Dioxygen Activation by Group 4 tritox Alkyls (tritox = t-Bu_3CO^-): Insertion and Oxygen Atom Transfer

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Abstract: Dioxygen treatment of (tritox)$_2$MMe$_2$ (M = Ti (**1a**), Zr (**1b**), Hf (**1c**)) and (tritox)TiMe$_3$ (**3**) afforded (tritox)$_2$M(OMe)$_2$ (**2a-c**) and (tritox)TiMe$_{3-n}$(OMe)$_n$ (n = 1 (**4**), 2, (**5**), 3 (**6**)), respectively, depending on the stoichiometry. Solid **4** is dimeric, consisting of two symmetry-related square pyramidal units linked by basal μ-OMe bridges (C_{2h}); the Ti atoms of [(tritox)-TiMe$_2$]$_2$(μ-OMe)$_2$ (**4$_2$**) lie 0.71 Å above the basal planes, and the short Ti-O(C-t-Bu$_3$) distance (1.752 (5) Å) concomitant with the 174.4 (6)° Ti-O-C (t-Bu$_3$) angle indicates strong O → Ti π-bonding. Crystal data: monoclinic, $C2/m$, a = 9.191 (3) Å, b = 13.810 (5) Å, c = 14.840 (4) Å, β = 76.105 (21)°, Z = 2, T = 25 °C, and R = 0.073 (926 reflections where $|F_o| \geq 3\sigma(|F_o|)$). Ligand exchange reactions were prevalent: **3** and **5** conproportionated to give **4**; **4** and **6** yielded **5**; **1b-d_6** and **1c** swapped Me groups; **2b-d_6** and **2c** exchanged methoxides; and **1b** and **2c** equilibrated ($K \sim 1$) to give **1c** and **2b**. The O_2 reactivity implicated η^2-OOMe intermediates. Upon exposure to dioxygen, (tritox)$_2$MMe(O-E-CH$_2$CR=CHR′) complexes degraded, perhaps due to fast Lewis acidic opening of formed epoxides. From treatment of (tritox)$_2$MMe(OCR$_2$CH=CH$_2$) (R = Me, M = Zr (**16b**), Hf (**16c**); R$_2$ = -(CH$_2$)$_4$-, M = Zr (**17**)) with O_2, the thermally sensitive epoxy alkoxides, (tritox)$_2$M(OMe)(OCR$_2$CHCH$_2$O) (R = Me, M = Zr (**18b**), Hf (**18c**); R$_2$ = -(CH$_2$)-, M = Zr (**19**)), were obtained, apparently via O_2 insertion followed by O-atom transfer, paralleling known TBHP epoxidations. The sporadic oxygenation rates of **1a**, **16b,c**, and **17**, combined with inhibition and initiation studies, suggest that autoxidation involving propagation by MeO$_2$• is the mechanism of O_2 insertion. The observation that **16b-d_3** and **17** (~1:1) epoxidize to **18b**, **18b-d_3**, **19**, and **19-d_3** (~1:1:1:1) supports this contention. Cp$_2$ZrMe$_2$ (**23**) reacted with O_2 to give Cp$_2$Zr(OMe)$_2$ (**24**), but Cp$_2$ZrMe(O-E-CRR′CH=CHR″) (R = R′ = Me, R″ = H (**25**); RR′ = -(CH$_2$)-, R″ = H (**26**); R = H, R′ = R″ = Me (**27**)) complexes exhibited increased decomposition rates relative to an inert atmosphere. These results suggest that tritox engenders a more electrophilic metal center than Cp, a feature crucial to the ligand exchanges and to S_H2 substitution processes occurring during autoxidation. The similarities of these O_2 activations to main group autoxidation reactions are also discussed.

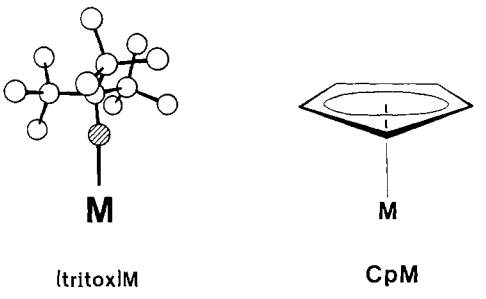
The diverse reactivity of molecular oxygen with transition-metal complexes is manifested in a variety of important processes.[1] Bioinorganic O_2 activations are responsible for critical selective oxidations[2,3] in addition to energy transduction.[4] Numerous commodity and specialty chemicals are produced via heterogeneous and homogeneous transition-metal-catalyzed oxygenations.[5-8] Several of these processes involve metal-mediated autoxidation reactions. Certain transition-metal complexes and metal oxide surfaces possess the ability to introduce a degree of selectivity to autoxidations that are otherwise indiscriminate. The control of such oxidations presents a conspicuous challenge to the inorganic and organometallic community. In order to more fully regulate the highly reactive nature of dioxygen, further understanding of its fundamental transformations must be attained.

In a preliminary communication,[9] the facile insertion of O_2 into early metal alkyl bonds and subsequent oxygen-atom transfer chemistry of presumed η^2-OOR intermediates was addressed. Emphasis was placed on the surprisingly clean nature of the oxygenations and indirect evidence for the existence of an alkyl peroxide obtained through the epoxidation of an allyloxide ligand. These investigations revolved around the utilization of tri-*tert*-butyl methoxide ((Me$_3$C)$_3$CO$^-$, tritox)[10] as an ancillary ligand.[11-13] Synthetic studies of group 4 tritox complexes suggested that tritox (cone angle ~125°) serves as a steric analogue to cyclopentadienyl (136°), while engendering a more electrophilic metal center.[11] As anticipated, the dioxygen activations of group 4 compounds may be interpreted with this characteristic in mind.

Table I. ^{1}H NMR Data for Group 4 Tritox Methoxide Complexes[a]

	tritox	OMe	Me
(tritox)$_2$Ti(OMe)$_2$ (**2a**)	1.46 (s, 54 H)	4.02 (s, 6 H)	
(tritox)$_2$Zr(OMe)$_2$ (**2b**)	1.41 (s, 54 H)	3.84 (s, 6 H)	
(tritox)$_2$Hf(OMe)$_2$ (**2c**)	1.42 (s, 54 H)	3.95 (s, 6 H)	
(tritox)TiMe$_2$(OMe) (**4**)	1.35 (s, 27 H)	4.06 (s, 3 H)	1.08 (s, 6 H)
(tritox)TiMe(OMe)$_2$ (**5**)	1.44 (s, 27 H)	4.12 (s, 6 H)	1.08 (s, 3 H)
(tritox)Ti(OMe)$_3$ (**6**)	1.46 (s, 27 H)	4.13 (s, 9 H)	

[a] Benzene-d_6; referenced to either Me$_4$Si (δ 0.00) or C$_6$D$_5$H (δ 7.15).



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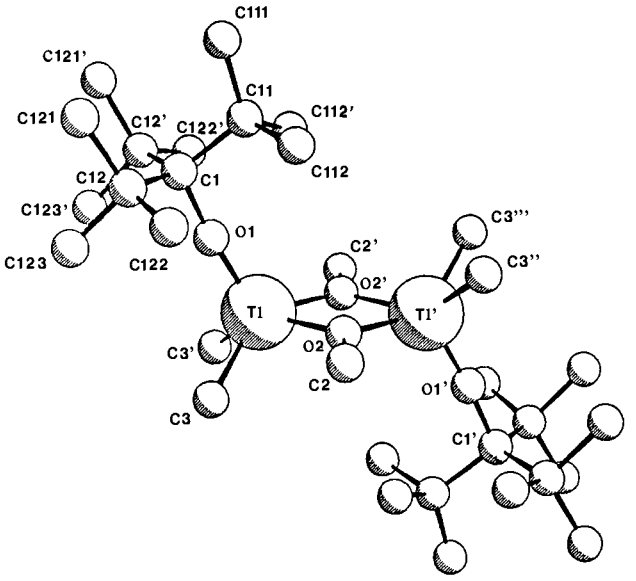

Figure 1. Molecular structure of [(tritox)TiMe$_2$]$_2$(μ-OMe)$_2$ (**4$_2$**).

While main group O_2 activations may be classified as autoxidation processes with some certainty,[14-16] similar transition-metal oxygenations are less well categorized.[17-19] Strong indications of parallel reactivity have been obtained for homoleptic metal-alkyl complexes of group 4[19] and through dioxygen treatment of Cp_2ZrRCl derivatives.[17] Alkyl peroxide intermediates resulting from formal dioxygen insertions into early metal M-R bonds are thought to be activated for O atom transfer by the binding of the proximal (β) oxygen to the electrophilic metal center.[20-22] Herein is presented a full account of the tritox-ligated group 4 oxygenations, including mechanistic information alluding to free-radical-based processes and a discussion pertaining to the importance of electrophilic metal centers in fomenting autoxidation.

Results and Discussion

Oxygenations of Metal Alkyls. When solutions of (tritox)$_2$MMe$_2$ (M = Ti, **1a**; Zr, **1b**; Hf, **1c**)[11] were exposed to either an excess (1 atm) or 1 equiv of dry dioxygen, the corresponding white, crystalline dimethoxide complexes, (tritox)$_2$M(OMe)$_2$ (M = Ti (**2a**), Zr (**2b**), Hf (**2c**)), were isolated in good yield (eq 1,

$$\underset{\textbf{1a}: M = Ti;\ \textbf{1b}: M = Zr;\ \textbf{1c}: M = Hf}{(\text{tritox})_2\text{MMe}_2} + O_2 \rightarrow \underset{\textbf{2a}: M = Ti\ (87\%);\ \textbf{2b}: M = Zr\ (94\%);\ \textbf{2c}: M = Hf\ (92\%)}{(\text{tritox})_2\text{M(OMe)}_2} \quad (1)$$

Table I). Absorption of O_2 by **1b** and **1c** occurred rapidly (<5 min) at −78 °C, while the formation of the Ti dimethoxide (**2a**) required extended, irregular reaction times (8-30 h) depending on which batch of precursor **1a** was utilized.[23] In all cases, the different batches of **1a** were spectroscopically (NMR, IR) identical. Varying the solvents in eq 1 (hexane, C_6H_6, toluene, CH_2Cl_2, CCl_4, Et_2O) or excluding light had no discernable effect on either the rate or cleanliness of the oxygenations. The addition of dioxygen to (tritox)TiMe$_3$ (**3**) afforded three different crystalline methoxides, depending on the stoichiometry (eq 2-4). Orange, crystalline [(tritox)TiMe$_2$]$_2$(μ-OMe)$_2$ (**4$_2$**) was obtained in 95% isolated yield from $^1/_2$ equiv of O_2, yellow (tritox)TiMe(OMe)$_2$

$$\underset{\textbf{3}}{(\text{tritox})\text{TiMe}_3} + (1/2)O_2 \rightarrow (1/n)\underset{\textbf{4}_n,\ n = 1\ (\text{soln});\ 2\ (\text{solid})}{[(\text{tritox})\text{TiMe}_2(\text{OMe})]_n} \quad (2)$$

$$\mathbf{3} + O_2 \rightarrow \underset{\textbf{5}}{(\text{tritox})\text{TiMe(OMe)}_2} \quad (3)$$

$$\mathbf{3} + (3/2)O_2 \rightarrow \underset{\textbf{6}}{(\text{tritox})\text{Ti(OMe)}_3} \quad (4)$$

(**5**) from 1 equiv (84%), and white (tritox)Ti(OMe)$_3$ (**6**) from $^3/_2$ equiv (74%), although the latter was more conveniently prepared from excess O_2. Varying the solvents or excluding light resulted in little or no effect. Curiously, **4** was colorless and monomeric in solution, yet it crystallized as a dimer (vide infra). Molecular weight measurements of **5** in benzene solution indicated the presence of a monomer/dimer (1:1.9) equilibrium, while ^{1}H NMR spectra gave rise to signals consistent with rapid dissociation of the dimer. Similarly, spectra of **6** are also indicative of a

Table II. Selected Interatomic Distances (Å) and Bond Angles (deg) for [(tritox)TiMe$_2$]$_2$(μ-OMe)$_2$ (**4$_2$**)

	Interatomic Distances		
Ti-O1	1.752 (6)	C1-C11	1.625 (15)
Ti-O2	2.015 (4)	C1-C12	1.586 (9)
Ti-C3	2.063 (10)	C11-C111	1.498 (16)
Ti···Ti′	3.290 (3)	C11-C112	1.530 (14)
C1-O1	1.433 (9)	C12-C121	1.575 (17)
C2-O2	1.492 (11)	C12-C122	1.530 (15)
O2···O2′	2.328 (8)	C12-C123	1.563 (13)
	Bond Angles		
O1-Ti-O2	114.3 (2)	C12-C1-C12′	114.5 (7)
O2-Ti-O2′	70.6 (2)	C1-C11-C111	114.2 (10)
O1-Ti-C3	106.8 (3)	C1-C11-C112	113.5 (6)
O2-Ti-C3	89.5 (3)	C1-C12-C121	112.6 (7)
C3-Ti-C3′	82.4 (4)	C1-C12-C122	112.6 (8)
Ti-O1-C1	174.4 (6)	C1-C12-C123	112.5 (7)
Ti-O2-C2	125.3 (1)	C111-C11-C112	107.9 (7)
Ti-O2-Ti′	109.4 (3)	C112-C11-C112′	105.9 (8)
O1-C1-C11	105.1 (7)	C121-C12-C122	105.8 (9)
O1-C1-C12	104.8 (5)	C121-C12-C123	99.8 (8)
C11-C1-C12	113.2 (5)	C122-C12-C123	112.7 (8)

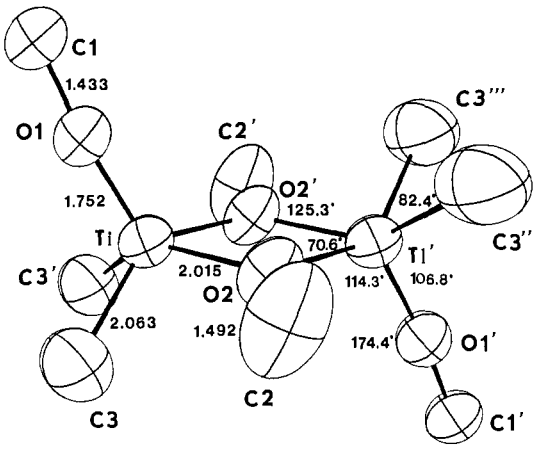

Figure 2. Inner coordination sphere of [(tritox)TiMe$_2$](μ-OMe)$_2$ (**4$_2$**).

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(23) Attempts to kinetically monitor the oxygenation of (tritox)$_2$TiMe$_2$ (**1a**) were hampered by stoppages of O_2 uptake. After variable time periods, readmission of O_2 restarted the reaction.

monomer, yet molecular weight measurements suggest the predominant species in solution is the dimer ([**6**]:[$\mathbf{6}_2$] ~ 1:5). Although written as monomers in eq 3 and 4, it is strongly suspected that both **5** and **6** possess dimeric structures in the solid state, akin to $\mathbf{4}_2$. The presence of higher order solution aggregates cannot be ruled out.

Molecular Structure of [(tritox)TiMe$_2$]$_2$(μ-OMe)$_2$ ($\mathbf{4}_2$). A single-crystal X-ray structure determination (monoclinic, $C2/m$) of $\mathbf{4}_2$ confirmed its dimeric nature. As Figure 1 illustrates, $\mathbf{4}_2$ exhibits overall C_{2h} symmetry, consisting of two symmetry-related square-pyramidal units linked by basal μ-OCH_3 bridges that lie on the twofold axis. A mirror plane contains the titanium, the centroid carbon (C1) and oxygen of tritox, and two *t*-Bu group carbons (C11, C111). Tritox occupies the apex of each pyramid, while two methyls and the two μ-methoxides compose the base; the Ti is positioned 0.71 Å above the basal plane. The Ti–O2 distances (2.015 (4) Å) and Ti–O2–Ti′ angles (109.4 (3)°) are typical of Ti$_2$(μ-OR)$_2$ moieties,[24-26] and the Ti–C3 (Me) bond length (2.063 (10) Å) is unexceptional (Figure 2, Table II). The Ti–Ti′ distance (3.290 (3) Å) remains well outside the sum of the covalent radii (2.64 Å), indicating no significant metal–metal interaction. The large O1–Ti–O2 (114.3 (2)°) and O1–Ti–C3 (106.8 (3)°) angles, accompanied by acute O2–Ti–O2′ (70.6 (2)°) and C3–Ti–C3′ (82.4 (4)°) angles, are in part a testament to the great steric bulk of tritox. An alternative C_i geometry of trigonal bipyramids joined by equatorial and axial μ-methoxides, [(tritox)$_{eq}$Me$_{eq}$Me$_{ax}$Ti]$_2$(μ-OMe)$_{ax}$(μ-OMe)$_{eq}$, would appear to be equally attractive.[26] Presumably the C_{2h} arrangement more effectively accommodates tritox's bulk and/or maximizes the orbital overlap necessary for strong μ-OMe bridges. It is likely, however, that these two structures are energetically close.[27,28]

Strong oxygen p$\pi \rightarrow$ dπ donation is manifested by the extremely short Ti–O1 (1.752 (5) Å) distance and near linear Ti–O1–C1 angle (174.4 (6)°). Similar combinations of short M–O bonds and obtuse M–O–R angles have been reported for a number of relevant complexes, including the following: (tritox)$_2$ZrCl$_3$·Li(OEt$_2$), 1.895 Å, 169°;[11] [(tritox)$_2$Cr(OCH-*t*-Bu$_2$)]$_2$, 1.838 Å, 171°;[12] [TiCl$_2$(OPh)$_2$]$_2$, 1.744 Å, 166°;[24] [TiCl$_2$(OEt)$_2$]$_2$, 1.77 Å, 165.5°;[25] and (2,6-di-*tert*-butylphenoxide)$_3$TiI, 1.798 Å, 157.5°.[29] Substantial stretching of tritox's C1–C11 and C2–C12 bonds (1.606 (28) Å average) and flattening of its tri-*t*-Bu core (∠O1–C1–C11(C12) = 105.1 (7)° (104.8 (5)°); ∠C12–C1–C11(C12′) = 113.2 (5)° (114.5 (7)°)) indicate the sterically distorted character of this bulky ligand.[11-13,30]

Ligand Exchanges. The formation of (tritox)TiMe$_2$(OMe) (**4**, eq 2) suggested that bimolecular methyl/methoxy exchange processes[31-33] play a vital role in this reaction. Confirmation was obtained through the clean conproportionation of **3** and **5** (1:1) to provide **4** (eq 5); in addition, a 1:1 mixture of **4** and **6** was immediately converted to **5** at 25 °C (eq 6). In each case, the equilibrium lay far to the right, at least within detectable limits

$$\underset{\mathbf{3}}{(\text{tritox})\text{TiMe}_3} + \underset{\mathbf{5}}{(\text{tritox})\text{TiMe}(\text{OMe})_2} \rightleftharpoons 2(\text{tritox})\text{TiMe}_2(\text{OMe}) \quad (5)$$

$$\mathbf{4} + \underset{\mathbf{6}}{(\text{tritox})\text{Ti}(\text{OMe})_3} \rightleftharpoons \mathbf{2\,5} \quad (6)$$

Scheme I

$$\underset{\mathbf{3}}{|\text{tritox}|\text{TiMe}_3} + O_2 \longrightarrow \underset{\mathbf{5}}{|\text{tritox}|\text{TiMe}|\text{OMe}|_2}$$

$$\mathbf{5} + \mathbf{3} \rightarrow 2\,\underset{\mathbf{4}}{|\text{tritox}|\text{TiMe}_2|\text{OMe}|}$$

(~2%) of ^{1}H NMR.[34] In conjunction with the above, **3** and **6** redistribute into a ~1:1 mixture of **4** and **5** (eq 7). Scheme I

$$\mathbf{3} + \mathbf{6} \rightleftharpoons \underset{\mathbf{4}}{(\text{tritox})\text{TiMe}_2(\text{OMe})} + \underset{\mathbf{5}}{(\text{tritox})\text{TiMe}(\text{OMe})_2} \quad (7)$$

indicates a plausible mechanism for the formation of **4** from **3** and O_2, corroborated by ^{1}H NMR and monitored via color changes. Upon admission of $^1/_2$ equiv of O_2 to a hexane solution of (tritox)TiMe$_3$ (**3**) at −78 °C, a fine, light-yellow powder diagnostic for (tritox)TiMe(OMe)$_2$ (**5**) precipitated. Over a ~15-min period, its color deepened to the bright orange of [(tritox)TiMe$_2$]$_2$(μ-OMe)$_2$ ($\mathbf{4}_2$). When a deficiency of O_2 was injected into an NMR tube containing **3**, the immediate appearance of **5** was noted followed by its depletion, concomitant with the growth of resonances attributable to **4**. As the O_2 content of the tube was increased, a mixture of **4** and **5** developed and (tritox)Ti(OMe)$_3$ (**6**) began to appear.[35] Under 1 atm of O_2, this mixture was completely converted to **6** in ~12 h. The latter observation and an independently monitored slow conversion of **5** to **6** (1 atm O_2, ~8 h) imply that disproportionation of **5**, giving **4** and **6** (eq 7), and subsequent oxygenation of **4** may be the predominant pathway in which (tritox)Ti(OMe)$_3$ (**6**) is formed. In accord with this proposal, **4** is rapidly converted to **6** under 1 atm of O_2 (~1 h).[35]

The ligand exchange reactions were not limited to the monotritox compounds. When equimolar amounts of (tritox)$_2$Zr(CD$_3$)$_2$ (**1b**-d_6) and (tritox)$_2$HfMe$_2$ (**1c**) were mixed in an NMR tube, an equilibrium with **1b**-d_3, **1c**-d_3, **1b**, and **1c**-d_6 was rapidly established (<5 min). Likewise, (tritox)$_2$Hf(OMe)$_2$ (**2c**) and (tritox)$_2$Zr(OCD$_3$)$_2$ (**2b**-d_6) equilibrated to give **2b**-d_3, **2c**-d_3, **2b**, and **2c**-d_6 (<5 min). A ~1:1 mixture of (tritox)$_2$ZrMe$_2$ (**1b**) and (tritox)$_2$Hf(OMe)$_2$ (**2c**) provided **1c** and **2b** (eq 8), indicative of Me/OMe exchange. An equilibrium constant (K_{eq}) of ~1 was obtained after a 4-day period. Unlike the Ti derivatives above, no indication of substantial (≳2%, ^{1}H NMR) conproportionation products, (tritox)$_2$MMe(OMe) (M = Zr, Hf), could be detected.

$$\underset{\mathbf{1b}}{(\text{tritox})_2\text{ZrMe}_2} + \underset{\mathbf{2c}}{(\text{tritox})_2\text{Hf}(\text{OMe})_2} \xrightleftharpoons{K_{eq} \sim 1} \underset{\mathbf{2b}}{(\text{tritox})_2\text{Zr}(\text{OMe})_2} + \underset{\mathbf{1c}}{(\text{tritox})_2\text{HfMe}_2} \quad (8)$$

Unfortunately, the latter compounds could not be independently prepared, thus the slight possibility that their spectra are superimposable on **1b**/**2b** and **2b**/**2c** could not be eliminated. The near unity value for K_{eq} (eq 8) substantiates the known similarities of Zr and Hf alkyl and alkoxide bond strengths.[36]

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(32) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.
(33) (a) Puddephatt, R. J.; Stalteri, M. A. *Organometallics* **1983**, *2*, 1400. (b) Jordon, R. *J. Organomet. Chem.* **1985**, *294*, 321.

(34) In principle, lower limits may be placed on these equilibrium constants given the NMR sensitivity. However, such calculations are dependent on the degree of aggregation of the species involved. Extrapolating monomer/dimer equilibrium constants obtained from ~5.5 °C molecular weight measurements to 25 °C is risky at best. If all species are predominantly monomeric at 25 °C the following sample calculation would hold: initial [**3**] ≃ initial [**5**] = 0.14 M; K_{eq} = [**4**]^2/[**3**][**5**] = [2x]^2/[0.14 − x]^2, [0.14 − x]/2x ≤ 0.02 (assuming ≤ 2% **3** and/or **5** relative to 2 equiv of **4** could not be detected by ^{1}H NMR); $K_{eq} \geq 2500$.
(35) These oxygenations are demonstrably faster when carried out in a flask (see experimental). Presumably the smaller surface area of the NMR tube solutions slows the interfacial passage of O_2, thereby permitting the direct observation of these reactions.

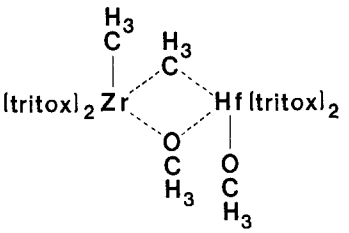
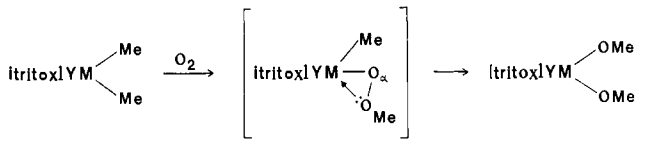


Figure 3.

Scheme II

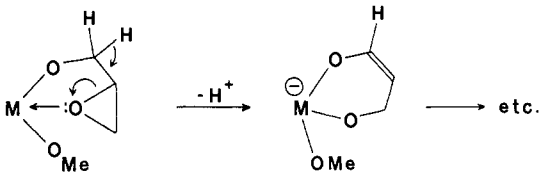


Y = Me, OMe; M = Ti

Y = tritox; M = Ti, Zr, Hf

Intuitively, one might have expected that the Me/OMe exchange reaction in eq 8 should have occurred at a rate qualitatively similar to the Me/Me and OMe/OMe exchanges of **1b**-d_6/**1c** and **2b**-d_6/**2c**, respectively. If the latter two exchanges involve transition states which can be described as (tritox)$_2$(CD$_3$)Zr(μ-CD$_3$)(μ-CH$_3$)Hf(CH$_3$)(tritox)$_2$[37] and (tritox)$_2$(CD$_3$O)Zr(μ-OCD$_3$)(μ-OCH$_3$)Hf(OCH$_3$)(tritox)$_2$,[38] an attractive transient for the Me/OMe exchange (eq 8) would be (tritox)$_2$(CH$_3$)Zr(μ-CH$_3$)(μ-OCH$_3$)Hf(OCH$_3$)(tritox)$_2$ (Figure 3), a transition state that is essentially an "average" of the prior two. In the Me/Me and OMe/OMe exchanges, $\Delta H = 0$, neglecting minor equilibrium isotope effects; in contrast, the Me/OMe "cross" reaction would logically involve the intermediacy of (tritox)$_2$MMe(OMe) species, whose formation is unfavorable ($\Delta H \gtrsim 4.6$ kcal).[39] The activation energy for the cross reaction consists of an inherent barrier for ligand exchange similar to the Me/Me and OMe/OMe cases, plus a component which reflects the unfavorable thermodynamics of methoxymethyl formation. The observed disparity in the qualitative self-exchange vs. cross-reaction rates corroborates this point.

While the facile ligand exchanges of **1**–**6** may be understood in terms of the intrinsic electronic unsaturation of these species, the conproportionations of the mono-tritox Ti complexes (eq 5–7) are in contrast to the disproportionations of the bis-tritox derivatives (eq 8). The former may result from minimizing the competition for vacant π-accepting orbitals on Ti by the π-donating OMe ligand.[32] Analysis of the various monomer/dimer equilibria suggests that their role is minor. No simple rationale can explain the disproportionation of eq 8; perhaps the bis-tritox coordination sphere causes significant distortions from pseudo-T_d symmetry in either the dimethoxide or dimethyl complexes, rendering the π-bonding arguments moot. Nevertheless, it is clear that the thermodynamic influences in these systems are subtle.



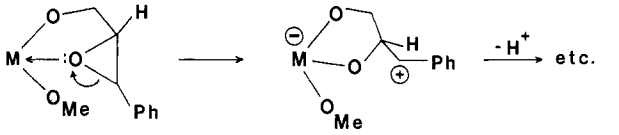


Figure 4.

Oxygen Atom Transfer. In each of the dioxygen insertion reactions above, the O–O bond was cleaved, implicating a methylperoxy methyl (M(η^2-OOMe)Me) intermediate (Scheme II). The subsequent transfer of the α-oxygen atom from the methylperoxy linkage[17-22,40] to an adjacent methyl would complete the methoxylation. Literature precedent for the alkylperoxy transient abounds. Early metal-catalyzed olefin and allylic alcohol epoxidations, utilizing *t*-BuOOH (TBHP) as an oxygen atom source, are proposed to occur via M(η^2-OO-*t*-Bu) intermediates.[41-43] Heterogeneous propylene oxide catalysis involves TBHP,[41] and Mimoun has structurally characterized (2,6-pyridinedicarboxylate)(H$_2$O)V=O(η^2-OO-*t*-Bu), a species which exhibits O atom transfer reactivity.[22] Schwartz[17] has proposed that Cp$_2$ZrCl(η^2-O$_2$R) is a crucial intermediate in the bimolecular formation of Cp$_2$ZrCl(OR) from the oxygenation of Cp$_2$ZrClR while Brindley and Hodgson have obtained PhCH$_2$OOH from aqueous quenches of Zr(CH$_2$Ph)$_4$ solutions which have undergone autoxidation.[19] Numerous late metal η^1-OOR species exist,[44] and Puddephatt has recently reported a Pt^{IV}(η^1-OO-*i*-Pr) complex which was obtained via the radical-based oxidative addition of *i*-PrI in the presence of O$_2$.[45]

Theoretical investigations[20] point to the η^2-binding in the early metal systems as the key feature in activating the α-O of an alkyl peroxide. The electrophilicity of the early metal is transposed to the α-O unit via η^2-ligation. Thus the O atom transfer in Scheme II may be thought of as a nucleophilic attack at the electropositive α-O by the M$^{\delta+}$–C$^{\delta-}$ polarized M–Me bond.

In order to demonstrate the feasibility of the purported η^2-OOMe intermediate, another neighboring group capable of nucleophilic attack at the α-O was sought. The aforementioned early metal catalyzed epoxidations of allylic alcohols by TBHP, in particular Sharpless' asymmetric Ti-catalyzed epoxidation procedure,[21,43] suggested that the inclusion of an allyloxide would serve this purpose. Treatment of (tritox)$_2$MCl$_2$ (M = Ti, **7a**; Zr, **7b**)

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(37) For μ-Me species, see: Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

(38) Bridging alkoxides are prevalent for the early metals. See: (a) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic: New York, 1978. (b) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 289.

(39) Given: (1) eq 8 shows that Me/OMe exchange can occur, (2) the equilibrium in eq 8 can be approached from both directions, and (3) solutions of **1b**/**2b** and **1c**/**2c** do not conproportionate to (tritox)$_2$ZrMe(OMe) and (tritox)$_2$HfMe(OMe), respectively (within ^{1}H NMR detection limits of ~2%). Therefore a lower limit can be placed on any cross reaction, (tritox)$_2$MMe$_2$ + (tritox)$_2$M′(OMe)$_2$ $\rightleftharpoons$ (tritox)$_2$MMe(OMe) + (tritox)$_2$M′Me(OMe). For example, consider the simple case where M = M′ = Zr: initial [**1b**] $\simeq$ [**2b**] = 0.08 M; K'_{eq} = [(tritox)$_2$ZrMe(OMe)]^2 /[**1b**][**2b**] = [2x]^2/[0.08 − x]^2, 2x/(0.08 − x) $\leq$ 0.02 (assuming $\leq$ 2% of 2 equiv of (tritox)$_2$ZrMe(OMe) could not be detected within limits of ^{1}H NMR); $K'_{eq} \leq 4.0 \times 10^{-4}$ and ΔG (and thus ΔG^*) $\geq$ 4.6 kcal/mol (25 °C).

(40) (a) Mimoun, H.; Carpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047. (b) Strukul, G.; Michelin, R. A.; Orbell, J. D.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3706.

(41) Sheldon, R. A. *J. Mol. Catal.* **1980**, *7*, 107.

(42) (a) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587. (b) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63. (c) Adam, W.; Griesbeck, A.; Staab, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 269.

(43) (a) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. *Pure Appl. Chem.* **1983**, *55*, 589. (b) Rossiter, B. E. In *Asymmetric Synthesis*; Vol. 5; Morrison, J. D., Ed.; Academic: New York, 1985; Vol. 5, p 193.

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Table III. ^{1}H NMR Data (δ, J(Hz)) for (tritox/Cp)$_2$MX(OCR^{1}R$^{1\prime}$CR^2=CR^{3}R^4) Complexes[a]

complexes	tritox/Cp	X	$R^1R^{1\prime}$	R^2	$R^{3\,b}$	$R^{4\,b}$
(tritox)$_2$TiCl(OCH$_2$CH=CH$_2$) (**8**)	1.42		4.74 (dd, ^4J = 1, ^3J = 6)	5.86 (ddt, ^3J = 6, ^3J_c = 9, ^3J_t = 17)	4.94 (dd, ^3J_c = 9, ^2J = 2)	5.19 (dd, ^2J = 2, ^3J_t = 17)
(tritox)$_2$TiCl(*E*-OCH$_2$CH=CHPh) (**9a**)	1.46		4.93 (dd, ^4J = 1, ^3J = 6)	6.19 (dt, ^3J = 6, ^3J_t = 15)	6.9–7.4	6.59 (d, ^3J_t = 15)
(tritox)$_2$ZrCl(*E*-OCH$_2$CH=CHPh) (**9b**)	1.41		4.65 (dd, ^4J = 1, ^3J = 5)	6.14 (dt, ^3J = 5, ^3J_t = 16)	6.9–7.4	6.53 (dd, ^4J = 1, ^3J_t = 16)
(tritox)$_2$TiCl(*E*-OCH$_2$CPh=CHPh) (**10a**)	1.44		5.28 (d, ^4J = 1)	6.8–7.3	6.8–7.3	*c*
(tritox)$_2$ZrCl(*E*-OCH$_2$CPh=CHPh) (**10b**)	1.40		4.94 (d, ^4J = 1)	6.8–7.3	6.8–7.3	*c*
(tritox)$_2$ZrCl(OCMe$_2$CH=CH$_2$) (**14b**)	1.39		1.39	5.97 (dd, ^3J_c = 10, ^3J_t = 17)	4.83 (dd, ^2J < 1.5, ^3J_c = 10)	5.06 (dd, ^2J < 1.5, ^3J_t = 17)
(tritox)$_2$HfCl(OCMe$_2$CH=CH$_2$) (**14c**)	1.40		1.41	6.05 (dd, ^3J_c = 11, ^3J_t = 17)	4.89 (dd, ^2J = 1, ^3J_c = 11)	5.11 (dd, ^2J = 1, ^3J_t = 17)
(tritox)$_2$ZrCl(OC(CH$_2$)$_3$CH$_2$CH=CH$_2$) (**15**)	1.40		1.6 (m, 4 H), 2.1 (m, 4 H)	6.07 (dd, ^3J_c = 10, ^3J_t = 17)	4.99 (dd, ^2J = 1, ^3J_c = 10)	5.26 (dd, ^2J = 1, ^3J_t = 17)
(tritox)$_2$TiMe(OCH$_2$CH=CH$_2$) (**11**)	1.44	1.37	4.79 (dd, ^4J = 2, ^3J = 4)	5.96 (ddt, ^3J = 4, ^3J_c = 9, ^3J_t = 17)	4.97 (dd, ^2J = 2, ^3J_c = 9)	5.20 (dd, ^2J = 2, ^3J_t = 17)
(tritox)$_2$TiMe(*E*-OCH$_2$CH=CHPh) (**12a**)	1.39	1.39	4.39 (dd, ^4J = 1, ^3J = 5)	6.26 (dt, ^3J = 5, ^3J_t = 16)	7.0–7.4	6.62 (d, ^3J_t = 16)
(tritox)$_2$ZrMe(*E*-OCH$_2$CH=CHPh) (**12b**)	1.42	0.79	4.76 (dd, ^4J = 1, ^3J = 5)	6.27 (dt, ^3J = 5, ^3J_t = 17)	7.0–7.4	6.64 (d, ^3J_t = 17)
(tritox)$_2$TiMe(*E*-OCH$_2$CPh=CHPh) (**13a**)	1.47	1.39	5.25 (d, ^4J = 1)	6.8–7.3	6.8–7.3	*c*
(tritox)$_2$ZrMe(*E*-OCH$_2$CPh=CHPh) (**13b**)	1.45	0.64	4.99 (d, ^4J = 1)	6.9–7.3	6.9–7.3	*c*
(tritox)$_2$ZrMe(OCMe$_2$CH=CH$_2$) (**16b**)	1.40	0.72	1.42	6.07 (dd, ^3J_c = 10.5, ^3J_t = 17.5)	4.91 (dd, ^2J = 1.5, ^3J_c = 10.5)	5.15 (dd, ^2J = 1.5, ^3J_t = 17.5)
(tritox)$_2$HfMe(OCMe$_2$CH=CH$_2$) (**16c**)	1.39	0.65	1.43	6.07 (dd, ^3J_c = 10.8, ^3J_t = 17)	4.91 (dd, ^2J = 1.2, ^3J_c = 10.8)	5.13 (dd, ^2J = 1.2, ^3J_t = 17)
(tritox)$_2$ZrMe(OC(CH$_2$)$_3$CH$_2$CH=CH$_2$) (**17**)	1.40	0.73	1.6 (m, 4 H), 2.0 (m, 4 H)	6.07 (dd, ^3J_c = 10.5, ^3J_t = 17)	5.02 (dd, ^2J = 1.5, ^3J_c = 10.5)	5.28 (dd, ^2J = 1.5, ^3J_t = 17)
(tritox)$_2$Zr(OMe)(OCMe$_2$CH=CH$_2$) (**21**)	1.42	3.92	1.43	6.10 (dd, ^3J_c = 10, ^3J_t = 17)	4.94 (dd, ^2J = 1, ^3J_c = 10)	5.20 (dd, ^2J = 1, ^3J_t = 17)
(tritox)$_2$Zr(OMe)(OC(CH$_2$)$_3$CH$_2$CH=CH$_2$) (**22**)	1.42	3.91	1.6 (m, 4 H), 2.0 (m, 4 H)	6.08 (dd, ^3J_c = 10, ^3J_t = 17)	5.05 (dd, ^2J = 1, ^3J_c = 10)	5.43 (dd, ^2J = 1, ^3J_t = 17)
Cp$_2$ZrMe(OCMe$_2$CH=CH$_2$) (**25**)	5.69	0.29	1.06	5.73 (dd, ^3J_c = 9, ^3J_t = 17)	4.78 (dd, ^2J = 1.5, ^3J_c = 9)	4.93 (dd, ^2J = 1.5, ^3J_t = 17)
Cp$_2$ZrMe(OC(CH$_2$)$_3$CH$_2$CH=CH$_2$) (**26**)	5.78	0.34	1.55 (m, 8 H)	5.86 (dd, ^3J_c = 10, ^3J_t = 17)	4.93 (dd, ^2J = 2, ^3J_c = 10)	5.04 (dd, ^2J = 2, ^3J_t = 17)
Cp$_2$ZrMe(*E*-OCHMeCH=CHMe) (**27**)	5.80	0.34	1.08 (3 H, d, ^3J = 6), 4.34 (1 H, dq, ^3J = 6, ^3J = 1)	5.41 (m)	1.59 (3 H, dd, ^3J = 5)	5.41 (m)

[a] Benzene-d_6; referenced to either Me$_4$Si (δ 0.00) or C$_6$D$_5$H (δ 7.15). [b] Allylic couplings (^4J) were not always resolved. [c] Resonance presumably obscured by Ph.

Table IV. ^{1}H NMR Data (δ, J (Hz)) for HOCR$_2$CHCH$_2$O and (tritox)$_2$M(OMe)(OCR$_2$CHCH$_2$O) Complexes[a]

complexes	R_2	H	H_t	H_c	other
HOCMe$_2$CHCH$_2$O[b]	0.96 1.06	2.49 (dd, ^3J_c = 3.9, ^3J_t = 2.7)	2.21 (dd, ^2J = 5.3, ^3J_c = 3.9)	2.45 (dd, ^2J = 5.3, ^3J_t = 2.7)	1.39 (OH)
HOC(CH$_2$)$_3$CH$_2$CHCH$_2$O[b]	1.47 (m, 6 H), 1.73 (m, 2 H)	2.59 (dd, ^3J_c = 4.3, ^3J_t = 2.9)	2.26 (dd, ^2J = 5.4, ^3J_c = 4.3)	2.52 (dd, ^2J = 5.4, ^3J_t = 2.9)	1.45 (OH)
(tritox)$_2$Zr(OMe)(OCMe$_2$CHCH$_2$O) (**18b**)	1.24, 1.38	2.93 (dd, ^3J_c = 4.2, ^3J_t = 2.9)	2.41 (dd, ^2J = 4.8, ^3J_c = 4.2)	2.56 (dd, ^2J = 4.8, ^3J_t = 2.9)	1.42 (tritox), 3.92 (OMe)
(tritox)$_2$Hf(OMe)(OCMe$_2$CHCH$_2$O) (**18c**)	1.24, 1.36	2.92 (dd, ^3J_c = 4.0, ^3J_t = 3.0)	2.39 (dd, ^2J = 4.5, ^3J_c = 4.0)	2.53 (dd, ^2J = 4.5, ^3J_t = 3.0)	1.40 (tritox), 3.94 (OMe)
(tritox)$_2$Zr(OMe)(OC(CH$_2$)$_3$CH$_2$CHCH$_2$O) (**19**)	1.7 (m, 2 H)[c]	3.01 (dd, ^3J_c = 4.0, ^3J_t = 3.1)	2.48 (dd, ^2J = 4.4, ^3J_c = 4.0)	2.66 (dd, ^2J = 4.4, ^3J_t = 3.1)	1.44 (tritox), 3.91 (OMe)

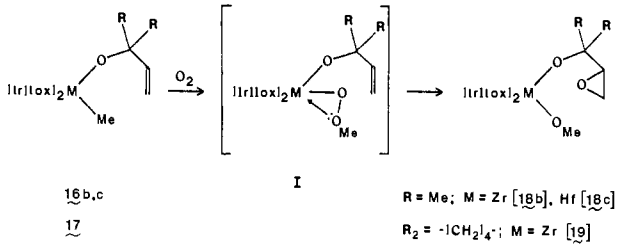
[a] Benzene-d_6; reference to either Me$_4$Si (δ 0.00) or C$_6$D$_5$H (δ 7.15). [b] Concentration dependent (spectra taken at 0.08 M). [c] Remaining 6 H's appear to be under the base of the tritox peak (δ 1.4–1.5).

Table V. $^{13}C\{^1H\}$ NMR Data (δ) for $HOCR_2\overline{CHCH_2O}$ and $(tritox)_2ZrX(OR')$ ($R' = CR_2CH{=}CH_2$, $CR_2\overline{CHCH_2O}$) Complexes[a]

complex	OC	R_2	CH	CH_2	$[((H_3C)_3C)_3CO]$	X
$HOCMe_2\overline{CHCH_2O}$	67.7	25.1, 27.2	58.7	43.8		
$HO\overline{C(CH_2)_3CH_2CHCH_2O}$	79.2	24.3,[b] 36.3, 38.4	57.3	43.9		
$(tritox)_2ZrCl(OCMe_2CH{=}CH_2)$ (**14b**)	82.5	30.6	146.1	111.1	33.5, 45.9, 99.5	
$(tritox)_2ZrCl(O\overline{C(CH_2)_3CH_2CH}{=}CH_2)$ (**15**)	94.0	23.2, 41.0	143.7	111.6	33.4, 45.9, 99.5	
$(tritox)_2ZrMe(OCMe_2CH{=}CH_2)$ (**16b**)	80.5	31.2	147.1	110.3	33.5, 45.8, 97.2	27.3
$(tritox)_2ZrMe(O\overline{C(CH_2)_3CH_2CH}{=}CH_2)$ (**17**)	92.1	23.6, 41.1	144.7	111.0	33.5, 45.8, 97.2	28.0
$(tritox)_2Zr(OMe)(OCMe_2\overline{CHCH_2O})$ (**18b**)	77.3	27.8, 28.2	58.8	44.8	33.5, 46.0, 96.0	60.1
$(tritox)_2Zr(OMe)(O\overline{C(CH_2)_3CH_2CHCH_2O})$ (**19**)	88.0	24.2,[b] 38.8, 39.1	58.3	46.6	33.5, 45.8, 96.3	59.9

[a] Benzene-d_6; referenced to C_6D_6 (δ 128.00). [b] Two-carbon resonance.

Scheme III



with the appropriate Li(*E*-$OCH_2CR{=}CHR'$) reagent led to the formation of the $(tritox)MCl(E\text{-}OCH_2CR{=}CHR')$ derivatives below (eq 9) in moderate yield (42–79%). The stoichiometric

$$(tritox)_2MCl_2 + Li(E\text{-}OCH_2CR{=}CHR') \xrightarrow{-LiCl}$$

7a: M = Ti
7b: M = Zr

$$(tritox)_2MCl(E\text{-}OCH_2CR{=}CHR') \quad (9)$$

R = R' = H; M = Ti (**8**)
R = H; R' = Ph; M = Ti (**9a**), Zr (**9b**)
R = R' = Ph; M = Ti (**10a**), Zr, (**10b**)

addition of MeLi to the allyloxy chlorides resulted in the desired Me derivatives according to eq 10 (35–75%). Initial oxygenation

$$(tritox)_2MCl(E\text{-}OCH_2CR{=}CHR') \xrightarrow[-LiCl]{CH_3Li}$$

8
9a,b
10a,b

$$(tritox)_2MMe(E\text{-}OCH_2CR{=}CHR') \quad (10)$$

R = R' = H; M = Ti (**11**)
R = H; R' = Ph; M = Ti (**12a**), Zr (**12b**)
R = R' = Ph; M = Ti (**13a**), Zr (**13b**)

efforts focused on the parent allyloxy Ti complex, **11**, the Zr analogue of which could not be prepared. Prolonged exposure of **11** to O_2 resulted in decomposition. Reasoning that rates of allyloxy epoxidation were known to be relatively slow, the cinnamyl (**12a,b**) and α,β-diphenyl derivatives were then investigated, since Ph substitution was shown to enhance the rate of O atom transfer in the catalytic diethyl tartarate/Ti(O-*i*-Pr)$_4$/TBHP system.[46] Again, oxygenation of these derivatives resulted in degradation to a multitude of products. Conceivably, Lewis acid-assisted openings of the desired epoxyalkoxy products were critically problematic. As Figure 4 indicates, electrophilic attack by the metal center on the coordinated epoxide, accompanied by proton loss, could serve to destroy the desired products, since all tritox-containing species are extremely sensitive to protolysis. The ability of Lewis acids to open epoxides is well-documented,[47] and spectra of the O_2 degradations showed substantial amounts of (tritox)H as well as –OMe residues, consistent with protolytic destruction. Furthermore, the allylic hydrogens present in the above derivatives could prove deleterious to radical-based processes (vide infra).

On the assumption that this scenario was correct, the preparation of $(tritox)_2MMe(OCR_2CH{=}CH_2)$ (R = Me, M = Zr (**16b**), Hf (**16c**); $R_2 = -(CH_2)_4-$, M = Zr (**17**)) complexes was accomplished in a fashion similar to the above. Dialkylation at

$$(tritox)_2MCl_2 + LiOCR_2CH{=}CH_2 \xrightarrow{-LiCl}$$

7b: M = Zr
7c: M = Hf

$$(tritox)_2MCl(OCR_2CH{=}CH_2) \quad (11)$$

R = Me; M = Zr (**14b**) (87%), Hf (**14c**) (63%)
$R_2 = -(CH_2)_4-$; M = Zr (**15**) (95%)

$$(tritox)_2MCl(OCR_2CH{=}CH_2) \xrightarrow[-LiCl]{CH_3Li}$$

14b,c
15

$$(tritox)_2MMe(OCR_2CH{=}CH_2) \quad (12)$$

R = Me; M = Zr (**16b**) (77%), Hf (**16c**) (30%)
$R_2 = -(CH_2)_4-$; M = Zr (**17**) (70%)

Cα and utilization of the unsubstituted (deactivated) olefin were considered sufficient to retard the rates of the plausible epoxide decompositions. As a consequence of the *gem*-dialkyl effect,[48] the substrate olefin may be more properly oriented for electrophilic attack by the α-O atom of the incipient alkyl peroxide.

When **16b,c** and **17** were treated with dioxygen (1 atm), diagnostic epoxide resonances attributable to $(tritox)_2M(OMe)(OCR_2\overline{CHCH_2O})$ (R = Me, M = Zr (**18b**), Hf (**18c**); $R_2 = -(CH_2)_4-$, M = Zr (**19**)) were observed by ^1H (Table IV) and ^{13}C NMR (Table V). As Scheme III indicates, an intermediate $(tritox)_2M(\eta^2\text{-}OOMe)(OCR_2CH{=}CH_2)$ complex (I) would logically undergo O atom transfer, as literature precedent suggested.[21,42,43] While **18b** and **19** can typically be prepared in ~90% purity (~90% yield) as clear, colorless oils, the hafnium derivative (**18c**) was somewhat less tractable (~80% purity, ~70% yield). Ethereal, hydrocarbon, and chlorinated solvents (e.g., CCl_4) may be utilized. Quenching studies supplied additional evidence in support of epoxide formation. When solutions of **18b,c** and **19** were subjected to excess H_2O, the epoxy alcohols, MeOH and

$$(tritox)_2M(OMe)(OCR_2\overline{CHCH_2O}) \xrightarrow{H_2O\ (xs)}$$

18b,c; **19**

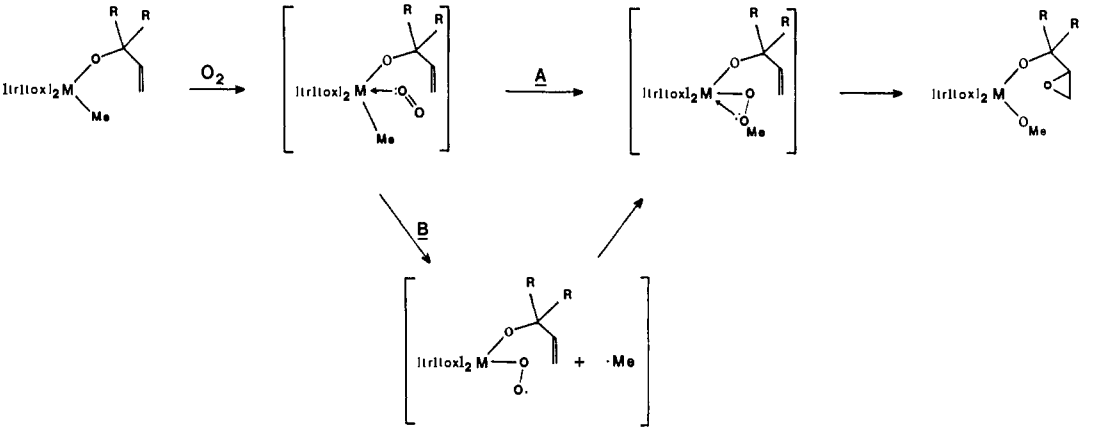
$$2(tritox)H + MeOH + HOCR_2\overline{CHCH_2O} + \text{"}MO_2\text{"} \quad (13)$$

R = Me; $R_2 = -(CH_2)_4-$

(tritox)H were cleaved from the metal center (eq 13). The resulting $HOCR_2\overline{CHCH_2O}$ (R = Me; $R_2 = -(CH_2)_4-$) species were correlated with authentic material[49] via ^1H NMR and capillary GC. From the spectral data, it was uncertain whether the epoxide oxygens were bound to the metal. Although significant shifts of the epoxide protons ($\Delta\delta \sim 0.4$ (CH); $\Delta\delta \sim 0.2, 0.1$ (CH_2)) of **18b,c** and **19** relative to their parent epoxy alcohols were noted, only the CR_2 carbon was distinctly different by ^{13}C NMR. Since

(46) Woodard, S. S. Ph.D. Thesis, Stanford University, 1981.
(47) Morgans, D. J.; Sharpless, K. B.; Traynor, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 462.
(48) (a) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; p 58. (b) Hammond, G. S. *Steric Effects of Organic Chemistry*; Wiley: New York, 1956; p 468.
(49) Payne, G. B. *J. Org. Chem.* **1962**, *27*, 3819.

Scheme IV



the Zr center is more electrophilic than a proton, this ~10 ppm downfield shift was easily rationalized. If the epoxide oxygen were bound to Zr, the CH and CH_2 carbons would be expected to show a similar downfield displacement. Attempts to crystallize the epoxy alkoxides for further structural study have proved fruitless. Once these species have reached their respective purity levels, degradation (apparently autocatalytic) then predominates. The formation of (tritox)H, concomitant with the disappearance of the epoxy resonances, was consistent with the decomposition pathways above.

In order to establish a link between the O_2 activations above and documented TBHP epoxidations, NaO_2-*t*-Bu was added to $(tritox)_2ZrCl(OCMe_2CH{=}CH_2)$ (**14b**, eq 14). Resonances signifying the formation of $(tritox)_2Zr(O\text{-}t\text{-}Bu)(\overline{OCMe_2CHCH_2O})$ (**20**, 30%) were observed, but considerable side products (e.g., (tritox)H, 30%) were also present, and rapid degradation of **20** ensued. Despite rigorous drying of the TBHP,[50] trace water[51] could be a source of NaOH, a significant impurity. Nonetheless, the NMR evidence for the occurrence of **20** supported the intermediacy of I in Scheme III.

$$\mathbf{14b} \xrightarrow{NaO_2\text{-}t\text{-}Bu} (tritox)_2Zr(O\text{-}t\text{-}Bu)(\underset{\mathbf{20}}{\overline{OCMe_2CHCH_2O}}) + \ldots \qquad (14)$$

The rates of epoxidation were decidedly sporadic. For example, spectroscopically (IR, NMR) indistinguishable batches of **16b,c** at similar concentrations (~0.02 M, 1 atm of O_2) were epoxidized over periods ranging from 5 to 36 h. In addition, some batches appeared totally inactive (no **18b** formation after 72 h). In one instance, an inactive batch of **16c** rapidly epoxidized (benzene, 1 atm of O_2) after standing (solid) in a drybox at −20 °C for 18 h. In order to circumvent these problems and obtain kinetic data, a solution of **16b** was separated into three vessels which were simultaneously exposed to 0.1, 0.5, and 1 atm of O_2. The epoxidations to $(tritox)_2Zr(OMe)(\overline{OCMe_2CHCH_2O})$ (**18b**) were simultaneously monitored, yet even under these conditions, the scatter in the rate data prevented meaningful interpretation. While the epoxidation was $[O_2]$-dependent, no order could be determined and kinetic analysis of the reaction was deemed untenable.

The addition of O_2 to *erythro*-Cp_2ZrClR (R = CHDCHD-*t*-Bu) results in the formation of 75% *erythro*-$Cp_2ZrCl(OR)$ and 25% *threo*-$Cp_2ZrCl(OR)$. This observation is consistent with bimolecular O atom transfer, with retention of configuration, from $Cp_2ZrCl(\eta^2\text{-}OOR)$ (50% erythro, 50% threo) to the starting *erythro*-Cp_2ZrClR.[17] When epoxidations of **16b** and **17** were carried out at concentrations ≳0.03 M, traces (~10%) of $(tritox)_2Zr(OMe)(OCR_2CH{=}CH_2)$ (R = Me (**21**); $R_2 = -(CH_2)_4-$ (**22**)) were detected (eq 15). Spectroscopic verification of these species

$$\underset{(17)}{\mathbf{16b}} \xrightarrow{O_2} \underset{(19)}{\mathbf{18b}} + (tritox)_2Zr(OMe)(OCR_2CH{=}CH_2) \qquad (15)$$
$$\mathbf{21}: R = Me\ (\sim 10\%)$$
$$\mathbf{22}: R_2 = -(CH_2)_4-\ (\sim 10\%)$$

$$\underset{(15)}{\mathbf{14b}} + LiOMe \rightarrow \underset{(22)}{\mathbf{21}} + (tritox)_2Zr(OMe)_2 \qquad (16)$$
$$\mathbf{2b}\ (15\text{–}25\%)$$

was accomplished via independent synthesis (eq 16). Treatment of $(tritox)_2ZrCl(OCR_2CH{=}CH_2)$ (R = Me (**14b**); $R_2 = -(CH_2)_4-$ (**15**)) with methoxide afforded the allyloxymethoxy complexes in respectable yield (**21**, 70%; **22**, 65%), although competitive displacement of the allyloxide results in ~15–25% inseparable **2** (eq 16). Although the apparent bimolecular α-O-transfer to form **21** and **22** was evidenced, a similar bimolecular epoxide-forming transfer has not been observed. Oxygenation of solutions containing equimolar (≳0.03 M) amounts of **14b** and **16b** provided **18b** as the sole product, leaving **14b** unchanged. In the ensuing mechanistic studies, the concentration of epoxide precursor was purposely kept low, keeping the bimolecular side reaction to a minimum. Exposure to light was not a factor; oxygenations of active **16b** in the dark proceeded smoothly.

The Nature of O_2 Insertion. While the O atom transfers were adequately rationalized via the purported η^2-OOMe intermediate, the mechanism of its formation was less certain. Consider the postulated mechanisms outlined in Scheme IV: step A depicts a concerted insertion of dioxygen into a M–Me bond, similar to the Cossee pathway[52] for the insertion of olefins, and step B corresponds to Schwartz's Cp_2ZrClR oxidation scheme,[17] essentially an attack on the metal center by O_2 to generate a radical pair (M–OO• and Me•) which recombine. The nonradical mechanism (A) appears implausible due to the sporadic nature of the epoxidation reactions; however, competitive binding by an impurity L (vs. O_2) could cause inhibition. Since active and inactive batches of **16b,c** are spectroscopically identical, such inhibition is considered very unlikely.

All evidence obtained was consistent with a radical-based process: (1) trace amounts of iodide quenched the epoxidation;[53,54] (2) when the oxygenation of **16b** was carried out in the presence of 1,4-cyclohexadiene (5–10 molar equiv), benzene was formed concomitant with inhibition of epoxide formation and an increase in the decompositions of **16b** and **18b**;[55] (3) AIBN initiated ep-

(50) (a) Hill, J. G.; Sharpless, K. B.; Exon, C. M.; Regenye, R. *Org. Synth.* **1984**, *63*, 66. (b) Hill, J. G.; Rossiter, B. E.; Sharpless, K. B. *J. Org. Chem.* **1983**, *48*, 3607.

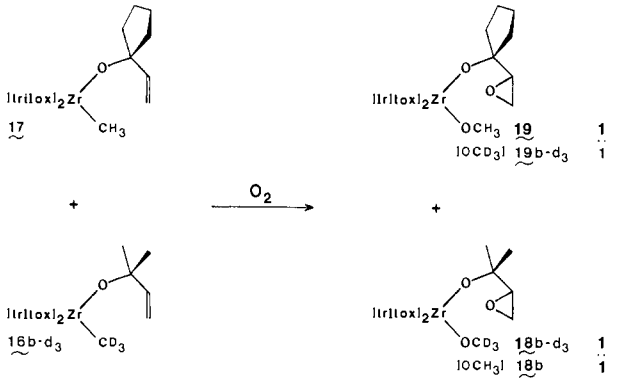
(51) Trace amounts of H_2O in "dry" TBHP have proved problematic in Sharpless's Ti-catalyzed epoxidations. See: Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922.

(52) (a) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99. (b) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377.

(53) This quenching is thought to occur via MeO_2• oxidation of I^- to iodine, an effective quenching agent (ref 54). Similar inhibitions by bromide have been observed (ref 13 and 14).

(54) (a) Brown, H. C.; Midland, M. M. *J. Am. Chem. Soc.* **1971**, *93*, 1506. (b) Suzuki, A.; Nozawa, S.; Harada, M.; Itoh, M.; Brown, H. C.; Midland, M. M. *Ibid.* **1971**, *93*, 1508.

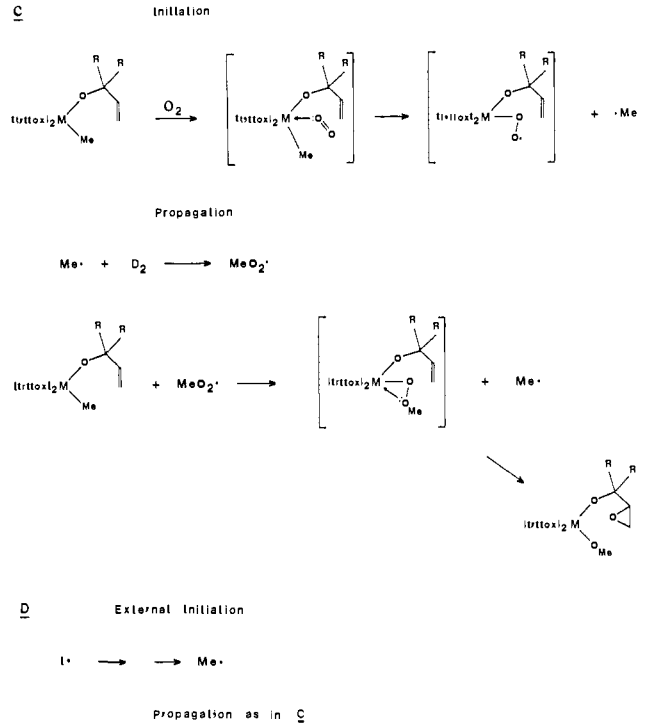
Scheme V



oxidation in inactive batches of **16b**; and (4) active **16b** was recovered with only slight decomposition (<5%, 24 h)[55] if the oxygenation was carried out in neat cyclohexene, whose allylic hydrogens may serve as radical scavengers. Although the epoxidations and alkoxylations involving dioxygen may be performed in chlorocarbon solvents (e.g., neat CCl_4), this result does not preclude the existence of radical intermediates. The rate constant for Cl atom abstraction from CCl_4 by Me$^\bullet$ is slow ($\sim$25 M^{-1} s^{-1}, 25 °C);[56] with this value as a maximum, in neat CCl_4 (10.36 M) the rate of Me$^\bullet$ abstraction of Cl$^\bullet$ would be $\sim 2.6 \times 10^2$ s^{-1}. The corresponding trapping of O_2 by $CH_3^\bullet$ is estimated to be near diffusion controlled (>10^9 M^{-1} s^{-1}). At 1 atm, [O_2] in solution (CCl_4) is approximately 0.012 M,[57] thus O_2 trapping ($\sim 1.2 \times 10^7$ s^{-1}) is $\sim 4.6 \times 10^4$ faster than Cl$^\bullet$ abstraction. Since the abstraction of a Cl atom from CCl_4 by $CH_3OO^\bullet$ is estimated to be thermodynamically unfavorable by as much as 44 kcal/mol,[58] it is clear halocarbon solvents pose no problems to an autoxidation process.

In both steps A and B, the epoxidation reaction is depicted as intramolecular. Scheme V illustrates a crossover experiment designed to test these pathways. Oxygenation of a $\sim$1:1 mixture of (tritox)$_2$Zr(CD$_3$)(OCMe$_2$CH=CH$_2$) (**16b-*d*$_3$**) and (tritox)$_2$Zr(CH$_3$)(OC(CH$_2$)$_3$CH$_2$CH=CH$_2$) (**17**) afforded a statistical mixture ($\sim$1:1:1:1) of labeled and unlabeled epoxides (**18b**:**18b-*d*$_3$**:19**:**19-*d*$_3$**). The exchange of Me groups between precursors **16b** and **17** did not appear to occur. Since the chemical shifts of their respective Me groups are very similar ($\Delta\delta$ = <0.01), the oxygenation of **16b-*d*$_3$** and **16c** ($\sim$1:1, $\Delta\delta$(Me) = 0.07) was also undertaken; no Me exchange was observed under epoxidation conditions. In the control experiment involving the products, independently synthesized **18b-*d*$_3$** and **19** exhibited *some* crossover of unknown origin. At high concentrations ($\sim$0.16 M), reproducible amounts of crossover ($\sim$20–30%) occurred immediately but remained constant with time and were independent of [O_2] present. At lower concentrations ($\sim$0.017 M), the amount of crossover was much less (<10%) and again remained unchanged as the conditions (time, [O_2]) were varied. Added (tritox)$_2$Zr(OMe)$_2$ (**2b**), a plausible and sometimes present impurity, did not catalyze the OMe exchange. Note that *only a statistical crossover* (1:1:1:1 of **18b-*d*$_3$**:**18b**:**19**:**19-*d*$_3$**) in this control reaction would render the experiment in Scheme V moot. However, it must be remembered that although the reaction conditions of the control mimic those of the crossover experiment as much as possible, some ambiguity regarding radical-based post-O atom transfer scrambling of methoxy groups persists. Exclusive of this possibility, the crossover clearly implies that steps A and B are *not* the mechanisms of choice.

Scheme VI



In order to account for the presumed crossover, two additional mechanistic postulations involving free radical chain processes are presented in Scheme VI. Pathway C involves O_2 binding to induce cleavage of the M–Me bond. The escape of Me$^\bullet$ and its diffusion-controlled capture by O_2 give rise to $MeO_2^\bullet$, which propagates the reaction by attacking the metal center, regenerating methyl radical. Mechanism D is a similar radical chain process whereby a spectroscopically invisible external I$^\bullet$ initiates the reaction. These pathways are consistent with the evidence, and both may explain erratic reactivity of spectroscopically indistinguishable batches of **16b**. The lack of an external initiator (I$^\bullet$) or the presence of trace quenching agents capable of lengthening the induction periods of C or D would logically explain the inactivity of certain batches. Curiously, the addition of significant amounts of MeLi, a plausible impurity, failed to initiate epoxidation of inactive **16b**.

In mechanisms C and D, the propagation steps involving attack by $MeO_2^\bullet$ on M to generate Me$^\bullet$ may be described as either synchronous or stepwise S_H2 homolytic substitution processes. This process is generally accepted as occurring in autoxidations of main group metal alkyls.[14,15] The parallels between these coordinatively unsaturated main group complexes and the group 4 species herein are self-evident. In seminal work by Davies et al., numerous R_2BOOR derivatives have been isolated from oxygenations of organoboranes. In some instances further activity of the alkylperoxy moiety has resulted in O atom transfer (i.e., $Me_2BOOMe \rightarrow (MeO)_2BMe$; $RZn(OOR) \rightarrow (RO)_2Zn$).

Initiation steps of BR_3 autoxidations involving direct O_2 attack at B to generate R$^\bullet$, analogous to mechanism C, have also been strongly implicated. Relative to propagation via $RO_2^\bullet$, these proposed initiations are very slow and extremely susceptible to inhibition, regardless of solvent.[54] In essence, the characteristics of the group 4 autoxidations above are comparable in every respect to those of organoboranes, except the rates of autoxidation are slower. Crude estimates of the propagation rates by $MeO_2^\bullet$ indicate that these are 10^2–10^4 slower than corresponding S_H2 rates for trialkylboranes.[59] Assuming the same factors which

(55) The decomposition would logically arise from MeO_2H, formed via allylic hydrogen atom abstraction (see ref 59).

(56) (a) Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511: k_{Cl}(Me$^\bullet$ + CCl_4) = 10 exp(8.8 ± 0.3)*e* exp[(−10.1 ± 0.5)/*RT*] M^{-1} s^{-1}; at 25 °C, k_{Cl} = 25 M^{-1} s^{-1} (with the given errors, the maximum k_{Cl}(25 °C) = 1.2 × 10^2 M^{-1} s^{-1}. It is assumed that these gas-phase values may be employed for CCl_4 solutions. See: (b) Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319.

(57) *Matheson Unabridged Gas Data Book*; Matheson Gas Products, 1974.

(58) Benson, S. D. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976. From known thermochemical data, $\Delta H_f°(H_3CO_2Cl)$ is calculated to be +7.11 kcal/mol and $D(H_3CO_2$–Cl) = 29 kcal/mol. $D(Cl_3$C–Cl) has been measured to be 73 kcal/mol, implying the minimum activation energy for Cl$^\bullet$ abstraction by $MeO_2^\bullet$ ≥ 44 kcal/mol.

are responsible for this disparity also affect the initiation rates (provided mechanism C is operative), the sporadic nature of the epoxidations can be rationalized on the basis of a sensitive initiation stage.

Alternate mechanisms involving charged propagating species such as MeO_2^- cannot be ruled out,[16] but the solvent independence of the qualitative epoxidation and alkoxylation rates suggests that such pathways are less likely. The initiation of RMgX oxidation has been proposed to occur via outer sphere electron transfer, providing $O_2^{\bullet-}$, MgX^+, and $R^\bullet$, which then propagates.[60] If outer sphere e^- transfers were operative, generating $O_2^{\bullet-}$ or MeO_2^-, complexes such as $(tritox)_2ZrMe(OCMe_2CH{=}CH_2)$ (**16b**) or $(tritox)_2MMe_2$ (M = Ti (**1a**), Zr (**1b**), Hf (**1c**)) may be electrochemically active. Cyclic voltammetric experiments of these species reveal *no* oxidation waves from +1.7 to −1.8 V (solvent limits of CH_2Cl_2), a region which encompasses the reduction potentials of O_2 and, presumably, $RO_2^\bullet$.[61] Extended Hückel calculations were performed on hypothetical, tetrahedral $(HO)_xMe_{4-x}Ti$ (x = 1, 2, or 3) species as models for the tritox derivatives. The data indicate that the HOMOs in these models are primarily Ti–O π-bonding in nature, with virtually no Ti–Me component. Although the electrochemical measurements do not provide explicit information, in concert with the calculations the data strongly support the contention that inner sphere processes are involved in both initiation and propagation steps.

Tritox vs. Cyclopentadienyl. The dioxygen reactivity of the complexes above verified the premise that tritox may function as a steric, yet less electron-donating equivalent of cyclopentadienyl.[11] Treatment of Cp_2ZrMe_2 (**23**)[62] with 1 atm of O_2 resulted in the formation of $Cp_2Zr(OMe)_2$ (**24**, 90%)[63] over a 48-h period at 25 °C, in contrast to the rapid oxygen insertion reaction of **1b**.

$$\underset{\mathbf{23}}{Cp_2ZrMe_2} + O_2 \rightarrow \underset{\mathbf{24}}{Cp_2Zr(OMe)_2} \qquad (17)$$

Allyloxymethyl derivatives of the Cp_2Zr fragment were prepared via the addition of the appropriate allyl alcohol to **23**, concomitant with the release of methane (eq 18). Exposure of

$$\underset{\mathbf{23}}{Cp_2ZrMe_2} + E\text{-}HOCRR'CH{=}CHR'' \xrightarrow{-CH_4} Cp_2ZrMe(E\text{-}OCRR'CH{=}CHR'') \qquad (18)$$

25: R = R′ = Me, R″ = H
26: RR′ = $-(CH_2)_4-$, R″ = H
27: R = H, R′ = R″ = Me

25–27 to 1 atm of O_2 resulted in decomposition with no evidence of epoxide formation. More importantly, no methoxy resonances indicative of O_2 insertion appeared during the course of degradation. For each complex, several (≥4 major) Cp-containing decomposition products were noted. While thermally stable for >4 days under an inert atmosphere (benzene solution), both **25** and **27** degraded within 24 h under O_2. Thermally sensitive **26** ($t_{1/2} \sim 24$ h) showed a similar acceleration with an oxygen atmosphere ($t_{1/2} \sim 8$ h).

Clearly, the mode of the Zr–Me bond oxygenation is markedly affected by the nature of the ancillary ligands, tritox vs. Cp. Since the 16e⁻ Cp_2ZrMe_2 (**23**) complex does react with O_2, albeit slowly, O-π-donation of the allyloxy ligands may electronically saturate the metal centers of **25–27**, thereby preventing an inner sphere attack by either O_2 or propagating $MeO_2^\bullet$ molecules. Perhaps the enhanced degradation rates of the latter species in the presence of O_2 are due to outer-sphere e^--transfer processes. Jordan[64] has recently shown that Cp_2ZrMe_2 is susceptible to oxidation by Ag^+ to give $[Cp_2ZrMe(S)]^+$ (S = solvent) and products derived from $Me^\bullet$. The tritox ligand, while sterically similar to Cp, engenders a more oxophilic metal center, thus allowing attack by O_2 (if mechanism C is operative) and $MeO_2^\bullet$. Provided t-Bu_3CO^- and allyloxide may be construed 4e⁻ donors, the $(tritox)_2MMe(allyloxy)$ complexes would be 14e⁻ species, therefore electron deficient.

The qualitative rates of the various oxygenations correlate with the electrophilicities of the metal centers. Oxygenations of $(tritox)_2MMe_2$ (M = Zr (**1b**), Hf (**1c**)) and $(tritox)TiMe_3$ are fast at −78 °C, while the trisalkoxy complexes, $(tritox)_2MMe(allyloxy)$ (M = Zr, Hf), are notedly slower. Since Ti is less electropositive, the slow (8–30 h), sporadic alkoxylation of $(tritox)_2TiMe_2$ (**1a**) is also in accord with this rationalization. Steric effects may also retard initiation/propagation, consistent with the slow epoxidations. Exposure of the extremely encumbered $(tritox)_3ZrMe$ (**28**)[11] species with O_2 (1 atm, 80 °C) slightly accelerated its thermal decomposition, with no evidence of methylperoxy formation. Lastly, repulsive, inner-sphere electrostatic interactions of $O_2/MeO_2^\bullet$ with the O-donor alkoxide ligands may serve to impede S_H2 processes.

Concluding Remarks

The experimental procedures utilized to delineate the apparent autoxidation mechanism fall short of full characterization, primarily because of the extreme sensitivities of the complexes involved. Nonetheless, the crossover experiment and supporting data are strongly indicative of radical processes. The indirect, yet fully substantiated intermediacy of the η^2-OOMe linkage, accompanied by its O atom transfer epoxidation reactivity, provides a clear rationalization for the alkoxylations. These observations also complement critical steps in O atom transfer processes which utilize TBHP, including Sharpless's Ti-catalyzed, enantioselective, allylic alcohol epoxidations.[21,43] Most importantly, it is clear that dioxygen need not be destructive to early metal systems. The above reactivity, especially the epoxidations, portends that molecular oxygen may be exploited as an oxygen atom source for a variety of transformations. The observed oxygen chemistry is potentially relevant to heterogeneous oxidations which implicate surface metal alkyl intermediates.[7] Surface alkyls may react directly with dioxygen through similar autoxidation steps rather via the attack of surface oxides. The primary function of dissociatively adsorbed dioxygen[7,65] may be limited to reoxygenation of surfaces depleted by loss of water, thus only indirectly related to C–O bond formation.

It is reassuring to note the parallels between these group 4 species and the main group alkyls (e.g., BR_3, AlR_3, ZnR_2).[14,15] The facile ligand exchanges of the Ti, Zr, and Hf complexes are analogous to redistributions common to main group metals.[66] Well-established autoxidation pathways of main group alkyls provide ample precedent for the proposed oxygenation mechanisms.

(59) Very crude estimates of the propagation rate ($k_p(MeO_2^\bullet + \mathbf{16b})$) can be made given data from the following: (a) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 722, 785. (b) Korcek, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U. *Ibid.* **1972**, *50*, 2285. Assuming the shutdown of **16b** epoxidation in neat C_6H_{10} is due to allylic H$^\bullet$ abstraction (≥10 faster) by propagating $MeO_2^\bullet$ and estimating this k_p' to be 10 times as fast (ref b) as $^sRO_2^\bullet$ autoxidation of C_6H_{10} (1.5 M^{-1} s^{-1}, ref a), $k_p'[MeO_2^\bullet][C_6H_{10}])/(k_p[MeO_2^\bullet][\mathbf{16b}]) = (15\ M^{-1}\ s^{-1}[9.86\ M])/k_p[0.0267\ M] \geq 10$; $k_p \leq 550\ M^{-1}\ s^{-1}$. Assuming cyclohexadiene reaction with $MeO_2^\bullet$ (giving benzene and $HO_2^\bullet$ under O_2, ref. a) competes equally with **16b** epoxidation, and this k_p' to be 10 times slower than the known k_{prop} by $HO_2^\bullet$ (370 M^{-1} s^{-1}, ref a) $(k_p'[MeO_2^\bullet][C_6H_8])/(k_p[MeO_2^\bullet][\mathbf{16b}]) = (37\ M^{-1}\ s^{-1}[0.8\ M])/(k_p[0.085\ M]) \sim 1$; $k_p \sim 350\ M^{-1}\ s^{-1}$. These numbers are extremely "soft", perhaps by as much as 10^2, due to (1) the lack of data pertaining to primary (and Me) peroxy radical abstractions, (2) the autoxidation of C_6H_8 actually propagates via $HO_2^\bullet$ (ref a), and (3) the ambiguities associated with estimating competitive rates when RO_2H species which form destroy **16b**. It is nonetheless heartening to note that similar k_p's for $RO_2^\bullet$ and organoboranes are expectedly faster: $(RBO)_3$, 10^3–10^6 M^{-1} s^{-1}; R_3B, 10^5–10^6 M^{-1} s^{-1} (ref 14a).

(60) Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1970**, *92*, 6609.

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In fact, the similarities of the group 4 oxygenations to those of trialkylboranes are so dramatic it is tempting to conclude that epoxidation mechanism C is favored over mechanism D. These autoxidations and the ligand exchanges rely on features common to both main and group 4 alkyls; electronic (coordinative) unsaturation and metal alkyl bonds that are distinctly $M^{\delta+}-R^{\delta-}$. In concert, these properties are manifested by the electrophilicity of the metal centers. The ability of ligands such as Me and OMe to span two metals[37,38] during the course of exchange and the susceptibility of these complexes to homolytic S_H2-type initiation and propagation steps during oxygenation[14] may be directly attributable to this characteristic.

Experimental Section

General Considerations. All manipulations were performed with use of either glovebox or high vacuum line techniques. Ethereal and hydrocarbon solvents were distilled under nitrogen from purple benzophenone ketyl and vacuum transferred from the same prior to use. Halocarbon solvents were refluxed over P_2O_5, distilled, and vacuum transferred from fresh P_2O_5. Benzene-d_6 and chloroform-d were dried over activated 4 Å molecular sieves, vacuum transferred, and stored under N_2. All glassware was washed with 1 M NaOH solution and dried at 160 °C. Li(tritox), (tritox)$_2$MCl$_2$ (M = Ti (**7a**), Zr (**7b**)), (tritox)$_2$MMe$_2$ (M = Ti (**1a**), Zr (**1b**)), (tritox)TiMe$_3$ (**3**), (tritox)$_3$ZrMe (**28**),[11] and Cp$_2$ZrMe$_2$[62] were prepared via published procedures as were 2-methyl-3,4-epoxybutan-2-ol and 1-cyclopentyl-2,3-epoxypropan-1-ol.[49] 1-Vinylcyclopentanol was prepared from cyclopentanone and vinyl magnesium bromide (Aldrich). Cyclohexane, 1,4-cyclohexadiene, and the remaining allylic alcohols (Aldrich) were dried over activated 4 Å molecular sieves and vacuum transferred prior to use. The Li allyloxides were prepared via deprotonation of the parent alcohols with *n*-BuLi (~quantitative) and isolated prior to use. $HfCl_4$ (Aldrich) was sublimed (10^{-4}, 180 °C) prior to use.

^{1}H NMR spectra were recorded on Varian EM-390, XL-200, or Bruker WM-300 spectrometers and ^{13}C NMR spectra on a JEOL FX90Q. Infrared spectra obtained on a Perkin-Elmer 357 spectrometer were not formally assigned, but were used as fingerprints to check purity. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 machine equipped with a capillary column (methyl silicone (HP No. 19095S-100), 5 m, 0.20/0.32 mm i.d.) and flame ionization detector. Cyclic voltammograms were obtained on a PAR Model 173 potentiostat, a Model 178 electrometer, and a Model 175 Universal programmer. Data were recorded with a Nicolet 4094 digital oscilloscope. Elemental analyses were conducted by Analytische Laboratorien, Elbach, West Germany. Molecular weights were determined by benzene freezing point depression.

Procedures. Routine oxygenations were carried out in the following manner. NMR tube samples (for convenient monitoring), typically 2–15 mg in benzene-d_6, were purged with O_2 (periodic shaking) dried via passage over KOH pellets. Larger samples were weighed into flasks which were evacuated, solvent was added via vacuum transfer, and the flask was subjected to O_2 dried via passage through a −78 °C trap. Occasionally, oxygenations were conducted in sealed NMR tubes. An NMR tube sealed onto a 14/20 joint was loaded with 2–15 mg of sample and ~0.2 mL of benzene-d_6. The tube was attached to a needle valve adapter, subjected to at least 3 freeze–pump–thaw cycles, exposed to ~500 Torr of O_2, and sealed with a torch.

1. (tritox)$_2$HfCl$_2$ (7c). To a flask containing $HfCl_4$ (1.16 g, 3.62 mmol) and Li(tritox) (1.50 g, 7.25 mmol) at −78 °C was distilled 70 mL of Et_2O. After the mixture was slowly warmed to 25 °C (4 h) and stirred a total of 6 h, the ether was stripped and replaced with 30 mL of hexane. After filtration, the filtrate was cooled and concentrated to yield 1.90 g of thermally sensitive, white crystalline **7c** (81%). ^{1}H NMR (C_6D_6) δ 1.34.

2. (tritox)$_2$HfMe$_2$ (1c). To a slurry of (tritox)$_2$HfCl$_2$ (**7c**) (1.62 g, 2.50 mmol) in 50 mL of Et_2O at −78 °C was added 3.57 mL of MeLi (5.00 mmol, 1.4 M in Et_2O). After the mixture was slowly warmed to 25 °C (4 h) and stirred an additional 5 h, the ether was removed. Hexane (35 mL) was added, the slurry filtered, and the filtrate cooled and concentrated to yield 1.28 g of white crystalline **1c** (85%). Anal. Calcd for $C_{28}H_{60}O_2Hf$: C, 55.28; H, 9.96. Found: C, 55.35; H, 9.82. ^{1}H NMR (C_6D_6) δ 1.33 (s, tritox, 54 H), 0.51 (s, Me$_2$, 6 H). ^{13}C{^{1}H} NMR (C_6D_6) δ 98.8 (CC_3), 47.3 ($HfCH_3$), 45.9 (CMe_3), 33.3 (CH_3).

3. (tritox)$_2$M(OMe)$_2$ (M = Ti (2a), Zr (2b), Hf (2c)). In 30 mL of benzene, 500 mg of (tritox)$_2$MMe$_2$ was dissolved and stirred under 1 atm of dry O_2. After 4 h (24 h for M = Ti), the benzene was removed and crystallization from ~15 mL of hexane yielded the white crystalline dimethoxide (**2a**, 87%; **2b**, 94%; **2c**, 92%). Anal. Calcd for $C_{28}H_{60}O_4Ti$: C, 66.11; H, 11.89. Found: C, 66.25; H, 11.87. Anal. Calcd for $C_{28}H_{60}O_4Zr$: C, 60.92; H, 10.96. Found: C, 60.84; H, 10.83. Anal. Calcd for $C_{28}H_{60}O_4Hf$: C, 52.61; H, 9.46. Found: C, 52.41; H, 9.31. M_r (**2b**) found 541 (calcd 551).

4. [(tritox)TiMe$_2$]$_2$(μ-OMe)$_2$ (4$_2$). In 10 mL of Et_2O at −78 °C, 138 mg (0.473 mmol) of (tritox)TiMe$_3$ (**3**) was exposed to 0.236 mmol of O_2, admitted via a gas bulb. Yellow precipitate formed immediately and gradually deepened to orange after 15 min. Upon warming to 25 °C, the solid dissolved to give a faint yellow solution. The Et_2O was removed and crystallization from 5 mL of hexane gave 138 mg of orange **4$_2$** (95%). Anal. Calcd for $C_{16}H_{36}O_2Ti$: C, 62.32; H, 11.77. Found: C, 62.20; H, 11.63. M_r found 316 (calcd 308).

5. (tritox)TiMe(OMe)$_2$ (5). In 10 mL of Et_2O at −78 °C, 139 mg (0.476 mmol) of **3** was exposed to 0.476 mmol of O_2, admitted via a gas bulb. A bright yellow color appeared immediately, and yellow crystals fell from solution. Upon warming to 25 °C, the crystals dissolved to give a pale yellow solution. The ether was removed and crystallization from hexane yielded 130 mg of yellow **5** (84%). Anal. Calcd for $C_{16}H_{36}O_3Ti$: C, 59.25; H, 11.19. Found: C, 59.39; H, 11.05. M_r calcd for monomer (M) 324, dimer (D) 648. At [**5**(monomer)]$_{total}$ = 0.222 *m*, M_r(found) = 537 (0.134 m_{eff}), D/M ~ 1.9; 0.139 *m*, M_r(found) = 502 (0.089 m_{eff}), D/M ~ 1.3; 0.034 *m*, M_r (found) = 453 (0.024 m_{eff}), D/M ~ 0.65.

6. (tritox)Ti(OMe)$_3$ (6). In 5 mL of pentane at −78 °C, 100 mg (0.342 mmol) of **3** was exposed to 1 atm of O_2. A yellow precipitate formed immediately and subsequently dissolved to give a colorless solution upon warming to 25 °C over the course of ~1 h. The solution was concentrated to <3 mL and cooled to −78 °C to provide white crystalline **6** (86 mg, 74%). Anal. Calcd for $C_{16}H_{36}O_4Ti$: C, 56.46; H, 10.66. Found: C, 56.64; H, 10.78. M_r calcd for monomer (M) 340, dimer 680 (D). At [**6**(monomer)]$_{total}$ = 0.160 *m*, M_r(found) = 626 (0.079 m_{eff}), D/M ~ 5.

General (tritox)$_2$MCl(allyloxy). Stoichiometric amounts of (tritox)$_2$MCl$_2$ (M = Ti (**7a**), Zr (**7b**), Hf (**7c**)) and LiOR (R = allyl) were dissolved in 50 mL of Et_2O at −78 °C and slowly warmed to 25 °C (2 h). After 4 h the ether was removed and hexane added. Filtration, concentration, and crystallization provided the highly soluble allyloxy chlorides. Since these derivatives merely served as precursors to the corresponding Me species, C and H analyses were not obtained, except for a representative complex, **14b**. ^{1}H, ^{13}C NMR, and IR were utilized to check their purity. In some instances, small amounts of impurities could not be removed by crystallization, as noted.

7. (tritox)$_2$TiCl(OCH$_2$CH=CH$_2$) (8). Treatment of **7a** (2.00 g, 3.87 mmol) with LiOCH$_2$CH=CH$_2$ (248 mg, 3.87 mmol) as above, except in THF, gave 1.65 g of white crystalline **8** (79%).

8. (tritox)$_2$MCl(*E*-OCH$_2$CH=CHPh) (M = Ti (9a), Zr (9b)). Treatment of **7a**/**7b** (1.09 g, 2.11 mmol/1.60 g, 2.81 mmol) with Li(*E*-OCH$_2$CH=CHPh) (340 mg, 2.43 mmol/430 mg, 3.43 mmol) as above yielded 540/1120 mg of white crystalline **9a**/**9b** (42/60%).

9. (tritox)$_2$TiCl(*E*-OCH$_2$CPh=CHPh) (10a). Treatment of **7a** (1.10 g, 2.13 mmol) with Li(*E*-OCH$_2$CPh=CHPh) (480 mg, 2.22 mmol) as above provided 1.00 g of white crystalline **10a** (68%).

10. (tritox)$_2$ZrCl(*E*-OCH$_2$CPh=CHPh) (10b). Treatment of **7b** (500 mg, 0.893 mmol) with Li(*E*-OCH$_2$CPh=CHPh) (171 mg, 0.893 mmol) as above gave an oil which, under dynamic vacuum (10^{-4} Torr), crystallized to provide light yellow **10b** (430 mg, 66%, >90% pure).

11. (tritox)$_2$MCl(OCMe$_2$CH=CH$_2$) (M = Zr, (14b), Hf, (14c)). Treatment of **7b**/**7c** (2.00 g, 3.57 mmol/600 mg, 0.927 mmol) with LiOCMe$_2$CH=CH$_2$ (328 mg, 3.57 mmol/85 mg, 0.924 mmol) as above provided 1.90 g/410 mg of white crystalline **14b**/**14c** (87/63%). Anal. Calcd for **14b**, $C_{31}H_{63}O_3ZrCl$: C, 60.99; H, 10.40; Cl, 5.81. Found: C, 60.76; H, 10.28; Cl, 5.65.

12. (tritox)$_2$ZrCl(OC(CH$_2$)$_3$CH$_2$CH=CH$_2$) (15). Treatment of **7b** (1.42 g, 2.54 mmol) with LiOC(CH$_2$)$_3$CH$_2$CH=CH$_2$ (300 mg, 2.54 mmol) resulted in a colorless oil. After 16 h under dynamic vacuum (10^{-4} Torr), 1.50 g of white, extremely soluble **15** was obtained (95%, ~95% pure).

General (tritox)$_2$MX(allyloxy) (X = Me, OMe). To a Et_2O solution of (tritox)$_2$MCl(allyloxy) at −78 °C was added a stoichiometric amount of MeLi (1.5 M in Et_2O). After the mixture was slowly warmed to 25 °C (2–4 h) and further stirred for 5 h, the Et_2O was stripped, hexane or pentane added, and the solution filtered. Cooling and concentrating the filtrate resulted in the extremely protolytically sensitive allyloxy methyl complexes. From similar procedures utilizing solid LiOMe, the allyloxy methoxy derivatives were obtained. Representative Me derivatives were subjected to C and H analyses. The high solubility of some of the complexes hampered recrystallization efforts, giving rise to variable purities, as noted.

13. (tritox)$_2$TiMe(OCH$_2$CH=CH$_2$) (**11**). Treatment of **8** (300 mg, 0.560 mmol) with 0.37 mL of MeLi (0.560 mmol) as above yielded 195 mg of white crystalline **11** (67%).

14. (tritox)$_2$MMe(*E*-OCH$_2$CH=CHPh) (M = Ti, (**12a**), Zr (**12b**)). Treatment of **9a**/**9b** (510 mg, 0.830 mmol/465 mg, 0.707 mmol) with 0.52/0.47 mL of MeLi (0.830/0.707 mmol) as above provided 170/320 mg of white crystalline **12a**/**12b** (34/71%). Anal. Calcd for **12a**, $C_{36}H_{66}O_3Ti$: C, 72.69; H, 11.18. Found: C, 72.48; H, 11.00. Calcd for **12b**, $C_{36}H_{66}O_3Zr$: C, 67.76; H, 10.42. Found: C, 67.54; H, 10.27.

15. (tritox)$_2$TiMe(*E*-OCH$_2$CPh=CHPh) (**13a**). Treatment of **10a** (960 mg, 1.39 mmol) with 0.93 mL of MeLi (1.39 mmol) as above gave 700 mg of light yellow crystalline **13a** (75%, >90% pure).

16. (tritox)$_2$ZrMe(*E*-OCH$_2$CPh=CHPh) (**13b**). Treatment of **10b** (300 mg, 0.409 mmol) with 0.27 mL of MeLi (0.409 mmol) as above resulted in an impure light yellow oil (~70%, ~75% pure by ^{1}H NMR).

17. (tritox)$_2$ZrMe(OCMe$_2$CH=CH$_2$) (**16b**). Treatment of **14b** (900 mg, 1.48 mmol) in 50 mL of Et$_2$O with 0.98 mL of MeLi (1.48 mmol) as above provided 670 mg of very soluble, white crystalline **16b** (77%). Anal. Calcd for $C_{32}H_{66}O_3Zr$: C, 65.13; H, 11.27. Found: C, 63.47; H, 10.57. The ^{13}C and ^{1}H NMR spectra indicated that <1.5% tritox-containing/organic impurities were typically present.

18. (tritox)$_2$Zr(CD$_3$)(OCMe$_2$CH=CH$_2$) (**16b**-d_3). Procedure 17 was followed with the following exception. When LiCD$_3$ was prepared with CD$_3$I and either Li wire or dispersion, spectroscopically pure **16b**-d_3 was inactive with respect to oxygenation. Iodide-free CD$_3$I was prepared as follows: to a slurry of Li dispersion (250 mg, 36 mmol) in 10 mL of Et$_2$O at −78 °C was vacuum transferred an ether solution of Zn(CD$_3$)$_2$ (11.4 mmol in 30 mL). Grey, metallic Zn metal precipitated from solution upon stirring at 25 °C for 1 h. The solution was decanted through a glass wool plug, stored under Ar at 0 °C, and titrated prior to use.

19. (tritox)$_2$HfMe(OCMe$_2$CH=CH$_2$) (**16c**). Treatment of **14c** (550 mg, 0.79 mmol) in 30 mL of Et$_2$O with 0.56 mL of MeLi (0.78 mmol) as above gave a clear oil which solidified under 15 min of dynamic vacuum (10^{-4} Torr). Recrystallization from 2 mL of pentane produced 310 mg of very soluble, white crystalline **16c** (58%, >95% pure by ^{1}H NMR).

20. (tritox)$_2$ZrMe(OC(CH$_2$)$_3$CH$_2$CH=CH$_2$) (**17**). Treatment of **15** (715 mg, 1.15 mmol) in 25 mL of Et$_2$O with 0.80 mL of MeLi (1.15 mmol) as above resulted in a clear colorless oil. After 3 h under dynamic vacuum (10^{-4} Torr), 482 mg of white crystalline **17** were obtained (70%). Anal. Calcd for $C_{34}H_{68}O_3Zr$: C, 66.28; H, 11.12. Found: C, 65.70; H, 10.88.

21. (tritox)$_2$Zr(OMe)(OCMe$_2$CH=CH$_2$) (**21**). Reaction of **14b** (300 mg, 0.50 mmol) with LiOMe (19 mg, 0.50 mmol) in 10 mL of Et$_2$O/10 mL of THF as above gave a colorless oil, consisting mostly of **21** (80% purity by ^{1}H NMR), which failed to solidify under vacuum. The major impurity (>15%) was identified as (tritox)$_2$Zr(OMe)$_2$ (**2b**).

22. (tritox)$_2$Zr(OMe)(OC(CH$_2$)CH$_2$CH=CH$_2$) (**22**). Reaction of **15** (300 mg, 0.47 mmol) with LiOMe (18 mg, 0.47 mmol) in THF as above provided **22** as an impure (60% pure by ^{1}H NMR), thermally sensitive yellow oil. The major impurity (>25%) was identified as **2b**.

Epoxy Alkoxides (Large Scale). For quenching and resultant GC studies, oxygenations of allyloxy methyl species were conducted in bomb reactors.

23. (tritox)$_2$Zr(OMe)(OCMe$_2$CHCH$_2$O) (**18b**). A glass bomb, pretreated by washing with 1.0 M NaOH and baking for 12 h at 160 °C, was loaded with **16b** (260 mg, 0.44 mmol) and 10 mL of hexane. Dry O$_2$ (1 atm) was introduced over the solution. After an equilibration period (15 min), the bomb was closed off and the solution stirred for 15 h. Evaporation of the solvent gave a thermally sensitive, colorless oil which failed to solidify after 1 h at 10^{-4} Torr (>90% pure, >90% yield by ^{1}H, ^{13}C{^{1}H} NMR). Attempts to crystallize the material under a variety of conditions only resulted in decreased purity, presumably due to thermal degradation.

24. (tritox)$_2$Hf(OMe)(OCMe$_2$CHCH$_2$O) (**18c**). As in procedure 23, exposure of **16c** (170 mg, 0.251 mmol) in 1 atm of dry O$_2$ for 24 h gave **18c** as a light tan oil in ~70% yield (80% purity).

25. (tritox)$_2$Zr(OMe)(OC(CH$_2$)$_3$CH$_2$CHCH$_2$O) (**19**). As in procedure 23, exposure of **17** to 1 atm of O$_2$ provided a thermally sensitive, light yellow oil (~90% yield, ~90% purity by ^{1}H NMR).

26. (tritox)$_2$Zr(O-*t*-Bu)(OCMe$_2$CHCH$_2$O) (**20**). To a flask containing **14b** (250 mg, 0.410 mmol) and NaOO-*t*-Bu (46 mg, 0.41 mmol), prepared via NaH and anhydrous (Sharpless procedure) *t*-BuOOH, was distilled 20 mL of THF at −78 °C. After the mixture was stirred for 3 h at 20 °C, the THF was removed and replaced with 10 mL of pentane. Filtration and removal of the pentane afforded **20** as an impure yellow oil (~20% (tritox)H, ~30% **14b**, ~30% **20**). The substantial quantities of (tritox)H and **14b** in addition to the rapid decomposition of **20** indicated that NaOH or H$_2$O impurities, presumably arising from NaOO-*t*-Bu,[50,51] were responsible for the mediocre purity. ^{1}H NMR **20** (C$_6$D$_6$) δ 1.37 (tritox), 1.18 (*t*-BuO), 2.40 (m, H$_t$ and H$_c$), 2.94 ("t", CH, ^3J = 3 Hz). The allyloxy methyl resonances could not be identified although shoulders on the upfield δ 1.37 peak were observed.

Table VI. Fractional Coordinates and Thermal Parameters[a] for [(tritox)TiMe$_2$]$_2$(μ-OMe)$_2$ (**4$_2$**)[b]

atom	*x*	*y*	*z*	*B*(iso)
Ti	0.0565 (2)	0.0000 (0)	0.0971 (1)	5.2 (1)*
O2	0.0000 (0)	−0.0843 (4)	0.0000 (0)	6.1 (3)*
C2	0.0000 (0)	−0.1923 (7)	0.0000 (0)	7.9 (7)*
C3	0.2207 (10)	−0.0984 (7)	0.1073 (6)	9.5 (5)*
O1	−0.0746 (6)	0.0000 (0)	0.2045 (4)	5.7 (3)*
C1	−0.1930 (10)	0.0000 (0)	0.2873 (6)	5.4 (5)*
C11	−0.3467 (11)	0.0000 (0)	0.2515 (7)	7.3 (6)*
C111	−0.4869 (17)	0.0000 (0)	0.3279 (11)	14.2 (13)*
C112	−0.3570 (13)	−0.0840 (8)	0.1861 (8)	11.7 (6)*
C12	−0.1692 (9)	−0.0966 (6)	0.3398 (5)	7.5 (4)*
C121	−0.0096 (14)	−0.1019 (8)	0.3612 (8)	12.5 (7)*
C122	−0.2821 (18)	−0.1072 (11)	0.4336 (9)	13.1 (7)*
C123	−0.1615 (14)	−0.1885 (6)	0.2773 (8)	11.7 (7)*
H3	0.2616 (0)	1.1185 (0)	0.1632 (0)	13.5 (31)
H3	0.2985 (0)	1.1204 (0)	0.0481 (0)	12.5 (31)
H3	0.1229 (0)	1.1306 (0)	0.1102 (0)	15.5 (35)
H111	−0.4864 (0)	0.0604 (0)	0.3708 (0)	12.3 (32)
H111	−0.5804 (0)	0.0000 (0)	0.3060 (0)	10.9 (64)
H112	−0.2604 (0)	1.1073 (0)	0.1386 (0)	17.2 (39)
H112	−0.4467 (0)	1.1058 (0)	0.1614 (0)	15.0 (35)
H112	−0.3601 (0)	1.1137 (0)	0.2479 (0)	20.2 (47)
H121	0.0265 (0)	1.1041 (0)	0.4207 (0)	19.9 (46)
H121	0.0869 (0)	1.1112 (0)	0.3057 (0)	15.2 (37)
H121	−0.0772 (0)	1.1593 (0)	0.3587 (0)	18.7 (43)
H122	−0.2793 (0)	1.1140 (0)	0.4981 (0)	17.5 (40)
H122	−0.2247 (0)	1.1665 (0)	0.3941 (0)	27.6 (63)
H122	−0.3966 (0)	1.1231 (0)	0.4287 (0)	16.2 (38)
H123	−0.2546 (0)	1.2082 (0)	0.2537 (0)	13.1 (31)
H123	−0.1599 (0)	1.2306 (0)	0.3340 (0)	12.5 (29)
H123	−0.0677 (0)	1.2061 (0)	0.2253 (0)	14.7 (33)

[a] From the anisotropic thermal parameters in the form exp[$-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$], the *B*(isotropic equivalents)'s are derived: *B*(iso) = 4.0[V^2 det (β_{ij})]$^{1/3}$. [b] The hydrogens attached to C2 (methoxy carbon) were disordered about the twofold axis and were not placed.

Hydrolyses of 18b,c and 19. Samples (~50 mg) of the epoxy alkoxide complexes were dissolved in Et$_2$O and subjected to excess H$_2$O. Analyses of the ether fraction were accomplished in two ways: (1) Capillary GC revealed the presence of (tritox)H and either 2-methyl-3,4-epoxybutan-2-ol (derived from **18b,c**) or 1-cyclopentyl-2,3-epoxypropan-1-ol (from **19**). Coinjection of the independently synthesized epoxy alcohols confirmed their presence. (2) Removal of residual ether enabled the ^{1}H NMR correlation of cleaved epoxy alcohols to the independently synthesized materials (the spectra are concentration dependent).

27. Cp$_2$Zr(OMe)$_2$ (**24**). Cp$_2$ZrMe$_2$ (**23**) (200 mg, 0.792 mmol) was dissolved in 15 mL of hexane and exposed to 1 atm of O$_2$ for 48 h. Removal of hexane resulted in white, crystalline **24** (>95%).[63]

28. Cp$_2$ZrMe(OCMe$_2$CH=CH$_2$) (**25**). To 500 mg (1.99 mmol) of **23** in 30 mL of hexane at 0 °C was added 208 μL of 2-methyl-3-buten-2-ol (1.99 mmol), resulting in the immediate release of CH$_4$. After the mixture was stirred for 1 h at 25 °C, filtration and crystallization yielded 470 mg of waxy white **25** (74%). Analytically pure crystals (400 mg, 63%) were obtained via sublimation (120 °C (10^{-4} Torr)). Anal. Calcd for $C_{16}H_{22}OZr$: C, 59.76; H, 6.90. Found: C, 59.62; H, 6.73.

29. Cp$_2$ZrMe(OC(CH$_2$)$_3$CH$_2$CH=CH$_2$) (**26**). Procedure 28 was repeated with 470 mg (1.87 mmol) of **23** and 255 μL (1.87 mmol) of 1-vinylcyclopentanol. The sublimed white crystals of **26** (130 °C (10^{-4} Torr)) melted to a clear oil near 25 °C (495 mg, 76%, >95% pure by ^{1}H NMR).

30. Cp$_2$ZrMe(*E*-OCHMeCH=CHMe) (**27**). Procedure 28 was repeated with 500 mg (1.99 mmol) of **23** and 203 μL (1.99 mmol) of (*E*)-3-penten-2-ol. Removal of solvent left **27** as a clear, analytically pure, colorless oil (>95%). Anal. Calcd for $C_{16}H_{22}OZr$: C, 59.76; H, 6.90. Found: C, 59.97; H, 6.81.

General Inhibition/Initiation Procedures. Oxygenation studies involving 1,4-cyclohexadiene and AIBN were conducted by simultaneously monitoring NMR tube scale reactions of the substrate (same batch) with and without varying amounts of inhibitor/initiator. A typical example

is delineated below. Exposure of **16b** (230 mg, 0.40 mmol) to 1 atm of dry O_2 in neat cyclohexene (15 mL) was carried out in a flask over a period of 24 h. Simultaneous monitoring of an NMR tube (C_6D_6, no C_6H_{10}) containing the same batch of **16b** indicated smooth epoxidation. In contrast, removal of the cyclohexene and subsequent analysis indicated that >95% of **16b** was recovered unchanged. Since **16b** is stable to cyclohexene, the small amount of decomposition (<5%) may result from scavenging of the C_6H_{10} allylic hydrogens by propagating $MeO_2^{\bullet}$.

Epoxidation in the Presence of 1,4-Cyclohexadiene. Three NMR-scale experiments were run simultaneously with 10-mg portions of **16b** (0.016 mmol, 0.085 M) in C_6D_6: (1) To the first sample was added 15 μL of 1,4-cyclohexadiene (0.16 mmol). No decomposition of **16b** was noted after 24 h. (2) A second NMR tube (no C_6H_8) was purged with dry O_2. Epoxidation to give **18g** proceeded to 70% completion after 24 h as judged by the OMe(**18b**):Me(**16b**) ratio. (3) The last sample, containing 15 μL of 1,4-cyclohexadiene, was exposed to dry O_2. After 24 h, epoxidation was <40%, and no **16b** remained. In similar runs, increasing the amount of inhibitor further lessened the percent of **18b** formed relative to the control.

Crossover Control. Individual 3-mg samples of **16b**-d_3 and **17** in 0.2 mL of C_6D_6 were submitted separately to dry O_2 for 20 h until conversion to **18b**-d_3 and **19** was judged complete. After the mixture was degassed and solvent removed, the two samples were combined in an NMR tube and monitored. Although several small peaks (<10% intensity of the OCH_3 attributed to **19**) were present between 3.8 and 4.0 ppm, these failed to increase in intensity over a 5-h period. The tube was then flushed with dry O_2 for several minutes. The **18b**-d_3/**19** mixture remained unchanged for >4 h. The control experiment was repeated for each crossover experiment.

Crossover Experiment (16b-d_3 + 17 + O_2). An NMR tube was charged with approximately 2 mg each of **16b**-d_3 and **17** in 0.2 mL of C_6D_6 (~0.017 M in each). After the exact molar ratio of the two allyloxy species was measured via ^1H NMR integration of the olefin region, the tube was purged with dry O_2. The reaction was monitored by ^1H NMR until <30% starting materials remained. Two methoxide resonances attributable to **18b** and **19**, as well as the epoxy oxide multiplets of **18b**/**18b**-d_3 and **19**/**19**-d_3, appeared immediately and grew in simultaneous in accord with the initial **16b**-d_3/**17** ratio. Because the methoxy peaks of **18b** and **19** differed by only 0.01 ppm, pure **18b** and **19** were sequentially added to the reaction mixture in order to confirm their identity. The crossover was conducted five times with varying concentrations of starting allyloxy substrates. All cases were consistent with immediate and sustained crossover (see text). In addition, no **16b** was observed during the course of the crossovers, indicating that CD_3/CH_3 exchange between **16b**-d_3 and **17** ($\Delta\delta < 0.01$) was not occurring prior to oxygenation. The latter observation was checked by epoxidizing equimolar amounts of **16b**-d_3 and **16c**. No crossover of their respective Me groups ($\Delta\delta = 0.07$) occurred prior to epoxidation. While this crossover experiment was also consistent with methoxy crossover, the less clean **16c** epoxidation prevented careful analysis.

Electrochemical Measurements. All experiments were conducted in a drybox. A silver reference electrode and platinum auxiliary electrodes were employed. Freshly distilled CH_2Cl_2 was chosen as the solvent and Bu_4NBF_4 (Southwestern Analytical), recrystallized from EtOAc/Et_2O and dried at 105 °C under vacuum, was the supporting electrolyte. Solutions (~1.0 mM) of **1a**, **1b**, and **16b** were scanned reversibly from +1.7 to −1.8 V at a typical rate of 200 mV/s. No oxidation or reduction waves were recorded. Variation of the scan speeds (50 mV/s to 100 V/s) had no effect. NMR analysis of the complexes upon removal of the solvent indicated some (~25% in the case of **16b**) decomposition, but all were still active to oxygenation.

Single-Crystal X-ray Diffraction Analysis of [(tritox)TiMe$_2$]$_2$(μ-OMe)$_2$ (4_2). A 0.4 × 0.3 × 0.2 mm, orange, rhomboidal-shaped crystal of [(tritox)TiMe$_2$](μ-OMe)$_2$ (4_2), obtained by slow evaporation of a pentane solution at −25 °C, was sealed in a thin-walled Lindemann capillary under N_2. Preliminary X-ray diffraction photographs displayed monoclinic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer measured 2θ values at 25 °C, were a = 9.191 (3) Å, b = 13.810 (5) Å, c = 14.840 (4) Å, and β = 76.105 (21)°. The cell volume was 1828.5 Å^3 with a calculated density of 1.120 g/cm^3. The space group was uniquely determined to be $C2/m$ and $Z = 2$. All unique diffraction maxima ($h,k,\pm l$) with $2\theta \leq 67.7°$ were measured on a four-circle, computer-controlled diffractometer with a variable 1° ω scan using graphite-monochromated Mo Kα radiation (0.71069 Å). After correction for Lorentz, polarization, and background, 926 (55%) of the 1686 reflections collected were judged observed ($|F_o| \geq 3\sigma(F_o)$).[67] Structure solution using heavy-atom techniques proceeded routinely.[68] The Ti was positioned from the Patterson synthesis, and the non-hydrogen light atoms were revealed by successive Fourier syntheses. Block-diagonal least-squares refinements (minimization of $\sum w(|F_o| - |F_c|)^2$, where w is based on counting statistics modified by an ignorance factor of $p = 0.03$) with 13 (some of which are symmetry restricted) anisotropic non-hydrogen atoms and all hydrogen atoms included at calculated positions have converged to a current residual (R) of 0.073 and a weighted residual (R_w) of 0.084 for the observed reflections.[69] The fractional coordinates and thermal parameters are listed in Table VI. Attempts to refine in the space group $C2$ did not lead to improvement in the residuals, corroborating the choice of $C2/m$.

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Registry No. 1c, 105372-84-7; **2a**, 94136-93-3; **2b**, 94136-94-4; **2c**, 105372-85-8; **3**, 89958-93-0; **4**, 94136-95-5; 4_2, 105373-08-8; **5**, 94136-96-6; 5_2, 105373-09-9; **6**, 94136-97-7; 6_2, 105373-10-2; **7a**, 89958-89-4; **7b**, 89958-87-2; **7c**, 105372-83-6; **8**, 105372-86-9; **9a**, 105372-87-0; **9b**, 105372-88-1; **10a**, 105372-89-2; **10b**, 105372-90-5; **11**, 105372-95-0; **12a**, 105372-96-1; **12b**, 105372-97-2; **13a**, 105372-98-3; **13b**, 105372-99-4; **14b**, 94136-98-8; **14c**, 105372-91-6; **15**, 105372-93-8; **16b**, 94136-99-9; **16b**-d_3, 105373-00-0; **16c**, 105373-01-1; **17**, 105373-02-2; **18b**, 94137-00-5; **18c**, 105373-05-5; **19**, 105373-06-6; **20**, 105373-07-7; **21**, 105373-03-3; **22**, 105373-04-4; **23**, 12636-72-5; **24**, 11087-29-9; **25**, 105373-11-3; **26**, 105373-12-4; **27**, 105373-13-5; $HFCl_4$, 13499-05-3; (tritox)$_2$TiMe$_2$, 89958-92-9; (tritox)$_2$ZrMe$_2$, 89958-91-8; Zn(CD$_3$)$_2$, 13001-41-7; Li(tritox), 89958-97-4; LiOCH$_2$CH=CH$_2$, 52203-12-0; Li(*E*-OCH$_2$CH=CHPh), 84987-71-3; Li(*E*-OCH$_2$CPh=CHPh), 105372-92-7; Li(OCMe$_2$CH=CH$_2$), 94137-01-6; LiOC(CH$_2$)$_3$CH$_2$CH=CH$_2$, 105372-94-9; LiCD$_3$, 15772-82-4; 2-methyl-3-buten-2-ol, 115-18-4; 1-vinylcyclopentanol, 3859-35-6; (*E*)-3-penten-2-ol, 3899-34-1.

Supplementary Material Available: Tables of bond distances, bond angles, fractional coordinates, and isotropic and anisotropic thermal parameters (5 pages); tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

(67) All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were as follows: REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, a system of computer programs for the automatic solutions of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

(68) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(69) $R = \sum||F_o| - |F_c||/(\sum|F_o|)$; $R_w = [\sum w|F_o| - |F_c|]^2/(\sum w|F_o|^2)^{1/2}$.