

Syntheses and Crystallographic Characterizations of $Ru_4(CO)_8(\mu_3-C_6H_2R_2O_2)_2$ ($R = H, t-Bu$), Complexes Containing 1,2-Semiquinone Ligands Which Bridge through Oxygen and η^6-C_6 Rings

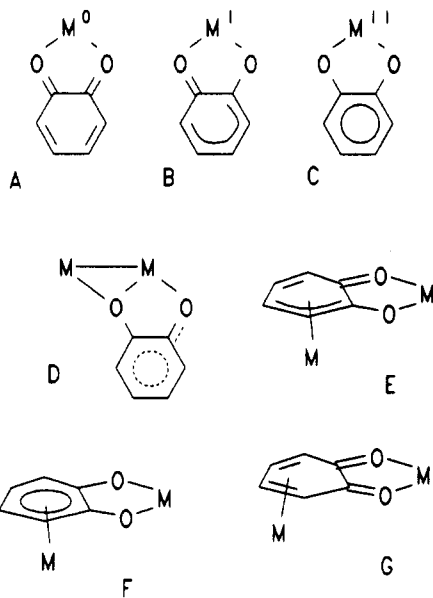
Melvyn Rowen Churchill,* Charles H. Lake, Witold Paw, and Jerome B. Keister*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214

Received September 13, 1993*

Summary: The reactions of $Ru_3(CO)_{12}$ with catechol and with 3,5-di-*tert*-butyl-1,2-benzoquinone yield the three clusters $Ru_4(CO)_8(\mu_3-O_2C_6H_2R_2)_2$ ($R = H, t-Bu$) which differ in the arrangement of metal atoms but which all contain μ_3 -semiquinone ligands coordinated via terminal and bridging O atoms and a $\pi-\eta^6-C_6$ ring. The substitution products $Ru_4(O_2C_6H_2(t-Bu)_2)_2(CO)_7L$ ($L = THF, NMe, PPh_3, C_2Ph_2$) were prepared from one isomer.

Transition-metal complexes of dioxolene ligands have been attracting increasing attention due to their structural and electrochemical properties. The most common coordination mode adopted by a 1,2-dioxolene is as an η^2 -chelate (structures A-C).¹ These complexes usually show



rich electrochemistry with ligand-localized redox processes corresponding to the reduction of the quinone ligand to a semiquinone and then to a catecholate, in addition to metal-localized redox processes.^{1,2} A few examples of bridging dioxolene ligands have been identified. Bridging via a single oxygen atom (structure D),¹ via an η^3-C_6 ring and oxygen atoms (structure E),³ and via terminal oxygen atoms and an η^6-C_6 ring (structure F)⁴ have been identified. Very recently complexes containing η^4 -1,2-benzoquinone

ligands (structure G) have been prepared.⁵ In this communication we report three new ruthenium clusters containing μ_3 -semiquinone ligands coordinated via terminal and bridging O atoms and a $\pi-\eta^6-C_6$ ring.

The reaction of $Ru_3(CO)_{12}$ with catechol has been very recently reported by Bohle and Goodson.^{5a} In refluxing *o*-xylene an insoluble species of the formula $[Ru_2(O_2C_6H_4)(CO)_4]_n$ was formed in high yield. In a very recent paper this material was crystallographically characterized as $[Ru_2(O_2C_6H_4)(CO)_4]_2$ and formulated as a η^5 -*o*-benzosemiquinone complex.^{5b} This compound produced $Ru(CO)_2-(PPh_3)_2(O_2C_6H_4)$, $Ru_4(CO)_8(AsPh_3)_2(\mu-O_2C_6H_4)_2$, and $Ru_2(CO)_4I(\mu-I)(\mu-O_2C_6H_4)$ by treatment with PPh_3 , $AsPh_3$, and I_2 , respectively. The ligands of the polymetallic products are bonded through both oxygen atoms to one metal atom and via a η^4 -arene ring to the other metal atom (structure G). The short C-O bond distances (1.27-1.30 Å) indicate that the bridging dioxolene ligands are most properly described as 1,2-benzoquinones.

We have also investigated this reaction with the goal of preparing trinuclear clusters with bridging dioxolene ligands for electrochemical studies. The reaction of $Ru_3(CO)_{12}$ with catechol in refluxing toluene gave an insoluble polymer, as previously reported. However, chromatographic separation of the filtrate enabled us to isolate in low yield a red compound which has been characterized as $Ru_4(CO)_8(1,2-C_6H_4O_2)_2$ (1).⁶ An X-ray crystallographic study⁷ revealed the novel structure shown in Figure 1.

The tetrametallic cluster 1 has crystallographically imposed C_2 symmetry (the 2-fold axis passing through Ru(2) and Ru(3)) and contains a linear array of three Ru atoms connected by metal-metal bonds ($Ru(1)-Ru(2) = Ru(1a)-Ru(2) = 2.846(1)$ Å) with each pair of metal atoms bridged by one dioxolene ligand through an oxygen atom and an η^6-C_6 ring. The fourth Ru atom, Ru(3), is connected via bridging oxygen atoms from the two dioxolene ligands.

(5) (a) Bohle, D. S.; Goodson, P. A. *J. Chem. Soc., Chem. Commun.* 1992, 1205. (b) Bohle, D. S.; Christensen, A. N.; Goodson, P. A. *Inorg. Chem.* 1993, 32, 4173.

(6) Synthesis and characterization of 1: $Ru_3(CO)_{12}$ (300 mg) and catechol (155 mg, 3 equiv) were heated under nitrogen in refluxing toluene for 3 h. The insoluble yellow-brown solid was removed and the filtrate evaporated to dryness. Separation of the residue by TLC (silica gel, 15% ethyl acetate in methylene chloride) gave a very deep red band, contaminated with free catechol. The yield of 1 was estimated to be ca. 15 mg (5%). Pure material and X-ray-quality crystals were obtained from crystallization from methylene chloride/methanol solution. Anal. Calcd for $C_{20}H_{12}O_{12}Ru_4 \cdot CH_2Cl_2$: C, 27.14; H, 1.08. Found: C, 27.76; H, 1.16. IR (CH_2Cl_2): 2064 w, 2036 vs, 2000 m, 1990 w, 1958 m, $br\ cm^{-1}$. 1H NMR ($CDCl_3$, 25 °C) 6.49 (t, 2H, $J = 6$ Hz), 6.28 (d, 2H, $J = 6$ Hz), 5.51 (t, 2H, $J = 6$ Hz), 4.96 (d, 2H, $J = 6$ Hz) ppm. EI MS: m/z 848 ($^{102}Ru_4$).

(7) Crystallographic data for 1: $C_{20}H_{12}O_{12}Ru_4 \cdot CH_2Cl_2$, $M_r = 929.5$, orthorhombic space group $Pnn2$, $a = 13.9003(20)$ Å, $b = 8.6481(21)$ Å, $c = 10.6075(16)$ Å, $V = 1275.1(4)$ Å³, $Z = 2$, $D_c = 2.421$ Mg/m³, $F(000) = 884$, $T = 298$ K, $R = 2.12\%$ and $R_w = 2.98\%$ for those 1676 reflect ions with $2\theta(Mo\ K\alpha) = 5-45^\circ$ and $|F| > 0.3\sigma(F)$.

* Abstract published in *Advance ACS Abstracts*, November 15, 1993.

(1) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* 1981, 38, 45.

(2) Hartl, F.; Vlcek, A., Jr. *Inorg. Chem.* 1992, 31, 2869 and references therein.

(3) Fox, G. A.; Pierpont, C. G. *J. Chem. Soc., Chem. Commun.* 1988, 806.

(4) Westcott, C. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J. *J. Chem. Soc., Chem. Commun.* 1991, 304.

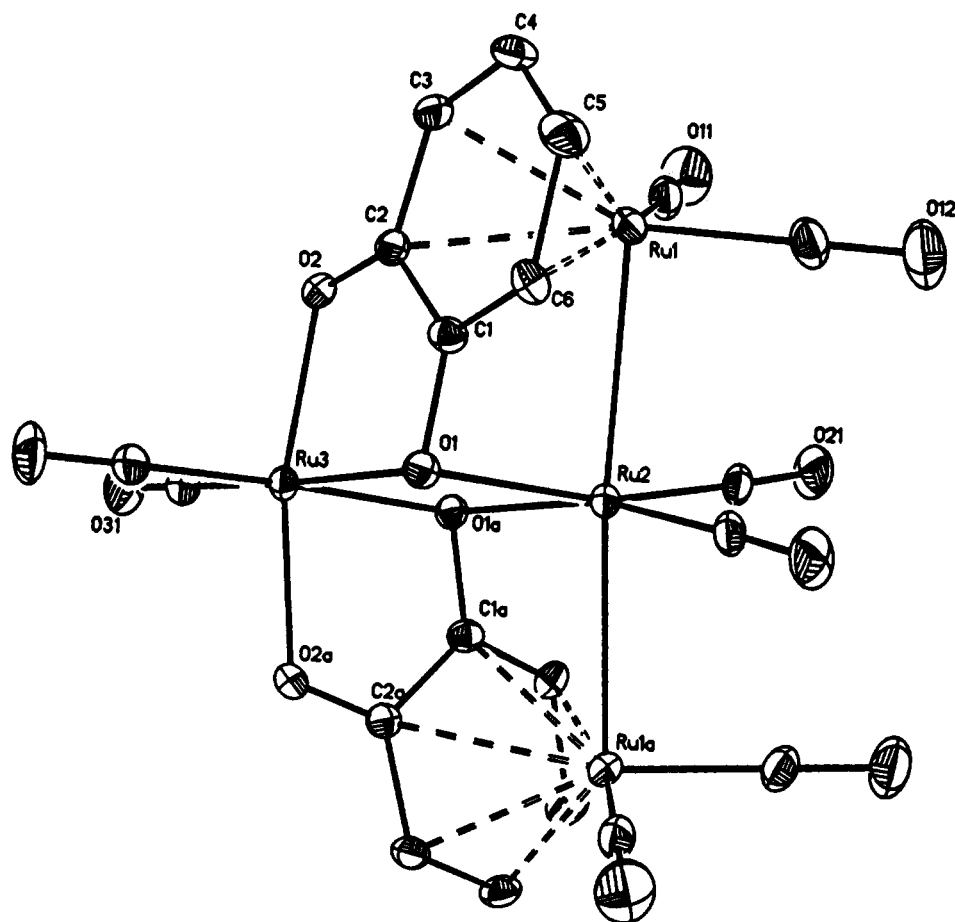


Figure 1. ORTEP drawing of 1. The molecule possesses precise C_2 symmetry. Selected bond distances (Å) and angles (deg): Ru(1)–Ru(2) = 2.846(1), C(2)–O(2) = 1.286(8), C(1)–O(1) = 1.366(6), Ru(3)–O(2) = 2.061(4), Ru(3)–O(1) = 2.120(4), Ru(2)–O(1) = 2.223(4), Ru(1)–C(1) = 2.315(5), Ru(1)–C(2) = 2.428(7), Ru(1)–C(3) = 2.306(8), Ru(1)–C(4) = 2.275(6), Ru(1)–C(5) = 2.284(6), Ru(1)–C(6) = 2.282(6); Ru(1)–Ru(2)–Ru(1A) = 175.1(1), Ru(2)–O(1)–Ru(3) = 102.2(1).

The short C–O distance associated with the terminally coordinated oxygen (C(2)–O(2) = 1.286(8) Å) and the long distance associated with the bridging oxygen (C(1)–O(1) = 1.366(6) Å) indicate that the dioxolene ligand might be best described as a semiquinone.

The reaction of $Ru_3(CO)_{12}$ with 3,5-di-*tert*-butyl-1,2-benzoquinone produced two clusters of the formulation $Ru_4(CO)_8(\mu_3-O_2C_6H_2R)_2$ ($R = t\text{-Bu}$), a red compound 2 and a yellow compound 3.⁸ The spectral data suggest that 2 is structurally analogous to 1. However, the X-ray crystallographic study⁹ of 3 (Figure 2) shows a structure

(8) Synthesis and characterization of "red" 2 and "yellow" 3: $Ru_3(CO)_{12}$ (200 mg) and 3,5-di-*tert*-butyl-1,2-benzoquinone (207 mg, 3 equiv) were heated under nitrogen in refluxing toluene for 4 h. The red solution was evaporated to dryness, and the residue was dissolved in 3 mL of methylene chloride. The insoluble yellow solid was filtered out and redissolved in methylene chloride. Concentration of this solution gave 100 mg (40%) of 3. Products contained in the filtrate were separated by TLC (methylene chloride). The first red-orange band was the main product, 2 (70 mg, 30%). X-ray-quality crystals of $3 \cdot 2CH_2Cl_2$ were obtained by slow evaporation of methylene chloride solution. Data for 3 are as follows. Anal. Calcd for $C_{36}H_{44}O_{12}Ru_4 \cdot 2CH_2Cl_2$: C, 36.84; H, 3.83. Found: C, 38.14; H, 3.50. IR (hexanes): 2035 vs, 1995 m, 1967 s, 1950 w cm^{-1} . 1H -NMR ($CDCl_3$, 25 °C): 6.52 (d, 2H, $J = 2$ Hz), 5.43 (d, 2H, $J = 2$ Hz), 1.56 (s, 18H), 1.28 (s, 18H) ppm. EIMS: m/z 1072 ($^{102}Ru_4$). Data for 2 are as follows. Anal. Calcd for $C_{36}H_{40}O_{12}Ru_4 \cdot CH_2Cl_2$: C, 38.51; H, 3.67. Found: C, 38.93; H, 3.60. IR (hexanes): 2058 m, 2032 vs, 1996 s, 1984 m, 1958 m, 1953 m cm^{-1} . 1H NMR ($CDCl_3$, 25 °C): 6.52 (d, 2H, $J = 2$ Hz), 5.14 (d, 2H, $J = 2$ Hz), 1.49 (s, 18H), 1.28 (s, 18H) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): 204.8 (2C, CO), 204.7 (2C, CO), 204.0 (2C, CO), 197.0 (2C, CO), 144.9 (2C, unprot ring C), 125.7 (2C, unprot ring C), 125.0 (2C, unprot ring C), 119.6 (2C, unprot ring C), 88.1 (2C, prot ring C), 85.9 (2C, prot ring C), 35.5 (2C, *t*-Bu C), 33.7 (2C, *t*-Bu C), 30.9 (6C, methyl C), 29.9 (6C, methyl C) ppm. EI MS: m/z 1072 ($^{102}Ru_4$).

analogous to that for $[Ru_2(O_2C_6H_4)(CO)_4]_2$ reported by Bohle and co-workers.^{5b}

The crystal contains two independent molecules of the cluster (each having precise C_i symmetry) and two independent CH_2Cl_2 molecules of solvation. The tetrametallic cluster 3 contains two diruthenium units, each pair of Ru atoms connected via a metal–metal bond and a dioxolene ligand bridge via an oxygen atom and a η^6 -C₆ ring. The two Ru_2 units are connected via bridging oxygen atoms from both dioxolene ligands. The ligands display the same coordination mode as in 1. The dioxolene terminal C–O distance is shorter than the other (1.292(12) vs 1.340(13) Å and 1.288(10) vs 1.357(11) Å in the two crystallographically independent molecules). These distances are very similar to the distances reported for $[Ru_2(O_2C_6H_4)(CO)_4]_2$ (1.292(3) vs 1.351(3) Å).^{5b} The dioxolenes are best described as semiquinones in 3, as in 1.

The unusual bonding of the ligands in these clusters would be expected to have a large effect on the electrochemical behavior. Indeed, although $Ru(CO)_2(PPh_3)_2(1,2-O_2C_6H_4)$ displays reversible oxidation at -0.36 V vs the ferrocene/ferrocenium couple, cyclic voltammograms of 1–3 in dichloromethane solution each showed only an irreversible one-electron oxidation at greater than 0.4 V.

(9) Crystal data for 3: $C_{36}H_{40}O_{12}Ru_4 \cdot 2CH_2Cl_2$, $M_r = 1238.8$, triclinic space group $P\bar{1}$, $a = 11.3503(13)$ Å, $b = 11.4188(11)$ Å, $c = 19.4541(19)$ Å, $\alpha = 93.680(8)^\circ$, $\beta = 102.682(8)^\circ$, $\gamma = 107.260(8)^\circ$, $V = 2326.3(4)$ Å³, $Z = 2$, $D_c = 1.769$ Mg/m³, $F(000) = 1224$, $T = 298$ K, $R = 4.34\%$, $R_w = 4.64\%$ for those 3540 reflections with $2\theta(\text{Mo K}\alpha) = 5\text{--}45^\circ$ and $F > 6\sigma(F)$.

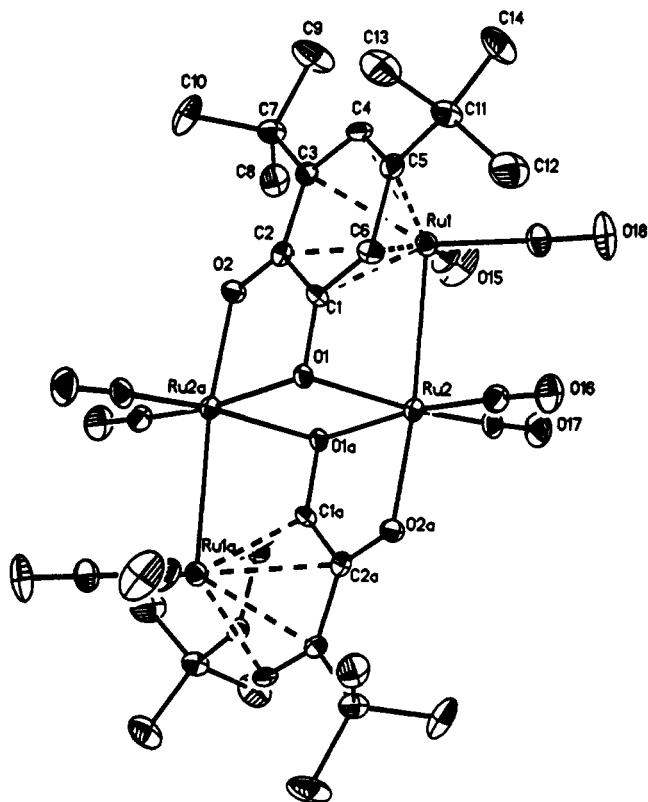


Figure 2. ORTEP drawing of one molecule of **3**. Selected bond distances (Å) and angles (deg) within this molecule: Ru(1)–Ru(2) = 2.791(1), C(2)–O(2) = 1.292(12), C(1)–O(1) = 1.340(13), Ru(2a)–O(2) = 2.083(7), Ru(2a)–O(1) = 2.192(6), Ru(2)–O(1) = 2.204(6), Ru(1)–C(1) = 2.328(8), Ru(1)–C(2) = 2.437(9), Ru(1)–C(3) = 2.357(10), Ru(1)–C(4) = 2.288(11), Ru(1)–C(5) = 2.314(9), Ru(1)–C(6) = 2.292(8); Ru(2)–O(1)–Ru(2a) = 103.2(2). Distances and angles within the second molecule are equivalent; e.g., Ru(3)–Ru(4) = 2.787(1).

The substitution chemistries of **2** and **3** are very different. At room temperature **2** does not react with PPh_3 , whereas **3** rapidly fragments to mainly $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)$. On the other hand, **2** reacts with trimethylamine *N*-oxide in THF or acetonitrile to form $\text{Ru}_4(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_2(\text{CO})_7\text{L}$ (L = THF,¹⁰ NCMe,¹¹ respectively). The THF complex is an excellent starting material for further substitution. The reactions with PPh_3 and diphenylacet-

ylene yield $\text{Ru}_4(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_2(\text{CO})_7\text{L}$ (L = PPh_3 ,¹² $\text{C}_2\text{-Ph}_2$ ¹³) after 30 min in refluxing heptane. No such products could be obtained from **3**.

The variety of coordination modes of the dioxolene ligand which arise from these reactions is surprising. We are continuing to examine the effect of the coordination geometry upon the electrochemical behavior of these clusters. The possibility of induction of the interconversion of the various coordination geometries of the dioxolene ligand via chemical or electrochemical methods is also under investigation.

Acknowledgment. We thank Dr. Scott Bohle for a preprint of ref 5b and for helpful discussions. This work was supported by the National Science Foundation through Grant CHE-9213695. Purchase of the diffractometer was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

Supplementary Material Available: Tables of crystal data, atomic positions, bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates for 1- CH_2Cl_2 and 3- $2\text{CH}_2\text{Cl}_2$ (19 pages). Ordering information is given on any current masthead page.

OM930629T

(10) $\text{Ru}_4(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_2(\text{CO})_7(\text{THF})$: IR (hexanes) 2030 s, 1991 s, 1952 m, 1947 m, 1938 w cm^{-1} ; ^1H NMR (CDCl_3 , 25 °C) 6.53 (d, 1H, $J = 2$ Hz), 6.45 (d, 1H, $J = 2$ Hz), 5.38 (d, 1H, $J = 2$ Hz), 4.89 (d, 1H, $J = 2$ Hz), 3.60 (m, 4H), 3.45 (m, 4H), 1.52 (s, 9H), 1.49 (s, 9H), 1.31 (s, 9H), 1.22 (s, 9H) ppm; FAB MS m/z 1116 ($^{102}\text{Ru}_4$). Anal. Calcd for $\text{C}_{39}\text{H}_{48}\text{O}_{12}\text{Ru}_4\cdot\text{CH}_2\text{Cl}_2$: C, 40.10; H, 4.21. Found: C, 38.14; H, 3.50.

(11) $\text{Ru}_4(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_2(\text{CO})_7(\text{NCMe})$: IR (hexanes) 2029 s, 1991 s, 1960 m, 1951 w, 1946 w cm^{-1} ; ^1H NMR (CDCl_3 , 25 °C) 6.51 (d, 1H, $J = 2$ Hz), 6.46 (d, 1H, $J = 2$ Hz), 5.18 (d, 1H, $J = 2$ Hz), 4.91 (d, 1H, $J = 2$ Hz), 2.38 (s, 3H), 1.51 (s, 9H), 1.48 (s, 9H), 1.29 (s, 9H), 1.24 (s, 9H) ppm. Anal. Calcd for $\text{C}_{37}\text{H}_{48}\text{O}_{11}\text{NRu}_4$: C, 41.07; H, 4.01; N, 1.29. Found: C, 40.10; H, 3.89; N, 0.92.

(12) $\text{Ru}_4(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_2(\text{CO})_7(\text{PPh}_3)$: IR (hexanes) 2027 s, 1988 s, 1950 s, 1944 w cm^{-1} ; ^1H NMR (CDCl_3 , 25 °C) 7.3 (m, 15H), 6.40 (d, 1H, $J = 2$ Hz), 6.17 (d, 1H, $J = 2$ Hz), 5.22 (d, 1H, $J = 2$ Hz), 4.37 (d, 1H, $J = 2$ Hz), 1.41 (s, 9H), 1.25 (s, 9H), 1.13 (s, 9H), 1.11 (s, 9H) ppm; ^{31}P NMR (CDCl_3 , 25 °C) 61.7 ppm; FAB MS m/z 1306 ($^{102}\text{Ru}_4$). Anal. Calcd for $\text{C}_{53}\text{H}_{56}\text{O}_{11}\text{PRu}_4\cdot\text{CH}_2\text{Cl}_2$: C, 46.72; H, 4.14. Found: C, 46.46; H, 3.70.

(13) $\text{Ru}_4(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_2(\text{CO})_7(\text{C}_2\text{Ph}_2)$: IR (hexanes) 2030 s, 1992 s, 1971 w, 1954 m, 1949 m cm^{-1} ; ^1H NMR (CDCl_3 , 25 °C) 7.54 (m, 10H), 6.45 (d, 1H, $J = 2$ Hz), 6.35 (d, 1H, $J = 2$ Hz), 5.25 (d, 1H, $J = 2$ Hz), 4.89 (d, 1H, $J = 2$ Hz), 1.27 (s, 9H), 1.24 (s, 9H), 1.20 (s, 9H), 1.07 (s, 9H) ppm; FAB MS m/z 1222 ($^{102}\text{Ru}_4$). Anal. Calcd for $\text{C}_{49}\text{H}_{50}\text{O}_{11}\text{Ru}_4\cdot\text{CH}_2\text{Cl}_2$: C, 46.05; H, 4.02. Found: C, 45.29; H, 3.97.