Photochemical Synthesis of Olefin–Carbonylosmium Complexes: Serendipitous Formation of a 1,2-Diosmacyclobutane Derivative

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The photochemical generation of highly reactive coordinatively unsaturated organometallic substrates as a means of synthesizing mononuclear metal carbonyl derivatives, and in particular carbonyl–olefin complexes, is well-known and has been applied to many transition metals.[1] Previously we have described the facile and efficient photochemical preparation of $Ru(CO)_4(olefin)$[2] and $Ru(CO)_3(olefin)_2$[3] complexes from $Ru_3(CO)_{12}$, **1-Ru**, and a variety of olefins. Here we report on the photochemical reaction between $Os_3(CO)_{12}$, **1-Os**, and olefinic ligand which, in addition to the anticipated $Os(CO)_4(olefin)$ compounds, also gave in an unprecedented fashion a rare example of 1,2-diosmacyclobutane derivative.[4]

Irradiation[5] of $Os_3(CO)_{12}$, **1-Os**, in the presence of a large excess of methyl acrylate results in the total consumption of **1-Os** and the formation of a mixture of two compounds, **2a** and **3a** (eq 1).

$$Os_3(CO)_{12} + \text{methyl acrylate} \xrightarrow[\text{benzene}, \approx 15\ ^\circ C]{h\nu,\ \lambda > 370\ \text{nm}} \mathbf{2a} + \mathbf{3a} \quad (1)$$

Compound **2a** and the corresponding fumarate complex, **2b**,[6] are shown to be the anticipated $Os(CO)_4(\eta^2\text{-olefin})$ derivatives.[7-9] The IR and ^{13}C NMR spectra of the molecules are consistent with trigonal-bipyramidal structures in which the olefin occupies an equatorial position, similar to the Fe and Ru analogues.[2] The molecules are fluxional. At low temperatures both olefin rotation and axial–equatorial carbonyl exchange is slow, as shown by the four CO resonances in the ^{13}C NMR spectrum of **2a**. Higher temperatures are required for carbonyl scrambling in **2a** and **2b** than in the respective tetracarbonyl ruthenium and iron derivatives.[2,10] This indicates that the $\Delta G^\ddagger$ for carbonyl scrambling is in the order **2-Fe** < **2-Ru** < **2-Os** and shows, as described elsewhere,[11,12] that metal–olefin back-bonding is most important in the osmium compounds.

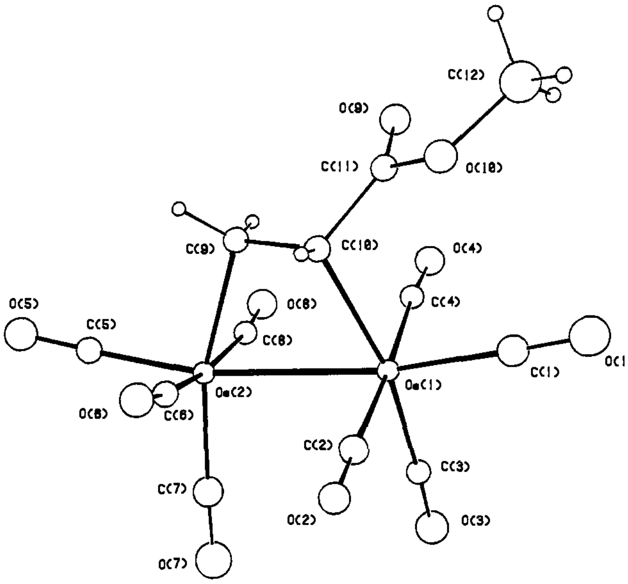

Figure 1. Molecular structure of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHCO_2CH_3)$ (**3a**). The hydrogen atoms, with the exception of one CH_3 hydrogen, were located and isotropically refined. Selected bond distances (Å): Os(1)–Os(2) = 2.8850 (5), Os(1)–C(10) = 2.223 (9), Os(2)–C(9) = 2.203 (9), C(9)–C(10) = 1.52 (1). Selected bond angles (deg): Os(1)–Os(2)–C(9) = 70.0 (2), Os(2)–Os(1)–C(10) = 71.0 (2), Os(2)–C(9)–C(10) = 106.5 (6), Os(1)–C(10)–C(9) = 103.5 (6).

More surprising and unexpected was the formation of another compound in these reactions. Compound **3a**[13] has been obtained in ~30% yield by crystallization of the crude reaction mixture. The dinuclear formulation, $Os_2(CO)_8(CH_2CHCO_2CH_3)$, indicated by the mass spectrum and analysis, has been confirmed by X-ray diffraction.[14] The molecular structure, with numbering scheme, is shown in Figure 1. The results clearly show the remarkable formation of a 1,2-diosmacyclobutane derivative in the photochemical synthesis. The Os–Os bond distance (2.8850 (5) Å) and Os–C bond lengths (Os(1)–C(10) = 2.223 (9) Å, Os(2)–C(9) = 2.203 (9) Å) are typical single-bond values[15] and the length of the μ-1,2-ethanediyl bridge (C(9)–C(10) = 1.52 (1) Å) is that

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(1) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(2) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *J. Am. Chem. Soc.* **1981**, *103*, 4069.

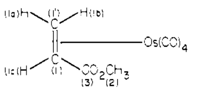
(3) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *Angew. Chem.* **1981**, *93*, 475; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 452.

(4) While this paper was in preparation we learned that a related 1,2-diosmacyclobutane has been synthesized: Motyl, K. M.; Norton, J. R.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325. The preparative procedure is quite different from ours and involves the reaction of $Na_2[Os_2(CO)_8]$ with $TsOCH_2CH_2OTs$.

(5) Irradiations were performed in an immersion lamp apparatus by using a Philips HPK 125-W high-pressure mercury lamp; the water-cooled compartment of the Pyrex immersion well also contained a GWV (Glasswerk Wertheim) cutoff filter sleeve ($\lambda > 370$ nm).

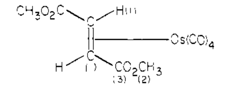
(6) The reaction with dimethyl fumarate also gave a mixture of compounds. So far only a pentane-soluble fraction, **2b**, slightly contaminated with free dimethyl fumarate has been isolated and identified.

(7) **2a**: white, air-stable solid; IR (pentane) ν_{CO} 2126, 2047, 2031, 2001, ν_{CO_2} 1718 cm^{-1}; ^1H NMR (25 °C, toluene-d_8, 200 MHz) δ 1.58 (H^{1a}, dd), 2.12 (H^{1b}, dd), 2.59 (H^{1c} dd), 3.38 (H^2, s) (J_{gem} = 4 Hz, J_{cis} = 8 Hz, J_{trans} = 10 Hz); ^{13}C NMR (–30 °C, toluene-d_8, 100.6 MHz) δ 10.5 (C(1′)), 23.6 (C(1)), 51.2 (C(2)), 176.7 (C(3)), 177.2, 175.9, 175.6, 174.4 (CO); mass spectrum (70 eV, 65 °C), M^+, $M^+ - n$CO (n = 1–4). Anal. Calcd for $C_8H_6O_6Os$: C, 24.74; H, 1.56. Found: C, 23.14; H, 1.43.



2a

(8) **2b:** white, air-stable solid; IR (pentane) ν_{CO} 2137, 2063, 2046, 2010, ν_{CO_2} 1713 cm^{-1}; ^1H NMR (25 °C, toluene-d_8, 200 MHz) δ 3.39 (H^1, s), 3.35 (H^2, s); ^{13}C NMR (25 °C, toluene-d_8, 100.6 MHz) δ 26.2 (C(1)), 51.4 (C(2)), 176.3 (C(3)), 173.7, 172.3 (CO); mass spectrum (70 eV, 80 °C) M^+, $M^+ - n$CO (n = 1–4).



2b

(9) $Os(CO)_4(\eta^2\text{-}C_2H_4)$, **2c**, was also obtained by thermal reaction of $Os(CO)_4(H)CH_3$ and ethylene in CH_2Cl_2: Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955.

(10) Coalescence temperatures, T_c, for **2a** ≃ 25 °C, for **2b** = 90 °C; on the basis of the approximate equation for two equally populated exchanging sites $\Delta G^\ddagger_{T_c}$ = 16.8 kcal/mol for carbonyl scrambling in **2b**.

(11) Kruczynski, L.; Martin, J. L.; Takats, J. *J. Organomet. Chem.* **1974**, *80*, C9.

(12) (a) Kruczynski, L.; LiShingMan, L. K. K., Takats, J. *J. Am. Chem. Soc.* **1974**, *96*, 4006. (b) Wilson, S. T.; Coville, N. J.; Shapley, J. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4038.

(13) **3a**: white, air-stable crystals; IR (pentane) ν_{CO} 2130, 2086, 2049, 2039, 2028, 2017, 2000, ν_{CO_2} 1713 cm^{-1}; ^1H NMR (25 °C, C_6D_6, 200 MHz) δ 1.53 (H^{1a}, dd), 1.98 (H^{1b}, t), 2.57 (H^{1c}, dd), 3.45 (H^2, s) ($J_{gem} = J_{trans}$ = 11 Hz, J_{cis} = 7.5 Hz); ^{13}C NMR (25 °C, C_6D_6 100.6 MHz) δ –24.9 (C(1′)), –4.3, (C(1)), 50.4 (C(2)), 166.9, 168.5, 171.9, 172.1, 178.7, 178.4, 179.1, 180.0, 182.4 (CO and C(3)); mass spectrum (70 eV, 70 °C), M^+, $M^+ - n$CO (n = 1–8). Anal. Calcd for $C_{12}H_6O_{10}Os_2$: C, 20.87; H, 0.88. Found: C, 21.26; H, 0.93.

(14) The structure determination was carried out by Dr. R. Ball of the Structure Determination Laboratory of the Department of Chemistry, University of Alberta. Crystal data for **3a**: space group $P2_1/n$, $Z = 4$, a = 16.707 (2) Å, b = 13.604 (2) Å, c = 6.997 (2) Å, β = 95.08 (2)° at –130 °C. In the final least-squares cycle 227 parameters were refined by using 2352 observations having $I > 3.0\sigma(I)$. The final agreement factors were R = 0.044 and R_w = 0.058.

(15) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1291.

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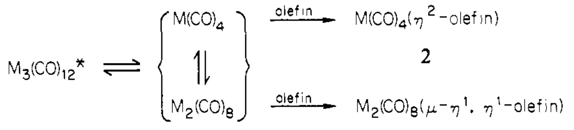
of a normal C–C single bond. Interestingly the four-membered ring is not planar but puckered and results in a skewed conformation of the two $Os(CO)_4$ moieties. The average twist angle about the Os–Os bond is 21°. The observed geometry is presumably due to the flexibility of the four-membered ring, which allows movement of the $Os(CO)_4$ moieties out of the sterically congested eclipsed configuration. The structure closely resembles, including the value of the twist angle, the unsubstituted parent molecule $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)$, **3c**.[4] Although two other examples of 1,2-dimetallacyclobutanes have been reported,[16] the photostability of **3a** is especially noteworthy and may indicate an extensive series of related 1,2-diosmacycles.[17]

The difference in the long-wavelength photoactivity of **1**-Os and **1**-Ru in the presence of olefins is striking and merits some considerations. Recent UV photoelectron spectral studies and theoretical investigations[18] deduced similar electronic structures for the two $M_3(CO)_{12}$ compounds. Thus the primary photoexcitation probably leads to a common photochemical intermediate (eq 2). Although there is no general agreement concerning the

$$M_3(CO)_{12} \underset{M\ =Ru,\ Os}{\overset{h\nu,\ \lambda\ >370\ nm}{\rightleftarrows}} M_3(CO)_{12}^* \qquad (2)$$

nature of the intermediate nor about the subsequent steps in the photoreaction,[19] we believe that with the present results, a previously postulated mechanism[2,19a] must receive serious consideration at least for the reaction with olefins (eq 3). The difference



(3)

in reactivity between **1**-Os and **1**-Ru is best explained by the relative M–M bond strength in these species, Os–Os > Ru–Ru, which may also account for the facile breakdown of $Ru_2(CO)_8$ and formation of **2**-Ru only.

The synthetic implications of the mechanism depicted by eq 2 are being evaluated by exploring the photoreaction of $Os_3(CO)_{12}$ with other unsaturated substrates and the interaction of olefinic ligands with other known metal-metal multiple bonded species.[20] The reactivity of **3a** is also under intense scrutiny.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the University of Alberta and the Max-Planck-Institute für Strahlenchemie for financial support, Professor J. R. Norton for a preprint of ref 4, and Professor R. Hoffmann for some relevant comments and preprints.

Registry No. **1**-Os, 15696-40-9; **2a**, 85702-38-1; **2b**, 85719-06-8; **3a**, 85702-39-2; methyl acrylate, 96-33-3; dimethyl fumarate, 624-49-7; osmium, 7440-04-2.

Supplementary Material Available: Detailed results of the X-ray molecular structure of $Os_2(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-}CH_2CHCO_2CH_3)$, tables of experimental details, positional and thermal parameters (*U*, *B*), bond distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

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[16] (a) Green, M.; Laguna, A.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1010 ($Pd_2(1,5\text{-}C_8H_{12})(\mu\text{-}\eta^1,\eta^1\text{-}C_2F_4)$). (b) Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, *1*, 1571 ($Co_2(CO)_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^1,\eta^1\text{-benzocyclobutene})$).

[17] Preliminary results indicate that photolysis ($\lambda \geq 370$ nm) of $Os_3(CO)_{12}$ with continuous ethylene purge gives conversion to a mixture of **2c** and **3c**.

[18] (a) Green, J. C.; Seddon, E. A.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1979**, 94. (b) Ajò, D.; Granozzi, G.; Tondello, E.; Fragalà, I. *Inorg. Chim. Acta* **1979**, *37*, 191. (c) Sherwood, D. E., Jr.; Hall, M. B. *Inorg. Chem.* **1982**, *21*, 3458. (d) Sherwood, D. E., Jr.; Hall, M. B. *Organometallics* **1982**, *1*, 1519. (e) Delley, B.; Manning, M. C.; Ellis, D. E.; Berkowitz, J.; Trogler, W. C. *Inorg. Chem.* **1982**, *21*, 2247.

[19] (a) Austin, R. G.; Paonessa, R. S.; Giordano, P. J.; Wrighton, M. S. *Adv. Chem. Ser.* **1978**, *168*, 189. (b) Malito, J.; Markiewicz, S.; Poë, A. *Inorg. Chem.* **1982**, *21*, 4337. (c) Desrosiers, M. F.; Ford, P. C. *Organometallics* **1982**, *1*, 1715.

[20] Preliminary work indicates that the reaction of ethylene and methyl acrylate with $[(\eta\text{-}C_5Me_5)Rh(CO)]_2$ results in cleavage of the Rh=Rh bond and formation of $(\eta\text{-}C_5Me_5)Rh(CO)(\text{olefin})$); Lin, G.-Y. unpublished observations.

Stereochemical Course of 5-Lipoxygenation of Arachidonate by Rat Basophil Leukemic Cell (RBL-1) and Potato Enzymes

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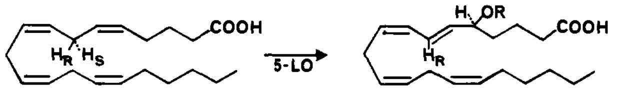
Metabolism of arachidonic acid by the 5-lipoxygenase pathway in response to triggering by IgE-dependent stimuli or by phagocytic leukocytes leads to the production of leukotrienes, a family of potent biological agents that function as regulators of the mammalian cellular microenvironment.[1] We report herein on the absolute stereochemistry of the conversion of arachidonate (**1**)



1

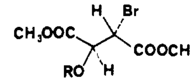
4 H_R=D

2 R=OH

3 R=H

to (5*S*)-hydroperoxy-6*E*-8*Z*,11*Z*,14*Z*-eicosatetraenoic acid (5-HPETE, **2**), the initial step in the leukotriene pathway, in two different enzyme systems—the 5-lipoxygenases (5-LO) derived from rat basophil leukemic (RBL-1) cells and potato tubers.[2] In this study (7*R*)-deuterioarachidonic acid was obtained by total synthesis and converted enzymically to 5-HPETE, which was reduced to the corresponding alcohol (5-HETE, **3**) and analyzed by mass spectrometry as a stable silyl derivative.

Synthesis of (7*R*)-Deuterioarachidonic Acid (4). The readily



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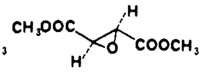

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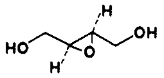

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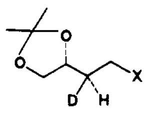
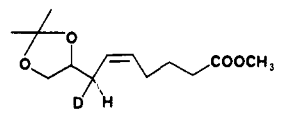
available dimethyl (2*R*)-acetoxy-(3*S*)-bromosuccinate (**5**)[4] was deacetylated (0.3 M hydrochloric acid in methanol, 0.1 M **5**, 46 h at 22 °C, 82% yield) and cyclized (6 equiv of potassium carbonate in acetone at 22 °C for 14 h, 69% yield) to the epoxy ester **6** [mp 70–73 °C; $[\alpha]^{25}_D$ −136.9° (*c* 1.07, methanol); enantiomeric purity >97%].[5] Reduction with sodium borohydride (3.7 equiv in ethanol at 0 °C for 4.5 h, 0.2 M **6**) gave 64% of the crystalline, C_2 symmetric diol epoxide **7**.[6] Stereospecific introduction of the deuterium label was achieved by epoxide opening with 95% ^{2}H lithium aluminum deuteride (2.5 equiv, tetrahydrofuran (THF), [**7**] = 0.06 M, 10 h at reflux), followed by in situ protection of



8 X=OH

9 X=$PPh_3^+Br^-$



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[1] For recent reviews see: (a) Bailey, D. M.; Casey, F. B. *Ann. Rep. Med. Chem.* **1982**, *17*, 203. (b) Clark, D. A.; Marfat, A. *Ibid.* **1982**, *17*, 291. (c) Corey, E. J. *Experientia* **1982**, *38*, 1259.

[2] Corey, E. J.; Albright, J. O.; Barton, A. E.; Hashimoto, S. *J. Am. Chem. Soc.* **1980**, *102*, 1435.

[3] Reactions involving air-sensitive reagents or substances were conducted under an Ar atmosphere. Satisfactory spectroscopic data (infrared, proton magnetic resonance, and mass spectral) were obtained for each synthetic intermediate by using chromatographically purified and homogeneous samples.

[4] Corey, E. J.; Marfat, A.; Hoover, D. J. *Tetrahedron Lett.* **1981**, *22*, 1587.

[5] Seebach, D.; Wasmuth, D. *Helv. Chim. Acta* **1980**, *63*, 197.

[6] Found for (2*S*,3*S*)-epoxy-1,4-butanediol (**7**): ^{1}H NMR (acetone-d_6 with water-d_2) δ 3.69 (dd, $J = 12, 3$ Hz, 2 H, CHHOH), 3.49 (dd, $J = 12, 5$ Hz, 2 H, CHHOH), 2.98 (7, 2 H); IR (neat) 3080 (OH), 1040, 875 cm^{-1}; MS, *m/e* 105 (M + 1), 104 (M^+), 73 ($M - CH_2OH$); $[\alpha]^{25}_D$ −30.57° (*c* 0.168, ethanol); mp 79–82 °C.

0002-7863/83/1505-4093$01.50/0