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Synthesis, Structure, and Catalytic Reactions of Dioxycarbene Complexes of Iron and Osmium

SHIAN-JY WANG, LANCE L. MILLER, ROBERT A. JACOBSON and ROBERT J. ANGELICI*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011, U.S.A.

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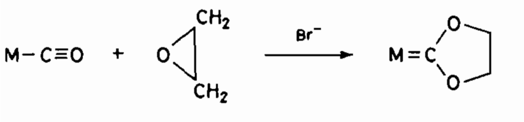
Abstract

$Os_3(CO)_{12}$ reacts with ethylene oxide in the presence of Br^- to give two of the few known dioxycarbene cluster compounds, $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$ (I) and $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (II). The structure of II, established by X-ray diffraction studies, shows the dioxycarbene ligands to be in terminal, equatorial positions. Investigations of reactions of the dioxycarbene ligand showed that $Fe(CO)_4(=\overline{COCH_2CH_2O})$ (III) decomposes with evolution of CO_2 and ethylene, but reacts with oxidizing agents, Me_3NO or O_2, to produce ethylene carbonate. The reaction of III with H_2 gas gives 1,3-dioxolane. In exploratory studies, ethylene oxide, CO and H_2 in the presence of Pt, Pd and Rh catalysts were found to give 1,4-dioxane, 2-methyl-1,3-dioxolane and 2-ethyl-1,3-dioxolane.

Introduction

Our group has recently synthesized a number of transition metal cyclic dioxycarbene complexes by the halide-catalyzed reaction of metal carbonyls [1–4] with ethylene oxide according to eqn. (1).



(1)

M = $CpFe(CO)_2^+$, $CpRu(CO)_2^+$, $CpMn(CO)(NO)^+$, $CpFe(CO)(PPh_3)^+$, $Mn(CO)_4X$ (X = Cl, Br, I), $Re(CO)_4X$ (X = Cl, Br, I), $Fe(CO)_4$, $Mn_2(CO)_9$, $Re_2(CO)_9$

In this paper, we describe the synthesis of dioxycarbene complexes derived from $Os_3(CO)_{12}$ and an X-ray structural determination of one of them. Also, various reactions of the dioxycarbene ligand in $Fe(CO)_4(=\overline{COCH_2CH_2O})$ are examined, and attempts to catalyze reactions of ethylene oxide, H_2 and CO are reported.

Experimental

General Methods

All reactions were performed under prepurified N_2. Unless noted otherwise, reagent grade chemicals were used without further purification. Methylene chloride, hexanes and acetonitrile were distilled from CaH_2 and stored under N_2 over type 4 Å molecular sieves. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2.

The starting compound $Os_3(CO)_{12}$ was prepared from OsO_4 by a modification of a literature procedure [5]. The compound $Fe(CO)_4(=\overline{COCH_2CH_2O})$ was synthesized from $Fe(CO)_5$ and ethylene oxide [4]. Trimethylamine oxide was purified by sublimation at 70 °C in vacuum. The catalysts (10% Pd/C, 10% Pt/C, 5% Rh/C, 10% Pd/Al_2O_3 and $PdCl_2$) were obtained from commercial sources. High pressure reactions were carried out in a 300 ml stainless steel pressure autoclave (Parr, model no. 4761).

Infrared spectra were recorded on a Perkin-Elmer 681 instrument. ^1H NMR spectra were recorded on a Nicolet NT-300 spectrometer. ^{13}C NMR spectra were recorded at −20 °C on a JEOL FX-90Q or Bruker WM-300 spectrometer; $Cr(acac)_3$ (0.1 M) was added to reduce ^{13}C data collection times. Melting points (m.p.) (uncorrected) of the compounds were determined in air on a Thomas hot-stage apparatus. GC-mass spectra were obtained on a Finnigan 4000 GC/MS instrument; FAB spectra of compounds I and II were obtained on a Kratos MS 50.

Synthesis of $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$ (I)

To a mixture of 0.15 g (1.4 mmol) of NaBr in 1 ml of $BrCH_2CH_2OH$ and 25 ml of ethylene oxide at 0 °C was added 0.12 g (0.13 mmol) of $Os_3(CO)_{12}$. The mixture was stirred at 0 °C for 3 days. When the reaction was complete (IR evidence), the solution was taken to dryness in vacuum. The crude compound was extracted with CH_2Cl_2, and the CH_2Cl_2 solution was filtered and chromatographed on a silica gel column (2.5 X 20 cm) using 1:2 CH_2Cl_2/hexanes as the eluent. The solvent was removed under vacuum from the yellow band eluting from the column. The residue was dissolved in CH_2Cl_2, and yellow needle

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*Author to whom correspondence should be addressed.

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crystals of the product were obtained from CH_2Cl_2/hexanes at −20 °C. Yield: 0.094 g, 73%; m.p. (dec.) 92–94 °C. *Anal.* Calc. for $Os_3C_{14}H_4O_{13}$: C, 17.67; H, 0.42. Found: C, 17.57; H, 0.45. IR(CH_2Cl_2) ν(CO): 2119(m), 2062(s), 2051(sh), 2036(vs), 2010(sh), 2001(m), 1991(s), 1970(m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.66 (s, OCH_2). ^{13}C NMR (CD_2Cl_2) at −20 °C: δ 212.15 (carbene C), 189.35, 189.17, 184.57, and 184.36 (CO), 71.10 (OCH_2) ppm. Mass spectrum: *m/e* 951.9 (parent ion).

Synthesis of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (II)

To a cooled mixture (0 °C) of 1.0 g (9.9 mmol) of NaBr and 5 ml of $BrCH_2CH_2OH$ in a pressure autoclave previously purged with N_2 was added 1.0 g (1.11 mmol) of $Os_3(CO)_{12}$. While stirring the mixture with a magnetic stirring bar, 30 ml of ethylene oxide was introduced. After closing the autoclave, its contents were stirred at room temperature for 52 h. Then, the pressure was released and the autoclave was opened. Unreacted ethylene oxide was evaporated by a rapid stream of N_2. The oily residue was dissolved in CH_2Cl_2, and the solution was chromatographed on a silica gel column (2.5 X 35 cm). The first band (yellow) which was eluted with 1:2 CH_2Cl_2/hexanes contained $Os_3(CO)_{11}(\overline{COCH_2CH_2O})$. The second band (orange) was eluted with 1:1 CH_2Cl_2/hexanes and contained $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$. The orange solution was evaporated under vacuum to yield an orange–yellow powder, which was recrystallized from CH_2Cl_2/hexanes at −20 °C. Orange needle crystals were obtained. Yield: 0.271 g of $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$, 26%; 0.381 g of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, 35%. m.p. of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$: 126 °C. *Anal.* Calc. for $C_{16}H_8O_{14}Os_3$: C, 19.30; H, 0.80. Found: C, 19.68; H, 1.03. IR(CH_2Cl_2) ν(CO): 2099(w), 2041(s), 2033(sh), 2010(vs), 2001(sh), 1971(m), 1948(mw) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.58 (s, OCH_2). ^{13}C NMR (CD_2Cl_2) at −20 °C: δ 214.11 (carbene C), 191.56, 191.18, 191.04, and 186.27 (CO), 70.04 (OCH_2) ppm. Mass spectrum: *m/e* 995.9 (parent ion).

Reactions of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ (III)

(a) Decomposition of $Fe(CO)_4(=\overline{COCH_2CH_2O})$

When $Fe(CO)_4(=\overline{COCH_2CH_2O})$ in CH_2Cl_2 was stirred at room temperature for more than 1 day, decomposition to a brown precipitate (probably Fe) and $Fe(CO)_5$ was evident; presumably the other products were CO_2 and C_2H_4; the CO_2 was identified as one of the products previously [4]. When a CH_2Cl_2 solution of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ was injected into the Finnigan GC-MS (injector block temperature was 250 °C, and capillary column was 45 °C), CO_2 and C_2H_4 were identified as the major decomposition products.

(b) Reaction of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ with H_2

0.25 g of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ in 5 ml of decalin was pressurized in an autoclave with 71.5 atm of H_2 gas at room temperature; it was heated to 200 °C and stirred for 24 h. After the pressure was released, the IR spectrum of the reaction mixture showed that $Fe(CO)_4(=\overline{COCH_2CH_2O})$ had reacted completely, and a brown precipitate (probably Fe) had formed. A GC and GC-MS spectrum of the reaction solution showed the formation of a 27% yield of 1,3-dioxolane.

(c) Reaction of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ with Me_3NO

To 0.12 g (0.50 mmol) of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ in 20 ml of CH_3CN at −78 °C, 0.197 g (2.5 mmol) of Me_3NO was added. The reaction mixture was allowed to stir at room temperature for 18 h. A brown precipitate was filtered from the mixture, and the solution was evaporated under vacuum. $Fe(CO)_4(NCMe)$ [6] [IR(CH_2Cl_2) ν(CO): 2050(m), 1953(s), 1931(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.70 ppm (s, CH_3CN)] was extracted from the residue with hexanes. The unextracted residue was ethylene carbonate (24% yield) [IR(CH_2Cl_2) ν(CO): 1810(vs), 1778(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.51 ppm (s, OCH_2)].

Catalytic Reactions of Ethylene Oxide, CO and H_2

The autoclave containing 2 ml (40 mmol) of ethylene oxide, 0.030 g (0.50 mmol) of NaCl, 2 ml of $ClCH_2CH_2OH$ and 0.04 mmol of catalyst was pressurized with 20.4 atm of H_2 and 20.4 atm of CO. The following heterogeneous and homogeneous catalysts were used: 10% Pd/C, 10% Pt/C, 10% Pd/Al_2O_3, 5% Rh/C, $PdCl_2$, $PdCl_2(PPh_3)_2$. The autoclave was heated with stirring at 175–190 °C for 10 h. After cooling to room temperature, the pressure was released and the autoclave was opened; the reaction mixture was analyzed by capillary GC (temperature programmed to 200 °C), which indicated the presence of several products. The major products of all of these catalytic reactions were 1,4-dioxane and 2-methyl-1,3-dioxolane. The yields (based on ethylene oxide) of 1,4-dioxane (17%) and 2-methyl-1,3-dioxolane (50%) in the 5% Rh/C-catalyzed reaction were determined by GC-MS using standard solutions of these compounds and t-butylbenzene as an internal standard.

Crystal Structure Determination of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (II)

Data Collection and Reduction

A crystal suitable for data collection, approximately 0.06–0.11 mm on a side, was selected, placed inside a glass capillary and mounted on a standard goniometer. All intensity data were collected at

TABLE I. Crystal Data for $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (II)

Empirical formula	$Os_3O_{14}C_{16}H_8$
Formula weight	994.80
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	15.391(4)
b (Å)	16.374(3)
c (Å)	17.911(2)
V (Å^3)	4493.(1)
Z	8
μ (Mo Kα) (cm^{-1})	180
ρ_{calc} (g cm^{-3})	2.94
T (K)	245
Diffractometer	SYNTEX P2$_1$
Monochromator	oriented graphite
Reflections measured	hkl, $hk\bar{l}$
Radiation	Mo Kα (λ = 0.71034 Å)
Scan type	ω-scan
Standard reflections[a]	1 (measured every 100)
Reflections collected	4155 collected, 1901 observed ($I > 2\sigma(I)$)
Maximum 2θ (°)[b]	40
Minimum 2θ (°)	3
No. unique reflections	1135 ($I > 2\sigma(I)$)
R_{av} [c]	0.103
Maximum no. parameters refined	120
R[c]	0.054 (unrestrained = 0.051)
R_ω [c]	0.058 (unrestrained = 0.055)

[a]No noticeable decay had occurred in the intensity of the standard. [b]The maximum in 2θ was limited due to a rapid fall off of intensity as a function of sin(θ). [c]$R_{av} = \Sigma|F_o - \langle F_o\rangle|/\Sigma\langle F_o\rangle$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_\omega = [w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. $w = \sigma^{-2}(F_o)$.

TABLE II. Atom Coordinates (fractional × 10^4) and Equivalent Isotropic Thermal Parameters[a] (Å^2 × 10^3) in $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (II)

Atom	*x*	*y*	*z*	*U*
Os1	3467(1)[b]	508(1)	1921(1)	54[c]
Os2	2809(1)	−247(1)	581(1)	53[c]
Os3	2152(1)	1312(1)	1064(1)	52[c]
O11	4559(27)	−889(22)	2536(28)	90[c]
O12	1947(27)	74(30)	2940(24)	113[c]
O13	5054(22)	988(25)	1002(23)	84[c]
O21	4141(22)	−1612(22)	487(22)	77[c]
O22	1412(36)	−537(36)	−593(28)	148[c]
O23	3923(33)	776(25)	−474(30)	116[c]
O24	1703(25)	−1214(22)	1700(22)	86[c]
O31	1698(29)	2668(25)	2152(25)	109[c]
O33	551(26)	395(30)	1570(25)	113[c]
O32	3647(29)	2308(23)	450(24)	97[c]
C10	3730(27)	1386(30)	2585(30)	55(14)[d]
O101	4448(25)	1927(27)	2544(34)	108(15)[d]
C101	4407(39)	2466(44)	3167(47)	86(19)[d]
C102	3513(42)	2407(46)	3553(47)	93(21)[d]
O102	3200(25)	1709(26)	3163(28)	105(14)[d]
C11	4171(32)	−332(36)	2309(33)	69(16)[d]
C12	2527(34)	220(39)	2540(39)	82(19)[d]
C13	4461(32)	850(31)	1385(34)	59(15)[d]
C21	3610(31)	−1114(31)	553(32)	62(15)[d]
C22	1976(38)	−399(40)	−178(40)	90(20)[d]
C23	3532(46)	371(50)	−55(47)	112(25)[d]
C24	2110(37)	−836(32)	1268(32)	65(15)[d]
C30	1506(35)	1577(34)	204(35)	75(17)[d]
O301	1844(24)	1930(24)	−456(27)	93(13)[d]
C301	1196(53)	2010(56)	−1021(60)	131(30)[d]
C302	379(52)	1581(55)	−712(52)	116(25)[d]
O302	641(22)	1358(24)	19(25)	84(12)[d]
C31	1870(35)	2157(42)	1731(39)	84(20)[d]
C32	3123(36)	1895(39)	722(41)	84(20)[d]
C33	1201(32)	681(31)	1371(32)	56(15)[d]

[a]$U = \frac{1}{3}\Sigma U_{ii} \times 10^3$ where the temperature factors are defined as $\exp(-2\pi\Sigma h_i h_j a_i^* a_j^* U_{ij})$. [b]Estimated standard deviations are given in parentheses for the least significant digit in this and all succeeding Tables. [c]Atom refined anisotropically. [d]Atom refined isotropically.

245 K. The unit cell parameters were initially calculated using an automatic indexing procedure [7]. The observed systematic absences of $0kl$: $k = 2n + 1$, $h0l$: $l = 2n + 1$, and $hk0$: $h = 2n + 1$ indicated the space group *Pbca*. Final lattice constants were determined by a least-squares fit to the 2θ values of 14 higher angle reflections. The intensities were corrected for Lorentz, polarization, and absorption effects (using an empirical absorption correction program [8] and includes a spherical correction with $\mu R = 3.2$). Table I contains information pertinent to the data collection and reduction.

Structure Solution and Refinement

Using an osmium–osmium vector for the three-dimensional Patterson superposition, analysis revealed the appropriate positions for the osmium atoms. The remaining non-hydrogen atoms were located via alternate cycles of least-squares calculations [9] and electron difference density calculations [10]. The atomic scattering factors were those found in the International Tables [11a]*. Positions of the hydrogen atoms were calculated assuming a C–H bond distance of 1.05 Å. Atomic coordinates and equivalent isotropic thermal parameters for II are given in Table II.

Restraints were added to the bond distances [12] due to the relatively small contribution to total scattering made by the individual carbon atoms in the presence of osmium and the large absorption effect due to the latter element (d(Os=C) = 1.64–

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*Hydrogen scattering factors were taken from ref. 11b. Real and imaginary corrections for anomalous dispersion of the osmium atoms were obtained from ref. 11c.

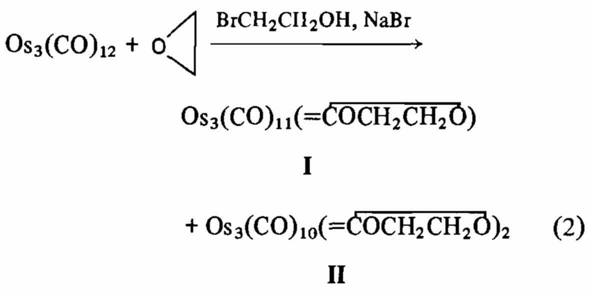
2.04 Å, $d(C{=}O) = 1.10-1.44$ Å prior to adding restraints). Analytical scattering factors for Os, O, and H were those found in the International Tables [13]. The 'ideal' standard deviation for bonded distances was set at 0.0133; the actual value was 0.0061 indicating a proper choice of restraint targets.

Accurate standard deviations were not possible to obtain from RESLSQ since a sparse normal equations matrix is used. The values reported throughout this paper were obtained from the full-matrix routine in ALLS, by inverting the normal equations matrix for atoms with the positions from RESLSQ, and thus they represent the maximum value for the standard deviations of the parameters.

Results and Discussion

Synthesis of $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$ *(I) and* $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ *(II)*

Since $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ [4], $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-CPh})[=C(OMe)_2]$ [14a], and $Fe_3S(CO)_9(=\overline{COCH_2CH_2O})$ [14b] are the only known clusters with dioxycarbene ligands, we explored the possibility that our previous method (eqn. (1)) of preparing cyclic dioxycarbene complexes from metal carbonyls could be extended to $Os_3(CO)_{12}$. Indeed, $Os_3(CO)_{12}$ reacts with ethylene oxide in the presence of Br^- (eqn. (2)) to form



$$Os_3(CO)_{12} + \text{O}\!\lhd \xrightarrow{BrCH_2CH_2OH,\ NaBr} \underset{\textbf{I}}{Os_3(CO)_{11}(=\overline{COCH_2CH_2O})} + \underset{\textbf{II}}{Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2} \quad (2)$$

the mono, **I**, and bis, **II**, carbene products. The preparations of **I** and **II** were performed under a variety of conditions (Table III); no $Os_3(CO)_{12}$ remained unreacted in any of the reactions. At 0 °C, the reaction gives only **I** (after 3 days); however, at 25 and 100 °C, both **I** and **II** are produced which suggests that $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ is produced by a further reaction of ethylene oxide with $Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$. Yields of both **I** and **II** are low when the reaction is run at high temperature (100 °C). This is presumably due to decomposition of the products at this temperature; in fact, the decomposition temperatures of the **I** and **II** solids are 92 and 120 °C, respectively.

TABLE III. Conditions for the Preparations of I and II

Temperature (°C)	CO pressure (atm)	Time	Yield (%)	
			I	II
0		3 days	73	
25	34	1 day	29	trace
25		52 h	26	35
100	34	1 h	14	10

The carbene ligands in **I** and **II** could either be in axial or equatorial positions. In other M_3 clusters whose structures have been established by X-ray diffraction, the non-carbonyl ligands are axial in $Os_3(CO)_{12-n}(NCMe)_n$ ($n = 1$ or 2) [15] and $Ru_3(CO)_{12-n}(CNBu^t)_n$ ($n = 1$ or 2) [16], but equatorial in $Os_3(CO)_{11}[P(OMe)_3]$ [17], $Ru_3(CO)_{11}(PPh_3)$ [18] and $Os_3(CO)_{10}(s\text{-}trans\text{-}C_4H_6)$ [19]. In an attempt to establish the structures of **I** and **II**, we compare their IR spectra in the $\nu(CO)$ region with those of clusters with known structures (Table IV). Because of the large number of absorptions in the spectra of both the axial and equatorial isomers, it is not possible to assign unequivocally structures to **I** and **II** on this basis.

The two cyclic dioxycarbene groups in compound **II** are equivalent, as indicated by the one sharp CH_2 singlet in the ^1H NMR spectrum and singlets for the carbene and CH_2 carbons in the ^{13}C spectrum. The ^{13}C NMR spectra of **I** and **II** recorded at room temperature showed only one broad band in the carbonyl region (~180 ppm downfield from Me_4Si), indicating that the CO ligands are fluxional; however, at −20 °C, four CO resonances were observed in both **I** and **II** indicating reduced fluxionality of the compounds. In $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, the carbonyl groups give rise to a sharp singlet at 204.1 ppm at room temperature in the ^{13}C NMR spectrum [4]. Thus, $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ is more fluxional than **II**. A similar difference in fluxionality is seen in the parent $M_3(CO)_{12}$ (M = Ru, Os) clusters where the Ru cluster shows a single CO resonance even at −100 °C [20], whereas, the CO doublet in $Os_3(CO)_{12}$ does not coalesce until 70 °C [21].

Structure of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ *(II)*

The solid state structure of compound **II** determined by X-ray diffraction is shown in Fig. 1. The basic coordination geometry is that of $Os_3(CO)_{12}$ [22] with the two cyclic dioxycarbene ligands occupying two equatorial carbonyl coordination sites. Each of the Os atoms has a distorted octahedral coordination geometry. All of the carbonyl ligands are terminal and nearly linear, Os–C–O, 170–174°. The three metal atoms define a triangle with an average Os–Os bond distance of 2.871 Å (Table V); this value is very close to the mean metal–metal distance (2.877(3) Å) [22] in $Os_3(CO)_{12}$. In **II**, the shortest Os–Os bond (2.854(3) Å) is between Os1

TABLE IV. IR Spectra of $M_3(CO)_{12-n}L_n$ Complexes

Complexes	
eq-$Ru_3(CO)_{11}(PPh_3)$ [a]	2087m, 2046s, 2030sh, 2023sh, 2014s, 1996sh, 1986m, 1972sh, 1960sh
ax-$Ru_3(CO)_{11}(CN^tBu)$ [a]	2093w, 2047s, 2040s, 2016m, 1998m, 1995m
ax-$Os_3(CO)_{11}(NCMe)$ [b]	2103w, 2052s, 2040s, 2020m, 2000vs, 1984sh, 1981m, 1969vw, 1960vw
$Os_3(CO)_{11}(=\overline{COCH_2CH_2O})$ [a]	2119m, 2062s, 2051sh, 2036vs, 2010sh, 2001m, 1991s, 1970m
eq,eq-$Os_3(CO)_{10}$(s-*trans*-C_4H_6) [b]	2109m, 2063m, 2047s, 2019vs, 1994s, 1975m, 1942vw
ax,ax-$Ru_3(CO)_{10}(CN^tBu)_2$ [a]	2065w, 2020s, 2007m, 1996s, 1990m, 1986m
ax,ax-$Os_3(CO)_{10}(NCMe)_2$ [b]	2077w, 2025sh, 2019vs, 1982s, 1953m
eq,eq-$Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ [b]	2099w, 2041s, 2033sh, 2010vs, 2001sh, 1971m, 1948mw

[a] In hexane. [b] In cyclohexane.

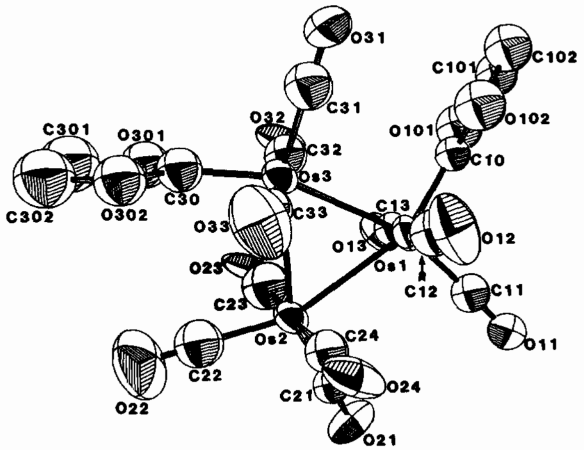


Fig. 1. ORTEP drawing of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (**II**).

and Os3, which are also the atoms that bear the cyclic dioxycarbene ligands. The shortest Os–Os distance in $Os_3(CO)_{10}(NCMe)_2$ [15] is also between the Os atoms that have the coordinated MeCN ligands. As in $Os_3(CO)_{10}$(s-*trans*-C_4H_6) [19] and $Os_3(CO)_{11}$-$(P(OMe)_3)$ [17] where the non-carbonyl ligands occupy the equatorial positions, the carbene ligands in **II** are also equatorial. The C_3O_2 carbene rings are nearly planar with the maximum deviation from planarity being 0.068 Å.

Both of the carbene ligands in **II** are terminal. Bridge bonding is observed in all other previously reported cluster-bound alkylidene (=CR_2) complexes, e.g. $(\mu_2\text{-}CO)(\mu_2\text{-}CH_2)Os_3(CO)_{10}$ [23] and $(\mu_2\text{-}H)_2$-$(\mu_2\text{-}CH_2)Os_3(CO)_{10}$ [24] and in some trimetal clusters with the =CR(OR′) ligand, e.g. $[(\mu\text{-}H)Os_3$-

TABLE V. Selected Bond Angles (°) and Distances (Å)[a, b] in $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (**II**)

	$N = 1$	$N = 2$	$N = 3$
$Os(N)-Os(N+1)$ [c]	2.883(3)	2.877(3)	2.854(3)
$Os(N)-C_{carbene}$	1.91(5)		1.88(6)
$Os(N-1)-Os(N)-Os(N+1)$	60.19(7)	59.42(7)	60.39(7)
$Os(N-1)-Os(N)-C_{ax}$	84(2), 99(2)	83(2), 94(3)	94(2), 83(2)
$Os(N+1)-Os(N)-C_{ax}$	97(2), 89(2)	85(2), 93(2)	94(3), 83(2)
$Os(N-1)-Os(N)-C_{eq}$	160(2)	154(2), 97(2)	158(2)
$Os(N+1)-Os(N)-C_{eq}$	101(2)	155(2), 96(2)	99(2)
$Os(N-1)-Os(N)-C_{carbene}$	98(1)		98(2)
$Os(N+1)-Os(N)-C_{carbene}$	156(2)		157(2)
$C_{ax}-Os(N)-C_{eq}$	92(3), 87(2)	90(2), 91(3), 92(3)	91(3), 92(2)
$C_{ax}-Os(N)-C_{carbene}$	89(2), 86(2)		92(3), 88(2)
$C_{ax}-Os(N)-C_{ax}$	174(2)	177(3)	177(3)
$C_{eq}-Os(N)-C_{eq}$		109(3)	
$C_{eq}-Os(N)-C_{carbene}$	102(2)		103(3)
$O_{ax}-C_{ax}-Os(N)$	177(6), 172(5)	175(6), 178(5)	171(6), 170(5)
$O_{eq}-C_{eq}-Os(N)$	175(5)	174(5), 173(6)	179(6)
$O_{carbene}-C_{carbene}-Os(N)$	127(4), 128(3)		129(4), 126(4)

[a] For the dioxycarbene groups, O–C–O, 104(4), 105(5); C–O–C, 118(4), 108(5), 115(5), 112(5); C–C–O, 111(5), 97(6), 106(7), 103(6). [b] All bond distances noted below were restrained to the target distances given: Os–CO, 1.88 Å; C–O, in CO groups, 1.16 Å; C–O at the carbene carbon 1.42 Å; and C–C distance in the carbene ligand, 1.54 Å. The standard deviations were all set to 0.013 Å. [c] N refers to the cyclic permutation 1, 2, 3, (note that for $N = 1$, '$N - 1$' is 3; for $N = 3$, '$N + 1$' is 1).

$(CO)_{10}(\mu$-CHOMe$)^-]$ [25] and $Pt_2W(CO)_6(PR_3)_2$-[μ-C(OMe)(Ph)] [26]; however, others have a terminal =CR(OR′) ligand, as in $Os_3[1$-η^1-C(OMe)(Me)][1,2-μ-H; 1,2-μ-O=C(Me)]$(CO)_9$ [27, 28]. Bis(alkoxy) (=$C(OR)_2$) and bis(thioalkoxy) (=$C(SR)_2$) carbene ligands are generally terminal in polynuclear complexes, e.g. $(\mu_3\text{-}S)_2Fe_3(CO)_8(=\overline{CSCH=CHS})$ [29], $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)$ [14] and $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ [4], but there are exceptions, e.g. $[Fe_3(CO)_9(\mu_3\text{-}\overline{CSCH_2CH_2S})(\mu_3\text{-}S)]$ [30a] and others [30b].

An ORTEP [31] drawing of **II** in Fig. 2 shows an explicit clockwise rotation for all groups of ligands when looking into the center of the osmium ring; the degrees of rotation are given in Table VI. A similar rotation is seen in other Os_3 clusters, $[Os_3(CO)_{10}$(*trans*-$CF_3(H)C=C(H)CF_3)(Br)]^-$ [32], $[Os_3(CO)_9$(*trans*-$CF_3(H)C=C(H)CF_3)(\mu\text{-}Br)]^-$ [32], and $Os_3(CO)_{11}[P(OCH_3)_3]$ [17], as calculated from data in the references (entries D, E, and F in Table VI). On the other hand, there is no evidence for such a rotation in $[Os_3(CO)_{11}(NCMe)]$ [15], $[Os_3(CO)_{10}(NCMe)_2]$ [15], $H_2Os_3(CO)_{11}$ [22], and $Os_3(CO)_{12}$ [22]. It is not clear what factors lead to these rotational distortions in some Os_3 clusters and not in others.

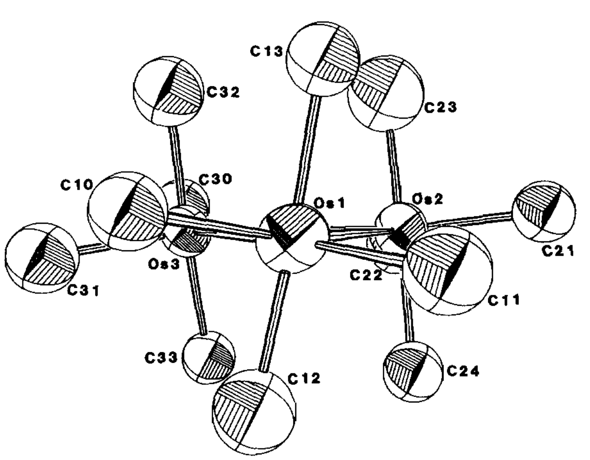


Fig. 2. Perspective view of $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (II) showing the clockwise rotation of the ligands around the pseudo-octahedral Os atoms.

Reactions of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ *(III)*

The complex, $Fe(CO)_4(=\overline{COCH_2CH_2O})$, is not stable in CH_2Cl_2 or THF even under N_2; about 30% of it decomposes in 18 h to give $Fe(CO)_5$ and a brown precipitate which is probably Fe. Previously [4] it was noted that solid **III**, when heated, evolves

TABLE VI. Comparison of Ligand Rotation[a] Values in $Os_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ (II)

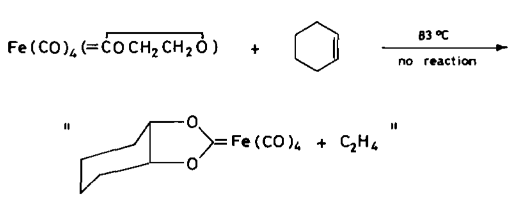
	I	II	III	IV
A	22.2 (C11)	6.3 (C13)	9.5 (C10)	11.3 (C12)
B	20.4 (C22)	8.3 (C23)	7.5 (C21)	8.2 (C24)
C	25.7 (C31)	12.5 (C32)	10.0 (C30)	13.5 (C33)
D	28.1	8.3	7.7	6.0
E	8.4	5.9	4.3	0.9
F	4.3, 14.5, 8.3	4.4, 4.1, 3.3	2.2, 0.6, 1.7	0.5, 1.1, −1.0
G	2.8, 3.0, 2.6	0.9, 0.6, 0.5	0.6, 1.4, 0.7	0.6, 1.0, 2.9
H	−4.4, 7.2, 5.1	1.2, −0.9, −0.7	−0.3, −1.3, 0.5	−0.8, 2.2, 2.4
I	5.9, 5.2, −0.8	4.0, 0.5, 0.3	2.8, 3.4, −0.4	3.7, 3.1, 0.4
J	7.6, 1.2, 2.6	2.8, 1.6, −0.6	5.8, 1.2, 0.5	5.7, −0.1, 2.5

I	Vector in plane of osmium atoms, arbitrary reference of 0°.
II	Vector perpendicular to plane, 90° anticlockwise rotation.
III	Vector in plane, 180° rotation.
IV	Vector perpendicular to plane, 90° clockwise rotation.
A, B, C	Atoms on Os1, Os2, and Os3, this structure
D	Atoms on Os3 in $[Os_3(CO)_{10}$(*trans*-$CF_3(H)C=C(H)CF_3)Br]^-$ [32].
E	Atoms on Os_3 in $[Os_3(CO)_9$(*trans*-$CF_3(H)C=C(H)CF_3)(\mu\text{-}Br)]^-$ [32]. The structure was inverted to give the clockwise rotation of the other structures.
F	Atoms on Os1, Os2, and Os3 in $Os_3(CO)_{11}[P(OCH_3)_3]$ [17].
G	Atoms on Os1, Os2, and Os3 in $H_2Os_3(CO)_{11}$ [22].
H	Atoms on Os1, Os2, and Os3 in $Os_3(CO)_{12}$ [22].
I	Atoms on Os1, Os2, and Os3 in $Os_3(CO)_{11}(NCMe)$ [15].
J	Atoms on Os1, Os2, and Os3 in $Os_3(CO)_{10}(NCMe)_2$ [15].

[a] Rotation values in degrees rotated from the vectors parallel and perpendicular to the metal atoms plane as given by the headings I, II, III, and IV.

CO_2 which was detected by the precipitation of $CaCO_3$ as the gas was passed through an aqueous solution of $Ca(OH)_2$. We have now detected both CO_2 and ethylene as products of this decomposition (eqn. (3)) when a CH_2Cl_2 solution of **III** is injected into a GC-MS instrument. It is not known whether or not the free carbene $=\overline{COCH_2CH_2O}$ is an intermediate in this reaction; however, this carbene, previously suggested [33] as an intermediate in the decomposition of the norbornadienone ketal, decomposes to CO_2 and C_2H_4. We considered the possibility that decomposition could occur by loss of C_2H_4 from **III**, leaving a CO_2 complex which might react with a different olefin to give a new dioxycarbene complex. However, refluxing (83 °C) **III** in cyclohexene (eqn. (4)) did not give the known stable dioxycarbene complex **IV** [34]; only decomposition of **III** (eqn. (3)) occurred.

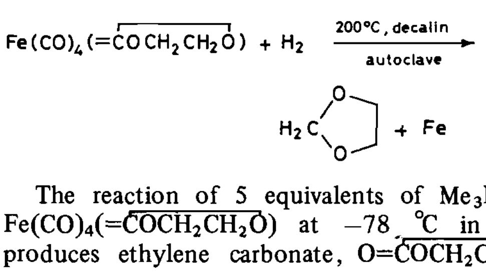
$$Fe(CO)_4(=\overline{COCH_2CH_2O}) \xrightarrow{CH_2Cl_2} CO_2 + C_2H_4 + Fe(CO)_5 + Fe + \quad (3)$$



IV

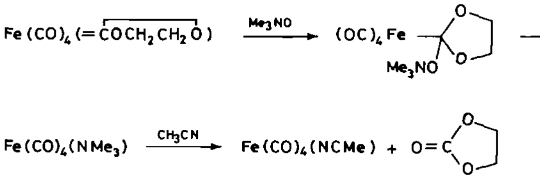
(4)

The reaction of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ with 71.5 atm of H_2 gas at 200 °C in the absence of CO gave a 27% yield of 1,3-dioxolane (eqn. (5)). However, in the presence of 34 atm of CO, this reaction did not produce any detectable 1,3-dioxolane. A possible interpretation of this result is that the initial step in the hydrogenation of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ is the loss of CO from $Fe(CO)_4(=\overline{COCH_2CH_2O})$ to give $Fe(CO)_3(=\overline{COCH_2CH_2O})$, which oxidatively adds H_2 to form an intermediate $H_2Fe(CO)_3(=\overline{COCH_2CH_2O})$ which transfers a H ligand to the carbene C and reductively eliminates 1,3-dioxolane. In this mechanism, CO inhibits the addition of H_2 and the eventual formation of 1,3-dioxolane.



(5)

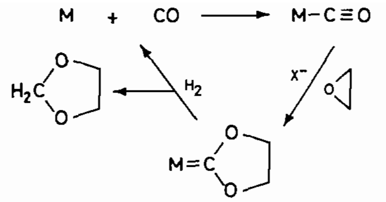
The reaction of 5 equivalents of Me_3NO with $Fe(CO)_4(=\overline{COCH_2CH_2O})$ at −78 °C in CH_3CN produces ethylene carbonate, $O=\overline{COCH_2CH_2O}$, in 24% yield. If only 3 equivalents of Me_3NO are used, the reaction is not complete even after one day. Also in CH_2Cl_2 solvent, the Me_3NO reaction does not go to completion. It is possible that Me_3NO oxidation of the Fe, rather than the carbene, leads to the low yield (24%) of ethylene carbonate. The formation of ethylene carbonate may occur by initial attack of Me_3NO on the carbene carbon atom as indicated by eqn. (6). Since a variety of other oxidizing agents including oxygen [35], pyridine *N*-oxide [36], dimethyl sulfoxide [37] and OH^-/Br_2 [38] have been reacted with carbene complexes to give organic products with C=O groups, several similar reactions were tried with **III**. Bubbling O_2 through a CH_2Cl_2 solution of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ at room temperature for 18 h gave only a low yield of ethylene carbonate, $Fe(CO)_5$ and a brown solid. A THF solution of $Fe(CO)_4(=\overline{COCH_2CH_2O})$ and excess $(CH_3)_2SO$ were refluxed for 4 h, but no ethylene carbonate was produced. Likewise, successive treatment of **III** with hydroxide and bromine in methanol did not give any of the carbonate. Ultraviolet photolysis (254 nm) of **III** with an equimolar amount of PPh_3 in THF gives both $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$. Similarly, refluxing **I** with PEt_3 in toluene gives $Os_3(CO)_{11}(PEt_3)$. Efforts to characterize the organic products formed in these reactions were not successful, but it is possible that the carbene ligand is lost as CO_2 and C_2H_4. A similar replacement of the carbene ligand was observed in reactions of $Re(CO)_4(Br)(=\overline{COCH_2CH_2O})$ with bipyridine of *o*-phenanthroline [39].



(6)

Catalytic Reactions of Ethylene Oxide, CO and H_2

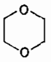
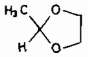
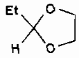
Since ethylene oxide reacts with $Fe(CO)_5$ in the presence of Br^- to form **III** (eqn. (1)), and **III** reacts with H_2 to form 1,3-dioxolane (eqn. (5)), it seems possible that $Fe(CO)_5$ and Br^- might catalyze the reaction of ethylene oxide, CO, and H_2 to form 1,3-dioxolane. Unfortunately, the hydrogenation step in this sequence is inhibited by CO (see above); so it appears that the $Fe(CO)_5/Br^-$ catalyst system will not be successful. However, in general, it seems possible that metals or metal complexes could catalyze the reaction of ethylene oxide, CO, and H_2 to form 1,3-dioxolane or other products derived from the dioxycarbene intermediate, **III** (Scheme 1). To explore this possibility, we examined several reactions using a metal catalyst with NaCl in $ClCH_2CH_2OH$ solvent as shown in Table VII. In a control experiment using no metal catalyst, but all other conditions being the



Scheme 1.

TABLE VII. Reaction of Ethylene Oxide (40 mmol), CO (20.4 atm) and H_2 (20.4 atm) in the Presence of NaCl (0.50 mmol) and Catalyst (0.040 mmol) at 180 °C in 2 ml of $ClCH_2CH_2OH$ for 11 h

Catalyst	Products[a]
10% Pd/C	A, B
10% Pt/C	A, B, C
10% Pd/Al_2O_3	A, B
5% Rh/C[b]	A, B
$PdCl_2$	A, B, C
$PdCl_2(PPh_3)_2$	A, B
–[c]	A

[a]A is 1,4-dioxane,  ; B is 2-methyl-1,3-dioxolane,  ; C is 2-ethyl-1,3-dioxolane,  . [b]The yields of A and B were 17% and 50%, respectively. [c]The yield of A using no metal catalyst was 28%.

same as in the catalyzed reactions, a 28% yield of 1,4-dioxane was obtained, probably from the dimerization of ethylene oxide. The cyclodimerization of ethylene oxide to 1,4-dioxane is possibly catalyzed by NaCl; Cl^- attack may open the ethylene oxide ring to give the alkoxide which would add to another ethylene oxide and then cyclize to form 1,4-dioxane; it is known that halide ions promote ethylene oxide ring opening in certain organic reactions [40]. In the presence of all the metal catalysts, not only was 1,4-dioxane formation observed but also 2-methyl-1,3-dioxolane. With 10% Pt/C and $PdCl_2$, 2-ethyl-1,3-dioxolane was also identified as a product. These three were the only products that were observed in the GC-MS spectra of the reaction mixtures. In none of the reactions was 1,3-dioxolane observed as a product. It is, however, possible that there are other non-volatile products. It is not clear how 2-methyl-1,3-dioxolane is formed; however, it has been found [41] as a byproduct in the polymerization of ethylene oxide catalyzed by $SnCl_4$ (92% dioxane and 8% 2-methyl-1,3-dioxolane are the volatile products in addition to the ethylene oxide polymer). A possible mechanism might involve isomerization of ethylene oxide to CH_3CHO, known to occur in the presence of $MnBr_2$ [42], followed by reaction with ethylene oxide to give 2-methyl-1,3-dioxolane [43]. A possible mechanism for the formation of 2-ethyl-1,3-dioxolane might proceed by the hydroformylation (H_2 and CO) [44, 45] of ethylene (generated by the decomposition of ethylene oxide) to give CH_3CH_2CHO which reacts with ethylene oxide to give 2-ethyl-1,3-dioxolane [43].

Although we are not aware of other attempts to catalyze reactions of ethylene oxide, CO, and H_2, epoxides are known to be deoxygenated to olefins and CO_2 by $[Rh(CO)_2Cl]_2$ [46], $Co_2(CO)_8$ [47], $Mo(CO)_6$ [48], and $Fe(CO)_5$ [49]. Also, the reaction of ethylene oxide with CO to give β-lactones is catalyzed by $RhCl(CO)(PPh_3)_2$ [50].

Supplementary Material

Listing of anisotropic thermal parameters, hydrogen atom positions, and calculated and observed structure factors (6 pages) are available from the authors on request.

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