)	0.0149(6)	0.0040(1)	0.0023(6)	0.0047(2)	0.0015(5)
C8	0.1718(2)	0.4196(4)	-0.1650(2)	0.0087(2)	0.0160(6)	0.0029(1)	0.0018(7)	0.0032(3)	0.0021(5)
C9	0.2898(2)	0.4039(4)	-0.1425(2)	0.0087(2)	0.0160(6)	0.0043(1)	-0.0026(7)	0.0064(3)	0.0026(5)
C10	0.3431(2)	0.3997(4)	-0.0467(2)	0.0058(2)	0.0155(6)	0.0044(1)	-0.0045(6)	0.0034(2)	0.0007(5)
C11	0.3011(2)	-0.1352(4)	0.1040(2)	0.0057(2)	0.0177(7)	0.0038(1)	-0.0037(6)	0.0039(2)	-0.0002(5)
C12	0.1576(2)	-0.1358(4)	0.0624(2)	0.0055(2)	0.0177(7)	0.0027(1)	0.0046(6)	0.0030(2)	0.0019(5)
C13	0.3313(2)	-0.0462(4)	-0.0971(2)	0.0065(2)	0.0183(7)	0.0033(1)	-0.0025(6)	0.0048(2)	-0.0004(5)
C14	0.1086(2)	-0.0288(5)	-0.1366(2)	0.0067(2)	0.0205(7)	0.0032(1)	0.0027(7)	0.0035(2)	0.0028(5)
CP1	0.2856(0)	0.2869(0)	0.1550(0)	4.0000(0)					
CP2	0.2429(0)	0.4129(0)	-0.0893(0)	4.0000(0)					

THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS:

EXP[-(B(1,1)*H*H + B(2,2)*K*K + B(3,3)*L*L + B(1,2)*H*K + B(1,3)*H*L + B(2,3)*K*L)].

Supplementary Material - 2

Compound 2: Interatomic Distances and Angles with Estimated Standard Deviations in Parentheses.

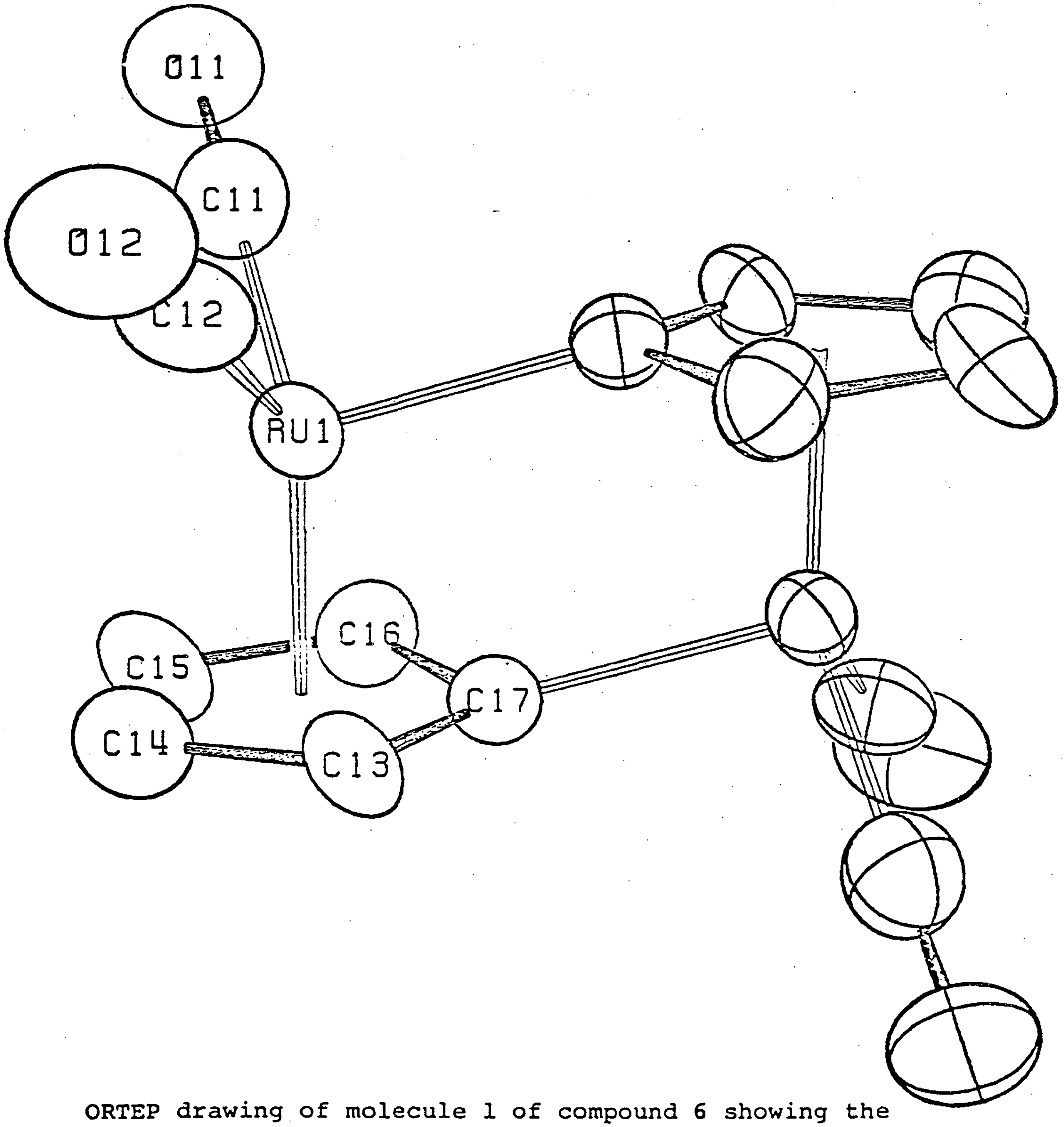
INTERATOMIC DISTANCES

ATOM 1	ATOM 2	DISTANCE
RU1	RU2	2.821(1)
RU1	C11	1.860(3)
RU1	C12	1.866(3)
RU1	C1	2.257(2)
RU1	C2	2.260(2)
RU1	C3	2.251(2)
RU1	C4	2.232(2)
RU1	C5	2.223(2)
RU1	CP1	1.894 *
RU2	C13	1.870(3)
RU2	C14	1.886(3)
RU2	C6	2.241(2)
RU2	C7	2.242(2)
RU2	C8	2.259(2)
RU2	C9	2.260(2)
RU2	C10	2.230(2)
RU2	CP2	1.896 *
C11	O1	1.151(3)
C12	O2	1.143(3)
C13	O3	1.129(3)
C14	O4	1.132(3)
C1	C2	1.425(3)
C1	C5	1.431(3)
C2	C3	1.398(3)
C3	C4	1.407(3)
C4	C5	1.417(3)
C5	C6	1.457(3)
C6	C7	1.424(3)
C7	C8	1.415(3)
C8	C9	1.411(3)
C9	C10	1.405(3)
C10	C6	1.427(3)

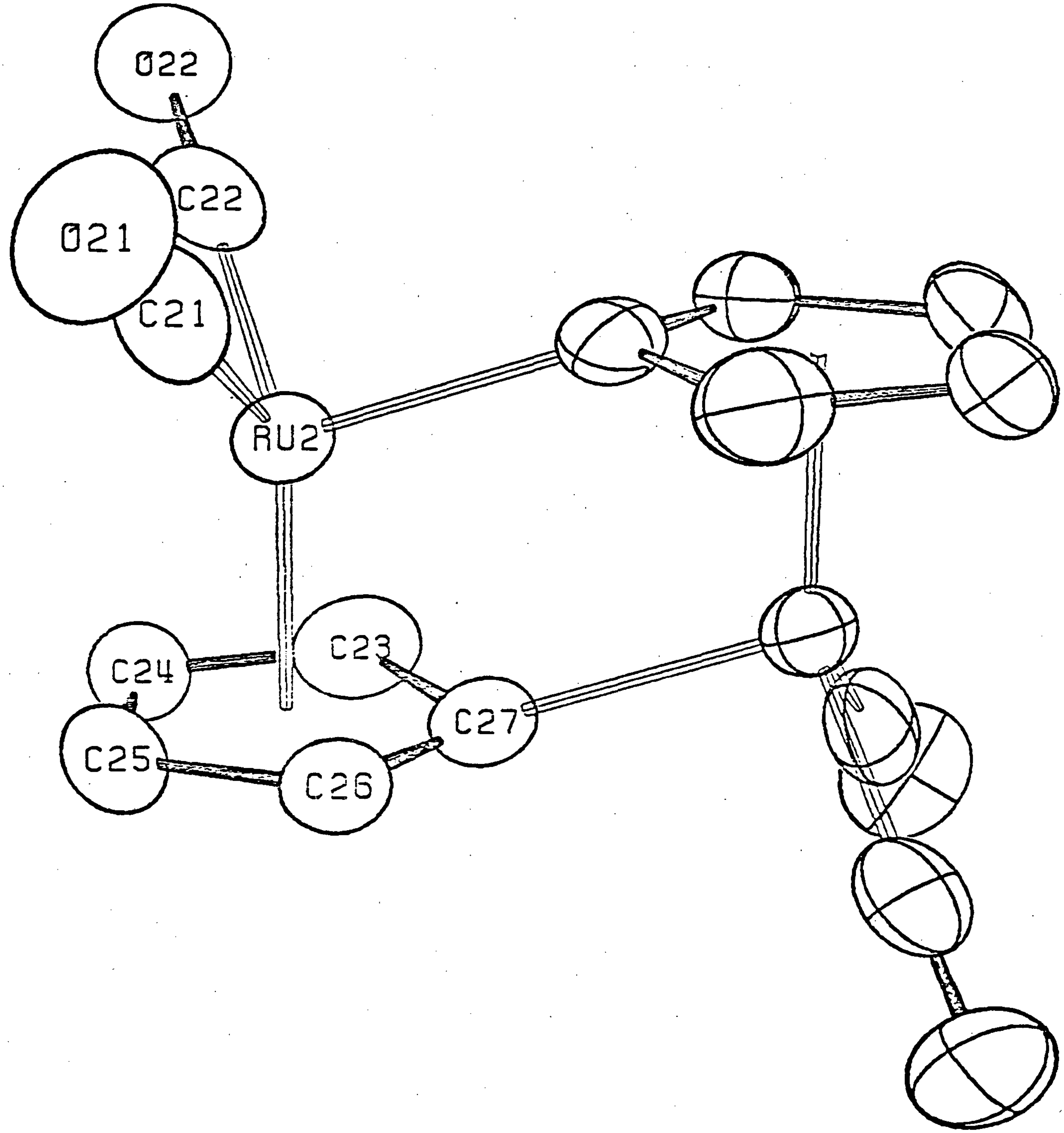
INTRAMOLECULAR ANGLES

ATOM 1	ATOM 2	ATOM 3	ANGLE
RU2	RU1	C11	94.40(8)
RU2	RU1	C12	93.32(7)
RU2	RU1	CP1	105.4 *
C11	RU1	C12	91.49(11)
C11	RU1	CP1	130.2 *
C12	RU1	CP1	131.1 *
RU1	RU2	C13	92.96(7)
RU1	RU2	C14	93.97(8)
RU1	RU2	CP2	104.7 *
C13	RU2	C14	90.50(11)
C13	RU2	CP2	130.1 *
C14	RU2	CP2	132.9 *
RU1	C11	O1	176.54(22)
RU1	C12	O2	176.86(21)
RU2	C13	O3	178.26(21)
RU2	C14	O4	179.20(23)
C5	C1	C2	107.66(19)
C1	C2	C3	107.67(20)
C2	C3	C4	109.28(20)
C3	C4	C5	107.97(20)
C4	C5	C1	107.40(20)
C4	C5	C6	125.73(18)
C1	C5	C6	124.69(19)
C5	C6	C7	124.38(21)
C5	C6	C10	125.51(19)
C10	C6	C7	107.17(21)
C6	C7	C8	107.67(21)
C7	C8	C9	108.71(22)
C8	C9	C10	107.79(21)
C9	C10	C6	108.65(20)

* CP1 and CP2 are the geometric centroids of each five member ring of the fulvalene.



ORTEP drawing of molecule 1 of compound 6 showing the labeling scheme used in the positional and thermal parameters and bond lengths and angles tables.



ORTEP drawing of molecule 2 of compound 6 showing the labeling scheme used in positional and thermal parameter and bond length and angles tables.

Table of Positional and Thermal Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
RU1	0.2586(1)	0.17097(10	-0.00920(6)	0.0204(2)	0.0107(1)	0.00471(6)	-0.0108(2)	0.0022(2)	-0.0032(1)
RU2	0.2968(1)	0.20707(9	0.49991(6)	0.0269(2)	0.0103(1)	0.00415(5)	-0.0155(3)	0.0019(2)	-0.0030(1)
O11	-0.062(1)	0.1673(11)	0.1814(6)	0.039(2)	0.029(2)	0.0080(6)	-0.029(3)	0.015(2)	-0.009(2)
O12	-0.036(1)	0.2528(12)	-0.1776(7)	0.042(2)	0.038(2)	0.0180(7)	-0.042(3)	-0.015(2)	0.001(2)
O21	-0.130(1)	0.2230(11)	0.5996(0)	0.032(2)	0.026(1)	0.0133(8)	-0.027(3)	0.002(2)	-0.013(2)
O22	0.309(1)	0.4303(9)	0.6391(6)	0.063(2)	0.020(1)	0.0093(5)	-0.030(2)	-0.008(2)	-0.012(1)
C11	0.059(2)	0.171(1)	0.1072(9)	0.029(3)	0.019(2)	0.0078(8)	-0.015(4)	-0.003(3)	-0.004(2)
C12	0.075(2)	0.222(1)	-0.1107(9)	0.032(3)	0.021(2)	0.0060(8)	-0.028(3)	0.002(3)	-0.002(2)
C13	0.522(2)	0.222(1)	-0.1160(8)	0.027(3)	0.011(1)	0.0060(7)	-0.014(3)	0.000(2)	0.001(2)
C14	0.383(2)	0.390(1)	-0.0948(10)	0.031(3)	0.018(2)	0.0082(9)	-0.019(4)	0.006(3)	-0.006(2)
C15	0.378(2)	0.370(1)	0.0179(11)	0.039(3)	0.014(1)	0.0118(10)	-0.028(3)	0.001(3)	-0.007(2)
C16	0.506(2)	0.188(1)	0.0704(8)	0.024(2)	0.017(1)	0.0078(7)	-0.015(3)	-0.001(2)	-0.012(1)
C17	0.606(1)	0.097(1)	-0.0150(8)	0.019(2)	0.013(1)	0.0049(6)	-0.012(3)	0.003(2)	-0.004(1)
C21	0.031(2)	0.219(1)	0.5641(9)	0.036(3)	0.013(2)	0.0078(8)	-0.021(3)	-0.010(2)	0.000(2)
C22	0.300(2)	0.344(1)	0.5878(8)	0.040(3)	0.016(2)	0.0044(7)	-0.024(4)	-0.000(3)	0.002(2)
C23	0.568(2)	0.201(1)	0.3793(9)	0.048(3)	0.017(2)	0.0062(8)	-0.036(3)	0.006(3)	-0.005(2)
C24	0.381(2)	0.353(1)	0.3332(8)	0.034(3)	0.013(2)	0.0045(7)	-0.015(3)	0.001(2)	-0.001(2)
C25	0.239(2)	0.290(1)	0.3181(8)	0.032(3)	0.016(2)	0.0040(7)	-0.011(4)	-0.000(3)	0.001(2)
C26	0.329(2)	0.096(1)	0.3580(8)	0.029(3)	0.015(2)	0.0045(6)	-0.015(3)	-0.000(2)	-0.005(2)
C27	0.536(2)	0.039(1)	0.3911(7)	0.036(3)	0.012(1)	0.0036(6)	-0.018(3)	0.006(2)	-0.003(1)

Atom	x	y	z	B,Å^2	Occ.
RU1'	0.158(2)	0.320(1)	0.0042(10)	3.0	0.065(2)
RU2'	0.149(1)	0.331(1)	0.4963(8)	3.0	0.001(2)
CP1 *	0.4791	0.2535	-0.0275		
CP2 *	0.4106	0.1950	0.3559		

The form of the anisotropic thermal parameter is:

$\exp[-(B(1,1)*h^2 + B(2,2)*k^2 + B(3,3)*l^2 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)]$.

Estimated standard deviations in the least significant digits are shown in parentheses

* CP1 and CP2 are the centroids of cyclopentadienyl rings C13-C17 and C23-C27 respectively.

Intramolecular Angles (deg.)

ATOM 1	ATOM 2	ATOM 3	ANGLE
CP1 *	RU1	C11	130.0
CP1 *	RU1	C12	129.3
CP1 *	RU1	C17	106.9
C17	RU1	C11	93.7(3)
C17	RU1	C12	95.1(3)
C11	RU1	C12	92.1(3)
CP2 *	RU2	C21	129.6
CP2 *	RU2	C22	130.9
CP2 *	RU2	C27	107.9
C27	RU2	C21	94.6(3)
C27	RU2	C22	94.2(3)
C21	RU2	C22	89.8(3)
RU1	C17	C13	123.9(5)
RU1	C17	C16	125.1(5)
C16	C17	C13	106.7(6)
C17	C13	C14	100.0(7)
C13	C14	C15	107.7(7)
C14	C15	C16	109.3(7)
C15	C16	C17	107.2(6)
RU2	C27	C23	122.6(6)
RU2	C27	C26	125.1(5)
C26	C27	C23	107.1(7)
C27	C23	C24	107.4(7)
C23	C24	C25	108.7(6)
C24	C25	C26	108.4(6)
C25	C26	C27	108.2(6)
RU1	C11	O11	178.0(8)
RU1	C12	O12	176.8(7)
RU2	C21	O21	177.1(8)
RU2	C22	O22	176.9(7)
RU1'	RU1	C11	68.5(5)
RU1'	RU1	C12	89.6(5)
RU1'	RU1	C17	161.8(4)
RU1'	RU1	CP1	83.2(4)
RU2'	RU2	C21	53.4(4)
RU2'	RU2	C22	67.6(4)
RU2'	RU2	C27	141.1(4)
RU2'	RU2	CP2	109.9(3)

* CP1 and CP2 are the centroids of the cyclopentadiene ligands.

Intramolecular distances.

ATOM 1	ATOM 2	DISTANCE
RU1	C11	1.870(9)
RU1	C12	1.849(9)
RU1	C17	2.077(6)
RU1	CP1 *	1.882
RU1	C13	2.207(7)
RU1	C14	2.249(8)
RU1	C15	2.270(8)
RU1	C16	2.221(7)
RU1	C17	2.242(7)
RU2	C21	1.889(10)
RU2	C22	1.868(9)
RU2	C27	2.099(7)
RU2	CP2 *	1.891
RU2	C23	2.233(8)
RU2	C24	2.240(7)
RU2	C25	2.270(7)
RU2	C26	2.238(7)
RU2	C27	2.277(7)
C11	O11	1.163(9)
C12	O12	1.155(9)
C21	O21	1.143(10)
C22	O22	1.168(9)
C13	C14	1.429(10
C14	C15	1.393(12)
C15	C16	1.430(10)
C16	C17	1.443(9)
C17	C13	1.425(9)
C23	C24	1.455(11)
C24	C25	1.397(11)
C25	C26	1.452(9)
C26	C27	1.435(11)
C27	C23	1.454(10)

* CP1 and CP2 are the centroids of the cyclopentadiene rings.

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