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Dioxy Carbene Complexes From Reactions of $Fe(CO)_5$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $Ru_3(CO)_{12}$ with Oxirane

MONO M. SINGH and ROBERT J. ANGELICI*

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

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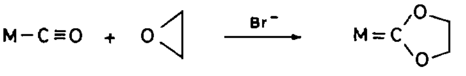
Abstract

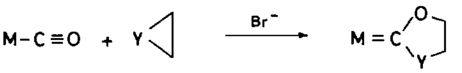
At 100 °C in the presence of Br^- catalyst, CO ligands in $Fe(CO)_5$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $Ru_3(CO)_{12}$ are converted upon reaction with oxirane (ethylene oxide) into dioxy carbene ligands as follows:



Products of these reactions are $Fe(CO)_4(L)$, $Mn_2(CO)_9(L)$, $Re_2(CO)_9(L)$, $Re_2(CO)_8(L)_2$, and $Ru_3(CO)_{10}(L)_2$, where L is the dioxy carbene ligand. Cleavage of the metal–metal bonds in $M_2(CO)_9(L)$, where M = Mn, Re, by reaction with Br_2 gives the expected $M(CO)_5Br$ and $M(CO)_4(L)Br$ products. Reaction of $Fe(CO)_5$ with aziridine $(\text{H}\overline{\text{NCH}_2\text{C}}\text{H}_2)$ yields the corresponding cyclic amino-oxy carbene complex $Fe(CO)_4(=\overline{\text{CNHCH}_2\text{CH}_2\text{O}})$.

Introduction

Ironpentacarbonyl is known to deoxygenate a wide variety of oxiranes to yield olefins [1]. We have recently demonstrated [2–4] that cationic as well as certain neutral metal carbonyls react with oxirane $(\overline{\text{OCH}_2\text{C}}\text{H}_2)$ and aziridine $(\text{H}\overline{\text{NCH}_2\text{C}}\text{H}_2)$ in the presence of a halide ion catalyst to form cyclic amino-oxy- and dioxy-carbene compounds according to eqn 1:



(1)

M = $CpFe(CO)_2^+$, $CpRu(CO)_2^+$, $CpMn(CO)(NO)^+$, $CpFe(CO)(PPh_3)^+$, $Mn(CO)_4X$, and $Re(CO)_4X$ (X = Cl, Br, I); Y = NH or O

The above reactions were carried out at room temperature. It was proposed [4] that reaction (1) depends upon the electrophilicity of the CO group and that $\overline{\text{YCH}_2\text{C}}\text{H}_2$ reacts at room temperature with only those metal carbonyl complexes which have CO stretching force constants, *k*(CO), higher than 17.0 mdyne/Å. Under these conditions, oxirane did not react with $Fe(CO)_5$, $M_2(CO)_{10}$ (M = Mn, Re) and $Ru_3(CO)_{12}$; aziridine also failed to react with $M_2(CO)_{10}$. We, therefore, undertook an investigation of the reactivity of oxirane with $Fe(CO)_5$, $M_2(CO)_{10}$ (M = Mn, Re) and $Ru_3(CO)_{12}$ at elevated temperatures. We describe here the results of these studies and the spectroscopic characterization of the resulting compounds.

Experimental

General Methods

Unless described otherwise, all reactions were performed under an N_2 atmosphere using standard Schlenk techniques. Reagent grade chemicals were used without further purification except as noted. Methylene chloride was dried over CaH_2 and distilled under N_2 before use. Acetonitrile was predried (CaH_2) and twice distilled from P_2O_5 and CaH_2 before final collection under N_2. Diethylether predried with CaH_2 was distilled from sodium benzophenone ketyl. Pentane was also dried and purified by distillation from CaH_2 and was stored over molecular sieves type 4 Å. Infrared spectra were run on Perkin-Elmer model 281 and 681 instruments. ^1H and ^{13}C NMR spectra were recorded on a Jeol FX-90Q spectrometer; $Cr(acac)_3$ was used to reduce the data collection time. Melting points of the compounds were determined on a Thomas hot stage and were uncorrected. Mass spectra of the complexes, except compound **V**, were obtained on a Finnigan 4000 GC/MS instrument; the FAB spectrum of **V** was obtained on a Kratos MS50 at the Midwest Center for Mass Spectrometry, Lincoln, Nebraska. Oxirane and aziridine are toxic substances; all preparations and manipulations were performed in an efficient hood. The starting compounds Fe-

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*Author to whom correspondence should be addressed.

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$(CO)_5$, $M_2(CO)_{10}$ (M = Mn, Re) and $Ru_3(CO)_{12}$ were obtained from commercial sources.

$Fe(CO)_4(=\overline{COCH_2CH_2O})$, *I*

To a cooled mixture (0 °C) of 0.25 g (2.4 mmol) of NaBr and 1 ml of $BrCH_2CH_2OH$ in a pressure bomb previously purged with N_2 was added 0.67 ml (0.98 g, 5.0 mmol) of $Fe(CO)_5$. While rapidly stirring the mixture with a magnetic stirring bar, 8 ml of oxirane was introduced into the bomb. After closing the bomb, the contents were pressurized with 700–800 psi of CO gas which had been purified by passing it through a stainless steel U-tube immersed in liquid N_2 to remove traces of $Fe(CO)_5$. The content of the bomb was stirred first at 0 °C for 2 h; then, it was allowed to warm to room temperature and heated to 100 °C (steam bath). At 100 °C, the pressure in the bomb was 900–1000 psi. After stirring for 20 h, the bomb was cooled to 0 °C in an ice bath, the pressure was released and the bomb was opened. Unreacted oxirane was evaporated by a rapid stream of N_2. A thick layer of a crystalline substance was suspended in the remaining viscous liquid. The mixture was dissolved in CH_2Cl_2, and the solution was chromatographed on a silica gel (230–400 mesh, kiesel gel, E. Merck) column (1.3 X 66 cm). The yellow band was eluted with CH_2Cl_2, and the solution was evaporated under vacuum to yield light-yellow crystals. These were redissolved in CH_2Cl_2 and filtered through a bed of anhydrous $MgSO_4$. The filtrate was evaporated under vacuum until crystallization began. After adding pentane, the mixture was allowed to stand at −20 °C overnight. The long light yellow needles of **I** which formed were collected, washed with pentane and dried under vacuum; yield 1.0 g (83%). *Anal.* Found: C, 34.78; H, 1.56. Calcd. for $C_7H_4O_6Fe$: C, 35.04; H, 1.68%. IR(CH_2Cl_2) ν(CO): 2068(s), 1982(s), 1956(vs); IR (Nujol): 2070(s), 1990(sh), 1960(vs), 1935(m) cm^{-1}. ^1H NMR (CD_3CN): δ 4.66 (s, OCH_2). ^{13}C NMR (CD_3CN): 250.75 (carbene C), 215.00 (CO), 72.46 (OCH_2) ppm. Mass spectrum, m/e 239.9 (parent ion).

$Mn_2(CO)_9(=\overline{COCH_2CH_2O})$, *II*

The same procedure as for the preparation of **I** was followed. From 0.78 g (2.0 mmol) of $Mn_2(CO)_{10}$, 0.16 g (1.6 mmol) of NaBr, 1 ml of $BrCH_2CH_2OH$ and 15 ml of oxirane, 0.62 g (71%) of **II** was obtained after recrystallization from CH_2Cl_2–hexane at −20 °C. M.p. 124 °C. *Anal.* Found: C, 32.86; H, 0.60. Calcd. for $C_{12}H_4O_{11}Mn_2$: C, 33.21; H, 0.93%. IR (CH_2Cl_2) ν(CO): 2095(m), 2048(w), 2029(s), 2014(sh), 2000(s), 1992(s), 1966(sh), 1946(m), cm^{-1}. ^1H NMR (CD_3CN): δ 4.63 (s, OCH_2). ^{13}C NMR (CD_2Cl_2): 259.28 (carbene C), 224.74, 224.57 and 223.61 (CO); 72.28 (OCH_2). Mass spectrum: m/e 433.8 (parent ion).

$Re_2(CO)_9(=\overline{COCH_2CH_2O})$, *III*

This compound was prepared by the same general method as described for **I**. A mixture of 0.66 g (1.0 mmol) of $Re_2(CO)_{10}$, 1 ml of $BrCH_2CH_2OH$, 0.11 g (0.98 mmol) of NaBr and 8 ml of oxirane at 0 °C was pressurized with 750 psi of CO in a bomb. After stirring at 0 °C for 1 h, the temperature of the bomb was slowly increased to room temperature. The reaction was stirred at ambient temperature overnight (8–10 h). Then the temperature of the bomb was increased to 100 °C causing a pressure rise to almost 900 psi; the contents were stirred at this temperature for 4 h. The bomb was cooled to 0 °C, and after releasing the pressure, the contents of the bomb were dissolved in warm CH_2Cl_2 (30 °C) and chromatographed on a silica gel column (1.3 X 66 cm) using CH_2Cl_2. The elution of **III** was monitored by IR spectroscopy. The fraction containing **III** was evaporated to dryness; the residue was redissolved in CH_2Cl_2 and the solution was filtered through anhydrous $MgSO_4$. The filtrate was concentrated and pentane was added. Upon standing overnight at −20 °C, snow white, long needles of **III** formed. They were collected, washed with pentane and dried under vacuum. Yield 0.50 g (71%). *Anal.* Found: C, 20.92; H, 0.60. Calcd. for $C_{12}H_4O_{11}Re_2$: C, 20.69; H, 0.58%. M.p. 165 °C. IR (CH_2Cl_2) ν(CO): 2106(w), 2048(s), 2000(vs), 1994(vs), 1965 (sh), 1938(s). IR (CH_3CN) ν(CO). 2106(w), 2047(s), 1998(vs), 1994(vs), 1967(sh), 1938(s) cm^{-1}. ^1H NMR (CD_3CN): δ 4.63 (s, OCH_2). ^{13}C NMR (CD_3CN): 232.02 (carbene C), 198.48 and 196.14 (CO), 72.46 (OCH_2) ppm. Mass spectrum: m/e 695.7 (parent ion).

$Re_2(CO)_8(=\overline{COCH_2CH_2O})_2$, *IV*

This compound was isolated as a by-product from the preparation of **III**. When the CH_2Cl_2 eluent from the column used in the synthesis of **III** showed no IR evidence for $Re_2(CO)_9(=\overline{COCH_2CH_2O})$, the column was eluted with a warm 1:1 mixture of CH_3CN and CH_2Cl_2 (30–35 °C) as rapidly as possible under a positive N_2 pressure of 6–10 psi applied to the top of the column. The progress of the elution was monitored by IR. Care was taken to strip the compound as completely as possible from the column. Fractions containing **IV** were collected and evaporated to dryness under vacuum. The white powder thus obtained was dissolved in excess warm CH_2Cl_2, and the solution was filtered rapidly while warm. Slow evaporation of CH_2Cl_2 followed by slow addition of pentane gave on standing at −20 °C 0.10 g (13%) of colorless microcrystalline **IV**. M.p. 244 °C. *Anal.* Found: C, 22.89; H, 1.05. Calcd. for $C_{14}H_8O_{12}Re_2$: C, 22.71; H, 1.09%. IR (CH_2Cl_2) ν(CO): 2080(m), 2032(s), 1974(vs), 1917(s). IR (CH_3CN) ν(CO): 2082(m), 2034(s), 1978(vs), 1918(s) cm^{-1}. ^1H NMR (CD_3CN): δ 4.56 (s, OCH_2). ^{13}C NMR

(CD_3CN): 234.28 (carbene C), 202.18 and 201.51 (CO), 71.85 (OCH_2). Mass spectrum: m/e 739.7 (parent ion). The separation of **III** and **IV** was also effected by fractional crystallization from CH_2Cl_2 and CH_3CN. By this method relatively pure **III** was obtained, but **IV** was found to be contaminated with **III**.

$Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$, V

This preparation was also carried out according to the procedure used for the synthesis of **I**. The reaction of 0.45 g (0.70 mmol) of $Ru_3(CO)_{12}$ with 20 ml of oxirane, 0.11 g (1.1 mmol) of NaBr and 1 ml of $BrCH_2CH_2OH$ under a CO pressure of 500 psi yielded after column chromatographic separation and crystallization from CH_2Cl_2–hexane at -20 °C (48 h) 0.25 g (49%) of orange-red crystals of V. M.p. 130–135 °C (decomposition). *Anal.* Found: C, 26.24, H, 0.86. Calcd. for $C_{16}H_8O_{14}Ru_3$: C, 26.42; H, 1.11%. IR (CH_2Cl_2) ν(CO): 2104(w), 2066(m), 2046(vs), 2040(sh), 2016(vs), 1990(s,br) cm^{-1}. ^1H NMR (CD_3CN): δ 4.63 (s, OCH_2). ^{13}C NMR (CD_3CN): 231.84 (carbene C), 204.13 (CO), 72.25 (OCH_2) ppm. Although the FAB mass spectrum of V in *o*-nitrophenyl octyl ether did not show a parent ion (M) at 729 (most intense peak expected for the isotope cluster), it did show clusters of peaks characteristic of trinuclear Ru +1 ions with the most intense peaks occurring at 685 (M–44), 654 (M–75), and 601 (M–128).

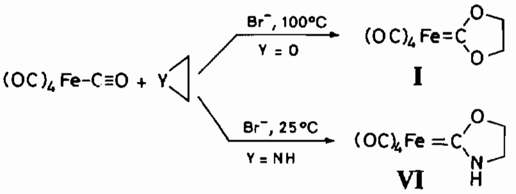
$Fe(CO)_4(=\overline{COCH_2CH_2NH})$, VI

A mixture of 1.0 g (4.9 mmol) of $[BrCH_2CH_2NH_3]Br$, 0.7 ml (1.0 g, 5.2 mmol) of $Fe(CO)_5$ and 0.27 ml (5.2 mmol) of aziridine in 10 ml of CH_3CN was stirred under N_2. After 1 h, another 0.74 ml of aziridine was added to the reaction mixture. When the IR spectrum of the mixture did not contain ν(CO) bands due to unreacted $Fe(CO)_5$, the mixture was taken to dryness under vacuum; the residue was washed once with Et_2O and finally extracted with CH_2Cl_2. The extract was filtered through $MgSO_4$ and evaporated to a yellow oil which could not be crystallized. The compound was identified by its IR, ^1H and ^{13}C NMR spectral features [5]. IR (CH_2Cl_2) ν(CO): 2056(s), 1970(s), 1940(vs) cm^{-1}. ^1H NMR (CD_3CN): δ 8.73 (NH), 4.59 (t, OCH_2), 3.63 (t, NCH_2). ^{13}C (CD_3CN): 229.51 (carbene C), 216.86 (CO), 72.46 (OCH_2), 45.50 (NCH_2) ppm.

Results and Discussion

Reactions of $\overline{OCH_2CH_2}$ and $\overline{HNCH_2CH_2}$ with $Fe(CO)_5$

Under pressure of CO (750 psi) and at 100 °C, oxirane reacts with $Fe(CO)_5$ in the presence of Br^- in $BrCH_2CH_2OH$ solvent to form the cyclic dioxy carbene compound, **I**, in excellent yield (83%) (eqn. 2a). On the other hand, aziridine reacts with $Fe(CO)_5$ in the presence of $[BrCH_2CH_2NH_3]Br$ at room temperature to give the amino-oxy carbene derivative, **VI** (eqn. 2b):

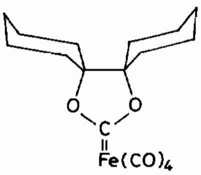


(2a)

(2b)

While the dioxy carbene complex, **I**, is a highly crystalline air-stable yellow solid, its solutions slowly decompose; these solutions are much more stable under one atmosphere of CO. The purpose of the CO pressure used in the preparation of **I** may be to stabilize this complex under the high temperature conditions of the reaction. When solid **I** was heated to its decomposition temperature, CO_2 was evolved, as detected by the precipitation of $CaCO_3$ as the gas was passed through an aqueous solution of $Ca(OH)_2$. It is interesting that the free carbene, $:\overline{COCH_2CH_2O}$, presumed to be generated in the thermal decomposition of the precursor norbornadienone ketal [6], decomposes to CO_2 and ethylene. The amino-oxy carbene compound, **VI**, is an extremely air-sensitive yellow oil. No attempts were made to purify the compound; its characterization is based on its infrared and ^1H and ^{13}C NMR spectra (see below).

Both **I** and **VI** exhibit three infrared ν(CO) bands. Other related, but less symmetric acyclic carbene compounds, $Fe(CO)_4[=C(OR)R']$ [7], $Fe(CO)_4[=C(OR)NR_2$ [7] and $Fe(CO)_4[=\overline{CN(Me)C(Me)C(H)S}]$ [8] show four or more ν(CO) bands. Known cyclic dioxy carbene compounds [9–11] $Fe(CO)_4[=\overline{COCR_2CR_2O}]$ in nujol mulls or KBr pellets exhibit four ν(CO) bands. However, in cyclohexane $Fe(CO)_4[=\overline{COCMe_2CMe_2O}]$ has a ν(CO) spectrum that is nearly identical to that of **I** [10]. An X-ray diffraction study [10] of



shows the cyclic carbene ligand in an axial position. The IR spectral features of **I** (ν(CO) (CH_2Cl_2): 2068(s), 1982(s), 1956(vs) cm^{-1}) and **VI**, (ν(CO) (CH_2Cl_2): 2056(s), 1970(s), 1940(vs) cm^{-1}) closely resemble those of $Fe(CO)_4[=\overline{CN(Me)CH_2CH_2N(Me)}]$ (ν(CO) (hexane): 2040(m), 1959(s), 1938(s) cm^{-1}) for which a trigonal bipyramidal structure with an axial carbene ligand has been proposed

[12]. Moreover, the IR spectra of **I** and **VI** match very closely those of axial isomers of $Fe(CO)_4L$, $Ru(CO)_4L$ and $Os(CO)_4L$ (L = group 5A donor ligand), as opposed to the equatorial isomers [13]. Thus, the number of carbonyl bands and their relative intensities in **I** and **VI** suggest that the dioxy- and amino-oxy ligands in these complexes occupy axial positions [14, 15], as is observed in $Fe(CO)_4[\overline{CN(Me)CH{=}CHN}(Me)]$ [16] which has been shown by an X-ray diffraction investigation to possess a distorted trigonal bipyramidal structure with an axial carbene ligand [17].

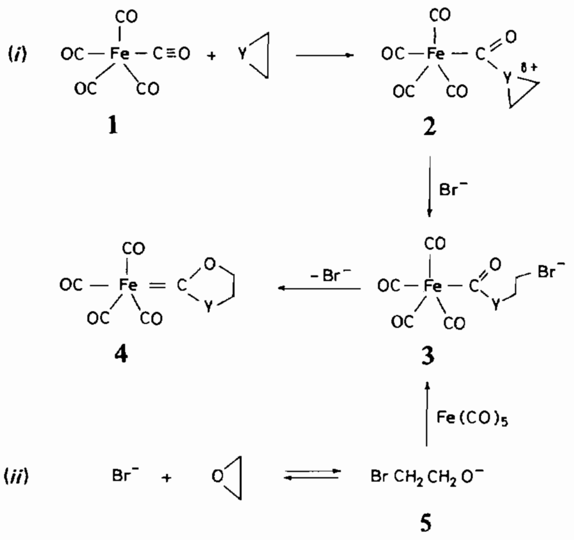
The $\nu(CO)$ values in compounds **1** (2068, 1982 and 1956 cm^{-1}), **VI** (2056, 1970 and 1940 cm^{-1}) and $Fe(CO)_4[\overline{CN(Me)CH_2CH_2N}(Me)]$ (2040, 1959 and 1938 cm^{-1}) [12] decrease in the order $=\overline{COCH_2CH_2O} > =\overline{COCH_2CH_2NH} > =\overline{CN(Me)CH_2CH_2N}(Me)$. This trend, which is also observed for other carbene compounds [3, 4], indicates that the dioxycarbene ligand has a greater π-acceptor/σ-donor ratio than either the amino-oxy or diamino carbene ligand.

The ^1H NMR spectrum of **I** shows a sharp singlet for the $-OCH_2-$ group at 4.66 ppm. The amino-oxy carbene derivative, **VI**, shows two triplets centered at 4.59 ppm and 3.63 ppm due to the $-OCH_2-$ and $-NCH_2-$ groups, respectively. Compound **VI** also has a broad NH signal at lower field (8.73 ppm). The ^{13}C NMR carbene carbon signal for **I** appears at lower field (250.75 ppm) than that for **VI** (229.51 ppm). A similar trend has been observed for other dioxy- and amino-oxy carbene compounds [2–5]. The single ^{13}CO signals which occur at 215.00 and 216.86 ppm in **I** and **VI**, respectively, show that both of these compounds are fluxional at room temperature.

In the mass spectrum of **I**, the parent ion $Fe(CO)_4L^+$ ($L = \overline{COCH_2CH_2O}$) peak occurs at m/e = 239.9. Other major peaks in the mass spectrum and the corresponding fragment ions are given below in Scheme 1.

The sequential loss of CO groups from **I** shows that the carbene ligand L, as reported for other acyclic carbene compounds [7], remains unchanged until all the CO groups are lost.

For reactions 2a,b we propose the following possible mechanisms (Scheme 2), which have been suggested earlier [2, 3] for the reactions of oxirane and aziridine with cationic carbonyl complexes:



Scheme 2.

Under the synthetic conditions used it was not possible to identify any of the intermediates suggested in this mechanism. However, initial attack by $\overline{HNCH_2CH_2}$ on one of the axial carbonyl groups in $Fe(CO)_5$ is supported by the known [15, 18] reaction of amines with $Fe(CO)_5$ to give $Fe(CO)_4[C(=O)NR_2]^-$ with the carbamoyl group in the axial position. The amine addition at an axial CO was previously [19, 20] rationalized in terms of the higher $\nu(CO)$ force constant for the axial CO ligands (k_{ax} = 16.98 mdyne/Å) than for the equatorial (k_{eq} = 16.41 mdyne/Å). The methylene carbons in the aziridine adduct **2** would then be susceptible to attack by Br^- causing ring-opening to intermediate **3**. Intramolecular displacement of Br^- in this intermediate by the acyl oxygen would give the carbene. This step is similar to intermolecular alkylation [7] of $Fe(CO)_4[C(=O)NR_2]^-$ with R'X to give the carbene complex $Fe(CO)_4[C(OR')(NR_2)]$.

The mechanism for the oxirane reaction may be similar to that for aziridine; however, an alternative mechanism (*ii* in Scheme 2) is perhaps more likely.

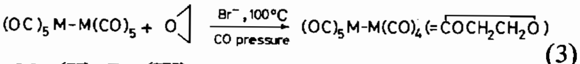
$$\begin{tikzcd}
\mathrm{Fe(CO)_4L^+} \arrow[r, "-\mathrm{CO}"] & \mathrm{Fe(CO)_3L^+} \arrow[r, "-\mathrm{CO}"] & \mathrm{Fe(CO)_2L^+} \arrow[r, "-\mathrm{CO}"] & \mathrm{Fe(CO)L^+} \arrow[dd, "-\mathrm{CO}"] \\
239.9 & 211.9 & 183.9 & 155.9 \\
\mathrm{Fe^+} & \mathrm{FeCO^+} \arrow[l, "-\mathrm{CO}"'] & \mathrm{Fe(CCH_2CH_2O)^+} \arrow[l, "-\mathrm{C_2H_4}"'] & \mathrm{FeL^+} \arrow[l, "-\mathrm{O}"'] \\
55.9 & 83.9 & 111.9 & 127.9
\end{tikzcd}$$

Scheme 1

In this mechanism, the initial step involves Br^- attack on oxirane to give intermediate **5**. Examples of such ring-opening reactions of oxiranes with halide ions are well known in organic chemistry [21]. The bromoethoxide **5** would be expected to attack an axial CO group in $Fe(CO)_5$ to give the alkoxycarbonyl complex **3**. Such reactions of other alkoxides with $Fe(CO)_5$ yield $Fe(CO)_4[C(=O)OR]^-$ rapidly even at room temperature [22, 23]. The rapid rates of these reactions and of the initial ring-opening step to **5** suggests that the slow step in reaction (2a) is the ring closure in which intermediate **3** is converted to the carbene product **4**. In contrast to this ring closure reaction, intermolecular alkylation [24] of $Fe(CO)_4[C(=O)OMe]^-$ with $MeOSO_2F$ does not give the carbene $Fe(CO)_4[=C(OMe)_2]$, but instead the methyl adds to the iron giving $Fe(CO)_4(Me)[C(=O)OMe]$. Thus, the acyclic derivatives $Fe(CO)_4[=C(OR)_2]$ are not known.

Reactions of $\overline{OCH_2CH_2}$ with $M_2(CO)_{10}$ (M = Mn, Re) and $Ru_3(CO)_{12}$

At 100 °C and a pressure (500–900 psi) of CO, oxirane reacts with $M_2(CO)_{10}$ in the presence of Br^- catalyst in $BrCH_2CH_2OH$ solvent to form the corresponding cyclic dioxy carbene compounds $M_2(CO)_9(=\overline{COCH_2CH_2O})$ in high yields (71%) (eqn. 3):



(3)

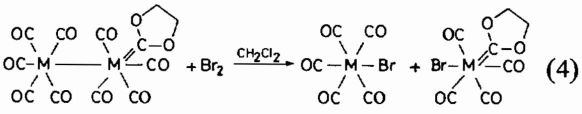
Mn (**II**), Re (**III**) **II**, **III**

The reaction of $Re_2(CO)_{10}$ with oxirane gives, in addition to **III**, the bis(dioxy-carbene) derivative $Re_2(CO)_8(=\overline{COCH_2CH_2O})_2$ in 13% yield. Attempts to prepare the corresponding amino-oxy carbene compounds by reacting $M_2(CO)_{10}$ with aziridine under these conditions did not produce the desired compounds.

A few acyclic carbene compounds of the type $M_2(CO)_9[=C(OR)R']$ (M = Mn, Re) are known [25–28]. The IR spectrum of **II** in the carbonyl region (ν(CO) = 2095(m), 2048(w), 2029(s), 2014(sh), 2000(s), 1992(s), 1966(sh), 1946(m)) compares well with those of other acyclic carbene complexes $Mn_2(CO)_9[=C(OR)R']$ [26] ($R = CH_3$; $R' = CH_3, C_2H_5$), where the carbene ligand occupies an equatorial position. The IR spectrum of **III** contains six carbonyl bands (ν(CO) = 2106(w), 2048(s), 2000(vs), 1994(vs), 1965(sh), 1938(s)) which are similar to those observed for $(CO)_5Re{-}Re(CO)_4[=C(OR)SiPh_3]$ [27], in which the carbene ligand is in an equatorial position as determined by an X-ray diffraction study [29].

Each of the compounds **II** and **III** in CD_3CN exhibits an ^1H NMR signal at 4.63 ppm for the $-OCH_2-$ groups. Conclusive evidence for the formation of cyclic dioxy carbene ligands in these compounds comes from the low-field resonances occurring below 200 ppm in their ^{13}C NMR spectra (δ(carbene) = 259.28 and 232.02 for **II** and **III**, respectively). While ^{13}C NMR spectra of **II** in CD_2Cl_2 at −10° to −20 °C reveal three ^{13}CO signals at 224.74, 224.57 and 223.61 ppm, compound **III** shows only two ^{13}CO signals at 198.48 and 196.14 ppm, the lower field resonance being of higher intensity. Likewise, the acyclic equatorial carbene compounds $(CO)_5Re{-}Re(CO)_4[=C(OR)SiPh_3]$ also show only two ^{13}CO signals [27]. Both compounds **II** and **III** give rise to a single $-OCH_2-$ ^{13}C peak at ~72.0 ppm as observed in other 5-membered cyclic dioxy carbene compounds [2].

The equatorial disposition of the dioxy carbene ligand in both compounds **II** and **III** is further supported by the isolation and characterization of $M(CO)_5Br$ (**VII**) and *cis*-$M(CO)_4Br(=\overline{COCH_2CH_2O})$ (**VIII**), from the reaction of the dinuclear complexes $M_2(CO)_9(=\overline{COCH_2CH_2O})$ (M = Mn and Re) with Br_2. Oxidative cleavage of the metal–metal bonds in **II** and **III** by one mol of Br_2 in CS_2 solution at room temperature instantly affords **VII** and **VIII** in 1:1 yield as established by an IR spectrum of the product mixture (eqn. 4):



(4)

II and **III** **VII** **VIII**

M = Mn, Re

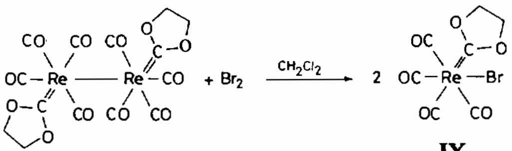
The mononuclear *cis* carbene compound **VIII** could be separated from the bromopentacarbonyl derivative by column chromatography on silica gel. Elution with CH_2Cl_2 gives **VII** followed by **VIII**. In the case of the colorless rhenium compounds, the elution was followed by IR spectroscopy. The IR, ^1H and ^{13}C NMR spectra of the $M(CO)_4Br(=\overline{COCH_2CH_2O})$ (M = Mn, Re) products are the same as those reported previously for these compounds prepared by another method [4]. Assuming that during oxidative cleavage no ligand-site exchange takes place, the equatorial isomers of **II** and **III** should form the corresponding *cis* mononuclear derivative **VIII** along with an equal amount of **VII**.

Further since the reactivity of oxirane with metal carbonyls depends, at least in part, on the electrophilicity of the CO group as suggested earlier [4], then $^-OCH_2CH_2Br$ generated in the reaction mixture (Scheme 2(*ii*)) should attack preferentially at one of the more electrophilic equatorial CO groups in $M_2(CO)_{10}$ forming the carbene ligand at this site. That the equatorial CO groups are more electrophilic than the axial ones is suggested by the higher CO stretching force constant (mdyne/Å) for the equatorial CO groups [30]:

	$k(CO)_{eq}$	$k(CO)_{ax}$
$Mn_2(CO)_{10}$	16.52	15.91
$Re_2(CO)_{10}$	16.67	15.82

The IR and ^{13}C NMR spectral data indicate that in the bis(dioxy carbene) compound $Re_2(CO)_8(=\overline{COCH_2CH_2O})_2$, **IV**, unlike in Re^1ax, $Re^2eqRe_2(CO)_8[=C(OEt)SiPh_3]_2$ [25, 31] where the carbene ligands are situated at axial Re^1 and equatorial Re^2 positions, the cyclic dioxy carbene ligands probably occupy equatorial positions at both Re^1 and Re^2. Compound **IV** exhibits a simpler IR spectrum in comparison to that for $Re_2(CO)_8[=C(OEt)SiPh_3]_2$ [31]. The ^{13}C NMR spectrum of **IV** shows only one carbene carbon signal at 234.28 ppm and two carbonyl signals at 202.18 and 201.51 ppm. This contrasts with two δ(carbene) and three δ(carbonyl) signals in $Re_2(CO)_8[=C(OEt)SiPh_3]_2$ [31]. Moreover, compound **IV** also gives rise to only a singlet ^1H resonance signal for the $-OCH_2-$ groups of the two cyclic dioxy carbene ligands. All of these spectroscopic data indicate that **IV** is more symmetric than the bis carbene compound prepared by Fischer, *et al.* [31].

When the bis(dioxy carbene) compound **IV** is treated with Br_2 in CH_2Cl_2 only *cis*-$Re(CO)_4Br(=\overline{COCH_2CH_2O})$ (**IX**) is formed as established by a comparison of its IR, ^1H and ^{13}C NMR spectral data with those of an authentic sample [4]; no $Re(CO)_5Br$ is detected in this reaction (eqn. 5).

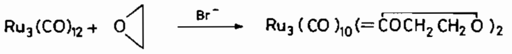


(5)

IV **IX**

This result may be taken as supporting evidence for both carbene ligands being in equatorial positions on the two different Re atoms in **IV**.

The reaction of the triangular $Ru_3(CO)_{12}$ cluster with oxirane in the presence of Br^- in $BrCH_2CH_2OH$ solvent at 100 °C under a 500 psi pressure of CO generates the bis(dioxy carbene) compound **V**, $Ru_3(CO)_{10}(=\overline{COCH_2CH_2O})_2$ in 49% yield (eqn. 6).



(6)

V

Although **V** was probably produced via a monocarbene complex $Ru_3(CO)_{11}(=\overline{COCH_2CH_2O})$, such a species was not identified under the reaction conditions. In the ^{13}C NMR spectrum, a single carbene carbon signal occurs at 231.84 ppm, a chemical shift which is very similar to that (227.08 ppm) of $CpRu(CO)_2(=\overline{COCH_2CH_2O})^+$ [3]. The $-OCH_2-$ carbon signal which occurs in the expected region at ~72.0 ppm, along with a sharp ^1H NMR resonance at 4.63 due to the $-OCH_2-$ groups, demonstrates that the compound contains a dioxo carbene ligand. All the carbonyl groups in **V** give rise to a singlet at 204.1 ppm at room temperature. Similarly, in the ^{13}C NMR spectrum of $Ru_3(CO)_{10}(CNBu^t)_2$ one observes only one ^{13}C carbonyl signal at 204.0 ppm [32]. The single ^{13}CO signal indicates that **V**, like other disubstituted Ru_3 cluster carbonyl compounds [32, 33], is fluxional at room temperature.

A comparison of the ν(CO) spectrum of **V** (in CH_2Cl_2: 2104(w), 2066(m), 2046(vs), 2040(sh), 2016(vs), and 1990(s,br) cm^{-1}) with that of $Ru_3(CO)_{10}(CNBu^t)_2$ [32, 34] (in hexane: 2065(w), 2020(s), 2007(m), 1996(s) 1990(m), and 1986(m)) shows that both have six ν(CO) absorptions; however, the ν(CO) values for **V** are at slightly higher wavenumbers than for $Ru_3(CO)_{10}(CNBu^t)_2$ indicating that the dioxy carbene ligand has a slightly greater π-acceptor/σ-donor ratio than $CNBu^t$. An X-ray diffraction study [32] of $Ru_3(CO)_{10}(CNBu^t)_2$ shows the $CNBu^t$ ligands to be on different Ru atoms in the triangular cluster and both to be in axial positions. Based upon the similar IR spectrum of **V**, the most likely structure of **V** is one with two axial carbene ligands on separate Ru atoms. This structure may form as a result of $^-OCH_2CH_2Br$ attack on axial CO groups of $Ru_3(CO)_{12}$ which have slightly higher ν(CO) force constants (16.673 mdyne/Å) than equatorial (16.641 mdyne/Å) [35].

To our knowledge, the only other known terminal carbene derivative of the Ru_3 cluster is $Ru_3(CO)_{11}[=\overline{CN(Et)CH_2CH_2N}(Et)]$ [12].

Conclusion

We previously observed [4] that CO ligands with ν(CO) force constants equal to or greater than 17.0 mdynes/Å would react with oxirane in the presence of Br^- at room temperature to give dioxy carbene complexes. In this paper, we report that at 100 °C metal carbonyls even with ν(CO) force constants below 17.0 mdynes/Å react similarly. This has been demonstrated for the following complexes (their highest ν(CO) force constant is given in parentheses): $Fe(CO)_5$ (16.98 mdynes/Å), $Mn_2(CO)_{10}$ (16.52), $Re_2(CO)_{10}$ (16.67), and $Ru_3(CO)_{12}$ (16.673).

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